Determination of Orientation in Aromatic Polyesters

by

David C. Oda

Submitted to the Department of Chemical Engineering in partial fulfillment of the requirements for the degree of

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Abstract

We have investigated the molecular scale orientation of two aromatic polyester ("polyarylate") systems using Wide Angle X-ray Scattering (WAXS) and Differential Scanning Calorimetry (DSC). The polyarylates studied were: poly(ethylene terephthalate) (PET) and the random terpolyester of hydroxybenzoic acid (HBA), isophthalic acid (IA), and hydroquinone (HQ) (abbreviated HIQ-x, where x is the mole percentage of HBA). Sample morphologies analyzed included unoriented bulk powders, axially symmetric fibers, and plane-strain deformed specimens which displayed three-dimensional scattering anisotropy.

A methodology for the analysis of multi-dimensional WAXS patterns is delineated. The method includes Gaussian deconvolution of the full experimental pattern to separate crystalline and non-crystalline portions. Analysis of the molecular orientation of the non-crystalline portion of the pattern is completed by series expansion using spherical harmonic terms and their coefficients. The series expansion allows us to separate the orientation from the structure factor contributions of the WAXS pattern. Each contribution can then be separately analyzed. To quantitatively characterize the orientation in a sample, molecular-scale simulations are conducted. Our model utilizes a Rotational Isomeric States (RIS) algorithm to simulate polymer chains which are then randomly placed on a 2-D lattice using a Monte Carlo (MC) sampling technique. Since we are modeling the non-crystalline phase, an ensemble of structures is required for the structure factor determination. The calculated structure factors are compared to their experimental counterparts to determine the orientation distribution function (ODF) of the molecular ensemble. The ODF offers a quantitative and concise method of characterizing the distribution of orientations that the generated molecular ensemble populates within the sample.

Our studies have shown that the oriented non-crystalline portion of these polyarylate materials is significant. Both the HIQ-40 fibers and plane-strain PET specimens studied showed more than 70% of the total material was oriented. This has major implications for the molecular modeling of these polymeric systems and their properties. Separating the 3-D WAXS pattern into its constituents allows us to quantitatively identify the amount of the various phases in any given sample. Our results indicate that in addition to the crystalline and isotropic amorphous phases present in these samples, there is also a substantial oriented non-crystalline phase as well. This implies the necessity of a three phase model to properly analyze the data. We also draw conclusions on the differences that mechanical and thermal processing have on orientation in our polyarylate materials. Our results show that thermal processing perfects orientation which has been initially established by mechanical deformation. Our results also show that in the non-crystalline phase a local packing structure is established upon initial mechanical deformation. This local structure remains intact through the thermal processing steps.

Thesis Supervisor: Gregory C. Rutledge
Title: Associate Professor of Chemical Engineering
To the Past and those who came before me, my great-grandparents:

Leong Boo
Leong Ching Ling
Kong Fat Chun
Margaret Chun
and
Emma Penny Bessho

And to the Future and those who shall walk with me,
My dearest Heart

Lisa Chalfin

"Et si pulcra et delectabilis est consideratio que dicta est, hec longe est pulcrior et delectabilior, ..."

("And if our deliberations to this point have been beautiful and delightful, the matters now to be considered are far more beautiful and delightful, ...")

- Roger Bacon, *Perspectiva*, Part I, Distinction 1, Chapter 1, ll. 15-16
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Chapter 1

Introduction

“Lo I the man, whose Muse whilome did maske,  
   As time her taught, in lowly Shepheardes weeds,  
   Am now enforst a far unfitter taske,  
   For trumpets sterne to change mine Oaten reeds;  
   Whose prayses having slept in silence long,  
   Me, all too meane, the sacred Muse areeds  
   To blazon broad amongst her learned throng:  
   Fierce warres and faithfull loves shall moralize my song.”

- Edmund Spenser, the Faerie Queene, Booke I, Stanza 1

1.1 Motivation

Aromatic polyesters are of great interest due to their favorable physical properties particularly in high strength, high modulus (HSHM) applications. Aromatic polyesters constitute the class of polymeric materials which contain aromatic moieties and ester linkages as the primary constituents of their polymer chain backbone. Also known as “polyarylates,” aromatic polyesters are a general class of materials with many uses, of which HSHM applications are merely a subset. One property nearly all polyarylates display is that they are semi-crystalline in nature. Often the interactions and differences between the crystalline and non-crystalline phases influence the bulk properties of the material.

The first polyarylate, poly(ethylene terephthalate) (PET), was introduced in the late 1940’s. PET is one of the most industrially important polymers in the U.S. today with annual production numbering in the billions of pounds. PET’s applications are myriad, ranging from carbonated beverage containers to film coatings and overhead transparencies. The HSHM field for polymers opened up in the early 1970’s with the commercial introduction of polyaramids (materials with aromatic moieties and amide linkages) such as, Nomex™ (poly(m-phenylene isophthalamide), MPIA) and Kevlar™ (poly(p-phenylene terephthalamide), PPTA). Since then, a number of different chain
architectures have been postulated. In particular, since Kevlar\textsuperscript{tm} can only be processed from solution, a melt processible alternative has been sought. One of these potential alternatives is HIQ-x. HIQ-x is a random rigid-rod terpolyester composed of the following three constituents: 1,4-hydroxybenzoic acid (HBA), isophthalic acid (IA), and hydroquinone (HQ). The x denotes the mole percentage of HBA in the polymer and completely defines the composition of the material.

The two materials studied in this thesis, HIQ-x and PET are both semi-crystalline polyarylates. HIQ-x displays a nematic liquid crystalline melt for the composition range of $20 < x < 80$. Many polyarylates are variations on the highly linear rigid structure of Kevlar\textsuperscript{tm} and HIQ-x is no exception. What makes HIQ-x interesting is that it has a melt processible phase, meaning that it can be injection molded. PET, on the other hand, is not a variant of Kevlar\textsuperscript{tm} (having been discovered before Kevlar\textsuperscript{tm}) and displays no liquid crystallinity. While PET has good HSHM behavior, its main attractions are its melt processibility, ease of production (in part due to its low production cost), and extensive recycle potential. All of these advantages have lead to a large literature presence for PET. Both HIQ-x and PET will be discussed more in depth in this chapter.

Studies on polyarylates continue to be done in order to enhance the performance capabilities of this class of materials. These types of improvements fall into two general categories: enhancement of strengths and mitigation of weaknesses. An example of the former is improving material tensile strengths and moduli by additional processing or the introduction of additives. Combating material weaknesses encompasses improvement of wear resistance, decreasing susceptibility to aging, or increasing thermal stability. For polymer and material scientists, product improvement is instituted on the molecular scale, whether through the introduction of new constituents or additives or by processing old materials in new ways. When dealing with these materials, many of the properties are greatly influenced by the molecular scale structure of the material. In turn, the molecular-scale structure is influenced by its processing history.
Therefore, molecular-scale analyses of these materials is important in gaining a fundamental understanding of the processing-structure-properties relationship in the material. In addition, since the chain alignments and their packing arrangements are often primary influences in the development of macroscopic properties, determination of the solid-state molecular-scale behavior of these polyarylates is of utmost importance. However, the molecular-scale packing behavior of the non-crystalline phase in many polyarylates is still not very well understood. A quantitative method of characterizing molecular-scale orientation is one of the main objectives of this thesis work. The non-crystalline (often termed the amorphous, both oriented or unoriented) phase of these materials often accounts for more than half of the material by mass in a given sample, making it the majority phase.

With the advent of the microcomputer and the doubling in computing power that occurs approximately every 18 months, the use of computer simulations has increased dramatically. Computer models are very useful in validation of theories and prediction of properties. With respect to polymers, computers are being applied to problems that were once thought to be intractable due to their sheer volume of calculations. Simulation techniques such as molecular dynamics and Metropolis Monte Carlo sampling are used on ever larger systems of atoms and molecules with dramatic effects. By using molecular modeling, we can build realistic molecular-scale ensembles and models which can aid in the analysis and evaluation of various material properties.

From the broad discussion above, we can specify the main objectives of this thesis work as follows:

1) To deduce a method for the quantitative description of oriented non-crystalline structure in the solid-state of aromatic polyesters. This method will encompass the use of theoretical structure factor calculations in conjunction with an analysis of experimental data to derive an orientation distribution function (ODF) which relates the two branches of the analysis.
2) To validate this method by analyzing various polyarylate samples with simple sample geometries and varying levels of spatial symmetry. This will include case studies of axisymmetric fibers (i.e. samples which display cylindrical symmetry) as well as uniaxially compressed plaques in plane strain deformation which exhibit three-dimensional orientation.

3) To evaluate the comparative effectiveness of this method relative to others. This will highlight the potential usefulness of comparisons made between related analyses on different size scales. It will also show the similarities and differences between such analyses.

With these objectives in mind, the rest of this chapter will discuss the state of the art with respect to the polyarylates of this study (PET and HIQ-x) and introduce the experimental techniques (WAXS and DSC) used in this study.

1.2 State of the Art

1.2.1 Aromatic Polyesters: Polyarylates

The field of polymers, particularly HSHM liquid crystal (LC) polymers, blossomed with the discovery of high tensile strength polymeric materials such as Nomex\textsuperscript{tm} and Kevlar\textsuperscript{tm} by Du Pont in the mid-1970's. Highly aligned and highly extended chain conformations in the fluid phase can be obtained by induction of an LC phase. There are two methods of producing liquid crystal phases: "lyotropic" (an LC phase induced by solvation) and "thermotropic" (an LC phase induced by heating). Aligned chains have a tendency to aggregate into larger structures, termed "domains." The degree of ordering can vary between simple aligned, extended chains, termed a "nematic" phase to phases which contain specific ordering between domains, for example smectic LC phases. When these liquid crystal domains are all aligned (as is the case in fiber spinning) a marked increase in the material's tensile modulus in the direction of the chain backbones is observed. Once these highly aligned domains are cooled below the crystal-to-nematic transition, \( T_{c-n} \), and annealed and crystallinity is induced, the material approaches the theoretical limit for the strength of the constituent covalent bonds. [Rutledge, G., 1990, Noel, C., 1985, Ciferri, A., 1991]
1.2.2 Defining the Role of Processing
Processing can affect a material's bulk properties, such as the tensile strength and sample geometry, after synthesis. Molecular-scale morphologies are greatly affected by processing history; this is especially true of polyarylates. One of the ultimate goals of polymer scientists is to determine the nature of the relationship of bulk properties with respect to structure and thereby relate it back to the composition and processing history of the material. This fundamental interplay of factors is a well known tenet of material science. [Davies, G.R., 1988]

\[ \text{composition, processing history} \rightarrow \text{Structure} \rightarrow \text{Relationship of Properties} \]

We focused on two factors of processing history in this thesis: mechanical bias and deformations and thermal or heat treatment (also referred to as “annealing”) of the material.

The initial mechanical processing step is often the point at which the bulk geometry and bulk morphology of the sample is determined, be it a powder, film, fiber, monofilament, rod, extruded part, or plaque. The nature of symmetry and orientation evidenced in a sample is highly dependent on its initial geometry and is often indicative of the amount and type of orientation seen on the molecular scale. Common specimen geometries include materials with two (2-D) or three (3-D) independent axes. Figure 1.1 shows examples of these spatial geometries.

Figure 1.1: Schematics of common processing symmetries a) axisymmetric or cylindrical requiring two variables \((r, \alpha)\) to characterize b) three-dimensional symmetry requiring three variables \((r, \alpha, \beta)\)
In this thesis, we studied the following sample geometries:

In 2-D: Fibers, Melt-spun and Solution-spun. Fibers can display widely varying degrees of orientation. Industrially produced fibers often show very high degrees of orientation due to the extreme processing conditions to which the material is subjected. Being industrially significant, fibers are a sample geometry which is very common. The HIQ-40 fibers studied in this thesis were obtained from Hoechst-Celanese in New Jersey.

In 3-D: We used a channel die to produce low to moderate molecular level orientation of a “pseudo-single crystal” nature. “Pseudo-single crystal” orientation arises because the material contains multiple crystallites, but due to the processing, all of these crystallites are forced to align in similar orientations. [Bellare, A., 1993] This unusual condition of macroscopically aligned microscopic crystallites allows one to study microscopic behavior much more easily and on a much larger scale within a material.

1.2.2.1 The Channel Die

Figure 1.2 shows a schematic of a channel die and the three independent orthogonal, spatial directions associated with it.

Figure 1.2: Schematic for channel die geometry showing the 3 orthogonal axes: LD = Load Direction, CD = Constraint Direction, FD = Free Direction
From the figure, the nomenclature for processing with the die becomes readily apparent. There are three spatially orthogonal axes, the constraint direction (CD), the load direction (LD), and the flow direction (FD). When the plunger is thrust downwards onto the sample, the load direction experiences a compressive force normal to the surface. In contrast, the constraint direction experiences an expansion or tensile force normal to its surface, yet is required (or constrained) to maintain its shape. The flow direction experiences a force similar to the constraint direction, but because it is unconstrained, it is allowed to freely expand or deform in that direction. Generally, the deformation caused by uniaxial compression in the solid state in a channel die leads to “plane-strain deformation.” That is, the material deforms and extends uniformly in the flow direction. If the walls are lubricated such that the friction between the channel die and sample surfaces is minimized (and therefore, slip between these surfaces is maximized), then the extensional bias experienced by the plane of the sample normal to the flow direction will proceed as a constant “front.” In polymeric systems, the backbones of the polymer chains align themselves with the direction of flow or deformation (that is, in the flow direction). Note that with plane-strain deformation, compressed samples should display two-fold rotational symmetry in each of the three orthogonal spatial directions.

1.2.2.2 Post-synthesis Processing

1.2.2.2.1 Mechanical and Orientational Bias

In our study, we limited ourselves to simple geometries to avoid the effects of a complicated flow and processing history from an already complex molecular-scale description of the material. Two-dimensional studies were limited to axisymmetric orientation in the form of fibers, both solution and melt spun. As noted in the previous section, uniaxial compression in a channel die yields macroscopic three-dimensional order, in the form of pseudo-single crystal order. Therefore, such samples can be of particular interest in this project, offering us a chance to study the effects of three-dimensional orientation of the crystalline and non-crystalline phases in the material. Starting from the unoriented powder of our materials ensures that any subsequent orientation we detect is a function of the processing that the sample undergoes.
Oriented non-crystalline phases in polymers are not unusual. For example, numerous studies on the various phases of drawn PET fibers discuss the nature of the oriented non-crystalline phase of PET and its relationship to both the crystalline and unoriented non-crystalline phases. [Fu, Y., 1994a, Hristov, H., 1991, Clauss, B., 1994, Fischer, E., 1976, Asano, T., 1973, Gupta, V., 1994] There have also been studies on plane-strain compressed poly(methyl methacrylate) (PMMA) samples. These studies deduced the average chain torsions and chain conformation of PMMA based on an analysis of Wide Angle X-ray Scattering (WAXS) data under the assumption of axisymmetric (or cylindrical) symmetry. [Mitchell, G.R., 1982, 1985a] Three-dimensional WAXS studies have been performed with Nylon-6,6 and polyethylene plane-strain deformed polymer specimens. [Galeski, A., 1991(a,b), Bartczak, Z., 1992(a,b)]. Galeski, et al. reported that at high strains in Nylon-6,6, the chains orient with their flexible backbones extended and aligned in the chain direction, packing much like hard cylinders in a 2-D hexagonally packed array.

1.2.2.2 Thermal Treatment or Annealing
Annealing is often referred to as a post-processing step. A thermal anneal usually does not change the bulk geometry of the sample appreciably (fibers remain fibers and a powder remains a powder, and while it may sinter, it will not preferentially obtain a uniquely oriented structure in the bulk). Studies have shown that varying the annealing temperature can significantly influence the molecular structure of a given bulk morphology. Generally, crystallinity is induced or enhanced. Thermal annealing is a solid-state processing step and as such is done below the melt transition (either the crystal-to-nematic transition, $T_{c-n}$, or the isotropic melt transition, $T_m$). However, to allow some chain mobility, annealing must be performed above the glass transition temperature, $T_g$. Thermal processing is often coupled with mechanical processing, where the coupling can be as simple as fixing the dimensions of the sample geometry or as complex as multistaged cycles of thermal and mechanical processing steps.
1.3 Materials: HIQ-x and PET

1.3.1 HIQ-x:
As previously mentioned, one of the polymers of interest in this thesis is HIQ-x, a rigid-rod polyarylate. Before proceeding to a detailed discussion this material, it is useful to examine some of the processing and physical problems encountered in with the material that predates it: Kevlar® (PPTA).

1.3.1.1 Sub-motivation: Problems with Kevlar®
The main reason that Kevlar® has such high strength is attributed to the presence of its long rigid-rod backbone. The rigid linear backbone causes PPTA chains to align preferentially making crystallization very facile. In fact, Kevlar® does not form either a liquid or vapor phase upon heating; it remains crystalline until degradation of the carbon-carbon bonds in the polymeric backbone occurs at about 600°C. However, Kevlar® is lyotropic, being soluble in a 100% sulfuric acid solution. While lyotropicity allows the processing possibilities of wet spinning of fibers and casting of films or plates from solution, the handling and storage of such a strongly acidic solution causes severe problems in large scale industrial applications. [Rutledge, G., 1990, Noel, C., 1985, Ciferri, A., 1991, Biswas, A., 1992] Also, lyotropic materials cannot be injection molded since the presence of solvent inhibits the ability of the material to be properly molded and the removal of solvent from such parts can be difficult. Lastly, Kevlar®, while stable under most conditions, degrades upon exposure to high intensity ultraviolet light (in a process commonly referred to as “aging”). These drawbacks have led polymer scientists to search for alternate materials which are melt processible, in the hope of making the many other thermoplastic polymer processing routes available.

1.3.1.2 Liquid Crystallinity
The search for melt processible polymeric HSHM materials has followed a general methodology. Given that PPTA does not melt, but degrades we ask the question: how can we produce a material which maintains a high tensile strength and whose melting
temperature is lower than its degradation temperature? Since the crystallinity of the PPTA is so high, disrupting the chain packing and making the crystalline phase less energetically stable has been the answer. However, one must remain cognizant of the fact that the aligned nature of the polymer chains is what leads to the high tensile strength and stiffness of these materials. Thus, steps must be taken to ensure that we do not disrupt the chain alignment and hence the material crystallinity "too much."

First, we can eliminate the hydrogen-bonded amides in the backbone, converting the polyaramid to a polyarylate. An example of the former is PPTA (Kevlar™) and an example of the latter is pHBA. Unlike PPTA, which is a copolymer of a diamine and a diol, pHBA is the homopolymer of 1,4-hydroxybenzoic acid (HBA), a difunctional molecule. However, like PPTA, pHBA has a tendency to degrade before melting. Again, this is attributed to the long, rigid, linear backbone of pHBA. [Lieser, G. 1983, Adams, J., 1976] As HBA is one of the three constituents of HIQ-x (the others being isophthalic acid and hydroquinone), pHBA can be thought of as HIQ-100. While, pHBA itself does not exhibit a melt phase (let alone a liquid crystalline one), as a simple limiting example of a rigid-rod chain its behavior has been simulated and studied. [Foulger, S., 1995, Rutledge, G., 1992]

A delicate balance must be achieved between disrupting the chain packing sufficiently to allow a material to exhibit a liquid crystalline phase and disrupting the chain packing so much such that an isotropic melt of unaligned chains results. That is, we require an anisotropic shape persistent mesogen. There have been a large number of variations on rigid-rod polymers postulated to overcome the high crystallinity of Kevlar™ and pHBA. On the molecular-scale, lowering of the melting point and increasing the processing window in these rigid rod polymers is generally accomplished in three distinct ways. All three categories rely on disrupting chain packing sufficiently to induce a transition to a more disordered melt (or liquid phase) before thermal degradation. The three categories of chain disrupters are delineated as follows:
1) Flexible “spacer” units in the backbone
2) Rigid disrupters or “kinks” in the backbone
3) Bulky side groups off of the backbone

The first two options are referred to as “main chain” methods because the nature of the linear rigid backbone is affected; the third is called a “side chain” method since the polymer backbone is unaffected. [Noel, C., 1985] An example of a polymer utilizing the first category to disrupt chain packing is poly(terphenyl-4,4” dicarboxylate). Note, PET (utilizing a -(CH$_2$)$_2$- spacer) and poly(butylene terephthalate) (PBT, with a -(CH$_2$)$_4$- spacer) utilize this method of chain disruption, but do not display liquid crystalline phases. Thus, they are examples where the backbone of the chain has been made too flexible for LC induction. An example of a material utilizing the second category is the random copolyester of 1,4-hydroxybenzoic acid and 2,6-hydroxynaphthaloic acid (HNA), a polymer with the trade name of Vectra$^{\text{tm}}$. In Vectra$^{\text{tm}}$, the naphthaloic moiety introduced at random intervals disrupts the periodicity of the chain backbone and prohibits the development of a fixed crystalline repeat distance. This is an example of a colinear kink, one that disrupt crystalline formation, but allows for the alignment of the polymer chains. An example of the third (or side chain) method of thermotropic LC phase induction is the random terpolyester of 1,4-hydroxybenzoic acid, terephthalic acid (TPA), and phenylhydroquinone (PHQ). The last constituent contains a phenylene ring off of the main backbone ring.

1.3.1.3 Literature: HIQ-x

One of the materials of focus in this thesis is the random terpolyester composed of the following three constituents: 4-hydroxybenzoic acid (HBA), isophthalic acid (IA), and
hydroquinone (HQ). These constituents are shown schematically in Figure 1.3.

![Figure 1.3: Schematic of the 3 constituents of HIQ-x: 1,4-hydroxybenzoic acid (HBA), isophthalic acid (IA), and hydroquinone (HQ)](image)

Because isophthalic acid contains a meta-linked phenylene moiety, the linear nature of the polyester backbone is disrupted. However, the polymer chain remains highly rigid. [Rutledge, G., 1992] HIQ-x utilizes the second category of inducing thermotropicity (delineated above) and has been reported to display a liquid crystalline phase when $20 < x < 80$. Additionally, the window of liquid crystallinity is $\sim 50^\circ \text{C}$ for HIQ-x compositions of $30 < x < 50$. [Blundell, D., 1989, Erdemir, A., 1986] A $50^\circ \text{C}$ range is the minimum temperature window necessary for viability in industrial processing. [Blundell, D., 1989] HIQ-x’s liquid crystalline behavior is shown in the phase diagram in Figure 1.4.

![Figure 1.4: Proposed phase diagram for HIQ-x [from Blundell, MacDonald, and Chivers, 1989]](image)
HIQ-x has been fairly extensively studied as a powder [Erdemir, A., 1985, Johnson, D., 1985], as fibers [Erdemir, A., 1986, Johnson, D., 1990], and as compression molded plaques [Blundell, D., 1988]. Synthesis of HIQ-x can done by a melt-acidolysis method [Spontak, R., 1991] or a non-aqueous dispersion route [Blundell, D., 1990, Spontak, R., 1991]. The latter enhances HIQ-x’s potential for industrial-scale production, as it allows the synthesis of high-molecular weight product. The non-aqueous dispersion process consists of a mixture of the constituents polymerizing in a liquid paraffin catalyzed by a supported metal catalyst. The development of a dispersed phase synthesis route allows the viscosity of the solution to be maintained at a low level. [Blundell, D., 1989] However, one of the major stumbling blocks for mass production of HIQ-x has been the complex morphological and phase behavior of the system. Given the large number of forces at work in the material (e.g. the rigid backbone, the $60^\circ$ kinks, and random copolymerization), it is not surprising that the structural behavior of HIQ-x is a strong function of both composition and processing history. Thus, developing an understanding of the molecular-scale morphology of HIQ-x is essential.

Table 1.1 summarizes a number of the material properties of HIQ-x. HIQ-x shows properties which, while not as impressive as Kevlar$^\text{tm}$, compare favorably to steel and other polymeric materials. In addition, as alluded to previously, HIQ-x has two major advantages over Kevlar: 1) it has the potential to be injection molded (because of its LC melt behavior) and 2) it shows improved compressive strength (albeit at the “cost” of some tensile properties).
Table 1.1: Material Properties of HIQ-x Fibers

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Crystallinity (&lt; 25%)</td>
<td></td>
</tr>
<tr>
<td>High Orientation</td>
<td></td>
</tr>
<tr>
<td>Extended Chain Structure</td>
<td></td>
</tr>
<tr>
<td>Relatively High Glass Transition Temperature</td>
<td>(~120°C)</td>
</tr>
<tr>
<td>Crystal-Nematic Transition Temperature</td>
<td>(~330°C)</td>
</tr>
<tr>
<td>Nematic-Isotropic Transition Temperature</td>
<td>(~360-400°C)</td>
</tr>
<tr>
<td>Low Density (&lt; 1.49 g/cm³)</td>
<td></td>
</tr>
<tr>
<td>Good Creep Resistance</td>
<td></td>
</tr>
<tr>
<td>Melt Processible</td>
<td></td>
</tr>
<tr>
<td>Excellent Tensile Properties:</td>
<td></td>
</tr>
<tr>
<td>Strength</td>
<td>0.55 - 1.26 GPa</td>
</tr>
<tr>
<td>Modulus</td>
<td>30 - 54 GPa</td>
</tr>
</tbody>
</table>

References:
1) Johnson, Karacan, Tomka, 1990
2) Blundell, MacDonald, and Chivers, 1989

1.3.1.4 HSHM Behavior

Like their cousins, the polyaramids, polyarylates have received a great deal of attention based on their enhanced mechanical properties. Generally, the improved specific tensile strength of polyaramids and polyarylates is attributed to two factors: the anisotropic nature of the chain (found in all polymers) and their inherent chain backbone rigidity which is primarily due to molecular-scale π-orbital conjugation of the phenylene ring and carbonyl carbons which dominate the backbone. These factors lead to a high packing density of chains. Coupled with the liquid crystalline behavior of HIQ-x, its high tensile modulus is especially attractive. Johnson, et al. have reported that the specific tensile modulus of annealed HIQ-33 fibers is 54 GPa and a specific tensile strength of 1.26 GPa [Johnson, D. J., 1990] which are lower than the strength and modulus values of Kevlar™ (Figure 1.5). Figure 1.5 has been taken from Adams and Eby (1987) and the strength and modulus data for the annealed HIQ-33 fibers added to it. The lower specific tensile modulus of HIQ-33 relative to PPTA is due to the disruption of chain packing by the m-phenylene units leading to lower packing efficiency and thus, lower degrees of crystallinity. [Johnson, D., 1990] Note that, in
general, these polymeric materials compare favorably to that of steel which is also shown in the lower left hand corner. This is primarily due to the low density (relative to steel) of polymers yielding higher strength-to-weight ratios.

![Graph: Specific Tensile Strength vs. Modulus for Various Fibers](image)

Figure 1.5: Plot of specific strength versus specific modulus for various fibers [modified from Adams and Eby, 1987]

1.3.1.4.1 Scattering Analyses of HIQ-x

WAXS is one of the main tools for comparison of the molecular structure of HIQ-x samples, especially in those samples which display a highly oriented nature (e.g. melt spun fibers). The length of annealing time affects the degree of crystallization in the material. This crystallization can be readily measured in WAXS scans. [Blundell, D., 1988, 1989, Erdemir, A., 1985]
At the present time, X-ray analysis on HIQ-x has focused on elucidating the unit cell structure of HIQ-33 and HIQ-50 fibers. Erdemir, et al. have determined the unit cell for the fiber structural unit to be orthorhombic with $a = 5.58\text{Å}$, $b = 3.92\text{Å}$, and $c = 24.32\text{Å}$. [Erdemir, A., 1988] This unit cell implies a density crystalline density of $1.49 \text{g/cm}^3$ at room temperature. Their work closely matches the results obtained by Blundell. [Blundell, D., 1989] Erdemir, et al., also report experimental data on the WAXS powder diffraction pattern of various compositions of HIQ-x. [Erdemir, A., 1986] They did not report any structural analysis on this WAXS data.

HIQ-100 (pHBA) has also been studied via WAXS quite extensively. The published values for the unit cell are as follows. It is an orthorhombic cell with 2 chains per cell. The unit cell parameters are listed as: $a = 7.62\text{Å}$, $b = 5.70\text{Å}$, $c = 12.56\text{Å}$. The c-direction is parallel to the polymer chain axis. [Geiss, R. 1984] Poly(pheynlene isophthalate) (PPI) is the copolymer of two of the components of HIQ-x, isophthalic acid and hydroquinone. Compositionally, PPI is HIQ-0. It is a regular alternating copolymer, since the components are either a diacid or a diol. The unit cell structure of PPI has been reported as a two-chain monoclinic cell with unit cell parameters: $a = 6.97\text{Å}$, $b = 6.92\text{Å}$, $c = 24.32\text{Å}$, $\alpha = 95^\circ$ [Cao, J., 1995] The density of the PPI unit cell is $1.37\text{g/cm}^3$. The difference in unit cells between PPI and that proposed for HIQ-x is actually quite small, requiring only a slight shift between chains. The HIQ-x powder pattern has been reported to contain reflections from both the HIQ-x fiber and PPI unit cell (at least the low index reflections). Thus, the as-synthesized powder of HIQ-x seemingly contains a highly disordered mixture of two similar, but distinct crystalline phases. The two unit cells are similar, having the same c-axis parameters and both are reported to contain chains a zig-zag conformation. However, the reported PPI unit cell is less dense. The orthorhombic cell found in the fibers is ostensibly preferred upon extension of the chains which may pack with greater efficiency in the denser unit cell.

Work has been done with neutron scattering on deuterated material by MacDonald, et
al. to determine some transesterification effects. [MacDonald, W., 1992] Transesterification is the transfer of segments between adjacent polymer chains via a mechanism which focuses on the ester linkages in the backbone. If the segment transfer is random, the primary effect of transesterification is to increase the distribution of chain lengths in the sample. If the segment transfer is not random (i.e. certain ester linkages attached to certain moieties are more easily broken than others), then a secondary effect of transesterification would be to produce regions that would be “rich” in certain monomer sequences. MacDonald et al. showed that transesterification between chains in HIQ-x became significant when processing temperatures were above approximately 150°C. They did not see any evidence of non-random transesterification statistics in HIQ-x chain segment transfers.

1.3.1.4.2 HIQ-x Characterization by Other Methods
Cheng, et al., have done work on interpretation of DSC results of rigid-rod polymeric materials (but not HIQ-x specifically) deriving properties like the melting temperature, \( T_m \), the perfect crystal enthalpy of fusion, \( \Delta H_f \), and the degree of crystallinity, \( \chi_{DSC} \). [Cheng, 1988, 1989, 1990, 1991] Economy, et al., have performed \(^{13}\)C-NMR experiments on \((^{13}\)C enriched) HBA/HNA copolyesters to determine monomer sequencing diad probabilities. [Economy, J., 1990, Lyerla, J., 1990] HIQ-x specific experimental IR work at Celanese concluded that the four diads of HIQ-x had independent and identifiably different signatures, which allowed the measurement of compositional changes as a function of processing. [Rafalko, J., 1993]

1.3.1.4.3 Simulation Studies
Simulation work on HIQ-x has focused primarily on the single chain and crystalline packing structures of the material. Erdemir et al., have looked at the extended chain behavior of HIQ-x. They discuss and characterize the extended chain nature of HIQ-x in fibers by matching experimental meridional WAXS peaks with those calculated from extended chain conformations. [Erdemir, A., 1988, Johnson, D., 1990, 1992] They concluded that the extended chains of HIQ-x displayed a zig-zag extended chain
conformation. This zig-zag formation is necessary for the proper extinctions to occur in the unit cell and for helical periodicity to be maintained in a crystal. Johnson also concluded that this planar chain configuration mitigated some of the modulus degrading effects of the introduction of the m-phenylene moieties.

O'Mahoney et al. investigated the unit cell analogs for a number of polyarylates, including HIQ-x. [O'Mahoney, C., 1990] They utilized single crystals of oligomeric analogs to study the higher order scattering reflections. These reflections gave more accurate and precise crystallographic information. They concluded that bis(4-benzoyloxyphenyl) isophthalate is the best oligomeric analog for HIQ-x. It produces a scattering pattern very similar to that of HIQ-x. It should be noted, however, that the oligomeric compound produces a two-chain monoclinic cell (with unit cell parameters: \(a = 7.508\, \text{Å}, b = 5.924\, \text{Å}, c = 60.664\, \text{Å}, \alpha = 93.05^\circ\)) which differs from the single chain orthorhombic unit cell for HIQ-x fibers and the monoclinic unit cell reported for PPI by Cao, et al. [Cao, J., 1995]

Rutledge has developed computer simulation code to study and model the solid state behavior of polyarylates. [Rutledge, G., 1992] He used a Rotational Isomeric States (RIS) algorithm for chain generation and a Metropolis Monte Carlo (MC) algorithm to sample acceptable chain packing arrangements on a two-dimensional lattice. He discusses, in depth, the single chain conformations of HIQ-x. Rutledge notes that for compositions approaching pHBA (HIQ-100) the chains stiffness, persistence length, and the anisotropy of the chains rise dramatically.

As one can see, extensive work has been done elucidating certain aspects of the single chains structure, as well as the periodic structure of the HIQ-x in the solid state. These simulation studies leave the questions dealing with simulations of solid state non-crystalline packing structures of these aromatic polyesters unresolved. Understanding and characterizing the disrupted crystalline structure of these polyarylates is key in understanding and more fully quantifying molecular-scale phenomena, whether they be diffusion or barrier properties or mechanical and structural properties.
1.3.2 PET

Poly(ethylene terephthalate) is an industrially important member of the polyarylates. With its annual production at the billions of pounds/year level, there has been intense study into its applications and processing behavior. Among the more interesting aspects of PET is the fact that its “oriented amorphous” phase is well documented [e.g. Fu, Y., 1994] and is often cited as the primary influence in a number of mechanical and structural properties. Yet, a detailed description of this oriented non-crystalline phases is not well documented in the literature. Presumably, this has been due in part to the difficult nature of modeling and characterizing this phase, since it is not perfectly periodic (like a crystal) nor totally unoriented (like the isotropic amorphous phase). Mathematically, this poor, but non-negligible sample orientation leads to a number of difficulties, as the macroscopic orientation of the phase is convoluted into the molecular-level structural detail, complicating experimental observations. Understanding the relationship between the macroscopic and microscopic level structures and the elucidation of the parameters which quantify that relationship is one of the main goals of this thesis work.

1.3.2.1 Literature

Note that while PET is a polyarylate, in much of the older literature, it is merely referred to as “polyester.” To avoid confusion, PET will always be used in reference to poly(ethylene terephthalate). While the chain backbone of PET is not composed purely of phenyl rings and ester linkages (in PET, there are also ethylene groups) over 85% of the material by weight is encompassed in the phenylene ring and ester moieties, so it is reasonable to consider it a member of the polyarylates.

1.3.2.1.1 Crystallization/Thermal Behavior

The crystalline structure of PET is well documented in the literature. Daubeny, et al. have reported a triclinic primitive cell of PET with the following unit cell parameters: \(a = 4.61\,\text{Å}, b = 5.953\,\text{Å}, c = 10.760\,\text{Å}, \alpha = 99.85^\circ, \beta = 118.20^\circ, \gamma = 111.37^\circ\). [Daubeny,
One particular aspect of crystallization that has received much attention is the rate of crystallization and thermal annealing behavior of PET. It has been shown (and will be discussed, in brief) that the nature of the processing of the material greatly affects the crystallization behavior. Thus, the duration of time a sample is maintained at the processing temperature is of primary concern.

The "half-time of crystallization" is the length of time which a sample takes to complete half of its crystallization to its final percentage. If the rate of crystallization is a simple exponential phenomena (such as in the case of one-dimensional growth [Avrami, M., 1939, 1940]), the half time to crystallization is a constant. Figure 1.6 plots the half-time of crystallization of PET as a function of temperature.

![Half Time Experimental Data for PET](image)

**Figure 1.6: Survey of literature values for crystallization rates of unoriented PET**

Note that, the values in the literature vary according to the nature of the experiment from which the data is derived. Still, the overall trend shows agreement with a maximum crystallization rate (and corresponding minimum half time) between 170\(^{\circ}\)C to
190°C. The minimum occurs because, as with all crystallization rates, the optimum rate is an interplay of two competing mechanisms: generation and nucleation of crystallites and the growth of those crystallites. In our case, only a rough estimate of the maximum crystallization temperature and its corresponding half-time was necessary. Using conservative estimates, the half time value at 190°C is 90 seconds. This value implies that in 15 minutes (900 seconds) a thermally equilibrated sample will have undergone ten half-times, i.e. approached to within 99.99% of its maximum extent of crystallization. After only five minutes (300 seconds) at 190°C over three half times will have passed and the crystallization approached to within 95% of its maximum extent. These estimates imply that crystallization in our PET samples (which deal with processing times on the order of minutes) is likely to be a major factor and a significant crystal phase can be expected.

There have been a number of studies into crystallization in oriented PET samples. Generally speaking, macroscopic processing has a tendency to orient the microscopic polymer chains in a material. Aligned chains crystallize more readily. In fact, cold-drawn crystallization processing relies on this very fact. [Salem, D., 1992(b), Alfonso, G., 1978, Fischer, E.W., 1976]

1.3.2.1.2 WAXS Characterization of PET
The molecular scale orientation of PET chains has been studied extensively via WAXS. Bellare, et al. created uniaxially deformed samples of PET in a channel die to induce “pseudo-single crystal” orientation of the crystallites. They tracked the progression of the crystallite orientation through a series of plaques deformed to different compression ratios. [Bellare, A., 1993] They showed that PET crystallites aligned in specific orientations based on their response to the deforming pressure. Chain backbones tended to align with the flow direction in proportion to increasing stress on the material. In their discussion, Bellare et al. restricted themselves primarily to the nature of orientation in the crystalline phase.
1.3.3 Orientational Studies on Other Polymeric Systems

The oriented non-crystalline phase of other polymers has been extensively studied. Bartczak and Galeski [Galeski, A., 1988, 1991, Bartczak, Z., 1992] investigated uniaxially deformed specimens of both polyethylene and Nylon-6,6 processed in a plane strain deformation. They observed that on the macroscopic scale, a hexagonal arrangement of chains predominates the non-crystalline structure for both polymer systems.

Mitchell and Windle have investigated poly(methyl methacrylate), PMMA, extensively. They used Legendre polynomials as a basis set in a series expansion analysis to separate the orientation and structural components of molecular-scale morphologies in their polymer specimens. They derived a cylindrical distribution function for the alignment of PMMA chains, but concentrated on the intrachain scattering aspects of the system (i.e. high scattering vector values). This scattering vector range allowed them to deduce information about the chain conformation, but did not enable them to make direct correlations concerning chain packing. [Mitchell, G.R., 1982, 1985a]

Pieper and Killian [Pieper, T., 1993] have developed a general methodology for building structural and orientational details into numerical simulations and calculations. They used a method which focuses on the various size ranges, from the microscopic scale through intermediate meso- and macrodomains to the macroscopic scale. While reasonably comprehensive, the method is computationally expensive and they restrict its application primarily to semicrystalline (not necessarily liquid crystalline) materials and to obtaining radial distribution functions (i.e. 1-D studies).

Biswas and Blackwell have analyzed and modeled the meridional portions of X-ray fiber patterns of HBA/HNA quite extensively. [Biswas, A., 1988(a,b,c), Blackwell, J., 1985] They showed that an aperiodic model of chains can still produce a cohesive set of constructive interference patterns. They demonstrated that a random copolyester, like Vectra™, may still yield a set of sharp meridional peaks without a regular repeat spacing along the chain backbone.
Three separate groups (Murthy, et al.; Fu, et al.; and Iannelli) have been working on the interpretation of the non-crystalline section of WAXS patterns in 1-D and 2-D. [Murthy, N.S., 1993, Fu, Y., 1993, Iannelli, P., 1993(a,b)] They espouse the necessity of being able to interpret the information contained in the amorphous halo to fully understand the molecular-scale structure of a polymer. In our case, given the low degrees of crystallinity that HIQ-x seems to have, non-periodic short range structure is especially important.

1.4 Experimental Analysis Techniques

A number of experimental techniques were utilized in this study. The primary analytical technique utilized was Wide-Angle X-ray Scattering (WAXS). However, other useful supplementary (and complimentary) information was obtained (especially in the last case study dealing with PET stress relaxation and recovery) from a number of other analytical techniques. The list of techniques includes: Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance (NMR, and more specifically, Carbon-13 Slow Magic Angle Spinning-Direct Exchange Correlation for Orientation Distribution Evaluation and Reconstruction or $^{13}$C SMAS-DECODER NMR), and Small-Angle X-ray Scattering (SAXS). The latter two methods will be discussed further in Chapter 5.

1.4.1 WAXS: 2-D and 3-D

Wide Angle X-ray Scattering (WAXS) is useful in elucidating the various bulk morphologies and spatial packing arrangements in materials. When studying the scattering characteristics of the system, we looked at both the periodic (i.e. constructive or Bragg) scattering as well as the aperiodic non-crystalline scattering. Since the degree of crystallinity in these materials is fairly low (less than ~25% for HIQ-x [Blundell, D., 1989] and less than 40% for PET [Mehta, A., 1978]), determination of characteristics of the dominant (non-crystalline) phase is also quite important.
1.4.1.1 General Theory

The basic scattering equation for WAXS can be summarized as follows [Guinier, A., 1963]:

\[
I_N(\bar{s}) = \sum_{n=1}^{N} f_n^2 + \sum_{n \neq n'} f_n f_{n'} \cos(2\pi \bar{s} \cdot \bar{x}_{nn'})
\]  

(1.1)

where \( I_N(\bar{s}) \) is the intensity of the scattering from a body of \( N \) scatterers (atoms in our case) and is spatially dependent. \( f_n \) and \( f_{n'} \) are the atomic scattering factors for atoms \( n \) and \( n' \) respectively. The summations are over all atomic pairs, either self-scattering in the first right-hand term or between different atoms in the second right-hand term. \( x_{nn'} \) is the real space vector between atoms \( n \) and \( n' \) and \( \bar{s} \) is the scattering vector in reciprocal space. The cosine term arises from the real part of the exponential used in the Fourier transform which relates reciprocal space to real space. To discuss this equation briefly, it makes no assumptions about the nature of the scatterers. Also, the scattering pair's local environment, i.e. which phase it is in, does not influence the pair's scattering properties (unless as a secondary effect, if for example the scattering factors were a function of temperature, connectivity or other structural parameter, which they generally are not). The equation is only concerned with types of atoms involved and the distances between the them. The phase of the material does not affect the scattering properties of its individual parts. One can analyze scattering data for different phases, but this is only due to the fact that periodic (i.e crystalline) systems contain only set spacings, where as aperiodic phases contain a distribution of spacings. In practice, the difference between the scattering properties of the two phases is not necessarily well defined.

When viewed as an infinite, periodic system of scattering bodies, crystalline systems are straightforward to analyze. For general theory on scattering, works by Cullity and Warren are considered to be essential to any experimentalist in the field. [Cullity, B., 1981, Warren, B., 1969] With respect to polymers, Alexander has an excellent treatment of the necessary modifications and expectations that one should have when dealing with X-rays and polymers. [Alexander, L., 1969] These authors note that
infinite, periodic systems have the advantage over the general scattering equation (Equation 1.1), in that they have simplified mathematical expressions. The pair-wise summation over all atoms in Equation 1.1 simplifies into two parts for a crystalline system: the contribution of each atom in a particular structural repeat (unit cell structure factor) and the translational lattice of the repeat units (the lattice factor). This separation occurs only for periodic systems. The Laue conditions (or its scalar equivalent, Bragg's Law) are simple quantitative characterizations the constructive interference patterns derived from these highly ordered arrangement of scattering objects.

Generally speaking, aperiodic (or non-crystalline) systems fall into 2 regimes, isotropic and anisotropic. Non-crystalline material is correlated in a like manner, as either unoriented or oriented, respectively. The former case corresponds to isotropic aperiodic scattering, while the oriented non-crystalline scattering can be viewed as anisotropic aperiodic scattering. Isotropic aperiodic scattering, also known as amorphous scattering, has been dealt with extensively by Guinier. [Guinier, A., 1963] The basis of aperiodic scattering is similar to that of period scattering. They both are derived from Equation 1.1, which consists of the summation of pairs of scattering distances. However, since there is no periodicity to simplify the calculation, the computational expense involved in the repetitive summation is very high. The advent of the use of computers (and supercomputers) to aid in these calculations, which are often performed iterative or via nested loops, has vastly improved our ability to solve or circumvent some of the former obstacles which restricted the applicability of such calculations.

1.4.1.2 Interpretations of Experimental WAXS Data
Quantitative interpretations of the experimental WAXS pattern is the desired goal of this thesis. To aid us in this endeavor, this section surveys some of the relevant features and basic interpretations reported in the literature. First, we outline some basic nomenclature. The scattering vector is often represented as $s (= f(2\theta))$. There are two orientation angles, generally denoted as $\alpha$ and $\beta$. $\alpha$ is the azimuthal angle and $\beta$ is the
polar angle (in the plane normal to the axis from which $\alpha$ is measured). The definition of $\alpha$ and $\beta$ is shown in Figure 1.1(b). In spherical coordinates, these two angles allow us to describe any location in space. Since we are describing the spatial orientation of a ray extending from the origin to point, a third Euler angle is not necessary in the spatial description. [Prince, E., 1992]

1.4.1.2.1 Distributions in 2$\theta$: Elements in Line Broadening

Practically speaking, we never deal with infinite, periodic objects. The finite dimensions of an object create an effect called “line broadening.” The perfect and discrete delta spikes of intensity at the Laue conditions, take on a breadth characteristic of the number of repeats present. That is, where as the infinite crystal WAXS pattern would have only diffracted intensity at specific points (points with infinitely narrow breadths) in space, the finite size of a real crystal produces a peak with a finite breadth. When dealing with line broadening in experimental WAXS data, one can account for a particular peak’s breadth with the following three general factors:

1) Instrumental
2) Macroscopic sample (or geometric)
3) Microscopic sample (or molecular)

Instrumental factors are a “catch-all” for effects introduced by a particular piece of equipment, for example, a finite beam thickness or the beam dispersion. Macroscopic sample factors deal with sample size, shape, and absorption properties. These factors can affect the breadth of a peak in the 2$\theta$ direction, but the effects are generally fairly small, unless dealing with a very narrow peak (not usually the case with polymers). With polymers, the largest factor in determining a crystalline peak breadth is the number of repeats or distances that constructively interfere. There is an inverse relationship between the number of repeats and the breadth of the peak measured from reciprocal space. This relationship is known as the Scherrer length [Guinier, A., 1963]:

$$L = \frac{k\lambda}{\beta_0 \cos \theta}$$ (1.2)
where \( L \) is the length of the crystallite in the direction of the scattering vector, \( \lambda \) is the wavelength of incident radiation, \( \beta_0 \) is the Full Width at Half Maximum (FWHM) of the peak in question, and \( \theta \) is one-half the scattering angle, \( 2\theta \). \( K \) is constant whose value depends on the geometry of the crystal, but is generally near unity. This formula derived for crystallites of finite sizes (between \( 10\text{Å} - 10,000\text{Å} \)) is reasonable for repeating systems, but for aperiodic systems is not valid. There is no analogous formula for amorphous or aperiodic systems. Use of Equation 1.2 on the aperiodic features offers dubious qualitative insight into the magnitudes of the atomic distances involved. The broad breadths of non-crystalline features can produce significant errors in estimations of distances using the Scherrer equation.

1.4.1.2.2 Distributions in Polar Angles: Spherical Harmonics (Polynomials)

In the two extremes of perfect alignment or fully isotropic distributions, the orientation distributions are simple to characterize, as they are either a delta spike or a constant-valued function respectively. Often, the deviations from the perfect delta spike are measured in terms of Gaussians, which for small symmetric variations about the preferred direction can work quite well. However, distributions not encompassed by the two limiting cases are not as well characterized. In determining an orientation distribution function (ODF) between the two extremes of perfect order and complete disorder, its shape is not known \textit{a priori}. Without knowledge of the ODF shape, a series expansion to model the distribution using a general basis set becomes the most feasible option available. If cylindrical or spherical coordinate systems are chosen to describe the spatial variance of the data, the ready choice for the basis set becomes Legendre polynomials (for the cylindrically axisymmetric case in two dimensions) and the spherical harmonics of the first kind (in the general three-dimensional case).

[Mitchell, G.R., 1982,1985a, deGennes, P., 1972] This implies that a Legendre polynomial series expansion would be appropriate for our fiber samples and a spherical harmonic series can be used for any plane-strain deformed specimens.
1.4.1.3 WAXS Summary
The advantages of WAXS are readily apparent. WAXS gives us a discrete, quantitative measure of the spatial orientation of atomic scale distances in a sample. Quantitative measurement of intensity can be easily taken with photomultiplier counters (either scintillation or proportional) at the appropriate atomic distances with the correct data collection range.

It is of note that WAXS is a bulk averaged sampling technique. The entire area under illumination by the beam undergoes scattering events (though these are in proportion to the type of material illuminated, so different materials will scatter X-rays to a greater or lesser extent based on the number of electrons present). Thus, the system does not necessarily differentiate between crystalline or non-crystalline scattering. This has its advantages. The amount of scattering due to either phase is in direct proportion to the amount of the phase present. However, this equality of scattering between phases means that determination of commingling of phases or phase separation is not as straightforward. Often the difference between periodic and aperiodic materials is the “sharpness” of features. Since crystalline peaks are generally narrower non-crystalline peaks (due to more constructive interference), WAXS is usually considered more sensitive to the crystalline phase. Inferences can often be made about macroscopic bulk phase morphologies (often referred to as “fine” structures); however, more often than not, this falls into the realm of SAXS (which in principle is very similar to WAXS).

1.4.2 DSC
Differential Scanning Calorimetry (DSC) can be used to verify the basic thermodynamic properties and transitions of the HIQ-x material reported in the literature. Various groups, such as Cheng, et al., have been able to determine such thermodynamic properties such as the standard heats of fusion ($\Delta H^\circ$) and perfect crystal melting temperature ($T_m$). [Spontak, R., 1992, Cheng, S., 1989, 1990, 1991, Johnson, R., 1993] Also, DSC provides an independent measurement of the degree of crystallinity of the material. Note that the DSC degree of crystallinity may not correlate directly to
that determined by WAXS, since crystallinity defined by thermodynamics (energetically favorable) is not necessarily the same as crystallinity in WAXS (long-range periodic order). [Wunderlich, B., 1976, Green D.l., 1990, 1992] We will discuss this point more concretely in later chapters when comparing the different degrees of crystallinity in our polyarylate samples.

Our primary purpose in using DSC is as a source of verification of literature values and as an independent measure of degrees of crystallinity for comparison to WAXS. The points at which phase transitions occur in our materials is of particular interest for us, but only from the standpoint of aiding us in choosing relevant and interesting processing histories for our materials. In particular, because HIQ-x does not have a reported enthalpy of formation, $\Delta H^0_f$, it is particularly difficult to gain an absolute measure crystallinity in a sample by DSC alone. While various other thermodynamic quantities may be derived using DSC, they are not the focus of this thesis.

DSC, while excellent for determining thermodynamic properties and phase behavior, suffers in that it is not overly sensitive to spatial orientations of a given sample, unless those spatial orientations lead to large differences in thermodynamic stability of a given phase. In any case, this is an indirect or secondary effect and unless substantial is not suitable for analysis by DSC alone.

1.5 Summary

Polyarylates are an important and interesting group of polymeric materials. They have excellent potential for HSHM applications. While extensive structural studies in a number of different areas have been done on these materials, to date there has been a lack of models describing the solid state packing behavior of these polymers. This is fertile ground for the use of simulation techniques which can help to ease the computational burden of both data analysis and simulation generation. Especially lacking for polyarylates is a bridge to linking the microscopic structure to larger scale
descriptions, from the atomic- and molecular-scale (angstroms to nanometers) to the size of chain domains, grains, and laboratory samples (microns to millimeters).

All of this makes the current research climate highly suitable for this thesis work. Whereas Mitchell and Windle concentrated on the intrachain scattering and high scattering vector range of the WAXS trace; Bellare, et al. chose to look at the crystalline portions of PET; Bartczak and Galeski looked at the non-crystalline phases of Nylon-6,6 and PE; and many have mentioned the presence of an "oriented amorphous" phase of PET, there lacks a cohesive study for pulling all of these facts and factors together. This thesis is a movement in that direction.

1.6 Thesis Organization

The rest of this document is dedicated to the elucidation of methods for quantitative interpretation of wide angle X-ray scattering information, primarily in the oriented non-crystalline portion, derived from aromatic polyester samples. Chapter 2 delineates a method of quantitatively measuring the molecular-scale orientation within a sample via use of a Legendre polynomial series expansion and correlating that to a molecular-scale model with explicit atomic positions. The method is demonstrated on an unannealed HIQ-40 solution-spun fiber specimen. Chapter 3 then uses the Legendre polynomial series expansion analysis to compare and contrast the role of certain processing variables in a set of HIQ-40 fiber samples. Chapter 4 deals with plane-strain deformed PET samples uniaxially compressed in a channel die. The degree of spatial anisotropy requires the full three-dimensional spherical harmonic series expansion analysis to study the oriented non-crystalline phase. In Chapter 5, a series of PET plaques are the main focus of a stress relaxation and recovery study. The spherical harmonic series expansion analysis is one of the techniques used to analyze this set of samples. This last chapter shows how the series expansion analysis may be coupled with other complimentary methods of determining molecular-scale orientation to aid in elucidating the role of processing in materials. Chapter 6 concludes the main body of this document; it summarizes the work found within this thesis and offers
recommendations for future studies in this area.

This document concludes with a number of appendices, which elaborate on various topics in more detail than is warranted for the main body. Topics included among the appendices are a discussion on the mathematical and functional forms of the spherical harmonics of the first kind and Legendre polynomials, supplemental analytical techniques, and copies of the computer code used to implement major aspects of the molecular simulations and theoretical structure factor calculations.
Chapter 2

The Spherical Harmonic Series Expansion Analysis

"... they are not the commandments of the gods, but the findings of men who were
gifted in reason, to discover the secrets of the physical universe, to find our what
ends were to be pursued and what avoided in the sphere of human behaviour,
and in the rules of reasoning, what valid inferences could be drawn, what
conclusions did not follow and what contradictions were entailed ..."
- St. Augustine, *City of God*, Bk II, Ch. 7

2.1 Purpose

As espoused in Chapter 1, the use of spherical harmonic series to characterize a
distribution in cylindrical or spherical coordinates is a natural choice. The use of this
set of functional forms is general in its application to problems in these coordinates
systems. For our purposes, they present a succinct and well-characterized basis set
for the elucidation of the spatial orientation in our samples. They offer a standardized
and informative method of characterizing features in an experimental trace. A spherical
harmonic series expansion does not pre-select a given distribution shape, but
theoretically can be used to model any distribution. Of course, there are practical limits
based upon the degree of noise and sharpness of feature which may limit the ultimate
application or use of spherical harmonics, but for smoothly varying functions (such as
most naturally occurring orientation distribution functions (ODFs)) we would anticipate
very few problems.

2.1.1 Methodology

Figure 2.1 shows a schematic of the steps required in the spherical harmonic series
expansion analysis. Starting with the experimental sample, we are required to collect
spatially dependent data on the sample. Our technique of choice is Wide Angle X-ray
Scattering (WAXS). Once, the raw experimental trace is obtained, the data must be
filtered, accounting for any instrumental or sample-geometry introduced artifacts. The
data is then separated into its crystalline and non-crystalline portions. Taking only the
non-crystalline portion of the trace, we must renormalize the data, so that it may be
compared to theoretical calculations. Lastly, we introduce a molecular model with explicit atomic coordinates and use those coordinates to calculate the model's structure factor. The structure factor calculations are compared to those of experiment and if the agreement of scattering features present is good, the model is said to accurately represent the molecular-scale structure of the sample.

Figure 2.1: Methodology schematic depicting the various steps, factors, and assumptions that enter the analysis. The middle column lists the various parts of the data which are accounted for. The analysis culminates in a correlation of a molecular model to structural information derived via the series expansion.
The experimental WAXS spherical harmonic series coefficients can be used for interpretation in comparison between samples; relative comparisons between coefficient traces of different samples can be made, since the data has been scaled to the common reference of the theoretical calculation. However, the coefficient traces are most useful when coupled with an explicit atom molecular model and theoretical structure factor calculations. Judicious selection and use of a relevant molecular model produce analogous coefficient traces which can imply a suitable molecular description for a material. In turn, this molecular model can be used for subsequent simulations to estimate and predict other properties and correlations, such as thermodynamic transitions or atomic and molecular pair correlations.

Once we have selected the spherical harmonics as a natural system of basis functions, it becomes incumbent upon us to set forth a working methodology to integrate their use into a meaningful analysis. This chapter sets forth such a methodology and designates the components and assumptions that must be made at each point. We start with the experimental analysis of data using a deconvolution of the pattern for the general two-dimensional case and then discuss semi-quantitatively the experimental structure factor coefficient traces which result. Matching these experimental structure factor coefficient traces to their theoretically calculated counterparts is the key to analysis and requires the introduction of an independent molecular model. Since we are dealing with the non-crystalline portion of the WAXS pattern, we will have to derive an ensemble of reasonable molecular-scale structures. The resultant ensemble from the molecular model may then be used as an accurate representation of the system's oriented non-crystalline portion in subsequent simulations. Additionally, the relationship between the theoretical and experimental coefficients is quantified in the ODF, yielding a concise means to correlate the molecular-level structure to a larger size scale.

2.1.2 Sample Legendre Analysis: HIQ-40, As-spun, Solution-spun Fibers
As an example of the spherical harmonic analysis, we demonstrate the technique on a fiber sample of HIQ-40 (designated hiq40fsa). The fiber is spun from a solution of 20%
dichloromethane (DCM) and 80% trifluoroacetic acid (TFAA) and unannealed (i.e. “as-spun”). A mixture of TFAA and DCM is a common solvent for polyarylates, such as HIQ-40. HIQ-40 is not known to be lyotropic (i.e. liquid crystalline phase forming from solution). Therefore, we anticipate that the fibers produced by this method will not necessarily have the chains as highly aligned as they would be if quenched from a liquid crystalline melt. What this means for the analysis is that the sample requires relatively few coefficient traces to characterize it, since the ODF of the molecular scale units should be fairly broad. Since we are dealing with a fiber, we have cylindrical symmetry. As such, our spherical harmonics degenerate into Legendre polynomials. Thus, for the remainder of this chapter we will deal exclusively with the Legendre polynomials as the basis set for the series expansion.

2.2 Experimental Data Analysis

The sheer number of data points in an experimental WAXS trace can be daunting. An average fiber diagram contains over 8000 discrete data points. In a three-dimensional WAXS trace, the number of data points increases even more dramatically with the introduction of a second orientation angle which must be sampled. Thus, with respect to the experimental branch of the analysis, the use of the spherical harmonic series expansion and its resultant coefficients to describe the WAXS pattern is a succinct way in which we may reduce the amount of calculations and parameters that we need to describe the WAXS pattern.

Utilizing an analytical approach similar to that used by Mitchell and Windle [Mitchell, G.R., 1982, 1985a], we have analyzed the non-periodic portion of a multi-dimensional WAXS traces using spherical harmonics. Whereas Mitchell and Windle looked at oriented non-crystalline patterns of PMMA (which is a completely non-crystalline polymer), both HIQ-\(x\) and PET are semi-crystalline. Thus, many of our samples have a non-negligible degree of crystallinity associated with them. This requires that we separate out the crystalline and non-crystalline parts. In principle, the crystalline parts can be analyzed with the series expansion analysis, the narrow azimuthal breadth of
the crystalline peaks requires a large number of terms in the series expansion to capture. In addition, it is easier to analyze the shape of the crystalline portions via other methods, as delineated later in Chapters 3 and 4. For the purpose of this current chapter, hiq40fsa does exhibit evidence of a crystalline phase; thus, we neglect the part of the analysis which calls for the removal of the crystalline phase.

Deconvolution of the experimental data via a Legendre polynomial series is as follows. A separation of spatial variables is implicit in the applicability of this method to analyzing any data. Separation of variables allows us to express the contributions of the scattering vector magnitude and its spatial orientation to the WAXS pattern as independent quantities, allowing them to be analyzed individually. Mathematically, this may be expressed as:

\[ I_{ex}(s, \alpha) = \sum_{n=0}^{\infty} A_{2n}(s)P_{2n}(\cos \alpha) \]  

(2.1)

where, \( P_{2n}(\cos \alpha) \) are the Legendre polynomials of even-order 2n. [Abramowitz, M., 1965] In Equation 2.1, the \( A_{2n}(s) \)'s are the Legendre polynomial coefficients, \( I_{ex}(s, \alpha) \) is the experimental intensity, \( s \) is the scattering vector magnitude, and \( \alpha \) is the azimuthal angle. \( \alpha \) is measured with respect to a reference axis, which for our purposes is equivalent to the fiber axis.

Equation 2.1 shows that the experimental data trace may be viewed as a series of Legendre polynomials and their coefficient traces. In theory, any axisymmetric function may be reproduced by this series. For processes such as fiber spinning, this is perfect. Practically speaking, the series is generally truncated at the point where the series obtains a desired tolerance. In the case of most semi-crystalline polymers, series of \( 2n > 20 \) (i.e. 11 terms) are generally not necessary. Still, with \( 2n = 20 \), there is a point of diminishing returns since the amount of data generated is on the order of that which was used to derive the series (i.e. the experimental fiber pattern).
It is readily apparent from Equation 2.1 that only the coefficient traces, the $A_{2n}(s)$'s, are functions of the scattering vector magnitude, $s$, and therefore the structure factors of the material in the sample. Given this, one of the advantages of this method is the ready deconvolution of a multi-dimensional WAXS trace into a (hopefully small) number of 1-D coefficient traces. These traces may be more readily analyzed since they are only a function of one variable (the scattering vector magnitude and not its orientation). In practice, the coefficient traces are derived from the numerical integration of the experimental trace:

$$A_{2n}(s) = \int_{\alpha} I_{ex}(s, \alpha) \cdot P_2(\cos \alpha) \sin \alpha \, d\alpha \quad (2.2)$$

We have found that for our evenly spaced data, the Alternative Extended Simpson's Rule (Numerical Recipes [Press, W.H., 1992]) was sufficient to attain the desired accuracy for the integration. This conclusion was based on a study of the convergence criterion for our numerical integration algorithm. We used a test peak of Gaussian shape. A Gaussian was chosen since its form is analytical and well characterized, but not one of the basis functions used in the analysis.

The experimental data is processed to account for experimental and geometric factors before being analyzed by separation into the Legendre polynomial series. We account for the following:

1) Crystallinity in the sample (as necessary)
2) Incoherent scattering, also known as Compton or multiple scattering events (section 2.2.3.1)
3) Self-scatter or uncorrelated electron gas scattering (section 2.2.3.1)
4) Normalization of the data to theoretical atomic units (section 2.2.3.2)

Subsequently, the coefficients can be compared to those that are derived or known from other sources (generally from theoretical calculations derived from a molecular model). The experimental and theoretical sets of coefficients are related to the each other as follows:

$$A_{2n}(s) = D_{2n} \cdot A_{2n}^{calc}(s) \quad (2.3)$$
That is, the experimental coefficient, $A_{2n}(s)$, on the left hand side is proportional to the theoretically calculated one, $A_{2n}^\text{calc}(s)$ by a scaling coefficient, $D_{2n}$. Note that only the structure factor coefficients (and not the scaling coefficient) are functions of the scattering vector. Thus, features between the two traces must correspond. The better the agreement between experimentally observed structure factor traces and the calculated ones, the more confidence we may have in our use of the scaling coefficients, $D_{2n}$. The $D_{2n}$'s are also the coefficients in an analogous Legendre polynomial series reconstruction of the ODF, $D(\alpha)$:

$$D(\alpha) = \sum_n D_{2n} \cdot P_{2n}(\cos \alpha) \quad (2.4)$$

Therefore, one of the keys to the analysis of these traces is determining the "correct" scattering unit that is associated with the ODF that is being determined. Here, "correct" implies that the features of the two set of coefficients match. Deriving such a model will be discussed subsequently in detail. For the time being, it is sufficient to say that there is no general model or technique that will always provide the explicit atomic coordinates that produce the desired calculated structure factor coefficient traces. Such a model must be built via a certain amount of experience and intuition.

One of the major advantages of the Legendre polynomial series analysis is that the overall pattern is separated into contributions which are easier to handle individually. Thus, the individual contributions to the pattern due to various factors can then be elucidated. That is, a particular "scattering unit" is chosen and the structure factor of that scattering unit are found in the radial or magnitude component of the separation of variables. The orientation of that particular scattering unit is then completely reflected only in the orientation distribution of the WAXS pattern.

The key to this analysis, then, is the proper elucidation of the "scattering unit" in the theoretical structure factor calculation. The proper scattering unit could be as simple as a monomer or as complex as a multichain structure, but for the purposes of the structure factor calculation must have explicit atomic coordinates (assuming that the
atomic structure factors are to be used). The range of interactions incorporated into the model ensemble is determined by the angular scattering range under inspection (i.e. the experimental data). For example, for most of the work presented in this thesis, we looked at a range of $2\theta = 10^0 - 50^0$, which implies that the most appropriate atomic pair spacings, $d$ (from Bragg's Law: $n\lambda = 2dsin\theta$), should range between values of $d = 8.84 \text{ Å} - 1.82 \text{ Å}$. This scattering vector range also corresponds to a reciprocal spacing ($s$, the scattering vector in reciprocal space, $s = 4\pi\sin\theta/\lambda = 2\pi/d$) range of $s = 0.710 \text{ Å}^{-1} - 3.44 \text{ Å}^{-1}$. Additionally, because the intensity of higher order reflections in WAXS of polymers tend to fall off fairly quickly, we expect that it will not be necessary to consider atomic scattering distances greater than a given cut off (somewhere in the $10\text{Å} - 20\text{Å}$ region).

2.2.1 Semi-Quantitative Interpretations of the $P_{2n}(\cos\alpha)$ Functional Forms

Before immersing ourselves in the full series expansion analysis, we present a semi-quantitative discussion of the functional forms of our basis functions, the Legendre polynomials. Appendix 8.3 gives the basic formulae (recursion and otherwise) for the Legendre polynomials. Appendix 8.3 also plots the functional forms for the Legendre polynomials up to $2n = 10$. In the appendix, we discuss the most rigorous definitions and forms of the Legendre polynomials. For our purposes here, we will be restricting the discussion to highlighting certain, semi-quantitative trend behavior.

$P_0(\cos\alpha)$ is unity for all values of $\cos\alpha$. This implies that it is a constant-valued function and as such, the $P_0(\cos\alpha)$ trace is a spatially averaged representation of the data. For axisymmetric geometries such as fibers, it is only azimuthally averaged (since the data as collected is already equatorially averaged).

$P_2(\cos\alpha)$ and the higher order Legendre polynomials may be viewed as the anisotropic contributors to the WAXS pattern. $P_2(\cos\alpha)$ would have intensity localized either parallel or perpendicular to the axis of symmetry (the fiber axis). Note, that the sign of the $P_2(\cos\alpha)$ coefficient specifies which axis has more intensity. A positive $P_2(\cos\alpha)$
would indicate the fiber axis, a negative $P_2(\cos \alpha)$ indicates positive intensity lateral (or perpendicular) to the fiber axis. Similarly, a negative $P_4(\cos \alpha)$ would be the localization of scattered intensity in the off-axis positions, while a positive $P_4(\cos \alpha)$ would result from contributions either parallel or perpendicular to the fiber axis. Therefore, these relative scattering positions correspond to the distribution of atomic spacing that were oriented in that particular direction. Another characteristic of the Legendre polynomials is the fact that higher index terms have narrower feature breadths. This implies that one can judge the “sharpness” of a given feature by the number of terms in the series required in the series expansion.

One would note the key to a good model would be to satisfy the macroscopic orientation constraint and the molecular-scale constraints, i.e. to ensure that the Legendre polynomial series features were reproduced while the composition and connectivity constraints were also met.

2.2.2 2-D WAXS Data Visualization: Fiber Diagrams

Fiber diagrams are a method to visualize WAXS data in two dimensions. Figure 2.2 shows a typical fiber diagram. In this case, the data are of hiq40fsa fibers.

Figure 2.2: An example of a fiber diagram showing broad and narrow features. The sample is HIQ-40 unannealed solution-spun fiber.
The diagram is a polar plot, where the 2θ direction is the radial coordinate and the azimuthal angle, α, corresponds to the angular or polar coordinate, α. The scattering intensity is then the dependent variable and is plotted as a contour level. Throughout this thesis, we will use the convention that the fiber direction (commonly referred to as the meridional direction) is α = 0° and perpendicular to the fiber axis (as known as the equatorial direction) is α = 90°. Since there are only two independent variables, the data is straightforward to visualize, requiring no projections or convolutions of either dimension to allow representation on a two-dimensional surface. The fiber diagram may be envisioned as a series of one-dimensional scans (θ/2θ) at various values of α.

Note in this fiber diagram, it contains an “amorphous halo” at 2θ = –20°, which stretches from the meridian to the equator and that this halo is asymmetric in the azimuthal direction, since the intensity at the equator is higher than that on the meridian. There are also features located on both the equator and meridian located at 2θ = ~45°.

2.2.3 Case Study: HIQ-40 As-spun Solution-spun Fiber: Experimental Results

The WAXS fiber pattern obtained was from a set of fibers as received from Hoechst-Celanese. They are HIQ-40 solution spun fibers. The fibers were 42.6μm (±0.6μm) in diameter as measured by optical microscopy. For more information on the basic characterization of these fibers (and others in the HIQ-40 series) see Chapter 3. The hiq40fsa fibers contain a negligible degree of crystallinity as detected by WAXS. However, the 2-D WAXS fiber pattern does display spatial scattering anisotropy. Even without assuming a model (and therefore without either presupposing a molecular-scale description or performing the structure factor calculation on that model), the experimental results from the hiq40fsa fiber may still be used to gain valuable insight into the sample fibers and into the series deconvolution analysis.

The experimental fiber pattern was taken using a Rigaku RU200B rotating copper
anode. The wavelength of radiation for the K\textsubscript{α} emission from copper is 1.54Å.

Scattering data was taken over an angular range of 2θ = 10° - 50° with steps (i.e. Δ2θ) of 0.1°. A pole figure attachment off of the θ/2θ goniometer allowed us to take sixteen θ/2θ traces over the entire azimuthal angular range, α = 0° - 90° with Δα = 6°. Since we were not dealing with crystalline scattering (except insofar as to remove it from the fiber pattern, if it is there), multiplicity which normally must be accounted for, is not a factor here.

2.2.3.1 Self-Scattering and Multiple Scattering Events

We were required to account for a number of other sources of scattering information. Figure 2.3 shows the functional forms of the Compton scattering, I\textsubscript{comp}, (multiple scattering events) and the self-scattering summation, Σf\textsuperscript{2} (commonly referred to as free electron gas scatter).

![Compton and Self Scattering Contributions](image)

**Figure 2.3:** Compton scattering, I\textsubscript{comp}, and the self-scattering summation, Σf\textsuperscript{2}, as functions of the scattering vector, s, where s = 4πsinθ/λ.

The data is taken from the International Tables of X-ray Crystallography [Henry, N., 1969]. The reason that we must remove the self scattering and the Compton scattering is so that the experimental data contains only the single scattering event data and
therefore may be compared to the theoretical calculations (in which only single
scattering events are accounted for).

2.2.3.2 Normalization
Before we can truly compare experimental and theoretical calculations, it is necessary
to normalize the data to some standard. To do this, we use the method of Krogh-Moe,
The method of Krogh-Moe for normalization of the experimental data to theoretical
units requires us to determine the normalization factor, \( k_{k-m} \), via the following equation:

\[
\begin{align*}
  k_{k-m} &= \frac{\int s^2 I'(s) ds - 2\pi^2 Zp}{\int s^2 I_{\text{raw}}(s, \alpha) \sin \alpha ds ds} \\
  &\quad (2.5)
\end{align*}
\]

where the numerator is comprised of two terms. The first is an integration over the total
theoretically uncorrelated scattering, \( I'(s) \) being comprised of the coherent self-scatter
and incoherent Compton scatter of all of the atoms in the specimen. We are required
to know the composition of the material to calculate either the self- or Compton scatter.
The second numerator term is the zero-angle scattering energy term, where \( Z \) is the
total electron charge and \( \rho \) is the atomic density of the material. The denominator of
the normalization factor is just the total area integration over the entire fiber pattern,
\( I_{\text{raw}}(s) \) being the raw experimental intensity. By equating the total experimental and
theoretical scattering intensities, the trace can be scaled to the realm of the theoretical.
The normalization constant is then applied to the experimental data and the self-scatter
sum, \( \Sigma f^2(s) \), and Compton scatter, \( I_{\text{comp}}(s) \) are subtracted from renormalized data. This
is shown mathematically in Equation 2.6:

\[
I_{\text{ex}}(s, \alpha) = k_{k-m} I_{\text{raw}}(s, \alpha) - I_{\text{comp}}(s) - \sum f^2(s) = k_{k-m} I_{\text{raw}}(s, \alpha) - I'(s) \quad (2.6)
\]

where \( I_{\text{ex}}(s, \alpha) \) is the renormalized experimental data which may now be analyzed via
the Legendre polynomial series expansion analysis.
After the application of Equation 2.6, the experimental trace has been normalized to atomic units (au), a measure of the theoretical scattering power of the material on a per atom basis. Because we have both shifted and rescaled the data, it may be considered a reallocation of scattering intensity from the uncorrelated average, I'(s), which was subtracted out. Thus, the resultant fiber pattern contains both positive and negative regions. The termination criteria chosen for the series was to resolve the experimental data to within 10% over the entire trace. This required 4 terms in the Legendre polynomial series (2n = 0 - 6) for the hiq40f4sa fibers. Figure 2.4 contains 4 parts, showing the raw observed data, the fiber diagram reconstruction from the Legendre series expansion, the difference between the two sets of fiber patterns, and the coefficient traces used for the reconstruction. As expected the first two diagrams have a similar visual appearance. The difference pattern, part c), has no discernible features, but is a random array of noise with both positive and negative values. The coefficient traces, parts d), also take on positive and negative values based on the azimuthal contribution of the corresponding Legendre polynomial. For example, the A_2(s) trace shows a negative coefficient value for the broad feature at θ = 20.3°. We know that the P_2(cosα) is negative near α = 90°, i.e. near the equator. Thus, the negative value of A_2(s) at 20.3° implies that the A_2(s)P_2 (cosα) term in the Legendre polynomial series would have a positive contribution on the equator (i.e. at α = 90°) of the fiber diagram. Similarly, for the peak in the A_2(s) trace at θ = 44.6°, the coefficient is positive, meaning that when P_2(cosα) is positive (at α=0° on the meridian) the A_2(s)P_2 (cosα) term would have a positive contribution.

The location of the peaks which comprise the coefficient traces of the experimental data remain consistent throughout each of the traces and are all present in the case of n = 0, since the term is a constant. In principle, the n = 0 term is equivalent to an azimuthal average of the scattering intensity at a given scattering distance (i.e. s). There are three consistent peaks in the coefficient traces.
Figure 2.4: Reconstruction of HIQ-40, as-spun, solution spun fiber. a) raw data, b) reconstructed data from the legendre series, c) subtraction of b) from a), d) experimental coefficient traces, $A_{2n}$ for $2n = 0 - 6$. All contour plots have 100 counts/contour: a) & b) 15 contours c) 3 contours

Table 2.1 summarizes the peak positions.

<table>
<thead>
<tr>
<th>Peak</th>
<th>$2\theta$ (°)</th>
<th>$d$ (Å)</th>
<th>$s$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>20.3</td>
<td>4.375</td>
<td>1.436</td>
</tr>
<tr>
<td>Peak 2</td>
<td>27.1</td>
<td>3.291</td>
<td>1.909</td>
</tr>
<tr>
<td>Peak 3</td>
<td>44.6</td>
<td>2.033</td>
<td>3.091</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of Spacings in hiq40fsa Experimental Coefficient Traces
Coefficient traces resulting from the series deconvolution may not have an immediately obvious physical interpretation. The traces represent the convolution of the scattering due to spacings oriented in a particular direction, or more accurately, the spacings that are oriented in a distribution that closely matches the functional form of a particular Legendre polynomial. The more a given spacing has a distribution that approaches that represented by the Legendre polynomial, the greater its contribution to that particular term in the series expansion.

2.3 The Molecular Model

Since, we are primarily interested in the oriented phase of the non-crystalline portion of our aromatic polyesters, we should employ a model which already incorporates some of those ideas. Particularly, since we are looking at an oriented phase, we can assume that some aspect of our system is anisotropic and that aspect of the system can be used as a reference. In 2-D, the focus of this anisotropy is the chain direction on the molecular scale and the fiber axis on the sample or laboratory scale. As noted previously in Chapter 1, polyarylates have reasonably high persistence lengths (on the order of 10Å - 100Å). Given this fact, as well as the fact that the size scale of WAXS is much less than that, we can safely assume that construction of a reasonable molecular model can center about the aligned chains and their packing behavior.

Starting with this supposition of aligned chains, we can then design a method by which the model grows in detail. In our case, we move from generating the single chain to placing them on a two-dimensional lattice. By varying the lengths of chains and the lattice parameters, we can simulate various chain conditions and therefore, get an idea of the nature of packing and interchain interactions in these materials.

2.3.1 Single Chain: Rotational Isomeric States (RIS)

Our efforts to model the solid state begin with the determination of the structure factor of a single chain. While the single chain is only a valid model for the gaseous state, it
also serves to introduce the concept of the intrachain scattering and allows us to interpret various features of the WAXS patterns and series expansion structure factor coefficient traces.

Building a realistic single chain is not trivial. [Rutledge G., 1992] Our simulations build chains ranging from monomers to oligomers of up to 15 units in length. Chains of this length should be more than adequate to capture the intrachain scattering that might occur since, the average contour length of a 15-unit oligomer is ~80Å and the interaction distances that we are primarily interested in are < 20 Å. Using such a large molecule is not necessarily wasted effort, since subsections of the chains can be considered separate and lead to additional averaging (i.e. an 80 Å chain may be viewed as approximately four 20Å chains) which implies that each chain produced adds multiple, uncorrelated distances to the ensemble.

Rutledge [Rutledge, G., 1992] used a Rotational Isomeric States (RIS) algorithm to create his chains. RIS reduces the number of states that need to be sampled by modeling the continuous torsion potential energy map as a set of finite and discrete energy states (rotational isomers). [Flory, P., 1989] While this assumption may seem rather restrictive, energetic considerations require that the molecules likely spend the most time in configurations incorporating these torsion potential minimums. Thus, when we sample them to exclusion of less energetically favorable torsions, it is not a gross error. By discretizing the energy map of the torsion potentials into only a few states (maximum of 4 different torsion states, in our case), the number of sampled states (and thus the size of parameters space) is drastically decreased. However, because this method utilizes those few states based upon where minimums occur in the bond torsion potentials, we do not create an unreasonable bias in the configuration space that we are sampling. Statistically speaking, most of the bond torsions in the backbone should be found in lowest energy states. The large number of possible conformations of a single polymer chain made it necessary to institute a method by which an reasonable ensemble of chain structures could be generated.
2.3.1.1 Intrachain Parameters
The parameters that are incorporated into the chain are the bond lengths, angles and torsions. The simulation assumes fixed bond lengths and angles. The backbone of these material is known to be fairly inflexible, so this is a fair assumption. The torsion angles chosen varied depending on which backbone component was chosen. Phenylene rings were chosen to be either in the plane of the ester group, if bonded to a carbonyl carbon, or were allowed to assume one of four states rotated out of the plane of ester (±45° or ±135°), if bonded to an ester oxygen. The ester torsion about the O-C bond in the backbone was allowed to vary freely between ±30° from the planar value. This was necessary to replicate the intrachain spacing in the experimental data at s = 3.027Å⁻¹. Figure 2.5 shows a representative trimer generated by the RIS computer code. Figure 2.5 gives an example of a trimer generated by the simulation and highlights the torsion about the C-O ester bond.

![Torsion about these C-O ester bonds](image)

Figure 2.5: A typical trimer of HIQ-40 as generated by the RIS code. Note the left most monomer relative to the middle monomer. This is due to the ester torsion between them.

2.3.2 Lattices: Monte Carlo Sampling
The packing structure of our polyarylates has been modeled as a two-dimensional lattice. Our reasoning is as follows: the chain packing structure in aligned materials is often seen to be hexagonally close packed. [Galeski, A., 1991(a,b); Bartczak. Z., 1992(a,b)] This is reasonable, since aligned polymeric chains are often envisioned as long (semi-)rigid cylinders. Due to their fairly rigid backbones, the assumption of long rigid cylinders is especially appropriate for our polyarylate materials which have high persistence lengths. [Rutledge, G.C., 1992] The most volumetrically efficient packing
structure for cylinders is a hexagonally closed packed arrangement.

We hypothesize that the local structure of our anisotropic non-crystalline material consists of a collection of polymer chains which are aligned parallel to each other. Thus, we envision these aligned chains as being placed parallel to each other on a distorted lattice. Thus, the lattice is a convenient method of representing the lateral packing behavior of the chains. We randomly choose an RIS generated chain and place it upon the lattice. We do this for all lattice sites in the simulation. Since, the lattice is meant to denote the packing behavior in the solid state, the chain's radius of gyration vector, \( R_{\text{gyra}} \), is calculated and its midpoint is placed on the lattice position and its direction aligned parallel to the z-axis (i.e. perpendicular or normal to the lattice plane). \( R_{\text{gyra}} \) is taken as the eigenvector corresponding to the largest eigenvalue in the radius of gyration tensor. The each element in the radius of gyration tensor for a chain containing \( m \) atoms may be calculated as follows:

\[
S_{jk} = \frac{1}{m} \sum_{i=1}^{m} x_{ij} x_{ik} - \frac{1}{m^2} \sum_{i=1}^{m} x_{ij} \sum_{i=1}^{m} x_{ik}
\]  

(2.7)

\( S_{jk} \) is the element in the radius of gyration tensor. \( x_{ij} \) is the coordinate, \( x_{i1} (= x) \), \( x_{i2} (= y) \), or \( x_{i3} (= z) \), for atom \( i \). \( R_{\text{gyra}} \) is a true measure of the chain director, because the chain backbone is not guaranteed to be absolutely straight. In the case of HIQ-x, the polymer chain contains \( m \)-phenylene moieties (and thus 60° kinks, via its isophthalic acid constituents), so this is especially true. Since explicit atomic coordinates are known for each structure in the molecular ensemble, determination of the radius of gyration is straightforward. Figure 2.6 shows a bird's eye view of the lattice building algorithm. It shows the parameter inputs (\( a, b, \) and \( \gamma \)), as well as the counterclockwise
spiral order upon which the RIS generated chains are placed on the lattice.

![Diagram of 2-D lattice](image)

Figure 2.6: Schematic of the 2-D lattice used in our simulations. \(a, b, \) and \(\gamma\) are the lattice unit cell parameters. Chains are placed in a counter-clockwise spiral.

Because of the large number of possible packing structures available to the RIS-generated chains, it was necessary to institute a method by which a reasonable ensemble of packing structures could be generated. The use of a Monte Carlo algorithm to generate such an ensemble was employed. Monte Carlo (MC) sampling is a method in which steps (individual structures, in our case) in the simulation are accepted or rejected based on a random number compared to a probability. In MC simulations, the probability of acceptance is related to a discriminating "quantity" in the simulation. Generally speaking, as this quantity approaches 0, the probability of accepting an MC step tends to 1, while at the other limit of the quantity approaching infinity, the probability tends towards 0. Most MC simulations chose energetics as their probability basis, but in principle, any property may be used. [Metropolis, N., 1953] The effect of Metropolis Monte Carlo sampling is to weigh or bias random sampling such that parameter space maybe sampled more efficiently. Steps which are less probable are less likely to be accepted and thus, less likely to be incorporated into the simulation results. [Rutledge, G., 1992]

Our use of MC sampling is to take a set of generated chains and to try and place them upon a lattice. Acceptance of the test structure into the molecular ensemble is based on two criteria: a geometrical or steric constraints (via a hard-core interaction model, which can be thought of as a two-state energy potential) and a "measure of merit" (via a comparison to experimental data).
An analogy for the measure of merit criterion can be drawn. The measure of merit can be viewed as a full-pattern refinement of the WAXS data. This is similar to a Rietveld analysis, which generates a structure factor based on an assumed structural model. In a Rietveld analysis, the calculated structure factor is compared to the experimental WAXS pattern through a sum of squared deviations calculated over the entire pattern. The parameters of the model are then refined to minimize this sum of squared deviations. Conceptually, our measure of merit analysis is quite similar. We use the full pattern to generate a series of coefficients which are then compared to calculated coefficients based on model. However, there are a couple of differences. Our analysis makes no explicit assumptions about the structure of the material. Generally, a Rietveld analysis is based on an explicit atom lattice model and used to fit the model parameters to generate the desired crystalline diffraction peaks. Thus, the analysis is a single calculation for a given set of model parameters. [Fu. Y., 1994, Busing, W., 1990]

In contrast, our analysis is based on modeling the non-crystalline material in a sample, so we are required to use a set of model parameters to construct our chains and lattice and take an ensemble average of their structure factors. Our structure factor calculation is computationally more expensive and must be repeated, but is also more general. Additionally, because the Rietveld analysis is generally based upon a crystalline model, assumptions must be made about the forms of the non-crystalline background of the pattern. In contrast, our analysis uses only a set of basis functions and does not explicitly define the functional form of the non-crystalline scattering. Thus, while related to our analysis, the Rietveld analysis is a “cousin” which falls under the same general category of the full-pattern refinement.

2.3.2.1 Interchain Parameters

Since we are dealing with a lattice model of sorts, the primary adjustable parameters are the lattice cell distances and the angles. Variations about the average unit cell distances were allowed. For all of our simulations, the displacements of the chains from the average lattice position were allowed to vary in a uniform distribution by up to ±50% of the average value. In the terminology of Hosemann, these are variations about
ideal lattice positions, or Type I distortions, and as such their primary effect in the calculations derived from ensembles using this averaging is that the feature intensity will be attenuated. The intensity being relegated to increasing the background and the feature shape does not appreciably change. [Hosemann, R. 1950, 1962] We will discuss paracrystalline order, a bit more in depth in section 2.3.4.

We used a two-dimensional lattice with random displacements from average positions. This was deemed to be the most expedient way to describe our aligned chain system, despite the fact that we desire to look at the uncorrelated packing structure of our materials. The portion of the scattering pattern that we are most interested in is, in fact, partially ordered. Also, a hexagonal closed packed (HCP) or other variant on a lattice can often be most easily described as a distortion from the rigid crystalline unit cell. This is especially true in light of the fact that we only deal with static structures and not a dynamic simulation which might correlate previous structures.

2.3.3 Alterations and Modifications to the Rutledge Code

The computer code used in this work is an extension of code developed by Rutledge [Rutledge, G., 1992] in his studies and simulations of HIQ-x chains. To summarize, he placed RIS-generated chains at random onto a two-dimensional lattice of average positions. The RIS-built chains incorporate the intrachain effects and the lattice model incorporates the solid state packing (or interchain effects). Since the chains are built before being placed on the lattice and the simulated structure is not allowed to relax energetically, the lattice does not influence the chain conformation, except when rejected due to a hard sphere overlap.

We summarize how the code used in this thesis work varies from Rutledge’s in the following list:

1) The only energetics incorporated in the simulations were via hard-core interactions (this is primarily a geometric constraint and only a crude energetic approximation).
2) None of the energetic optimization calculation option in the code were utilized.
3) Output is the structure factor coefficients of the spherical harmonic series expansion analysis for the generated molecular ensemble.

4) The structure factor of the simulated ensemble is used for comparison to the experimental data, which in turn, is used as one of the criteria for acceptance of a structure into the ensemble. Thus, the measure of merit parameter, $\beta_x$, was introduced.

These modifications were required for the reasons delineated below. Because we are dealing with a static structure calculation, the energy calculating subroutines in the code were not necessary for our purposes. In order to compare our simulation results to the experimental data, we were required to introduce a subroutine which derived the structure factor coefficients based on the atomic positions of the atoms in the molecular ensemble. The introduction of the "measure of merit" acceptance criterion required the introduction of the $\beta_x$ parameter into the simulation.

2.3.4 Distortions and Paracrystalline Considerations

Practically speaking, the chains are not always placed precisely at the specific lattice position. While the lattice specifies the average positions, some variation about that position is allowed in the directions lateral (i.e. in the plane of the lattice) to the chains. The "absolute position" of a chain is not always a fixed distance from its neighbors. Thermal effects, especially at room temperature (300 K) can cause such variations about a set lattice position. This is a Type I paracrystalline distortion as delineated by Hosemann. [Hosemann, R., 1962] Since we are looking at a partially disordered system, the distortions from the average lattice positions gives our model a method to mimic this disorder.

We did not allow longitudinal variations in our simulations. The reason for this is that given the RIS-generated chains already encompass variations in composition and the MC sampling should generate any given interchain interaction in time. Thus, shifting a chain longitudinally should will produce no additional types of interactions that the model does not already incorporate.
While the simulation did encompass Type I distortions, Type II paracrystalline distortions were neglected. In brief, Type II distortions consist of placement of lattice sites, not as distributions about set positions, but as distributions about set distances from nearest neighbors. That is, previous distortions in the lattice have a tendency to compound in a given direction based on the additive nature of the distortions. This type of paracrystalline lattice distortions were not considered for the following reasons. At the distances that we are concerned with, the nature and influence of Type II distortions will not be readily apparent and are reasonably approximated with Type I distortions, which are incorporated. Tied to this fact, the size of the lattices involved (at a maximum of 5x5) are not large enough to effectively incorporate Type II distortions. Hosemann indicates that long range order is more effectively disrupted in Type II, but the number of sites indicated as necessary for this is still much greater than five.

2.3.5 Structure Factor Calculations

Given a molecular ensemble, a structure factor can be calculated as a function of the scattering angle. By assuming the separation of variables implicit in the series expansion analysis, the intensity, which is a function of the scattering vector, may be broken up into individual components, which are functions of single variables only. This deconvolution of the various contributions to the scattering intensity may be viewed as a simplification of an otherwise mathematically complex (as well as very expensive computationally) problem. From the Legendre polynomial series expansion, the coefficients ($A_{2n}(s)$) of the Legendre polynomial terms are solely functions of the scattering vector magnitude. Given an explicit atomic coordinates model (such as delineated in the previous sections), we can calculate an equivalent structure factor coefficient ($A_{2n,\text{calc}}(s)$) for the model ensemble and compare them to the $A_{2n}(s)$.

From a general scattering equation, such as one from Guinier [Guinier, A., 1963] (see section 1.4.1.1), we can derive an explicit expression which computes the structure
factor coefficient as a function of the scattering vector:

\[ A_{2n}^{\text{calc}}(s) = \sqrt{\frac{(4n+1)}{N}} \sum_{j}^{N} \sum_{k \neq j}^{N} f_j(s)f_k(s)J_{2n}(r_{jk}s)P_{2n}(\cos \alpha_{jk}) \]  \hspace{1cm} (2.8)

Equation 2.8 is a summation of contributions by all of the atom pairs in a given structure. For proper use of the equation, all atoms types and relative distances must be known. Equation 2.8 has four main parts: a prefactor, the atomic scattering factors for a given atom pair, an even-integer order Bessel function, and a weighting distribution. The prefactor is an outgrowth of the orthogonality of the basis functions and ensures proper proportion between coefficient traces and that the calculated coefficient is scaled to a per atom basis. \( f_j(s) \) and \( f_k(s) \) are the atomic scattering factors for each of the atoms in a given pair. The summations denote that we sum over all atom pairs. The Bessel function, \( J_{2n}(r_{jk}s) \), is derived from the symmetry of the sample scattering geometry. The Legendre polynomial is a basis function to relate the structure factor calculation to the axisymmetric coordinate system (and the analysis in general). \( r_{jk} \) is the distance between atoms \( j \) and \( k \) and \( \alpha_{jk} \) is the angle between the vector connecting atoms \( j \) and \( k \) and a reference axis (the fiber axis in our case).

Note, that Equation 2.8 makes no assumption about the connectivity or relationship of the atomic distances relative to one another. As is generally the case with scattering, only a bulk average of spacings is given. How those spacings are related to each other is a matter of interpretation. To go any further, some other set of observations, assumptions, and information must be invoked, which is the point of the molecular model we are postulating.

The structure factor calculation highlights one of the aspects of the model. The summation in calculation is over all of the explicit atomic pairs. Because the model does not make use of periodic boundary conditions, the lattice size effectively limits number and distance of the interactions reproduced in the model. Our long range interactions are effectively set to zero. In relation to Hosemann paracrystallinity
distortions, unlike the gradual decay of order seen with large Type II paracrystalline lattices, our simulation cuts off long range interactions abruptly. Essentially, we have approximated the decay with a step function. The fact that we limit our lattice size means that our simulation does not incorporate any effects or influences outside of its boundaries.

2.3.6 Structure Acceptance Criteria for the Ensemble
Once we have the ability to calculate a comparison to the experimental data, we have to determine proper conditions for acceptance of a given structure into our molecular ensemble. We have two means to do that and utilize both within the simulation. One is the geometrical constraint of non-overlapping atoms (often referred to as hard-core potential) and the other is a “measure of merit” criterion which accepts a particular structure based on whether its scattering improves the fit of the theoretical calculation with respect to the experimentally derived coefficients.

2.3.6.1 Configuration Acceptance in Monte Carlo Sampling
General Monte Carlo sampling is a method where one samples parameter space at random and deduces the probability (and hence the contribution to the statistical mechanical partition function, Z) of that set of parameters by weighting them with a Boltzmann factor, \( \exp(-E/kT) \). The Metropolis Monte Carlo sampling technique (also known as “importance sampling”) is a variation on the standard Monte Carlo method. In Metropolis MC, a given configuration in parameter space is weighted by the Boltzmann factor. Subsequently, that configuration's contribution to the partition function is weighted evenly (i.e. without the Boltzmann factor, which already been accounted for). This has the effect of sampling parameter space more effectively without biasing the final result. [Metropolis, N., 1953]

2.3.6.2 Hard Sphere Overlaps: \( K_{vdw} \)
The first ensemble acceptance criterion is a steric or geometric constraint: hard-core interactions, also referred to as hard-sphere overlaps. To model this we introduce the
hard sphere interaction volume, \(d_{\text{hard sphere}}\). This is the simplest energetic constraint that can be placed upon a model simulation. The potential function used has only two values and is solely a function of the distance between the two atoms, \(d_{12}\). For \(d_{12} > d_{\text{hard sphere}}\), the energy of interaction, \(E\), is zero (and therefore, all distances have equal Boltzmann weighted probabilities) and for \(d_{12} < d_{\text{hard sphere}}\), the energy of interaction is infinite (again, all distances here are equally unlikely, having the same infinitely high energy). In mathematical terms, we express these criteria as:

\[
\begin{align*}
&\text{if } d_{12} \geq d_{\text{hard sphere}}, \text{ then } E = 0 \\
&\text{if } d_{12} < d_{\text{hard sphere}}, \text{ then } E = \infty
\end{align*}
\]

Estimates of proper \(d_{\text{hard sphere}}\) can be made via two routes: 1) the excluded volume integral and 2) as a function of the Van der Waals radii. Both types of analysis deal with functional forms of the potential energy curve as a function of distances. Both functional forms consist of two parts, short-range repulsive term and a long-range attractive portion. When these two competitive portions equal each other, one can argue that the forces balance and that is the "proper" interaction distance.

The excluded volume distance, \(d_{\text{excl. vol.}}\), is calculated from the 9-6 energy potential.

\[
E(d_{12}) = \varepsilon \left[ \left( \frac{\sigma}{d_{12}} \right)^9 - \left( \frac{\sigma}{d_{12}} \right)^6 \right]
\]

where \(\sigma\) and \(\varepsilon\) are characteristic parameters for each atom type and whose values may be found in Biosym's CFF91 forcefield file. [MSI Simulations Inc, 1994] The excluded volume (B) integral was solved numerically using Maple V [Waterloo Maple Inc., 1996] and is of the form:

\[
B = 4\pi \int_{d_{12}}^{\infty} \left[ 1 - \exp \left( -\frac{\varepsilon}{kT} \left( \frac{\sigma}{d_{12}} \right)^9 - \left( \frac{\sigma}{d_{12}} \right)^6 \right) \right] d(d_{12})
\]

The final form of the integral, utilizes a change of variables, in which \(x = (\sigma/d_{12})^3\).
Substituting this variable transformation into Equation 2.10 yields:

\[
B = \frac{4\pi\sigma}{3} \int_0^\infty x^2 \left( 1 - \exp\left( -\frac{e}{kT} \left( x^3 - x^2 \right) \right) \right) dx
\]  

(2.11)

Table 2.2 shows the distances at which this balance point occurs in the excluded volume integrals (i.e. \(d_{12} = d_{\text{excl.vol}}\) when \(B = 0\)) and compares these values to the Van der Waals radii are for the various types of atoms in our aromatic polyesters:

<table>
<thead>
<tr>
<th>Atom Type</th>
<th>(C_{ph})</th>
<th>(C^*)</th>
<th>(O')</th>
<th>(O)</th>
<th>(H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma)</td>
<td>4.01</td>
<td>3.308</td>
<td>3.535</td>
<td>3.535</td>
<td>2.995</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>0.064</td>
<td>0.12</td>
<td>0.267</td>
<td>0.240</td>
<td>0.02</td>
</tr>
<tr>
<td>(d_{\text{excl.vol}})</td>
<td>2.0635</td>
<td>2.1314</td>
<td>2.4040</td>
<td>2.3396</td>
<td>2.0183</td>
</tr>
<tr>
<td>(d_{vdw})</td>
<td>1.96</td>
<td>2.03</td>
<td>1.60</td>
<td>1.60</td>
<td>1.37</td>
</tr>
<tr>
<td>(d_{vdw}/d_{\text{excl.vol}})</td>
<td>95%</td>
<td>95%</td>
<td>67%</td>
<td>68%</td>
<td>68%</td>
</tr>
</tbody>
</table>

Table 2.2: Parameters used in Excluded Volume Integrals and a Comparison of the Excluded Volume and Van der Waals Overlap Distances.

For Table 2.2, the following nomenclature is used: \(C_{ph}\) is a phenylene ring carbon, \(C^*\) is a carbonyl carbon, \(O'\) is a carbonyl oxygen, \(O\) is an ether oxygen, and \(H\) is a general hydrogen. The van der Waals radii are obtained from Rutledge's code. [Rutledge, G., 1992] The van der Waals radii, \(d_{vdw}\), are lower than the excluded volume distances calculated. The percentage of \(d_{\text{excl.vol}}\) that \(d_{vdw}\) covers is listed for each atom type as well in Table 2.2.

Our simulations calculate \(d_{\text{hard sphere}}\) as a percentage of the sum of the van der Waals radii of atoms 1 and 2. That is,

\[
d_{\text{hard sphere}} = K_{vdw} \cdot (d_{vdw,1} + d_{vdw,2})
\]  

(2.12)
Thus, one of the parameters specified in our simulation is $K_{vdw}$. If the value is less than one, then our cutoff is placed firmly within the repulsive core of the atomic interaction distances. Note that a "hard-core potential" is a type of forcefield. The geometric criterion used here can be viewed as conventional Boltzmann sampling based on an energy potential which utilizes only two energy states define using the hard-code interactions above.

However, one should note that the presence of overlaps in the ensemble affects the structure factor calculation only indirectly. The Bessel function, $J_{2n}(r_{jk}s)$, could potentially introduce an overlap artifact in the structure factor calculation based on its shape (e.g., $J_0(x)$ approaches its maximum value of one as $x$ approaches zero). Since, we are only looking at scattering vector magnitudes no smaller than $2\text{Å}$, which implies that any overlaps will likely be much further downfield and thus, will not enter the range of $s$-values that we explicitly define for the simulation. However, if we chose a $K_{vdw}$ too small (and decrease the allowable distance between atoms in the ensemble) overlap artifacts would become much more prevalent in the structure factor calculation.

2.3.6.3 Measure of Merit
The second acceptance criteria we utilize is a "measure of merit." We compare the theoretical structure factor coefficients to their experimental counterparts; the level of "agreement" between the two is the measure of acceptance of the structure into the simulation ensemble. In order to make the comparison, we introduce $\beta_\chi$, and define it as follows. In this case, the objective function:

$$\text{OBJF} = \chi_i^2 = \frac{1}{n_{2n}n_s} \sum_{k} \sum_{2n} \sum_{s} \frac{1}{i} (A_{2n}(s) - D^{' \text{calc}}_{n_{2n}}(s))^2$$

which simplifies to an average value based on all $i$ previously accepted structures. As
shown below in Equation 2.14:

\[
\chi_i^2 = \frac{1}{n_{2n}^i} \sum_{j=1}^{n_{2n}} \sum_{s} \langle (\Delta A_{2n}(s))^2 \rangle_i
\]  

(2.14)

\(\chi_i^2\) is a sum of least squares deviations between the theoretical and experimental structure factor coefficients. The theoretical coefficients must be scaled for the comparison. Since, the test scaling parameters, \(D'_{2n}\), are unknown, we must find the \(D'_{2n}\)'s which gives the lowest \(\chi_i^2\) for the ensemble incorporating the new structure. \(\chi_i^2\) is then used as a basis for an acceptance probability. Note \(\chi_i^2\) behaves as a proper discriminating variable (see section 2.3.2), as \(\chi_i^2\) tends to zero, we would desire to accept the new structure into the ensemble, as the theoretical structure factor deviates very little from the experimental. If the addition of the new structure leads to large deviations in \(\chi_i^2\), then we would not desire to add the new structure to our simulation ensemble. The criteria is used to measure the “measure of merit” of the currently generated structure as it adds to the ensemble average. The structure factor coefficient is calculated for the new structure and added into the average structure factor calculated for all other accepted structures. If the fit is improved, the new structure is automatically accepted into the ensemble. However, if the fit is not improved, there is still a finite chance that the structure will be accepted. The probability of acceptance is equal to the exponential of the magnitude of the decrease of fit encountered by the addition of the structure in question, divided by the square of the weighting factor, \(\beta_x\). A random number between 0 and 1 is drawn and compared to the probability. If the number is higher than the probability the new structure is rejected. If the random number is lower or equal to the probability of acceptance the structure is accepted.

Mathematically, both acceptance criteria can be combined and summarized as follows, the total probability of acceptance equal to the product of the two individual probabilities:

\[
P_{i-1,i} = P(E) P(\chi_i^2)
\]  

(2.15)
The criteria for this set of probabilities is then:

\[
\text{if } d_{jk} < K_{\text{vdw}}(d_{\text{vdw},j} + d_{\text{vdw},k}) \text{ for any pair of atoms } j \text{ and } k
\]

then \( P(E) = 0 \), else \( P(E) = 1 \)

\[
\text{if } \chi_i^2 \leq \chi_{i-1}^2
\]

then \( P(\chi_i^2) = 1 \)

\[
\text{if } \chi_i^2 > \chi_{i-1}^2
\]

then \( P(\chi_i^2) = e^{-(\chi_i^2 - \chi_{i-1}^2)/\beta_\chi} \)

This acceptance probability would be exactly like a Metropolis Monte Carlo algorithm, if instead of squared deviations and \( \beta_\chi \), we used the energy difference between the ensemble fit with and without the new structure. There is one major difference between Metropolis MC sampling and the sampling we do here. \( \chi_{i-1}^2 \) is dependent on all previous structures generated, being an average of all the accepted structure factor calculations up to that point.

The better the features match (i.e. the better the “measure of merit,” conversely the lower the \( \chi_i^2 \) value) between the calculated and experimental traces, the more representative the generated structure is of the local structure in the experimental sample. The measure of merit criterion accomplishes the goal of developing a molecular-scale model which characterizes a given sample. Essentially, we have let the data direct the flow of the analysis. What comes out of the comparison of the coefficients is the orientation distribution function (ODF). The ODF completes the quantitative description of the molecular model relative to the experimental scattering data from a given sample.

What is \( \beta_\chi \)? Primarily, it is a weighting parameter. For a qualitative physical interpretation consider the following limits on \( \beta_\chi \). If \( \beta_\chi \) is “large,” most (if not all) of the structures generated in the simulation are accepted. If the \( \beta_\chi \) is “small,” the acceptance rate drops and the simulation acts like an optimization, becoming highly discriminating. This implies that \( \beta_\chi \) simulates a type of annealing, allowing one to incorporate a desired level of sensitivity of the simulation to the experimental data. How large is “large” depends on the absolute magnitudes of the data and is especially sensitive to noise.
$\beta_x$ is normalized with respect to the number of points taken, the number of traces compared, and the number of RIS-generated structures accepted.

2.3.7 Model Heuteristics: Getting a good first guess

One of the key goals in elucidating the correct structure is not only finding the final structural ensemble, but understanding the steps required to arrive at that ensemble. Ultimately, the matching of experimentally derived coefficient factors is an iterative process. But, it can be done more intelligently than through calculation of all possible structural combinations. A good first guess can be essential in reducing the time necessary to arrive at a reasonable set of structures. There are a number of ideas which can be incorporated into making a good first guess. The two main ones are:

1) A variation on the unit cell structure of the crystalline material in question
2) A hexagonal close packed structure of a given density

Generally speaking, options 1 and 2 often converge to similar (if not the same) routes fairly quickly; understandably so, since often the crystalline structure of a material is often a variation on hexagonal structure. [Bartczak, Z., 1992, Daubeny, P., 1954, Galeski, A., 1988, O'Mahoney, C., 1990] For example, the HIQ-x unit cell is an orthorhombic cell with $a = 3.95\text{Å}$ and $b = 5.58\text{Å}$ and is depicted in Figure 2.7.

![Figure 2.7: Diagram of HIQ-x unit cell. $a$ and $b$ are unit cell parameters and $\phi = \tan^{-1}(b/a)$](image)

As shown in Figure 2.x, the angle $\phi$, which is between the [100] and [110] rays of the two-dimensional lattice is $54.7^\circ$ (i.e. very close to the regular hexagon angle of $60^\circ$). Thus, only a slight distortion from the unit cell is necessary to have the chains arrange
themselves in a hexagonally closed packed (HCP) structure. Conversely, HCP chains in the melt or non-crystalline phase only need to overcome a slight energy barrier to crystallize. The fact that many polymeric unit cells arrange in near HCP order is well established; specific examples include Nylon-6,6 [Galeski, A., 1988] and polyethylene. [Bartczak, Z., 1996]

2.3.7.1 Some Nuances of the Molecular Model
How can one systematically get a cohesive model as delineated from the experimental data? Modeling aids us in relating a molecular-scale picture to the macroscopic observations (in this case, of the WAXS patterns). Again, judicious use of computing power is necessary, since molecular dynamics simulations on full length polymers in the solid state is not yet a reality due to computational speed limitations. However, methods and techniques to gain additional insight with respect to the molecular model and minimal amounts of additional effort are relevant and will be discussed here.

One might hope that one could use the same model molecular ensemble to describe data for all experimental samples. One can use the ensemble derived from comparison of a given experimental sample and compare it to a different sample. The ODF that results would be acceptable only insofar as the calculated structure factor coefficient traces from which it was derived are comparable to the new sample. This comparability is measured quantitatively by the sum of squared deviations between the calculated and experimental coefficient traces, the $A_{2n}(s)$. Put another way, the molecular model and any additional simulation results from the model (e.g. correlations between phenyl ring in the backbone or other pair correlations or the ODF) are appropriate insofar as the match between the experimental and theoretical data is acceptable. Since the structure factor calculation only depends on the static distances between atoms and their atom types, it does not uniquely specify a “molecular condition.” The molecular model incorporates additional information dealing with the material compositions and connectivities. By introducing these molecular-level constraints, we define a subset of solutions that will fulfill all of the criteria, both
macroscopic \( (A_{2n}(s))^s \)'s and microscopic (connectivities and compositions). The use of the RIS and MC algorithms are invoked to produce more efficient sampling, thus, further refining model space.

Once the model is set, further refinements are done iteratively. Since the major features fall on similar spacings for each coefficient trace, we need only focus on matching one or two of the coefficient traces initially. Often, a comparison with the results from the \( A_2(s) \) coefficient traces are also used simultaneously to fitting the \( A_0(s) \) coefficient traces. The \( A_2(s) \) trace contains information about the meridional and equatorial regions of the WAXS traces based on its sign; thus, allowing easily interpretable results to be garnered from the comparison of the theoretical trace with its experimental counterpart.

2.3.8 Simple Examples of the Structure Factor Calculation

In order to ensure that the structure factor calculation code was running correctly and consistently, the following tests were run: a single aromatic polyester chain, a simple two-dimensional lattice with only point masses at the lattice sites (which may be viewed as a lattice of lateral spacings where the chains are all represented as points), and a two-dimensional lattice with real aromatic polyester chains upon it. We are essentially building up complexity in our scenarios systematically. Thus, each step added gives an idea of the salient features of the model and their relative influence on the calculated structure factor coefficient traces.

2.3.8.1 Single Chain

The model and the subsequent computer code may be used in simple cases to verify the proper behavior. The simplest realistic scenario for our purposes is the 1x1 lattice or single chain. This case is considered simple, since no interchain (or packing) considerations are accounted for in the simulation. For our tests, we used a pHBA pentamer with a random setting angle. The output for the single chain case is shown in Figures 2.8 and 2.9.
The temperature and pressure chosen for this simulation were 300K and 1 bar, respectively. 50 RIS-generated chains were randomly oriented and their structure factor coefficients calculated. $\beta_\chi$ and $K_{vdw}$ were not appropriate to this simulation since we were not comparing to experimental data nor dealing with multiple chains per structure.

As can be seen, the calculated axisymmetric structure factor coefficient traces show reasonable behavior. For the pHBA pentamers generated, coefficient traces show the proper behavior; the positions of the features of the structure factor coefficient traces show peak maximums at s-values of $2.105\AA^{-1}$ and $3.072\AA^{-1}$. These reciprocal spacings correspond to d-spacing values of $3.07\AA$ and $2.04\AA$, respectively. These two
values are similar to those listed in the literature for pHBA whose chain axis unit cell parameter is listed as 12.4Å. [Lieser, G., 1976] This c-value yields d-spacings of 3.10Å for the (004) and 2.07Å for the (006) index reflections. Given the wide breadth of the features in the calculated coefficient traces, the fact that the maximums lie within 2% of the literature values gives us confidence in the output of our structure factor calculations.

2.3.8.2 Simple Points/Atoms on a Lattice
The simplest lattice case is one which consists of only one atom placed per lattice site. If there are no displacements from that site (e.g. if one neglects thermal displacements or a Hosemann Type I distortions, see section 2.3.4, for further discussion of the Hosemann paracrystalline types), then the structural ensemble formed is a perfect two-dimensional lattice. Lattice spacings of \( a = b = 5.0\text{Å} \) on a square lattice where chosen. The number of sites chosen were either 9, 25, or 49, (corresponding to lattices of 3x3, 5x5 or 7x7 in size respectively). Figures 2.10 and 2.11 show the coefficient traces of these simulation runs. For the three scenarios, the figures depict comparisons between the various calculated structure factor coefficient traces.

![Graph](image)

**Figure 2.10:** Calculated structure factor coefficient traces, \( A_{0,\text{calc}}(s) \) and \( A_{2,\text{calc}}(s) \), for square lattice of carbon atoms. Lattice sizes are 3x3, 5x5, and 7x7. \( a = b = 5.0\text{Å} \).
Since, this is a simple structure factor calculation, temperature, pressure, $K_{vdw}$, and $\beta_\chi$ are not appropriate and thus, not assigned values.

In comparing the three lattice sizes, we see that the conclusions from the results for the four sets of coefficients run ($2n = 0 - 6$) are similar. All of the coefficient traces show the same overall feature positions, although the feature FWHM (i.e shape) in the larger lattices are narrower and more refined. Larger lattices should lead to narrower features since we are not dealing with periodic boundary conditions and therefore, the size of the lattice effectively denotes the maximum interaction distance in the simulation. Outside of that distance, all of the “other” material is background not contributing to the structure factor calculation. The decrease in feature breadth is a well known understood in crystallography to be due to the nature of reciprocal space. Essentially, the more repeats a given spacing has in a sample in reciprocal space, the more constructive interference it creates. This leads to a shorter peak breadth in real space. [Guinier, A., 1963] The Scherrer equation is mathematical formulation of this particular effect. The scattering distance of $1.26\text{Å}^{-1}$ ($d = 5.00\text{Å}$) is prevalent in the traces, since that corresponds to the distance between the lattice sites specified (5.0Å). These
observations imply that structure factor calculation for the lattice portion of the model is working correctly. One can also note that the coefficient traces display the alternating positive and negative magnitudes of features present when modeling a scattering perpendicular to the reference axis of the series expansion.

2.3.8.3 Real Chains/Molecules on a Lattice
The next step in testing is to replace the single atoms (or point masses) with explicit chains. These have been produced using RIS code developed by Rutledge [Rutledge, G., 1992], as described above in section 2.3.1. For the purposes of the code, which produces only polyarylates, the simplest oligomeric structure derivable was that of poly(1,4-hydroxybenzoic acid) or pHBA. We used a temperature and pressure of 300K and 1 bar, respectively. The $K_{vdw}$ was set at 0.0 and no $\beta_X$ parameter was used. The structure factor coefficient traces for this simulation are shown in Figure 2.12. Twenty-five structures were generated and accepted in the simulation.

By placing pHBA on the same size lattice as in the simple lattice of atoms and studying the effect upon the derived structure factor coefficients, we can discern that the added detail of a real molecule on the lattice structure to the structure factor calculation.

![Figure 2.12: Calculated structure factor coefficients $A_{2n,calc}(s)$ for 3x3 square lattice of pHBA trimers. The lattice is cubic with $a = b = 5.0\text{Å}$](image)

Figure 2.12: Calculated structure factor coefficients $A_{2n,calc}(s)$ for 3x3 square lattice of pHBA trimers. The lattice is cubic with $a = b = 5.0\text{Å}$
We can see that the trimers placed on a 3x3 lattice show a mixture of features of both the lattice and chain. The features are "oriented" correctly as well. The intrachain peaks at 2.105Å⁻¹ and 3.072Å⁻¹ are positive in the A₂,calc(s) trace and the interchain (or lattice) spacing of 1.26Å⁻¹ is negative in the A₂,calc(s) trace. By use of simulations, we can effectively distinguish the individual effects of the inter- and intrachain influences on the coefficient traces (and thus, the WAXS pattern itself). Figure 2.13 denotes the comparison of the A₀,calc(s) traces for the single chain, simple lattice, and lattice with real chains. This graphically highlights the interplay of the lattice and chain features, the real lattice displaying a readily apparent combination of both sets of features.

![Graph showing comparison of coefficient traces for single chain, simple lattice, and lattice with real chains.]

**Figure 2.13: Comparison of single chain, simple lattice, and lattice with real chains structure factor calculations. All chains are pHBA pentamers and all lattice spacings are 5.0Å.**

### 2.3.9 Parametric Evaluations

After establishing that the structure factor calculations for a 3-D structure produced from the model are performing correctly (i.e. as expected), we can then begin to study the behavior of varying parameters in the simulation. For all of our subsequent simulations, the temperature was fixed at 300K and the pressure at 1 bar.
2.3.9.1 Single chain behavior
As the length of a chain increases, we anticipate that certain trends should be observed. This is amply demonstrated by a comparison of simulation runs which vary only in the lengths of the oligomers involved. Figure 2.14 shows an example of the resultant theoretical structure factor coefficient traces for a two-dimensional case, in which \( 2n = 4 \) in runs which varied only the oligomer lengths. We notice two trends: first, the FWHM (Full Width at Half Maximum) of the features decreases with increasing monomer length as shown in Figure 2.15. Second, with increasing oligomer length more features become accentuated and the intrachain peak grows in size relative to the interchain feature near \( s = \sim 1.25\text{Å}^{-1} \). Secondary and higher reflections (\( n > 1 \), in \( n\lambda = 2\text{d}\sin\theta \)) at \( s \sim 1.20\text{Å}^{-1} \) and \( 2.05\text{Å}^{-1} \) become more pronounced at the longer oligomer lengths as well. These reflections are to be expected, since the longer lengths generally leads to more constructive interference of certain scattering distances down the chain. In our case, this is especially germane, since the composition of our chains is primarily ester linkages and phenylene rings. The slight shift of peak positions represents a measure of the sampling error in the simulation.

![Figure 2.14: Comparison of \( A_4(s) \) coefficient traces as a function of the oligomer length](image-url)
Figure 2.15: Intrachain peak breadth as a function of the number of units in the simulated oligomer

2.3.9.2 Lattice parameters

While intrachain factors influence the behavior of the scattering properties of the simulations perpendicular to the plane of the lattice, the spacings that we assign between lattice sites must also affect the average scattering distances observed in the coefficient traces. The results of these studies is shown in Figures 2.16 - 2.17. The series of data are for the simulation of HIQ-40 as-spun solution spun fibers.

Figure 2.16: Intrachain feature as a function of unit cell spacing. In the cases shown we have a square lattice, i.e. $a = b$
Similar to the conclusions from the intrachain scattering, the simulation and structure factor calculation performs as expected. Decreasing the lattice size moves features to higher scattering vectors (i.e. smaller scattering spacings in reciprocal space). As with the intrachain results, the number of average repeat spacings (i.e. the lattice size) affects the FWHM of the peaks involved. Figure 2.17 shows the dependence of the peak breadths as a function of lattice spacing. The peaks' FWHM decrease with increasing size of the lattice. As we saw with the intrachain features, the larger lattices correspond to a larger number of repeats. The larger spacings when Fourier transformed into reciprocal space, correspond to a smaller reciprocal spacing. Thus, in the coefficient traces, the peak breadth decreases.

2.3.10 Modeling Results and Discussion: hiq40fsa Fibers
Dimers on a 3x3 lattice were required to yield a pattern which displayed the proper features out to the $A_8(s)$ coefficient trace which were observed in the experimental data analysis. Lattice parameters of $a = 4.25\text{Å}$, $b = 3.75\text{Å}$, and $\gamma = 80^\circ$ were used. As previously mentioned, four RIS states were allowed for a phenylene ring if bonded to
an ester oxygen. Otherwise, the ring was constrained to be coplanar with the carbonyl group, due to π-orbital conjugation. The ester torsion was allowed to vary randomly by up to ±30° out of the plane of the backbone with a uniform distribution. The molar percentage of HBA was set at 40%. 25 chains were specified in the chain build. The parameters for the acceptance criteria for the ensemble structures were \( \beta_\chi = 20,000 \) and \( K_{vdw} = 0.5 \). The \( \beta_\chi \) value is large, because it allows most of the structures which pass the hard-core geometric constraint into the ensemble of accepted structures. A \( K_{vdw} \) factor of 0.5 implies that with standard 9-6 interaction potential that the hard sphere cutoff we used is approximately 48% of the excluded volume balance point. This value of hard-core radius is well below the energetic balance point, implying that many structures allowed are likely to be highly strained (i.e. have some atom pairs well within the repulsive force region). The number of accepted structures for this set of parameters was 647 out of 6000 attempted.

The relative amount of the material phases postulated to be present within an aromatic polyester can now be looked at in a quantitative manner. For hiq40fsa fibers, there is no crystalline portion subtracted before Legendre polynomial series analysis. The fact that there are no discernible crystalline features (i.e. features with a FWHM in the 2θ direction of 5.0° or less) of the fiber pattern makes this assumption reasonable.

2.3.10.1 The Isotropic Trace
The isotropic coefficient trace, \( A_0(s) \), is a special case in terms of the components which contribute to its structure factor. The \( A_0(s) \) trace is composed of (at least) two phases, the oriented and unoriented non-crystalline phases. The unoriented non-crystalline phase can also be properly referred to as the “amorphous phase.” The unoriented non-crystalline phase may or may not be present in a sample. \textit{A priori}, we do not know the relative contribution of the phase to the overall trace, however, it may be non-negligible. Therefore, we must account for the presence of the non-crystalline phase, in our data. Since, the amorphous phase is purely isotropic, its influence extends only to the \( A_0(s) \) trace and no other higher order term in the series expansion.
We have assumed an additional completely isotropic non-crystalline phase, because we are not sure that all of the chains in our experimental sample are necessarily aligned, even locally. Since, our model only encompasses aligned chains, we can envision that not all of the material in our samples would display this packing behavior. The assumption of a completely isotropic non-crystalline phase implies that any unaligned chains would be completely uncorrelated with respect to their neighbors. This proved to be sufficient to model the scattering characteristics of our experimental sample.

Obtaining an unoriented non-crystalline trace can be done either experimentally or via simulation. We have chosen the latter, since our polymer powder samples all contained a crystalline phase implying that processing (either data or material) would be required to obtain a measure of the purely amorphous scattering characteristics of HIQ-40. The amorphous phase was modeled using the Biosym\textsuperscript{tm} software. [MSI Simulations Inc., 1994] We used the Builder, Polymerizer, and Amorphous Cell modules to construct a simulation cell of HIQ-40. These results were then used to simulate the amorphous scattering behavior of the material. 50-unit oligomers were placed in a cubic cell with edge lengths of 20Å. The box was filled with chains until the specified density ($\rho = 1.35 \text{ g/cc}$) was reached. This density was estimated from data listed by Hsiao and Shaw for HIQ-20 under high pressure. [Hsiao, B., 1990] The temperature of the simulation was 300K. The system was allowed to equilibrate for 50,000 time steps and 10 snapshots of the system were taken every 100,000 time steps. We ran one simulation of 1,000,000 time steps. Each time step was 1 ps. A sample of the structure factor calculation from the simulation cell is shown in Figure 2.18.
One will note that the structure factor for the amorphous cell shows three characteristic spacings. These are generally interpreted as one intrachain scattering peak along the backbone of the chain, and the other two as interchain peaks, indicative of the packing properties of the material. For these simulations, Table 2.3 summarizes the spacings we found and their corresponding $s$, $d$, and $2\theta$ values.

<table>
<thead>
<tr>
<th></th>
<th>$2\theta$ (°)</th>
<th>$s$ (Å$^{-1}$)</th>
<th>$d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interchain 1</td>
<td>15.65</td>
<td>1.109</td>
<td>5.665</td>
</tr>
<tr>
<td>Interchain 2</td>
<td>23.10</td>
<td>1.631</td>
<td>3.852</td>
</tr>
<tr>
<td>Intrachain</td>
<td>42.50</td>
<td>2.953</td>
<td>2.128</td>
</tr>
</tbody>
</table>

Table 2.3: Simulated Amorphous HIQ-40 Feature Positions

It is unusual for an amorphous trace to display more than one readily distinct interchain spacing. However, due to the rigid nature of the chains in HIQ-x, we believe that the two features appearing near $2\theta \sim 20^\circ$ are due to separate distributions of lateral packing spacings. This is likely due to the rigidity of the polymer backbone, and the propensity of the phenyl rings to align edge to face. These spacings correspond very closely to the unit cell parameters for the crystalline phase of the material, which is
known to contain primarily edge-to-face and face-to-face interactions. These edge-to-face and face-to-face interactions have also been studied in pHBA in our own group and seen to be significant at lower temperatures. [Foulger, S.H., 1995] Also note that these values bracket the commonly quoted value of \(~4-5\)Å for the average van der Waals interaction distance for non-bonded interactions. [Galeski, A., 1992]

In fitting, the isotropic trace of the non-crystalline portion of the pattern, we determined two factors, the isotropic scaling coefficient for the first term in the ODF reconstruction, \(D_0\), and the fraction of oriented non-crystalline material, \(\chi_{ONC}\). By minimizing the squared deviations between the combined oriented and unoriented structure factor coefficient traces and the experimental coefficient trace, \(A_0(s)\), we determined that a \(D_0 = 80.7\) (unitless) was required and \(\chi_{ONC} = 0.73\) was determined to give the best fit.

2.3.10.2 ODF Scaling Factors
The \(D_{2n}\)’s are specifically what we are looking for in determining the orientation distribution function (ODF) of the material. Figure 2.19 shows a comparison of the experimental and calculated structure factor coefficients for hiq40fsa fibers. Only three coefficients were required (the fourth coefficient trace for \(A_6(s)\) was negligible).

![Figure 2.19: Comparison of experimental and calculated structure factor coefficient traces for hiq40fsa fibers, a) \(A_0(s)\) coefficients, b) \(A_{2n}(s)\) coefficients (2n = 2,4)](image)

Table 2.x shows the values for the scaling coefficients, \(D_{2n}\), required for each of the
coefficient traces including the 0th term. The table also includes the squared deviation totals for each coefficient trace, $\chi^2_{2n}$, for the individual trace comparisons. $\chi^2_{2n,max}$ is the squared deviation if calculated coefficient were identically 0 at all s-values (i.e. the null option). The average of $\chi^2_{2n}$ for all of the traces is a number which may be compared to $\beta_x$. For the hiq40fsa fibers, $(\chi^2_{2n})_{ave}$ is 85.40. Upon comparison of $(\chi^2_{2n})_{ave}$ with $\beta_x$, we now can assess that a $\beta_x$ value of 20,000 is large.

<table>
<thead>
<tr>
<th>2n</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{2n}$</td>
<td>80.7</td>
<td>6.40</td>
<td>2.49</td>
<td>~0</td>
</tr>
<tr>
<td>$\chi^2_{2n}$</td>
<td>115.0</td>
<td>96.8</td>
<td>48.6</td>
<td>33.4</td>
</tr>
<tr>
<td>$\chi^2_{2n,max}$</td>
<td>304.4</td>
<td>174.3</td>
<td>79.7</td>
<td>33.4</td>
</tr>
</tbody>
</table>

Table 2.4: Scaling Coefficients, $D_{2n}$, for hiq40fsa Fibers

These coefficients when placed in a Legendre series summation, determine the values for the ODF as a function of the azimuthal angle. Figure 2.20 shows the ODF as a function of azimuthal angle.

Figure 2.20: ODF for HIQ-40, As-Spun, Solution-Spun Fiber
The anisotropic portion of the distribution has a FWHM of 64.6° and a significant isotropic portion (the ordinate of Figure 2.20 starts at 0.075 and only ranges up to 0.095). This implies that while chains are aligned locally in the hiq40fsa fibers with respect to each other, they are not necessarily aligned with the fiber axis.

2.4 Discussion of Case Study Results

The presence of the oriented non-crystalline phase is in the absence of the presence of a crystalline phase in this sample. Therefore, we may conclude that, while one of the sources for an oriented non-crystalline phase may be the interface between the amorphous and crystalline regions in a polymer, this is not a necessary condition. In the case of the HIQ-40 unannealed solution-spun fiber sample, this type of oriented non-crystalline material does not exist within the sample. In fact, our results indicate that the oriented non-crystalline material exists as a distinct type, or morphology, of the polymer chain packing structure within the material. One should also note, that while there is a physical reason for the alignment of chains (the mechanical bias induced in the act of drawing), the crystalline phase is not necessary to have orientation develop in this material. Thus, the oriented non-crystalline portion of the material is not necessarily a phenomenon found only at the interface between crystalline and amorphous regions.

Only two phases are needed to describe this sample. Both are non-crystalline and aperiodic. While, the oriented phase is envisioned as a highly disordered lattice model, periodic boundary conditions are not invoked as an assumption. Therefore, the "interaction distance" of the oriented phase is limited. We do not know a priori what lies outside the boundary. In fact, as per the nature of an aperiodic structure, it is uncorrelated.

One should also note that the analysis implies that the size of the oriented non-crystalline domains are quite small. Since WAXS data encompasses a bulk average, it is not possible, with this analysis to determine whether or not the domains of oriented
material are evenly dispersed amongst the unoriented areas or if they form a distinct and separate phase. The analysis only tells us that they are a majority of the scattering contribution. Figure 2.21 shows a schematic representation of this two-phase model. As drawn, the oriented and unoriented phases are intermingled quite intimately. It must be remembered that the oriented phase contains an isotropic part, but this is still a locally organized structure. Truly isotropic amorphous material is completely randomly oriented both microscopically and macroscopically with chains not necessarily aligned relative to the each other.

![Figure 2.21: Two phase schematic showing the oriented non-crystalline phase interspersed in the isotropic amorphous phase](image)

The ODF in Figure 2.20 only rigorously applies to the ensemble of structures for which it is derived, (in this case, a set of dimers set upon a 3x3 rhombic lattice). The analysis does not account for how these trimers link together, nor does the structure factor calculation take into account any molecular or atomic structure outside of the simulation's interaction distance (the volume covered by the placement of the explicit atoms of the model). We have quantitatively correlated a molecular model to an experimental sample through an ODF. The ODF is intrinsically tied to its model (rigorously speaking, it is only valid insofar as it pertains to the molecular ensemble for which it is derived). However, the ODF bridges the gap between the microscopic description and the experimental observations which are a bulk average the scattering properties of microscopic description. For example, one could use the quantitative breakdown of phases as inputs to an aggregate model or move to a more sophisticated representation since we no longer have only the second moment of the distribution specified, but an entire series of coefficients.

We make the following conclusions about the ensemble and its characteristics. First,
the density of the cell may be calculated, it is 1.825 g/cm$^3$. This value is high relative to
the crystal density of 1.495 g/cm$^3$ reported for the crystalline unit cell of HIQ-x.

[Erdeimir., A., 1986] Note, that the simulated density we list may not be the true density
of the structures in the simulation. Our density is calculated from the average lattice
positions input into the simulation. However, since we do not have any boundaries to
the simulation and we have an acceptance criteria which favors more open structures,
the structures accepted into our molecular ensemble are likely to be less dense than
the input parameters would indicate. If the lattice parameters of the simulation were
expanded by 10% (they were allowed to vary by up to 50% uniformly in the simulations)
in each direction, the density of the ensemble drops to 1.51 g/cm$^3$. A 15% expansion in
the unit cell, yields a density of 1.37 g/cm$^3$. These densities are quite reasonable and
well within the range of the simulation sampling space. If the high density of the
ensemble is correct, this would imply that some aphysical overlaps of atoms may be
occurring in the model. This is partly expected since the hard-sphere cut off was
$\sim1.0\text{Å}$, well within the attractive portion of the 9-6 interaction potential. While, these
overlaps do not directly affect our structure factor calculations, they may present
problems for future simulations using these specific parameters and this ensemble of
molecules.

2.5 Chapter Summary and Conclusions

We have delineated in this chapter the applicability and versatility of the series
expansion analysis to the determination of orientation distribution functions in a general
two-dimensional case. We demonstrated the complete analysis on a polyarylate fiber
sample. This allowed us to highlight all of the major steps in the analysis as well as
the various conceptual details, while not inundating the reader with an undue amount of
data or too many coefficient traces. By using a “real” data set, we have demonstrated
the applicability of the analysis to engineering applications and have highlighted some
of the conceptual advantages of the analysis, such as, the determination of the ODF, a
quantitative correlation between theory and experiment and the reduced computational
load required for the full pattern analysis. In addition, the method derives a molecular ensemble. The molecular ensemble is a powerful tool; it may be further characterized and used in subsequent simulations to study, determine, and predict a number of thermodynamic properties or phenomena.

The analysis is most suited for describing samples with orientation which requires few terms in the expansion. These are generally low levels of orientation. While, in theory we can study any axisymmetric distribution and break it down in terms of a Legendre polynomial series expansion, very narrow distributions (i.e. high molecular orientations) require large number of series terms to be employed. For highly anisotropic systems, such as some products formed in industrial fiber processes, one can find that the number of coefficient traces necessary for a proper description of the orientation can exceed the number of data points that have been measured in the fiber pattern. In such cases, obviously, the reduction of data (and the subsequent reduction in computational expense) espoused by the analysis is lost. Also one runs the risk of “manufacturing” new data.

For the aromatic polyester used in the example, we have deduced a 2-phase system to account for the features in the experimental results. The two phases are oriented and unoriented non-crystalline phases of the material. The analysis shows that the sample contains no detectable (by WAXS) crystalline phase, but displays over 70% oriented material. This shows quite clearly that the mechanical bias of the fiber drawing process leads to overall chain orientation, but not crystallization. It also shows that the crystalline phase is not necessary for presence of the oriented non-crystalline phase. While some of the oriented non-crystalline material may be associated with the interfacial area of aligned crystallites and the unoriented amorphous phase of the material, the bulk of the oriented non-crystalline section is unassociated with this interface. Because the analysis takes a bulk average of the material, it is unclear whether the oriented and unoriented portions of the system form a single commingled phase or two discrete phases.
Chapter 3

2-D Analysis Case Study: HIQ-40 Fibers

“In the preceding books I have laid down the principles of philosophy; principles not philosophical but mathematical: such, namely as we may build our reasonings upon in philosophical inquiries. These principles are the laws and conditions of certain motions, and powers and forces, which chiefly have respect to philosophy; but lest they should have appeared dry and barren, I have illustrated them here and there with some philosophical scholioms, giving an account of such things as are of more general nature, and which philosophy seems chiefly to be founded on;”

- Sir Isaac Newton, Principia, Bk 3, p. 397

3.1 Introduction

In this chapter, we use the Legendre polynomial series expansion analysis on multiple fiber samples. Whereas in Chapter 2, we had only one sample, in this chapter, we have a set of four HIQ-40 fibers which vary in their processing history. Thus, the Legendre polynomial series expansion analysis will help us to quantify a number of parameters to characterize the various processing routes, as well as elucidate ensemble structures for each of the fiber samples.

3.1.1 Experimental Processing: Fiber Spinning

Fibers are of great industrial importance. They are produced for a myriad number of uses and applications ranging from the reinforcing phase in composites (e.g. fiber glass) to the basic material in woven (e.g. ballistic weave in bulletproof vests) and non-woven (e.g. electrospun PET) fabrics. The geometry of fibers takes advantage of a polymer chain’s anisotropic geometry. Often, the chain axis is aligned (at least roughly) in the fiber direction.

The changes that the material morphology undergoes during fiber drawing and the physical characteristics of such extreme processing conditions discussed by Middleman [Middleman, S., 1977], Schultz, Prevorsek and Oswald [Schultz, J., 1990]. Figure 3.1 shows a general fiber production schematic, consisting of a reservoir, spinneret, and take-up reel. The reservoir can contain either a melt or solution of the
desired material. The spinneret generally ranges from the sub-millimeter to micron range in size. Often a plunger is used to force material through the spinneret die (often there is more than one hole in the die).

Die swell is often observed with fibers, since the outside surface is allowed to relax once it is free of the spinneret walls. Before the take-up reel, a post-spinning step can occur, in which excess solvent and/or annealing and crystallization of the material can be facilitated by heating or washing the fiber.

The speed at which the take-up reel spins can differ from that of the speed of the material exiting the spinneret die. This speed differential can cause additional mechanical bias (and combat the relaxation experienced in die swell) and is characterized by the quantity known as the draw ratio, which as its name implies is the ratio of the take-up reel speed to the spinneret exit velocity.

![Figure 3.1: General schematic of a fiber spinning process](image)

The general terms which help to characterize physically a fiber process are the draw ratio and the final fiber diameter. The comparison of the final fiber diameter to the spinneret die opening gives a measure of die swell, but one must remember to account for additional factors, such as solvent evaporation and thermal expansion or contraction. For our purposes, we are not concerned with die swell in the present study.
3.2 Experimental

3.2.1 Fiber Sources
HIQ-40 fibers were obtained from Hoechst-Celanese in New Jersey. Two types of fibers were received: solution-spun and melt-spun. Solution-spun fibers were spun from a solution of 20% dichloromethane and 80% trifluoroacetic acid. The melt-spun fibers were spun from a nematic melt ($T_{C-n} = 333^\circ$C for HIQ-40). Bundles of both the melt- and solution-spun HIQ-40 fibers were subsequently thermally annealed at 300 °C for 68 hours with fixed ends to produce heat treated (or “annealed”) samples. The set of HIQ-40 fiber samples allows comparison of two separate processing variables: the type of spinning process (solution or melt) and the effect of annealing (unannealed versus thermally annealed samples).

The fiber samples are designated with an eight character code. The first three characters denote the material constituents; the next two characters denote the mole percentage of HBA; and the last three characters denote the bulk geometry of the sample (e.g. fiber or powder), whether it is solution- or melt-spun, and whether the samples is as-spun (unannealed) or heat treated (annealed). Table 3.1 delineates the naming designations for our four HIQ-40 fiber samples.

<table>
<thead>
<tr>
<th>Fiber sample</th>
<th>Composition</th>
<th>Geometry</th>
<th>Spinning Condition</th>
<th>As-spun or heat treated</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HIQ-40</td>
<td>fiber</td>
<td>solution</td>
<td>as-spun</td>
<td>hiq40fsa</td>
</tr>
<tr>
<td>2</td>
<td>HIQ-40</td>
<td>fiber</td>
<td>solution</td>
<td>heat treated</td>
<td>hiq40fsh</td>
</tr>
<tr>
<td>3</td>
<td>HIQ-40</td>
<td>fiber</td>
<td>melt</td>
<td>as-spun</td>
<td>hiq40fma</td>
</tr>
<tr>
<td>4</td>
<td>HIQ-40</td>
<td>fiber</td>
<td>melt</td>
<td>heat-treated</td>
<td>hiq40fmh</td>
</tr>
</tbody>
</table>

Table 3.1: Nomenclature for the HIQ-40 Fibers

3.2.2 Optical Microscopy: Physical Characterization of the Polymer Samples
All of the fibers have diameters on the order of tens of microns. Measurements were taken off of the optical micrographs using a Mitutoyo dial caliper allowing measurement
down to 0.2 mm (±200μm). Coupled with the reference scale bar, the calipers enabled us to gain an accuracy on the fiber diameter measurements on the order of hundredths of microns (1/100 μm). Optical micrographs were taken on instant processing film using a Nikon AFX-II photomicrographic attachment on a Nikon Optiphot-pol polarized light microscope. All of the photographs shown in this thesis are with unpolarized light.

3.2.3 Thermal Characterization: DSC
DSC was used to characterized the thermodynamic transitions (and their associated parameters) in our HIQ-40 fiber samples. A Perkin-Elmer DSC-7 was used with a scanning rate of 10°C/minute. The scanning range tested was 100°C (373.16 K) to 450°C (723.16 K). Each sample weight was measured so that comparisons of enthalpies could be made between samples. The Perkin-Elmer DSC-7 used is located in the Center for Material Science and Engineering (CMSE). This work made use of MRSEC Shared Facilities supported by the National Science Foundation under Award Number DMR-9400334.

Thermal characterization studies on HIQ-x have been done primarily on powders and fibers at various compositions. As shown previously in Chapter 1, Figure 1.3 (reproduced from Chapter 1) diagrams the published thermal behavior of HIQ-x as a function of composition. From the Figure 1.3, the crystal-to-nematic transition temperature ($T_{c-n}$) of HIQ-40 is 333°C (606.16 K).

Figure 1.3: Proposed phase diagram for HIQ-x [from Blundell, MacDonald, and Chivers, 1989]
3.2.4 WAXS Characterization Parameters and Procedures

Two-dimensional Wide Angle X-Ray Scattering (WAXS) patterns (also referred to as fiber diagrams, see section 2.2.2) of the four fiber samples were obtained using a Rigaku RU 200B Rotating Copper Anode with $\theta/2\theta$ goniometer and a pole figure attachment. The wavelength of the incident Cu$_{K\alpha}$ X-ray radiation was 1.5425Å. The sample was tested for maximum intensity as a function of azimuthal angle, $\alpha$, for constant $2\theta = 42.5^\circ$. This intensity maximum was assumed to be on the meridian ($\alpha = 0^\circ$). The equatorial scan from the samples was then obtained by rotating the pole figure attachment by $90^\circ$ in $\alpha$. The 2-D pattern was taken, by combining sequentially taken one-dimensional $\theta/2\theta$ traces using a detector with a proportional intensity counter.

Only one quadrant of data was taken ($\alpha = 0^\circ$ to $90^\circ$), since the other four quadrants must be similar by symmetry. The steps in the azimuthal angle, $\Delta \alpha$, varied from $4^\circ$ to $6^\circ$ depending on the sharpness of crystalline features in the fiber. The scattering angle ($2\theta$) ranges measured were $10^\circ$ to $52^\circ$ with steps ($\Delta 2\theta$) of $0.1^\circ$. The detector was held at each $2\theta-\alpha$ combination for a minimum of 5 seconds in an effort to ensure reasonable signal to noise ratio.

Once collected, the fiber diagrams were analyzed using the Legendre polynomial series expansion analysis. However, before we can use the Legendre analysis we need to account for the following factors in the fiber diagrams:

1) the crystalline phase,
2) incoherent (Compton) scatter,
3) self-scatter, and
4) renormalization of data for comparison to theory

3.2.5 The Crystalline Phase Contribution

The last three factors are covered in depth in Chapter 2. The first factor, that of crystallinity, will be dealt with here. The experimental traces are characterized using Gaussians in order to fit the crystalline peaks of the trace, so that they may be
removed. The objective function to be minimized was of the following form:

$$\text{OBJF} = \sum_{2\theta} \sum_{\alpha} (I_{\text{obs}}(2\theta, \alpha) - I_{\text{calc}}(2\theta, \alpha))^2$$  \hspace{1cm} (3.1)

where:

$$I_{\text{calc}}(2\theta, \alpha) = a2\theta + b\alpha + c + \sum_{i=1}^{N_{\text{peaks}}} A_i e^{-\ln 2\left(\frac{(2\theta - \omega_2\theta)}{(\omega_{2\theta}/2)}\right)^2} -\ln 2\left(\frac{(\alpha - \omega_\alpha)}{(\omega_{\alpha}/2)}\right)^2$$  \hspace{1cm} (3.2)

The background for the system was assumed to be linear in the two spatial variables, $2\theta$ and $\alpha$. Thus, three variables were required to account for the background: two slopes and an intercept. Gaussians were chosen as the functional form, since thermal vibrations and other theoretical displacements from the mean value often display a normal statistical distribution. Five variables are needed for each two-dimensional Gaussian (and thus, for each peak): the maximum amplitude, $A_i$; the mean position in $2\theta$, $\omega_{2\theta}$; the Full Width at Half Maximum (FWHM) in $2\theta$, $\omega_{2\theta}$; the mean position in the azimuthal angle ($\alpha$), $\omega_{\alpha}$; and the FWHM in $\alpha$, $\omega_{\alpha}$. In principle, Gaussians are not justified in the azimuthal direction of $\alpha$; however, for the fairly narrow distributions of the crystalline peaks, the use of Gaussians is appropriate. However, as we shall see, some artifacts will be introduced based on the choice of a Gaussian peak shape in both the $2\theta$ and $\alpha$ directions. For $N_{\text{peaks}}$ and five variables per peak, plus the three background variables, we have a total of $5N_{\text{peaks}} + 3$ variables to account for in each sample. For the crystalline deconvolution, we also add a number of additional Gaussians to simulate the amorphous regions. This is solely for the purposes of subtraction for the crystalline peaks.

For our purposes, we assumed that features with a FWHM in $2\theta$ of $5.0^0$ or less were indicative of relatively high numbers of repeats. At a FWHM of $5.0^0$, the Scherrer equation (Equation 1.2) yields a value of $L \sim 16\AA$ for the corresponding crystallite size. Given that our simulations had an upper bound of approximately that limit, this FWHM cutoff seemed appropriate. A size of $16\AA$ is generally about 3 - 5 scattering bodies in a row (corresponding to 2 - 4 similar spacings between these scatterers) at $\sim 3.5\AA - 5\AA$. 

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per spacing. Three to five scatterers is on the lower bound of resolution for constructive interference. [Guinier, A., 1963]

Once the crystalline phase has been accounted for the data analysis proceeds as delineated in Chapter 2. The remaining scattering from the sample is solely due to the non-crystalline portion of the material and thus we can use a Legendre polynomial series to characterize the scattering properties of the system. If we are to use the method of Chapter 2, we had to account for incoherent (Compton) and self-scatter, as well as renormalize the data to atomic units for comparison to theory. Once that is done the Legendre polynomial series coefficients may be determined.

Once the experimental data has had all of these factors accounted for and been normalized, it can be considered a reallocation of scattered intensity about an average value. This reallocation directly affects the convergence criteria. Now that some of the values of the diagram are negative in magnitude, testing for convergence via a point-by-point basis becomes less tractable, since one or more values in data can take on a value of zero. Additionally, while experimental data is shifted to an average value closer to zero, the noise in the trace is unaffected (on an absolute scale) by the shift of the average. It therefore becomes more significant in the fiber pattern (compared to the total integrated area which is now reduced in relative value). The sum of squared deviations is still used as a basis for comparison between the experimental data and its reconstruction. However, keeping in mind that the noise in the trace has been made more significant by the renormalization, the Legendre polynomial series expansion does not converge to within approximately $10\%$ of the square root of the sum of the squared deviations divided by the square root of the sum of the squared deviations of the experimental curve relative to zero.

If the Legendre analysis is run on the experimental data without renormalization and subtraction of the self- and Compton scattering and the series deconvolution is carried out to the same number of terms, it generally yields better agreement. This is understandable as, nothing has changed except for the scaling and the average value
of the intensity over the entire diagram. The better fit is attributed solely to the fact that the integrated area under the curve is larger and that the ratio of the sum of squared deviations to the total integration of the squared areas yields a smaller value. However, the raw experimental data cannot be compared directly to the simulation structure factor calculations. The simulation results would have to be renormalized and the factors neglected in the experimental analysis accounted for in the theoretical coefficients. Thus, we would gain nothing by not accounting for these factors here in the experimental data. Therefore, it was chosen to go with the shifted and renormalized experimental data sets and a slightly more lax series termination criterion. Given the 10% noise limit, the termination criterion chosen for the Legendre polynomial series expansion was that the entire experimental pattern be fit within 12% of the total integrated area for all four fiber patterns studied. Smaller features which are best modeled in terms of higher order Legendre polynomial terms may be uncovered, if the noise level in the data is reduced. The shape of the lower order Legendre series coefficients (except $A_0(s)$) do not change after normalization to atomic units.

3.2.6 Visualization of WAXS Data

As per our discussion in Chapters 1 and 2, the standard method of displaying 2-D WAXS patterns is termed the fiber diagram (see section 2.2.5). Figure 3.2 shows an example of a typical fiber diagram. In this case, it is for an hiq40fmh fiber. The diagram is a polar plot, where the 2θ direction is the radial coordinates and the azimuthal angle, $\alpha$, corresponds to the angular or polar coordinate. Since there are only two independent variables, the data is straightforward to visualize. The fiber
diagram may be thought of as a series of 1-D scans \((\theta/2\theta)\) taken sequentially.

![Diagram showing fiber features](image)

Figure 3.2: Example of a fiber diagram showing broad and narrow features. The sample is annealed HIQ-40 melt-spun fibers

In the example given, we can see that a number of spatial features become visually apparent when plotted in this manner. Many of the contours have a very narrow distribution in the radial direction. These are the crystalline peaks. The presence of the peaks in horizontal and vertical layer lines becomes readily apparent when we plot the data as a polar plot. Such an inference would not have been as easily recognized from the separate one-dimensional \(\theta/2\theta\) traces.

### 3.3 Characterization Results: Expectations and Observations

#### 3.3.1 Optical Microscopy Results

Figure 3.3 (a-d) shows reproductions of unpolarized light optical micrographs for all four of the HIQ-x fiber samples. Table 3.2 shows a collation of results for the four HIQ-x fiber samples used in the study. It lists the fiber diameters as well as the error
associated with the measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>hiq40fsa</th>
<th>hiq40fsh</th>
<th>hiq40fma</th>
<th>hiq40frmh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Diameter (μm)</td>
<td>42.6 (±0.7)</td>
<td>30.8 (±0.2)</td>
<td>27.1 (±0.7)</td>
<td>24.8 (±0.2)</td>
</tr>
</tbody>
</table>

Table 3.2: HIQ-40 Fiber Diameter Measurement Results

Visually, the solution spun fibers showed far more macroscopic curvature than their melt spun counterparts despite all the fibers having their ends fixed during the heat treatment. The solution-spun fiber sinuosity is presumed to be due to a shorter scale less extended chain conformations present in the sample prior to annealing. Since the solution spun fibers are not from a lyotropic solution, we do not expect that the chains in a solution-spun fiber are necessarily aligned relative to the fiber axis \textit{a priori}. Nor do we expect that there will be nematic domains that will then line up in the fiber direction when subjected to mechanical deformation. Thus, the overall local and meso-scale structures are expected to be less ordered in the solution-spun fibers than in the melt.

This implies that subsequent thermal processing does not necessarily reorient the chains nor their domains with respect to the fiber axis. This is understandable, since annealing takes place in the solid state and thus, the processing temperature is below the crystal-to-nematic temperature ($T_{c-n} = 333^\circ C$) for HIQ-40. While, the chains are mobile during the annealing process (the processing temperature is above $T_g$), they may not take on the entropically unfavorable extended chain conformation that readily, implying that the energy barrier to the nematic phase is still fairly high.
The annealed samples are a darker brown, which contrasts with the light golden color of the as spun samples. This color change is presumably due to degradation brought on by the annealing process. In addition, the annealed fibers show cracking or flaking on the outer surfaces implying that the anneal may be inducing relaxations and reorganizations in small domains, which subsequently peel away from the surface. It is unknown if the flaking occurred during the annealing time itself or afterwards when being handled. In either case, the flaking and discoloration show that the anneal has some morphological effect on the material and that this effect is taking place on a fairly
large (~ 1μm - 10μm) size scale.

3.3.2 DSC Results

Figure 3.4 shows a typical DSC trace for an HIQ-x fiber. In this particular case, the DSC trace is of the annealed melt-spun HIQ-40 (hiq40fmh) fiber. The trace does not cover the entire range that had been measured by this scan, but focuses on the melting peak for clarity. The baseline for this system is curved with a positive slope and the small spikes at T ~ 350°C, 390°C, and 430°C are instrumental artifacts.

![DSC Trace](image)

Figure 3.4: Example DSC trace for an HIQ-40 fiber. In this case, the sample depicted is hiq40fmh.

The literature reported value for T_{c-n} for HIQ-40 as-synthesized powders is 333°C. [Blundell, D., 1989] For quenched PPI (poly(p-phenylene isophthalate) or HIQ-100) powders, T_m (there is no LC phase for PPI) is listed as 388°C. [Cao, J., 1995] We found that the HIQ-40 fibers in our study displayed transitions at or below the reported values for the powders. Table 3.3 summarizes our DSC results for the four fiber samples, listing the melting peak range (a measure of the peak size which can be
related to the distribution of crystal sizes), the peak maximum, $T_{c-n}$, the peak onset, as measured by extrapolation of the initial slope, and integrated area under the peak or melting enthalpy, $\Delta H_f$.

<table>
<thead>
<tr>
<th></th>
<th>hiq40fsa</th>
<th>hiq40fsh</th>
<th>hiq40fma</th>
<th>hiq40fmh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak range ($^\circ$C)</td>
<td>286 - 339</td>
<td>312 - 345</td>
<td>264 - 328</td>
<td>324 - 352</td>
</tr>
<tr>
<td>$T_{c-n}$ ($^\circ$C)</td>
<td>318</td>
<td>335</td>
<td>318</td>
<td>344</td>
</tr>
<tr>
<td>Onset ($^\circ$C)</td>
<td>290</td>
<td>325</td>
<td>306</td>
<td>335</td>
</tr>
<tr>
<td>Enthalpy (J/g)</td>
<td>5.01</td>
<td>24.98</td>
<td>9.01</td>
<td>25.98</td>
</tr>
</tbody>
</table>

**Table 3.3: HIQ-40 Fiber DSC Results**

We can see from the DSC data that $T_{c-n}$ for the as-spun fiber samples is lower than that reported for the powder. This is attributed to the fact that the crystallites in the fibers are smaller than those generally encountered in the as-synthesized powder. That is, the surface to volume ratio of the fiber crystallites is higher than that of the ones in the powder implying that the fiber crystallites should be less energetically stable, thus lowering their $T_{c-n}$. The annealed fibers display $T_{c-n}$'s comparable to the reported literature data. Peak ranges are broader for the unannealed samples implying that the degree of crystal perfection is also lower in these samples. Thus, we conclude that the unannealed fiber samples have both smaller crystallites and a lower degree of crystallite perfection.

As there is no reported $\Delta H^0_f$ value in the literature to our knowledge, determination of an absolute degree of crystallinity difficult. However, comparisons of enthalpies of melting between samples gives a measure of the relative increase of crystallinity in the samples. Our results shows that the degree of crystallinity drastically increases during annealing, increasing the amount of crystalline material by 3 - 5 times over that produced by the fiber spinning process (either solution- or melt-spinning). Erdemir, et al., note that as-spun melt fibers of HIQ-x display a very broad endotherm in the
temperature ranges that we observed. [Erdemir, A., 1988] However, they list no numbers on the degree of crystallinity. We know of no published data to date which numbers on the degree of crystallinity found in annealed fibers for comparison.

3.3.3 WAXS Results: Experimental Data and its Representations, and Analysis

As reported in Chapter 1, section 1.3.1.4.1, the unit cell for HIQ-x is an primitive orthorhombic cell with $a = 5.58\text{Å}$, $b = 3.95\text{Å}$, and $c = 24.32\text{Å}$. [Johnson, D., 1991] $0/2\theta$ 1-D WAXS traces taken in our laboratory correspond well with that reported in the literature, so we have no reason to suspect the reported unit cell to be in error.

First, WAXS fiber patterns are corrected for instrumental effects and scaled for comparison to the theoretical structure factor calculations. The crystalline phase is accounted for and subtracted off by the use of Gaussians as explained earlier in section 3.2.5. In accounting for the crystalline phase, we used a Gaussian peak shape in the two directions and their mean position in $2\theta$ was checked to ensure that it corresponded to a position that should be present from the unit cell. The corresponding $d$-spacing must match within $0.25\text{Å}$ of the reported literature value.

Table 3.4 lists the crystalline peaks and their characterization parameters for each of three HIQ-x fiber samples which contained crystalline peaks (hiq40fsh is the lone sample which did not). The table lists the assigned Miller Index for each peak based on the literature unit cell, literature value of that $2\theta$ spacing and the observed $2\theta_i$ and $\alpha_i$ parameters for the Gaussian peak used to model it. The parenthetical values after each mean value is the FWHM for that spatial direction. All values are in degrees.

<table>
<thead>
<tr>
<th>Miller Index</th>
<th>Reported $2\theta$</th>
<th>hiq40fsh $2\theta_i$</th>
<th>hiq40fsh $\alpha_i$</th>
<th>hiq40fma $2\theta_i$</th>
<th>hiq40fma $\alpha_i$</th>
<th>hiq40fmh $2\theta_i$</th>
<th>hiq40fmh $\alpha_i$</th>
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</thead>
<tbody>
<tr>
<td>004</td>
<td>14.5</td>
<td>--</td>
<td>--</td>
<td>14.5(0.9)</td>
<td>0.4(15.4)</td>
<td>14.5(1.0)</td>
<td>-0.1(12.9)</td>
</tr>
<tr>
<td>100</td>
<td>16.4</td>
<td>16.1(1.2)</td>
<td>89.3(47.3)</td>
<td>--</td>
<td>16.1(1.2)</td>
<td>90.0(9.6)</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>17.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>17.6(4.1)</td>
<td>88.7(35.7)</td>
<td></td>
</tr>
<tr>
<td>010</td>
<td>21.7</td>
<td>22.7(1.3)</td>
<td>91.8(48.0)</td>
<td>--</td>
<td>21.4(4.6)</td>
<td>90.2(13.6)</td>
<td></td>
</tr>
<tr>
<td>006</td>
<td>21.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>21.8(1.7)</td>
<td>-0.1(10.6)</td>
<td></td>
</tr>
</tbody>
</table>
One can see from Table 3.4 that very few crystalline features are needed for most of the samples. This is common for these materials, where degrees of crystallinity as measured by WAXS are often reported to be less than 25%. [Blundell, D., 1989] Our own results from WAXS tell us that the highest degree of crystallinity for our samples was 28% for the annealed melt spun fiber (hiq40fmh). Our quantitative analysis bears this out, since the hiq40fmh fiber has the highest number of crystalline peaks. Table 3.5 summarizes the crystalline data by reporting the WAXS degree of crystallinity, \( \chi_{WAXS} \), for the four fiber samples.

<table>
<thead>
<tr>
<th>Miller Index</th>
<th>Reported ( 2\theta )</th>
<th>hiq40fsh ( 2\theta_i )</th>
<th>hiq40fsh ( \alpha_i )</th>
<th>hiq40fma ( 2\theta_i )</th>
<th>hiq40fma ( \alpha_i )</th>
<th>hiq40fmh ( 2\theta_i )</th>
<th>hiq40fmh ( \alpha_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>22.5</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>21.8(2.2)</td>
<td>47.3(11.7)</td>
</tr>
<tr>
<td>110</td>
<td>27.7</td>
<td>27.9(1.8)</td>
<td>92.8(47.3)</td>
<td>--</td>
<td>--</td>
<td>27.7(1.5)</td>
<td>90.1(9.0)</td>
</tr>
<tr>
<td>112</td>
<td>29.4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>28.5(1.8)</td>
<td>75.9(12.4)</td>
</tr>
<tr>
<td>008</td>
<td>29.4</td>
<td>29.4(0.8)</td>
<td>-3.2(28.1)</td>
<td>29.4(0.9)</td>
<td>0.0(12.6)</td>
<td>29.3(0.9),</td>
<td>-0.1(9.5)</td>
</tr>
<tr>
<td>116</td>
<td>33.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>30.6(4.1),</td>
<td>60.8(17.1)</td>
</tr>
<tr>
<td>0010</td>
<td>37.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>36.8(1.7),</td>
<td>0.0(8.7)</td>
</tr>
<tr>
<td>0012a</td>
<td>44.5</td>
<td>--</td>
<td>--</td>
<td>44.6(1.3)</td>
<td>0.0(15.1)</td>
<td>44.1(2.2),</td>
<td>-0.9(27.0)</td>
</tr>
<tr>
<td>0012b</td>
<td>44.5</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>44.6(0.9),</td>
<td>0.0(8.2)</td>
</tr>
</tbody>
</table>

Table 3.4: HIQ-40 Fiber Crystalline Peak Deconvolution Results

As can be noted from Table 3.5, annealing causes a marked increase in the amount of crystalline material present. More than the processing change from solution to melt spun. However, the melt spun fibers, ostensibly, display a higher starting point and, possibly a higher maximum degree of crystallinity. The trend in the WAXS degree of crystallinity is the same as for the enthalpy of the melting peak in DSC. However, unlike DSC, there is no measurable crystallinity in the as-spun solution-spun fiber and

<table>
<thead>
<tr>
<th>( \chi_{WAXS} )</th>
<th>hiq40fsa</th>
<th>hiq40fsh</th>
<th>hiq40fma</th>
<th>hiq40fmh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
<td>18.2%</td>
<td>9.2%</td>
<td>27.6%</td>
</tr>
</tbody>
</table>

Table 3.5: HIQ-40 WAXS Degree of Crystallinity, \( \chi_{WAXS} \), Results

As can be noted from Table 3.5, annealing causes a marked increase in the amount of crystalline material present. More than the processing change from solution to melt spun. However, the melt spun fibers, ostensibly, display a higher starting point and, possibly a higher maximum degree of crystallinity. The trend in the WAXS degree of crystallinity is the same as for the enthalpy of the melting peak in DSC. However, unlike DSC, there is no measurable crystallinity in the as-spun solution-spun fiber and
the degree of crystallinity between annealed samples, while fairly close are not the same (as implied by DSC). The presence of a melting endotherm in the hiq40fsa samples where no crystallinity is measured by WAXS is likely due to the melting of disordered paracrystalline regions. Similar observations (and conclusions) were drawn by Erdemir and coworkers on HIQ-x fibers. [Erdemir, A., 1988] The fact that DSC shows a melting transition were no crystallinity is measured by WAXS reinforces the assertion that DSC is less sensitive to defects and distortions in a crystallite than WAXS is. This also highlighted by the fact that the long tail preceding the melting peak was included in the enthalpy calculation for the melting peak. The tail of the melting peak is often associated with small or defective crystals melting prematurely. They melt prematurely because of excess energy due to high defect densities or high surface-to-volume ratios.

If the thermal transition in the fiber sample is (at least, in part) due to a paracrystalline phase, then this paracrystalline phase is thermodynamically stable (or meta-stable). If this paracrystalline material exists, then its scattering properties (though diffuse) should be observable in the WAXS fiber patterns. Our Legendre polynomial series analysis is well suited for this purpose for examining this moderately oriented, but diffuse scattering phase

Figures 3.5 - 3.7 and 2.4(a) show the WAXS fiber patterns of the raw, crystalline and the remaining non-crystalline material after the crystalline peaks have been subtracted for the four fiber samples. One can see from the series of figures that the as-spun fibers show very little in the way of crystalline peaks. In fact, only one of the fiber samples, hiq40fmh, displays 3-D order and periodicity. While two other samples, hiq40fsh and hiq40fma, display some periodic peaks, these are restricted to certain directions (the equator for hiq40fsh and the meridian for hiq40fma). The reasons for this will be discussed further in the following paragraphs.
Figure 3.5: Fiber Patterns for HIQ-40 annealed melt spun fiber (hiq40fmh) a) raw experimental data trace, b) crystalline peak subtractions, c) non-crystalline portion of trace.

As noted in section 3.2.5, the fiber diagram makes visualization of lattice features easier. This is particularly germane for the hiq40fmh sample which displays the highest degree of crystallinity of the four HIQ-40 fiber samples. The fiber diagram in Figure 3.5 makes it quite clear that three-dimensional order is present in the samples since there
are a number of well-defined crystalline peaks in the pattern on both axes as well as off-axis. In addition, from Table 3.4, we note that reflections in each of all three unit cell directions are present in the WAXS data. Not all of the peaks listed in Table 3.4 appear in Figure 3.5(b). Since the contour plot displays iso-intensity layers, it may appear that some features are not diminished in size or do not appear in either the crystalline or non-crystalline traces after subtraction. These are artifacts of the contour levels and the plotting style chosen.
Figure 3.6: Fiber Patterns for HIQ-40 as-spun melt spun fiber (hiq40fma) a) raw experimental data trace, b) crystalline peak subtractions, c) non-crystalline portion of trace.

Figure 3.6 shows the raw experimental data and its breakdown into crystalline and non-crystalline portions of hiq40fma. It is readily apparent from the crystalline fiber diagram (b) that the amount of order that we would consider periodic is concentrated on the meridian. Three narrow peaks appear in the hiq40fma fiber diagram. They correspond to the (004), (008) and (0012) indexed reflections. No three-dimensional order is
implied in the sample, since there are no equatorial or off-meridional peaks in the fiber diagram. These three peaks are often termed “liquid crystalline” peaks and correspond to the hypothesis that due to processing from a nematic melt, most of the polymer chains in the fiber have extended chain conformations aligned in a nematic mesophase. When the fiber is drawn, these nematic domains preferentially align, aligning the extended chains as well. Despite much chain alignment, there is very little lateral periodicity. Thus, no crystalline peaks appear off-axis or on the equator.
Figure 3.7: Fiber Patterns for HIQ-40 annealed solution spun fiber (hiq40fsh) a) raw experimental data trace, b) crystalline peak subtractions, c) non-crystalline portion of trace.

The results of the crystalline deconvolution of hiq40fma contrast starkly with the hiq40fsh results shown in Figure 3.7. In hiq40fsh, we see hardly any indication of extended chain conformation in the meridional direction and the primary crystalline
peaks lie on the equator. Their spacings correspond to the (100), (010), and (110) indexed reflections. Ostensibly, the effect of annealing has been to cause refinement of molecular structure in the directions lateral to the chain (i.e. on the equator). The fact that very little refinement of reflections in the fiber direction occurs is understandable, because there is very little driving force to go to an extended chain conformation in the annealing process. A large entropic barrier must be overcome due to the connectivity inherent in the polymer chain. Note that the chains must have a general direction associated with them, since most of the peaks associated with the lateral directions of the chains are centered on the equator. However, the azimuthal spread is high. $\omega_{\text{cd}} \sim 48^\circ$ for all 3 equatorial peaks in Figure 3.7. We do see some development of weak LC peaks on the meridian.

The last figure, a reproduction of Figure 2.4(a), displays the experimental fiber diagram. Since there is no WAXS-measurable crystallinity in the hiq40fsa sample, the non-crystalline portion of the fiber diagram and the raw data are the same. We concluded that there were no crystalline (or liquid crystal or paracrystalline peaks) visually as no features displayed the characteristic narrow peaks breadth in the radial direction.
3.3.3.1 Qualitative Results: Description and Salient Features

We can readily see that the processed and filtered fiber patterns all display a number of similarities. All contain a broad feature of positive intensity centered at $2\theta = \sim 20^\circ$ on the equator. This makes sense, since this diffuse scattered intensity is likely due the distribution of lateral spacings between chains. Since any given polymer chain axis is likely to align itself with the fiber draw axis, periodic coherent scattering along the meridian, especially in the melt-spun fibers, makes sense. In the case of the two melt-spun fiber samples, the LC peaks are readily apparent in the raw data traces. The solution-spun fibers, not having been drawn from a liquid crystalline solution, do not display the same chain alignment propensities. The chains must pack, however. The packing in the lateral direction is aperiodic, but is distributed about a mean value. There is a mean separation distance at approximately 4.5 Å$^{-1}$. There is also a broad distribution about this spacing, indicating wide fluctuations of the interchain distance.

After annealing, both solution- and melt-spun fibers show increased amounts of crystallization via DSC. WAXS measurements agree with this finding and also indicate that there is not only an increase in the amount of crystalline material in the samples tested, but that size of the crystals also increases. That is, not only does the integrated area under the peaks attributed to the crystalline phase increase, but their full-width at half maximum (FWHM) also decreases implying more diffracting planes available (and therefore, greater crystal perfection) for constructive interference.

The fact that the annealed fibers show more crystallinity is not surprising, since thermal annealing should yield enhanced crystal growth, if the $T_m$ (or in our case the $T_{c-n}$) of the material is not exceeded. However, tied to this increase in crystallinity and crystal growth is also the idea that the non-periodic or amorphous material about the crystallites must also be undergoing a certain amount of structural reorientation. Indeed, our results show that this is the case. The non-crystalline portions of the WAXS fiber patterns show distributions that are narrower for the annealed samples than for their as-spun counterparts. This indicates that a narrower ODF will be
necessary to characterize the samples and their molecular arrangements within these materials. A narrower ODF also indicates that more terms will be necessary in the Legendre polynomial series expansion.

3.3.4 Quantitative Interpretations: Legendre Analysis

As discussed in Chapter 2, the use of a series expansion analysis can be used to make the copious amount of data more succinctly interpretable. In the case of samples which display a cylindrical axis of symmetry, the analysis is greatly simplified since the spherical harmonics of the first kind reduce to Legendre polynomials of only even order. Symmetry allows a reduction in the number of polar angles necessary to describe the system. In the fiber samples, the obvious choice of the axis of symmetry is the fiber axis. The two orthogonal directions lateral to the symmetry axis are combined, yielding equivalent directions perpendicular to the fiber axis. The convention we used for the azimuthal angle, $\alpha$, is that the direction parallel to the axis (also referred to as meridional) is $\alpha = 0^\circ$ and the direction perpendicular to the symmetry axis (which is equatorial) is $\alpha = 90^\circ$.

To normalize the data (rescaling it in terms of atomic units), we followed the methodology outlined by Mitchell and Windle [Mitchell, G.R., 1982,1985a] who in turn adapted the normalization method from Krogh-Moe [Krogh-Moe, J., 1956]. See Chapter 2, section 2.2.3.2 for more of the mathematical details. The normalization may be envisioned as a reallocation or redistribution of scattering intensity. The normalization is based on the supposition that the total scattering intensity remains the same and it is merely the spatial location of the scattered intensity that has been altered. The normalization forces the experimental data into a common frame of reference that of a given amount of scattering events per unit time and volume. One of the main effects of the data processing on the fiber diagrams is to enhance the difference between the minima (negative areas) and maxima (positive areas) of the scattered intensity. In fact, due to the subtraction of the incoherent and self-scatter from the pattern the processed scattered intensity is actually a representation of the
redistribution of the scattered intensity due to the presence of order and orientation.

Once we have renormalized the non-crystalline portion experimental fiber pattern, we can apply the Legendre polynomial series expansion analysis to the data. Figure 3.8(a-d) show the experimentally derived coefficient traces of the four HIQ-x fiber samples. These data are derived from the non-crystalline 2-D WAXS traces in Figures 3.5 - 3.7 (parts d) and Figure 2.4(a).

![Graphs showing Legendre series coefficient traces for HIQ-40 fibers](image)

Figure 3.8: Legendre series coefficient traces for HIQ-40 fibers, a) hiq40fsa, b) hiq40fsh, c) hiq40fma, d) hiq40fmm, as a function of the scattering vector, s. $A_{10}(s)$ is the maximum coefficient shown (if necessary)

When initially characterizing the experimental structure factor coefficient traces, $A_{2n}(s)$, one can get a qualitative feel for the distribution represented by looking at the total
number of coefficients used in the series to characterize the fiber diagram and which coefficient trace has the highest maximum value. These factors are shown in Table 3.6.

<table>
<thead>
<tr>
<th></th>
<th>hiq40fsa</th>
<th>hiq40fsh</th>
<th>hiq40fma</th>
<th>hiq40fmh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum number of coefficients</td>
<td>$4(A_6(s))$</td>
<td>$5(A_8(s))$</td>
<td>$7(A_{12}(s))$</td>
<td>$9(A_{16}(s))$</td>
</tr>
<tr>
<td>Largest coefficient (absolute value)</td>
<td>$A_0(s)$</td>
<td>$A_2(s)$</td>
<td>$A_2(s)-A_4(s)$</td>
<td>$A_2(s)-A_4(s)$</td>
</tr>
</tbody>
</table>

Table 3.6: Qualitative Comparison of Experimental Coefficient Traces for HIQ-40 Fibers

Qualitatively speaking, the more terms needed in the series the narrower the ODF. As well, the larger coefficients contribute more to the series reconstruction. Thus, if a higher order coefficient has a large magnitude, the ODF more closely approaches the shape of that basis function. Relating these ideas back to our samples, it would appear that the hiq40fsa fibers should have the lowest degree of orientation and the hiq40fmh the highest. Hiq40fsh should have the second lowest degree of orientation and hiq40fma the second highest. The fact that the melt-spun fibers require a larger number of Legendre polynomial series terms implies that melt-processing induces the highest degree of orientation in fibers. While, annealing also, has a tendency to increase orientation, its effect is not as great.

From the traces shown, there appear to be two distinct features: an asymmetric one which lies on the equator near $s = 1.45\text{Å}^{-1}$ ($-2\theta = 20^\circ$) and one that lies on the meridian near $s = 3.1\text{Å}^{-1}$ ($-2\theta = 45^\circ$). From the coefficient traces we can tell that the feature at $s = 1.45\text{Å}^{-1}$ lies on the equator since its $P_2(\cos\alpha)$ coefficient is negative at that $s$-value.

Likewise, the feature at $s = 3.1\text{Å}^{-1}$ lies on the meridian since it's $P_2(\cos\alpha)$ coefficient is positive for that $s$-value. The equatorial feature is termed an interchain peak or feature and is due to spacings lateral to the chain direction. The meridional feature is considered an intrachain peak, since its spacings lie along (or parallel) to the fiber axis which is associated with the polymer chain axis. The asymmetry of the interchain peak
may be characterized for the present discussion as two symmetric features. We assumed the two interchain features to lie at $s \sim 1.45\text{Å}^{-1}$ and $1.75\text{Å}^{-1}$.

Figure 3.9 compares the first 4 experimental coefficient traces for the HIQ-40 fiber samples.

![Graphs showing experimental coefficient traces for HIQ-40 fiber samples]

Figure 3.9: Comparison of the experimental coefficient traces for the four HIQ-40 fiber samples

We note the following things about the comparison between fiber coefficient traces. First, there is very little shift in the position of the maximums for each of the interchain or intrachain features. The relative contributions of each trace to the series expansion...
varies, but the similarity between the coefficient traces implies that we will be able to use the same molecular ensemble for the theoretical structure factor calculation. Second, the second interchain feature is much weaker in intensity than the first interchain feature.

The roughness of the coefficient traces for the hiq40fmh fibers is due to the Gaussian peak subtraction. As previously noted, when looking at the hiq40fmh fiber diagrams, some intensity from the crystalline peaks remains. We can now see the magnitude of some of these crystalline peak artifacts more readily. The crystalline subtraction affects the traces in two ways: it decreases the overall intensity and it introduces subtraction artifacts. As noted previously, there is no a priori reason to presuppose that the shape of the crystalline peaks is Gaussian, especially in the azimuthal direction. The overall reduction of intensity occurs since a larger portion of the trace is crystalline and with a larger portion of the trace removed, the hiq40fmh coefficient traces (derived from the portion of the fiber diagram remaining after the crystalline subtraction) are more sensitive to noise and artifacts in the data. Thus, intensity which is missed by the assumed functional form will be incorporated into the non-crystalline pattern and subsequently into the coefficient traces which are derived from the subtraction of the crystalline peaks from the experimental data.

3.3.4.1 Coefficient Modeling and Theoretical Calculations
Semi-quantitatively, the melt-spun fibers show a higher degree of orientation than the solution-spun ones. One can discern this conclusion from the fact that the number of terms in the series expansion is higher. We noted in Chapter 2, section 2.2.1 that the functional forms of higher order Legendre polynomials contained narrower features. Thus, the distribution of spaces described by the Legendre polynomial series for the melt-spun fibers is narrower. In addition, the magnitudes of the higher order terms is more significant in the annealed and melt-spun samples. Only in the hiq40fssa sample is the $A_0(s)$ coefficient term the largest in absolute value. In the other fiber samples, the $A_2(s)$ or $A_4(s)$ coefficients are more significant. This implies that these annealed
and melt-spun samples again, have a narrower orientation distribution of scattering units.

Thus, qualitatively, we can conclude that we expect the melt spun fibers, hiq40fma and hiq40fmh, to show the higher degrees of orientation and the hiq40fmh fibers should display the highest degree of orientation. Ostensibly, hiq40fsh fibers should display more orientation than hiq40fsa fibers, but less than hiq40fma fibers. This conclusion is based on the fact that the hiq40fsh has fewer non-negligible series coefficients than hiq40fma, but more than hiq40fsa.

3.3.5 Modeling Comparisons
3.3.5.1 The Amorphous Trace, $A_0(s)$
As noted in Chapter 2, the $P_0(\cos\alpha)$ coefficient trace, $A_0(s)$, has two contributing factors to it. Because we are dealing with all of the non-crystalline scattering, it may contain both oriented and unoriented non-crystalline material. By definition, the unoriented phase is isotropic. Thus, it will add only to the isotropic coefficient, $A_0(s)$. Its contribution to all of the higher order coefficients (i.e. $2n > 0$) must be identically zero. The isotropic amorphous trace that we have chosen to use has been derived from a Biosym™ simulation. A more detailed description of the parameters is contained in Chapter 2, section 2.4.1.6. To summarize, we simulated 50-unit chains in a 20Å x 20Å x 20Å box with a density of 1.35 g/cm³. The resultant isotropic scattering curve is given below in Figure 3.10.
3.3.6 Modeling results

We are utilizing a molecular model with explicit atomic coordinates. The model consists of RIS-generated aromatic polyester chains placed via a Monte Carlo sampling method on a two-dimensional lattice. The basic inputs are the ester torsions allowable (which influences the chain sinuosity) and the unit cell parameters, a, b and γ. The RIS states are hard coded and allow the esters to rotate up to ±30° out of the plane of the backbone. The phenyl rings are allowed 4 states (±45 or ±135) if they are attached to an ester oxygen. Otherwise, they are planar with the ester carbonyl. Two termination criteria are used: a hard-core interaction characterized by $K_{vdw}$, and a “measure of merit,” which involves a sum of squared deviations comparison to a set of experimental traces, characterized by $\beta_X$. The determination of the proper parameters is done iteratively with variations on a HCP or the crystalline lattice of the material used as starting points.

3.3.6.1 Orientation Distribution Functions (ODFs)

Once the features of all relevant coefficient traces have been matched, the scaling factors between traces indicates their relative contributions to the ODF for that
ensemble (insofar as the model represents that sample). As seen in Chapter 2, when we have an axisymmetric system, the ODF is composed of the scaling coefficients, $D_{2n}$, derived from the comparison of theoretical calculations to the experimental data. Mathematically, this is shown in equation 3.x:

$$A_{2n}(s) = D_{2n} \cdot A_{2n}^{calc}(s) \quad (3.3)$$

The $D_{2n}$'s are then used to reconstruct the ODF in a Legendre series summation:

$$D(\alpha) = \sum_{2n} D_{2n}P_{2n}(\cos \alpha) \quad (3.4)$$

It is just a series summation of a Legendre polynomial series analogous to the deconvolution of the experimental data, except that the equation is only a function of $\alpha$. As previously mentioned, Legendre series coefficients are not intrinsically associated with a particular scattering reflection or spacing. However, they do offer general insight into the nature of the “orienting body” in the system. For example, as the distribution being described becomes more narrow, the number of terms (and therefore number of coefficient traces) increases since only the higher order Legendre series terms display the narrow features required to match a narrow intensity distribution.

3.3.7 Ensemble Comparisons

Two sets of molecular ensembles may be compared to the experimental HIQ-40 sample traces. In the first case, a single sample is used to develop an ensemble, which is then compared to all other samples. We expect that the ensemble used will best fit the experimental data from which it was originally validated. However, this method allows the most direct comparison of ODFs since all distributions are derived from the same ensemble. The second case is one in which each set of the HIQ-40 fiber coefficient traces is used to derive its own characteristic ensemble and ODF. This case gives us the most accurate representation for each sample, though theoretically, the ODFs derived only relate to the specific ensembles that generated them. As noted previously, there is very little difference in the feature positions found in the four fiber experimental coefficient traces. As such, we are not required to utilize the multiple ensemble analysis in this case.
3.3.7.1 Iso-structural Analysis

The single ensemble method allows for the most direct comparison of ODFs between samples. As we have noted previously, all of the HIQ-40 fiber coefficient traces show similar feature positions. However, the $A_{2n}(s)$ traces do display markedly different relative contributions to the ODF. This is actually ideal, since the model and analysis parameters influence feature positions and shape, but make no suppositions about the individual coefficient contributions to the ODF. One can view the iso-structural analysis as an attempt to enforce a common molecular model (or ensemble) upon a group of samples. Thus, the scaling is a reflection of exactly how this particular ensemble of structures orients within this sample. The sum of squared deviations (a function of $\chi^2$) measure how accurately the model ensemble describes the molecular scale structure of the sample.

The resultant ODFs from the iso-structural analysis are shown in Figure 3.11. The ensemble used was the one derived in Chapter 2 for the hiq40fsa sample. The parameter values for the simulation were as follows. Each structure generated consisted of HIQ-40 dimers on a 3x3 lattice. Lattice parameters used were $a = 4.25$ Å, $b = 3.75$ Å, $\gamma = 80^0$. The temperature and pressure of the simulation were fixed at 300K and 1 bar. The van der Walls cutoff factor, $K_{vdw}$, was 0.5 and the measure of merit parameter, $\beta_X$ was 20,000. 647 structures out of 6000 attempted were accepted.
Figure 3.11: ODFs for the four HIQ-40 fiber samples in the iso-structural analysis.

Table 3.7 shows the scaling coefficient values, \(D_{2n}\), used in the equation 3.4 and whose distributions are pictured in Figure 3.10.

<table>
<thead>
<tr>
<th></th>
<th>hiq40fsa</th>
<th>hiq40fsh</th>
<th>hiq40fma</th>
<th>hiq40fmh</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_0(s))</td>
<td>80.7</td>
<td>70.8</td>
<td>66.4</td>
<td>61.4</td>
</tr>
<tr>
<td>(A_2(s))</td>
<td>6.40</td>
<td>35.8</td>
<td>33.0</td>
<td>34.4</td>
</tr>
<tr>
<td>(A_4(s))</td>
<td>2.49</td>
<td>14.9</td>
<td>26.7</td>
<td>31.5</td>
</tr>
<tr>
<td>(A_6(s))</td>
<td>~0</td>
<td>3.98</td>
<td>19.8</td>
<td>28.1</td>
</tr>
<tr>
<td>(A_8(s))</td>
<td>--</td>
<td>~0</td>
<td>9.94</td>
<td>19.4</td>
</tr>
<tr>
<td>(A_{10}(s))</td>
<td>--</td>
<td>--</td>
<td>3.31</td>
<td>13.4</td>
</tr>
<tr>
<td>(A_{12}(s))</td>
<td>--</td>
<td>--</td>
<td>~0</td>
<td>8.90</td>
</tr>
<tr>
<td>(A_{14}(s))</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>6.77</td>
</tr>
<tr>
<td>(A_{16}(s))</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>~0</td>
</tr>
</tbody>
</table>

Table 3.7: Scaling Coefficients for HIQ-40 Fibers in the Iso-Ensemble Analysis. All values of \(D_{2n}\) are \(x \times 10^{-3}\).
We can see that the D_{2h}'s show the trends we expect, i.e. the value of the higher level coefficients are lower than the low index ones. [Bower, D., 1981] Table 3.8 shows a collation of results based on the iso-structural analysis.

<table>
<thead>
<tr>
<th></th>
<th>hiq40fsa</th>
<th>hiq40fsh</th>
<th>hiq40fma</th>
<th>hiq40fmh</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODF_{max}</td>
<td>0.0902</td>
<td>0.1254</td>
<td>0.1591</td>
<td>0.2032</td>
</tr>
<tr>
<td>FWHM</td>
<td>64.6°</td>
<td>61.0°</td>
<td>38.0°</td>
<td>27.9°</td>
</tr>
<tr>
<td>%XTAL</td>
<td>0.0%</td>
<td>18.2%</td>
<td>9.2%</td>
<td>27.6%</td>
</tr>
<tr>
<td>%ONC</td>
<td>85.6%</td>
<td>66.8%</td>
<td>88.0%</td>
<td>64.4%</td>
</tr>
<tr>
<td>%UNC</td>
<td>14.4%</td>
<td>15.0%</td>
<td>2.8%</td>
<td>8.0%</td>
</tr>
<tr>
<td>χ_i^2</td>
<td>47.2</td>
<td>85.6</td>
<td>112.5</td>
<td>99.2</td>
</tr>
</tbody>
</table>

Table 3.8: Collation of Orientational Structural Parameters for HIQ-40 Fibers. %XTAL, %ONC, and %UNC are the relative fractions of the crystalline, oriented non-crystalline and unoriented non-crystalline material, respectively.

It lists two parameters which partially characterize the ODF, its maximum value and FWHM. The FWHM is taken only on the anisotropic part of the ODF. If the ODF were Gaussian in shape, these two parameters would fully specify it. However, because we have not specified a normal distribution, these two parameters only supply part of the picture. However, the numeric comparisons offer some insight. Also, as concluded in the discussion of the experimental traces, the melt-spun fibers show more orientation than the solution-spun and the unannealed samples display broader more diffuse ODFs than their heat treated counterparts. However, we now have a more quantitative feel for what that means. Table 3.8 also displays the final χ_i^2 for the comparison of the experimental and calculated structure factor coefficients. Again, one notes that the value of β_χ = 20,000 is much larger than the average deviations in the trace. This means that we accepted most of the structures that passed the steric constraint.

Table 3.8 also contains a breakdown of the relative percentages of the three phases.
used to describe the system: the crystalline (%XTAL), oriented non-crystalline (%ONC), and unoriented non-crystalline (%UNC) phases. All of the ODFs show a significant proportion of unoriented, but locally structured, aligned material. This implies that the one of the effects of processing is that it can induce local orientation without leading to macroscopic orientation.

One can see that the relative percentages of the unoriented non-crystalline material for the annealed samples relative to their unannealed equivalents are the same (or slightly higher). This leads us to believe that the primary contributor of material used in crystallization is the oriented non-crystalline material. Thus, the effect of annealing seems to cause the oriented chains in the non-crystalline portion to crystallize. This fits our intuition, since the oriented chains are in an arrangement that is fairly similar to the crystal unit cell. It would require little energy to overcome the barrier to crystallization for these oriented chains. This would imply that the oriented non-crystalline chains could crystallize much more readily than the unoriented non-crystalline chains. It is well established in the literature that oriented chains crystallize more rapidly than their unoriented counterparts. [Mandelkern, L., 1964, Kawai, T., 1967, Adams, A., 1995]

From the FWHM of the ODF peaks, we can see that annealing causes an increase in the degree of alignment of oriented chains. It is likely that small scale defects and imperfections are being reduced during the annealing process. The elimination of such disruptions to order can only occur on a small (i.e. local) size scale in the material. The annealed melt-spun fibers show a larger decrease in the FWHM of their ODF relative to the unannealed melt-spun fiber than the annealed solution-spun fiber does to the unannealed solution-spun fiber. This implies that the orientation of the unannealed material can have a large effect on the degree of chain reorientation that occurs. It may also influence the maximum degree of crystallinity attainable by a material.

Our results also show that the amount of unoriented non-crystalline material does not decrease upon annealing. This fact implies the oriented phases are not pulling material from the unoriented phase in order to induce additional orientation in the material. Put another way, annealing of the sample only perfects any orientation that is already
present, it will not create it anew. In the melt-spun fibers, it appears that there is also a relaxation effect going on in the unoriented non-crystalline phase leading to more of the isotropic phase being generated.

The solution-spun fibers have much broader peaks in their ODF in comparison to the melt-spun fibers. This implies that the solution-spinning process does not cause an extended chain conformation, nor does it align the chains. The spinning process must induce the initial orientation in the material, since as discussed above, annealing will not create orientation, only perfect it. The high degree of orientation in the melt-spun fibers is attributed to the presence (and alignment under mechanical bias) of nematic domains in the liquid crystalline phase of the melt from which the fibers were spun.

3.4 Discussion of Results

3.4.1 3-Phase Model

In Chapter 2, we noted that the presence of two phases were required to account for all of the scattering features in the fiber sample. Now that we have multiple samples, we have determined for the more general case that three phases are required. The three phases are: a crystalline, an isotropic amorphous, and an oriented non-crystalline phase. The first two phases are well excepted in the literature. The third has been postulated, especially in some polymers such as PET [Fu, Y., 1993, Hristov, H., 1991, Galeski, A., 1992, Fischer, E., 1976, Clauss, B., 1995, Asano, T., 1973] Our WAXS results and Legendre polynomial series analysis agree with the assertion that the oriented non-crystalline phase exists. Additionally, we assert that the amount of oriented material is not restricted to the interface of the crystalline and amorphous sections of the polymer alone. Instead, our results indicate that the crystalline phase is generated within the oriented portion of the non-crystalline phase, preferentially consuming the material from that phase over the unoriented portion. A significant portion of the material in a fiber is oriented and a significant portion of the oriented material is non-crystalline. For example, over 84% of the chains in the hiq40fma fibers are oriented, where less than 10% of these oriented chains are in the crystalline
phase. This fact reinforces the assertion that the non-crystalline section of the material should be of great interest to anyone who desires to understand the behavior of the material, since it comprises such a significant proportion of the material.

3.4.2 Comparisons of Series of Data
One can see from the experimental coefficient traces, the spacings for all of the HIQ-40 fiber samples are similar. This implies that the morphology for the various samples is rather similar, even in the solution-spun fiber cases. The orientation of these units is much less in the solution-spun fibers, but the mean interchain spacings are similar in the non-crystalline portions of the traces and have a common value of \( s = 1.416 \text{Å}^{-1} \) \( (d = 4.456 \text{Å}) \). This is very close to the general Van der Waals interaction distance quoted of \(-4\text{Å} - 5\text{Å}\). However, in HIQ-40, there is also an additional interchain spacing of lesser magnitude between \( s = 1.443 \text{Å}^{-1} - 1.687 \text{Å}^{-1} \) (corresponding to \( d = 4.354 \text{Å} - 3.724 \text{Å} \)). This secondary spacing varies between solution- and melt-spun fibers.

Assuming a paracrystalline structure, these mean spacings can give us insight into the type of quasi-unit cell needed to capture various scattering features in the experimental data. Obviously, that is not the whole story. Modeling allows us to interpret some of the features as having correlations between molecular scale structure and macroscopic measurements. We concluded that the melt-spun fibers contained a higher degree of chain orientation as demonstrated by the presence of only the liquid crystalline peaks in the hiq40fma fibers. Thus, we have seen that the effect of melt spinning is to induce a higher degree of orientation and extended chain conformations in fibers produced by that route. The annealed samples (hiq40fsh and hiq40fmh) displayed a higher degree of periodicity in the directions lateral to the chain. This implies that the directions lateral to the chain crystallize more readily than directions along the chain. This seems reasonable, since the directions lateral to the chain are generally less constrained by the connectivity of the chain backbone. We envision the chain direction to be highly conformationally constrained due to connectivity between atoms.
We noted also that the multiple-ensemble analysis was not needed to compare the HIQ-40 fiber samples. This is based upon the similarity found in the experimental series expansion coefficients. This similarity implies that for this set of fiber samples, the local-scale structures contained within the samples are also very similar. The short chains in our simulations means that we are primarily modeling the lateral packing behavior of HIQ-40 fibers. Thus, the ODFs derived for each sample show how much chain packing is occurring in each direction with respect to the fiber axis. There are large isotropic components to our ODFs, implying that these interactions between chains are occurring at all directions of the sample.

Most, if not all, of our expectations made in the qualitative analysis section are met. We can see from the modeling results that increase in either mechanical or thermal bias leads to greater alignment and orientation down to a molecular scale. This fact is made more readily, concisely, and quantitatively when we use the Legendre polynomial series analysis to derive coefficient traces, molecular ensembles and ODFs for the HIQ-40 fiber samples. The differing effects of fiber spinning and annealing are readily apparent for our results.

Thermal bias, or annealing, has the function of eliminating defects and creating a higher degree of crystalline perfection in our fiber samples. The increased degree of perfection is associated with directions lateral to the chain, whether the chain is in an extended conformation or not. This conclusion is based on the observation that equatorial peaks appear in both annealed fiber samples, but enhancement of meridional peaks is not necessarily seen in the annealed samples. This implies that the directions lateral to the chain are more mobile than those along the chain. The annealed samples show a higher degree of orientation of chains and, more importantly, the oriented non-crystalline phase of the material is preferentially consumed in the growth of the crystalline phase. In fact, the melt-spun fibers seem to indicate that the unoriented non-crystalline material also undergoes some relaxation which withdraws a minor amount of material from the oriented non-crystalline phase. The spinning process is very important in the establishment of orientation on the microscopic scale.
Whereas, annealing can perfect partial alignment of chains, it will not initiate orientation of them. The initial orientation of chains is accomplished in the spinning step. The comparison of the solution-spun fibers from a non-lyotropic solution and the melt-spun fiber from the nematic melt highlight this fact. The hiq40f4sa fibers show almost no chain orientation, where hiq40fma samples a measurable amount of orientation. This degree of orientation is then built upon by the annealing step.

3.5 Chapter Conclusions and Interpretations

We have used the Legendre polynomial series analysis to compute and compare the ODFs for a set of HIQ-40 fibers. The series analysis yields a set of quantitative parameters for description of an oriented molecular model as well as the ODF. The model parameters allow a more accurate description of the system on a molecular level and affords us insight into the relative effects of various processing parameters on the molecular-scale structure of the HIQ-40 fiber samples. We have seen that annealing leads to both higher degrees of chain orientation as well as crystallization of the material. Also, comparison of the melt-spun and solution-spun fibers demonstrates the range of chain alignments possible through varying processing. The mere fact that we can spin from the melt highlights the processing versatility of HIQ-x and validates study of it for the purposes of exploring its potential as a Kevlar™ alternative.

Up to this point, we have only considered samples of HIQ-40, but conclusions about the applicability of the three phase model to other systems are also possible. The intuitive assumption that the extension of this methodology to other aromatic polyester systems, as well as other polymers (or other materials displaying molecular-level anisotropy) would be a straightforward process and is supported in the upcoming chapters. We shall see that even when studying a different polyarylate system (PET), the methodology of a series deconvolution analysis translates over almost completely and a number of analogous conclusions dealing with the nature of the polymer chains and their alignment can be made.
Chapter 4

3-D Analysis: Plane-Strain Deformed PET

"... the sciences are defined by necessity, utility, and difficulty, since art is concerned with the difficult and the good, as Aristotle says in Ethics, book 2. For if what is sought is easy, it is unnecessary to create a science [out of it]; likewise, if it is difficult but useless, we do not create a science out of it, since such effort would be foolish and futile..."

- Roger Bacon, Perspectiva, Part I, Distinction 1, Chapter 1, l. 37-41

4.1 Motivation and Objectives

This chapter presents the complete spherical harmonic series analysis with respect to a three-dimensionally anisotropically oriented sample of PET produced under plane-strain compression. We do not desire to have a highly anisotropically oriented sample, as that would require a large number of series terms and their coefficient traces to be studied and reproduced, but do require some measurable spatial anisotropy to display the merits of the analysis.

As espoused in Chapter 1, the use of a spherical harmonic series to characterize an unknown function or distribution in spherical coordinates is a natural choice. For our purposes, they present a succinct and well characterized method for the elucidation of spatial orientation in the system. They offer a standardized and informative method of characterization for the experimental traces. The functional forms of the spherical harmonics do not a priori preselect a given distribution; they can be used to model any theoretical distribution in spherical coordinates. Of course, there are practical limits based upon the degree of noise and sharpness of any features which may limit the ultimate applicability of the spherical harmonic series deconvolution. However, for smoothly varying functions (such as most naturally occurring orientation distribution functions (ODFs)), we would anticipate very few problems due to the feature breadths. Noise, on the other hand, can always limit the applicability of the series expansion, as it becomes more significant in the determination of coefficients of higher order terms in the series expansion. This is due to the fact that the higher order series terms have narrower features, and thus “model” the noise more readily.
The WAXS spherical harmonic series coefficients can be used in two ways: 1) in comparison of different samples and 2) coupled with molecular modeling. Comparison of samples highlights the relative differences of varying processing parameters and can show the development of structural detail through a series of samples. Judicious selection of a relevant molecular model produces analogous series structure factor coefficients which are then correlated to the experimental ones. In turn, the model is correlated to the sample as a suitable local- or molecular-scale description of the material. This molecular model can then be used for subsequent simulations to estimate other properties and correlations.

4.1.1 Objectives
Once we have selected the spherical harmonics as a natural system of basis functions, it becomes incumbent upon us to set forth a working methodology to integrate their use into a meaningful analysis. This chapter sets forth such a methodology and designates the components and assumptions that must be made at each step. We start with the analysis of experimental data using a spherical harmonic series deconvolution of the pattern in the general three-dimensional case. Then we discuss semi-quantitatively the scattering coefficient traces which result. Matching these scattering coefficient traces is the key to analysis and requires the introduction of an independent molecular model which we can then correlate to the experimental data. The resultant ensemble from the model parameters allows the comparison to experiment and enables us to deduce the ODF.

We refer the reader to Figure 2.1 for the general methodology in the spherical harmonic series deconvolution analysis. As presented, Figure 2.1 needs no modification to the overall scheme. The details of many of the equations, while conceptually similar do require modifications based upon the use of spherical coordinates instead of cylindrical. These modifications are described more in depth later in this chapter. We begin with a brief recap of processing via channel die and a description of the method for producing the experimental sample used in this phase of the study.
4.2 Experimental Processing

4.2.1 Channel Die

Figure 1.1 shows a schematic of a channel die and the three independent orthogonal spatial directions associated with it. There are three spatially orthogonal axes, the constraint direction (CD), the load direction (LD), and the flow direction (FD). The deformation caused by uniaxial compression in the solid state in a channel die leads to plane-strain deformation. In polymeric systems the long axes, or chain backbones, of the polymer chains eventually align themselves with the direction of the deformation, that is, in the flow direction. Note that with plane-strain deformation, compressed samples should display mirror planes in each of the three orthogonal directions.

4.2.1.1 Heated Press

We used a heated platen press, Carver Model C (no. 2086), with specially modified heating platens which allowed us to process materials at temperatures up to 450°C. The press is manual in its operation and the limiting value on hydraulics is 25,000 lbs of force. The press itself is a constant displacement apparatus, allowing one to control the distance between the platens more accurately than the actual force applied (though
they are obviously related). The platen areas are 6" x 6". The press allows quick cooling of the platens by flushing cooling water through them. This allows the temperature of the platens to be brought from 500°C to 30°C (room temperature) within 3 minutes. This is the fastest quench that we can achieve with the apparatus and still remain under load. Note that as cooling occurs, there is material contraction leading to the possibility of variation of stress on the sample as a function of quenching. Strain should not vary, since the nature of the press which uses a lever-to-screw mechanism for adjusting platen displacements makes it a constant strain device.

4.2.1.2 Sample Production and Processing Parameters

We analyzed one plane-strain deformed PET sample for this study. The sample was held at a processing temperature of 190°C for 15 minutes as a thermal equilibration step. The sample was held in the channel die which was placed between the platens of the press for this time under no load. The platens and channel die had been heated beforehand for a minimum of 2 hours at the target temperature to ensure that they had thermally equilibrated. The sample before the thermal equilibration step registers no crystallinity by WAXS and residual crystallinity (~5%) by DSC. As noted previously in Chapter 1, a processing temperature of 190°C indicates that the degree of crystallinity of the sample should be near maximum (~40%) by the time we begin the deformation process. In turn, this implies that the sample will already have a significant number of crystallites nucleated which will subsequently align in the plane strain deformation. Reorientation of crystallites has been one of the main mechanisms associated with the aligning of chains in plane-strain deformed PET. [Bellare, A., 1993] The sample was deformed at 190°C with 20,000 pounds of force. This amount of force is equal to a final stress of 48.0 MPa on the sample. The sample was allowed to cool overnight dropping to room temperature within 6 hours of deformation. We have designated this sample as PET190SC (processed at 190°C, slow-cooled). The initial sample measured 25mm x 12mm x 6mm. The channel width in the channel die was 12mm. The final compression ratio (CR) of the sample was 2.5. This compression ratio is smaller than expected based on the compressive stress as a function of CR reported
by Bellare [Bellare A., 1993]. While Bellare reports no strain rates for the deformation, we believe the discrepancy in CR at a given applied load to be due to different strain rates in our deformation steps. Our deformation occurred over a 3 second period, implying an average strain rate of 0.8 s\(^{-1}\).

4.2.2 Sample Characterization

4.2.2.1 Wide Angle X-ray Scattering (WAXS): The Pole Figure Attachment

In order to measure the spatial scattering orientation of a material accurately we employed a pole-figure attachment to the \(\theta/2\theta\) goniometer mounted on a Rigaku RU200B Rotating Copper Anode. Essentially, the pole figure attachment consists of a set of nested rings which allows the sample to be placed in any spatial orientation which is described by two polar angles, \(\alpha_L\) and \(\beta_L\). Figure 4.x shows a simple schematic of the definitions and relationships of the laboratory frame, sample frame, and polar angles, \(\alpha_L\) and \(\beta_L\).

![Diagram showing definitions of \(\alpha_L\) and \(\beta_L\) with respect to the sample and laboratory frames.](chart.png)

Figure 4.1: Schematic showing definitions of \(\alpha_L\) and \(\beta_L\) with respect to the sample and laboratory frames.
The x, y, and z-axes are in the reference frame of the laboratory. The sample has a normal, \( \vec{n} \), which always lies in the xy-plane (which is horizontal in the laboratory frame). The angle between the sample normal and the y-axis is \( \alpha_L \). Rotations of the sample about the normal, \( \vec{n} \), is movement in the second polar angle, \( \beta_L \). Note that the scattering angle \( \theta \) is also in the xy-plane, since (by construction) the X-ray source and detector both lie in the xy-plane. \( I_0 \) and \( I \) are the incident and scattered beam intensities, respectively. \( \vec{S}_0 \) and \( \vec{S} \) are the incident and detected X-ray beams in the laboratory frame, respectively. The difference between the incident and detected beams is the scattering vector, \( \vec{s} \). By definition, \( \vec{s} = \vec{S} - \vec{S}_0 = 4\pi\sin\theta/\lambda \), where \( \lambda \) is the wavelength of the X-ray radiation (in this case, \( \lambda_{K\alpha} = 1.5425\text{Å} \)).

4.2.3 3-D WAXS Data Visualization: Pole Figures and 3-D Spatial Diagrams

4.2.3.1 Pole Figure Stereographic Projections

The pole figure diagram is a common technique for visualizing the spatial dependence of scattered intensity from a given set of diffracting planes. Both crystalline and non-crystalline (as in the case of PE or Nylon-6,6 [Bartczak, Z., 1992, Galeski, A., 1988]) scattered intensity can be visualized using a pole figure diagram. The pole figure diagram is a stereographic projection of scattered intensity at a given 20 value as a function of its spatial orientation (i.e. the two polar angles). As with the fiber diagram, there are only two independent variables. Unlike the fiber diagram which uses one polar angle and the scattering vector magnitude as the coordinate axes, the pole figure diagram uses the two polar angles. The intensity is then plotted as contours. Figure 4.2 shows one quadrant of a typical pole figure.
Figure 4.2: An example of a pole figure diagram. This example is of the $\overline{1}05$ reflection (along the chain axis) of a PET plane-strain deformed specimen.

This example is the PET190SC plane-strain deformed sample. The $2\theta$- value is $42.5^\circ$. For PET, this $2\theta$ value is associated with the $(\overline{1}05)$ reflection which lies approximately $5^\circ$ from the chain axis. Figure 4.x shows that the chains in the sample display a high degree of orientation (described by the darker contours) in a particular direction, “on a pole” so to speak. In this case, this orientation is in the FD indicating that many chains are lining up in that direction. For further discussion of pole figure diagrams, the reader is directed to Alexander, Chapter 4. [Alexander, L., 1969]

4.2.3.2 Three Spatial Dimension Data Sets: The 3-D WAXS Pattern
In the case of a three spatial dimension data set, the visual representation is slightly more difficult. In this case, we have 3 independent spatial variables (the scattering vector magnitude, $2\theta$ or $s$, and the two polar angles, $\alpha$ and $\beta$, and a fourth dependent variable, the intensity $(I(s,\alpha,\beta))$) to represent. Visualization of the data is most easily accomplished conceptually, if we think of the 3-D scan being composed of a series of fiber diagrams taken over a number of $\beta$-values. This is analogous to the fiber diagram...
being composed of a number of simpler $\theta/2\theta$ traces. In fact, the 3-D data set contains within it all of the information of pole figure diagrams, fiber diagrams, and conventional $\theta/2\theta$ scans (i.e. 1-D scans). Figure 4.3 shows the 3-D WAXS pattern of the raw scattered intensity from the same plane-strain compressed PET sample that the pole figure is taken from in the previous section (section 4.2.3.1). Also demonstrated in Figure 4.3 are some of the various components that may be taken from it for interpretation.

Any ray emanating from the origin can be considered a single $\theta/2\theta$ scan. Examples of this are shown on two of the 3D-WAXS pattern axes: the load (LD) and constraint (CD) directions. Since these traces are of PET and contain both crystalline and non-crystalline portions of the trace, they should show results analogous to those found for crystalline orientation of Bellare, et al. [Bellare, A., 1993] In the load direction, we do indeed see the (100) peak at $2\theta = 25.7^\circ$. Analogously, in the CD the (010) peak at $2\theta = 17.3^\circ$ dominates the $\theta/2\theta$ trace. Additionally, if we wish to look at a set of intensities as a function of orientation angle, then a “shell” of data is taken. Each shell would contain the data at constant scattering angle for all spatial orientations. An example of this is also shown in Figure 4.3, which depicts scattered intensity of the (105) reflection as a function of the spatial orientation of the sample. We can see that, if we take the shell of data only at $2\theta = 42.5^\circ$, the stereographic projection of that reproduces a quadrant of a pole figure diagram which again matches the data reported by Bellare, et al. [Bellare, A., 1993] Lastly, the three flat faces of the octant of data can be seen to represent 2-D fiber patterns of data (the fiber patterns are shown in black contours on each of the octant faces). In fact, any plane taken from the 3-D WAXS pattern which passes through the origin will produce a fiber diagram.
Figure 4.3: A 3-D WAXS pattern and its breakdown into 1-D and 2-D scans.
Note that, due to the effects of symmetry (the mirror plane in each of the 3 orthogonal directions of a plane-strain deformed sample), the 3-D WAXS patterns that are in this thesis require only one octant of the entire sphere to be taken. In our experiments we used the following convention. The CD corresponded to $\alpha_L = 0^\circ$, $\beta_L = 0^\circ$, the FD corresponded to $\alpha_L = 0^\circ$, $\beta_L = 90^\circ$, and the LD corresponded to $\alpha_L = 90^\circ$, all $\beta_L$ values. This means that $\bar{n}$ (re: Figure 4.1) is also the normal to the LD. As such, the LD has no set $\beta_L$-value due to geometric constraints of the experimental set-up. The data at $\alpha_L = 90^\circ$ must be taken in reflection mode (i.e. the detected X-ray beam reflects off of the surface of the sample as opposed to transmission mode where the detected beam passes through the sample). As such, diffracting distances in the LD are parallel to the bisector of the incident and detected X-ray beams. Given this, the rotation of those planes about $\beta_L$ (which is rotation about the normal to LD and is also a bisector of the incident and scattered beams) will all yield the sample configuration of the scattering distances (i.e. parallel to the normal of LD and the bisector of $\bar{S}$ and $\bar{S}_0$). Figure 4.4 shows a simple schematic of the transmission verses reflection geometries.

![Figure 4.4: Schematic showing the relationship between the transmitted and reflected scattering X-ray beams.](image)

For the purposes of our molecular model, it was necessary to transform the convention by which our experimental data was taken. The molecular model we used consists of aligned chains, which should eventually line up in the FD. Therefore, the convention best suited for the structure factor calculations was that the FD corresponds to $\alpha = 0^\circ$, $\beta = $ all values, the CD corresponds to $\alpha = 90^\circ$, $\beta = 90^\circ$, and the LD corresponds $\alpha = $
90°, β = 0°. This convention is shown in Figure 4.5, which depicts both the laboratory and molecular frame conventions.

Figure 4.5: Axes conventions for the molecular frame ($\alpha$, $\beta$) and the laboratory frame ($\alpha_L$, $\beta_L$) with respect to the sample frame (FD, LD, CD).

The transformation between conventions is straightforward with $\alpha$ and $\beta$ related to $\alpha_L$ and $\beta_L$ as follows:

$$\alpha = \cos^{-1}\left(\frac{\cos(90 - \alpha_L)}{\sqrt{((\sin(90 - \alpha_L))^2 (\cos \beta_L)^2 + (\cos(90 - \alpha_L))^2)}}\right)$$  \hspace{1cm} (4.1)

and

$$\beta = \cos^{-1}(\sin(90 - \alpha_L) \sin \beta_L)$$  \hspace{1cm} (4.2)

Once the experimental data is transformed to the molecular frame convention, we may proceed using $\alpha$ and $\beta$ as our polar angles though the spherical harmonics series expansion.

4.2.4 Differential Scanning Calorimetry, DSC

Differential Scanning Calorimetry (DSC) is used to measure thermodynamic properties and transitions of a material. The thermodynamic properties of an unknown sample can be investigated by comparing the thermal input into the sample relative to a known reference.
PET has a glass transition, $T_g$, reported between 67°C (for the purely amorphous PET) and 81°C (for PET at its maximum degree of the crystallinity). [Kolb., H., 1949] The melting point of PET, $T_m$, has been reported as 265°C. [Bellare, A., 1993, Kolb., H., 1949]. The maximum degree of crystallinity, $\chi_{DSC}$, for PET is generally reported to be about 40%. Mehta et al., derive a value of $\Delta H^0_f = 140$ J/g $\pm$ 20 J/g for the heat of fusion in surveying literature and experimental values from a number of different sources. [Mehta, A., 1978] Under very high strain rates at moderate to low temperatures, strain induced crystallinity becomes a significant factor, but generally does not increase the maximum degree of crystallinity. [Clauss, B., 1992]

We used a Perkin-Elmer DSC-7 with the following experimental parameters in our DSC runs: a heating rate of 20°C/min and a temperature range of 50°C (323.16 K) to 300°C (573.16 K). Sample weights were measured on a microbalance and ranged from 5.000mg to 20.000mg. The weight is needed as a reference to calculate standard enthalpies of thermal phenomena in the DSC trace. The Perkin-Elmer DSC-7 used is located in the Center for Material Science and Engineering (CMSE). This work made use of MRSEC Shared Facilities supported by the National Science Foundation under Award Number DMR-9400334.

4.3 Characterization Results

The main two polymer characterization techniques utilized in this chapter were DSC and WAXS. The two techniques are highly complimentary in that, whereas DSC is a bulk-averaged, spatially independent measure of the thermodynamic (and thus, energetic) differences within the material, WAXS is a bulk-averaged, spatially dependent measure of the local (i.e. atomic-scale) distances within the material. Another contrast between the two techniques is that DSC is an invasive analysis technique and WAXS is a non-invasive, static technique. These two allow us to look at different (though obviously related, since they come from the same sample) properties.
of a material. DSC gives a measure of the thermodynamic stability of a given solid-state phase, where WAXS gives us the spacings and structure contained within that same solid-state phase.

4.3.1 DSC
With the literature values quoted in section 4.2.4, we now have a set of reference values to compare to our own experimental data. Figure 4.6 shows the DSC traces for the PET190SC plane-strain deformed sample.

![DSC scan for PET190SC showing a melting peak at 260°C](figure)

Table 4.1 shows the numerical parameters which characterize the main peak depicted in Figure 4.6.

<table>
<thead>
<tr>
<th>PET190SC</th>
<th>Onset (°C)</th>
<th>Tm (°C)</th>
<th>ΔHf (J/g)</th>
<th>χDSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>260.2</td>
<td>53.21</td>
<td>38.0%</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: DSC Melting Peak Parameters for PET190SC sample

PET190SC displays an endothermic peak at 260°C. Since, PET is not documented to exhibit an LC phase, this endothermic peak has been assigned as the isotropic melting peak. The melting peak maximum occurs at 260°C for PET190SC. This value agrees
well with the reported literature value of 265°C. Using Mehta and Wunderlich’s $\Delta H^0_f$ value of 140 J/g for the $\Delta H^0_f$ yields a DSC degree of crystallinity ($\chi_{\text{DSC}}$) of 38.0% for the PET190SC sample. $\chi_{\text{DSC}}$ is below 40%, which is consistent with the observed maximum degree of crystallinity generally seen. The DSC scan shows no pre-melting peaks which would indicate additional crystallization or phase changes.

Since this is DSC, we can make no inference about the spatial orientation of the crystallites in the material. We assume that we have crystallites of varying sizes, since the DSC peaks show long tails preceding the melting peak. Larger crystallites have a lower surface-to-volume ratio. Consequently, the long tails of the pre-melting peak is due to the smaller crystallites melting earlier than the larger, more stable ones. From Figure 4.6 it is apparent that we do not see any noticeable T_g for the two samples, despite the fact that we have the range of 67°C - 81°C (where the reported value of T_g for PET is supposed to be) encompassed in the range of temperatures studied with DSC. One can argue that a slope change (indicative of a second-order transition, which T_g is), is occurring between 50°C and 100°C in the scan, but given the values in the data set, no further quantitative estimate can be given.

4.3.2 WAXS: Experimental Data Set
PET processed in a channel die shows “pseudo-single crystal” order, a type of three-dimensional orientation. [Bellare, A., 1993] Given that we have three-dimensional orientation in our sample, we were required to analyze the sample with a technique that would measure a sample’s three-dimensional structural morphology. Wide Angle X-ray Scattering (WAXS) techniques fit the bill perfectly. The use of the pole figure attachment on a standard $\theta$/2$\theta$ goniometer enabled us to measure the spatial orientation at varying $\theta$ values of the scattered intensity from a sample.

The following data collection ranges were used in obtaining the 3-D WAXS patterns from our samples. Due to symmetry, we were required to measure the scattering from
only one octant of the great sphere. We chose $\alpha_L = 0^\circ$ to $90^\circ$ and $\beta_L = 0^\circ$ to $90^\circ$ in steps of $10^\circ$ (i.e. range $\alpha_L$ = range $\beta_L$ = $0^\circ$ - $90^\circ$, $\Delta \alpha_L = \Delta \beta_L = 10^\circ$). The $2\theta$ range collected was between $2\theta = 10^\circ$ to $50^\circ$ in steps of $0.25^\circ$ (i.e. range $2\theta$ = $10^\circ$ - $50^\circ$, $\Delta 2\theta = 0.25^\circ$). A finer mesh in $2\theta$ was not required since our main focus in the study was to measure the oriented non-crystalline material, whose features are very broad in $2\theta$. The crystalline peaks which were to be subtracted out from the trace required only a few points to characterize. With $\Delta 2\theta = 0.25^\circ$ and crystalline peak Full Widths at Half-Maximum (FWHM) of at least of $2.0^\circ$ or more (up to $5.0^\circ$) in size, we were assured of a minimum of eight (8) points to resolve the crystalline peaks. This ensured that our statistics for the peak subtractions were reasonable.

4.3.2.1 PET190SC: 3-D WAXS Pattern

Since it was processed at $190^\circ$C for over 15 minutes, PET190SC should show close to the maximum degree of crystallinity (~40%). Via DSC, we have demonstrated that this is the case. This coupled with the fact that the sample is allowed to cool for a number of hours at temperature under load means that the sample is likely to have a high degree of oriented crystallites. Our purpose here is to determine what the degree of non-crystalline material is in the sample and to make inferences about whether the high degree of crystalline orientation translates into non-crystalline material orienting in a similar fashion.

Figure 4.7 shows the separation of the total experimental 3-D WAXS pattern into its crystalline and non-crystalline portions. We can see from the Figure 4.7(a) that the raw data shows many features which are narrow in the radial direction. These are the crystalline peaks and their contributions are shown graphically in Figure 4.7(b). The remainder of the scattering is shown in Figure 4.7(c). This is assigned as the non-crystalline portion of the pattern.
Figure 4.7: 3D-WAXS patterns for PET190SC. a) Raw, b) crystalline, c) non-crystalline
Contours: a) 16 lvls, 400 counts/lvl, b) 16 lvls, 400 counts/lvl, c) 11 lvls, 200 counts/lvl
There are a couple of things to note about Figure 4.7. First, the chains appear to orient in the manner described by Bellare, et al [Bellare, A., 1993] with their chain axes preferentially aligning in the FD direction, although the distribution is fairly diffuse. The peak is centered on the FD-axis and has polar angle FWHM of approximately $30^\circ$. The crystalline material is primarily axisymmetrically oriented. There are fairly large crystals, as indicated by the small FWHM in the $2\theta$ direction. There is also some differentiation of crystalline directions between the LD and CD-axes. The LD is “preferred.” For example, the crystalline peak for the (100) reflection displays intensity about an annular ring in the LD-CD plane. Its intensity is not isotropic, however, and displays a maximum in the LD.

The non-crystalline scattering does not show the same degree of orientation that the crystalline scattering does. However, the trend behavior is quite similar, with the LD-CD plane showing a distinct amount of fairly diffuse scattering in the $2\theta$ direction, more than the FD. However, the difference is not as large as with the crystalline material. There is also concentration of the LD scattering over the CD. We do not expect the non-crystalline material to be as well organized as the crystalline material; therefore, it is understandable that the non-crystalline material is more diffuse in both structural (i.e $2\theta$) and spatial (i.e. $\alpha$ and $\beta$) orientations of its constituent chains. The fact that the oriented non-crystalline phase mimics the trend behavior of the crystalline phase implies that the oriented non-crystalline phase is linked to the crystalline phase. The chains within each phase are chemically bonded. The viscosity-average molecular weight of the PET is 18,000 amu (which corresponds to $\sim$100 ethylene-terephthalate units). A 100-unit chain should be long enough to tie from one oriented phase into another. With this length of chain, entanglements and chains anchored in two or more crystallites are not uncommon. Thus, as the crystallites orient, some of that orientation will translate over into non-crystalline phase.

4.3.3 Reference Plaque: Purely Amorphous Sample
In order to quantify our results, we used a purely amorphous reference sample to
account for geometrical or instrumental factors introduced by our plaque geometry and the actual physical dimensions of our samples. The spatial orientation of an amorphous reference shaped like our oriented plaques enabled us to quantify and subtract off the geometric effects of the beam passing through varying amounts of material as the sample was rotated in the pole-figure attachment. To model our sample geometry a completely amorphous sample was machined with plaque dimensions similar to that of PET190SC (both were cut to 25.0mm x 12mm x 1.25mm). The reference sample had its 3-D WAXS pattern taken. Any residual orientation in the 3-D WAXS data would have been solely due to the bulk sample dimensions. The sample had not undergone any mechanical strain and was quenched from the melt by immersion in an ice-water bath. Therefore, no crystalline peaks should have been present in the WAXS pattern, a fact which we verified. A representative WAXS θ/2θ trace from the reference sample is shown in Figure 4.8.

![Figure 4.8: PET amorphous reference 2θ scattering curve. Taken at α = 0° and β = 0°. All other α–β combinations show similar shapes, but different scalings due varying thicknesses of sample illuminated by the beam.](image)

DSC results on the reference sample indicate that it contains ~5% residual crystallinity. These crystallites must be too small to resolve by WAXS.

The amorphous reference serves two purposes. In the experimental analysis, it is used to correct the WAXS pattern for any artifacts due to the path length of the beam.
passing through the sample. We take a full 3-D WAXS pattern on our amorphous reference, using the same \((\alpha_L, \beta_L, 2\theta)\) mesh as the sample we wished to analyze. Since the sample is rotated and not spherical in shape, different values of \(\alpha_L\) and \(\beta_L\) can display differing thickness of sample normal to the incident radiation beam. Since, in theory, all of the traces of the amorphous reference sample should register the same total amount of scattering if they presented the same sample thickness to the beam at each \(\alpha_L-\beta_L\) combination, we can deduce the effect of the sample geometry on the beam path length at a given \(\alpha_L-\beta_L\) combination. By taking the ratio between the scattering at the given \(\alpha_L-\beta_L\) combination and a reference \(\alpha_L-\beta_L\) combination, we can account for the varying beam path length in the experimental WAXS data. We chose data collected at \(\alpha_L = 0^\circ\) and \(\beta_L = 0^\circ\) to be the base reference trace in the amorphous reference.

The second purpose of the amorphous reference is that we can also use it as a measure of the unoriented non-crystalline contribution to the isotropic \((n = 0, m = 0)\) term in our series expansion analysis. This is discussed further in section 4.6.5 after we introduce the series expansion analysis.

4.4 Experimental WAXS Results

4.4.1 Pre-processing the 3-D WAXS diagrams

Once collected, the 3-D WAXS patterns were analyzed via deconvolution with a spherical harmonic series. However, before the spherical harmonic analysis can be applied to the experimental data, we need to account for the following factors in the 3-D WAXS diagrams:

1) the crystalline phase,
2) renormalization of data
3) incoherent (or Compton) scatter,
4) and self-scatter

The second step is required, since both the Compton and electron gas scatter are listed in terms of the normalized units. Also, the renormalization makes comparisons
between various samples and theoretical structure factor calculations much more facile, as they are all give a common reference.

4.4.1.1 Accounting for the Crystalline Phase
To account for crystallinity in our samples we used the following technique. The experimental traces were modeled using Gaussians in order to fit the crystalline peaks of the trace. Gaussians were chosen as the functional form, since thermal vibrations and other theoretical displacements from a mean value often display a normal statistical distribution. The Gaussian peak shape was not found to be universally acceptable in modeling the crystalline scattering distributions in the polar angles. Given this fact, we decomposed each of the one-dimensional 0/2θ traces separately. We then checked for consistency between the results of the individual decompositions to ensure that the peaks were of similar positions and shapes between traces that were “adjacent” (i.e. ±1 a_L or β_L step) in the data collection mesh. The objective function to be minimized was of the following form:

\[ OBJF = \sum_{2\theta} (I_{\text{obs}}(2\theta) - I_{\text{calc}}(2\theta))^2 \]  

(4.3)

where:

\[ I_{\text{calc}}(2\theta) = a2\theta + b + \sum_{i=1}^{N_{\text{peaks}}} A_i e^{-\ln2\left(\frac{(2\theta - 2\theta_i)^2}{(\omega_{2\theta_i}/2)}\right)^2} \]  

(4.4)

The background for the system was assumed to be linear in the 2θ; thus, two variables (a and b) are needed to account for the background (a slope and a constant). Three variables are needed for each one-dimensional Gaussian (and thus, for each peak): the maximum amplitude, A_i; the mean position in 2θ, 2θ_i; and the full width at half maximum in 2θ (FWHM), ω_{2θ_i}. With three variables per peak and two background variables, we have a total of 3N_{\text{peaks}} + 2 variables to account for in each θ/2θ trace of the 3D-WAXS pattern. For the crystalline decomposition, we also add a number of additional peaks to approximate the non-crystalline regions. Normally, three peaks were needed to represent the non-crystalline region: one at 2θ ~ 45° to represent the
intrachain spacings and two at 2θ ~ 20° to represent the asymmetric intrachain feature. This is solely for the purposes of subtraction for the crystalline peaks. These non-crystalline peaks are not used subsequently in the analysis.

As with the HIQ-40 fibers, we assumed that features with a FWHM of 5.0° (in the 2θ direction) or less were indicative of relatively high numbers of repeats. At a FWHM of 5.0°, the Scherrer equation (Equation 1.2) yields a value of ~16Å for the corresponding crystallite size. This is an appropriate lower limit on crystallite sizes from both a practical and modeling standpoint.

We may determine the WAXS degree of crystallinity, χ_{WAXS}, as follows: each Gaussian peak has an area equal to 1.06*A_i*σ_i. We summed the contributions in all of the peaks in each of the 1-D θ/2θ traces for each α_L–β_L combination. We then integrated over all α_L–β_L combinations and summed their crystalline contributions. Since these are polar angles, a factor of sinα_L was necessary for the proper weighting in the spherical coordinate system. The numerical spatial integration of the crystalline portions of the θ/2θ traces yields the following result. χ_{WAXS} for PET190SC is 25.9%. Given the processing conditions and the long time that the sample was allowed to anneal after deformation, PET190SC shows a high degree of periodicity (i.e. crystalline perfection). The number, however, is much lower than its corresponding DSC value. As found with the HIQ-40 fibers, χ_{DSC} is categorically higher than χ_{WAXS}.

Once the crystalline phase has been subtracted from the experimental data, the analysis proceeds in a manner similar to that delineated in Chapter 2. The remaining scattering from the sample is solely due to the non-crystalline portion of the material. A spherical harmonic series is used to characterize the scattering pattern of the sample, since we are now dealing with three-dimensional data in spherical coordinates. If we are to use the methodology delineated in Chapter 2, we must account for incoherent (Compton) and self-scatter, as well as renormalize the data to atomic units for comparison to theory.
4.4.1.2 Incoherent (Compton) and Electron Gas (Self-) Scatter

As discussed in Chapter 2, the series deconvolution analysis requires that we account for a number of other sources of scattering information. Figure 4.9 shows the functional forms of the Compton scattering, $I_{\text{comp}}$, (multiple scattering events) and the self scattering summation, $\Sigma I^2$. The data is taken from the International Tables of X-ray Crystallography [Henry, N., 1962]. The reason that we must remove the self scattering and the Compton scattering is so that the experimental data contains only the single scattering event data and therefore may be compared to the theoretical calculations (in which only single scattering events are accounted for). Both the Compton and self-scatter are not orientationally dependent, since both types of scattering are uncorrelated with respect to spatial variations. Thus, they are only functions of the scattering angle magnitude, $s$.

![Figure 4.9: Compton scattering, $I_{\text{comp}}$, and self-scattering summation, $\Sigma I^2$, for PET as a function of the scattering vector magnitude, $s$, where $s = 4\pi \sin \theta / \lambda$.](image)

4.4.1.3 Normalization of the Experimental via the Method of Krogh-Moe

Before we can truly compare experimental and theoretical calculations, it is necessary to normalize the data to a common standard. To do this, we use the method of Krogh-
Moe, as reported by Mitchell and Windle. [Mitchell, G.R., 1982, 1985a, Krogh-Moe, J., 1956] This method of normalization scales the experimental data to theoretical units and requires us to determine the normalization factor, $k_{k-m}$, via the following equation:

$$k_{k-m} = \frac{\int s^2 I'(s)ds - 2\pi^2 Z\rho}{\int\int\int s^2 I_{raw}(s, \alpha, \beta) \sin\alpha d\alpha d\beta ds} \quad (4.5)$$

Equation 4.5 is just the three-dimensional version of Equation 2.5. The numerator is comprised of two terms. The first is an integration over the total theoretical scattering, $I'(s)$ being comprised of the electron-gas, self-scattering and incoherent, Compton scattering of all of the atoms in a material:

$$I'(s) = I_{comp}(s) + \sum f^2 \quad (4.6)$$

The second numerator term in Equation 4.5 is the zero-point scattering energy term, where $Z$ is the total electron charge and $\rho$ is the density of the material. The denominator of the normalization factor is just the total volumetric integration over the entire 3-D WAXS pattern. $I_{raw}(s, \alpha, \beta)$ is the total experimental intensity (sans crystalline scattering). By equating the total experimental and theoretical scattering integrated intensities a constant is obtained that converts the experimental intensities to atomic units (au). The normalization constant is then applied to the experimental data and the self-scattering sum, $\Sigma^2(s)$, and Compton scattering, $I_{comp}(s)$ subtracted from renormalized data. This is shown mathematically in equation 4.7:

$$I_{ex}(s, \alpha, \beta)$$

where $I_{ex}(s, \alpha, \beta)$ is the renormalized experimental data which may now be analyzed via the spherical harmonic series analysis. Because we have shifted the data, it may be considered a redistribution of scattering power about the isotropic average. The resultant 3-D WAXS pattern contains both positive and negative regions. Note that the redistribution affects the convergence criteria of the series expansion. Now that some of the values of the diagram are negative in magnitude, testing for convergence by
measuring the squared deviations on a point-by-point basis over the entire WAXS pattern becomes less tractable, since one or more data points in the set can take on a value of zero. Additionally, while experimental data is shifted closer to zero, the noise in the trace is unaffected by the shift of the average. Therefore, the signal-to-noise ratio is lowered. The sum of squared deviations may still be used as a basis for comparison, however, one must careful of how it is applied. As such, the spherical harmonic series used in the series expansion converges to within 15% of the sum of squared deviations over the entire pattern.

4.4.2 Spherical Harmonics: Extensions from 2-D to 3-D
4.4.2.1 General Equations
The WAXS pattern, while conceptually straightforward, can present a complicated situation from which meaningful information is to be deduced. The sheer number of data points involved with a three-dimensional pattern can be daunting, by its mere size (over 16,000 data points are involved with our patterns (which have range \( \alpha = \text{range } \beta = 0^\circ - 90^\circ, \Delta \alpha = \Delta \beta = 10^\circ; \text{range } \theta = 10^\circ - 50^\circ, \Delta \theta = 0.25^\circ \)). With the advent of modern computing, this set of numbers is no longer intractable to sample and store, but requires the judicious use of computing power to analyze. The use of a spherical harmonic series and its spherical harmonic coefficients to describe the WAXS pattern offers a succinct method in which we may reduce the number of parameters required to describe the WAXS pattern and thus, the amount of calculations needed. In theory, because the functional forms of the spherical harmonics are analytical and the series converges, we lose very little information in the series deconvolution.

Using an analytical approach similar to that espoused by Mitchell and Windle [Mitchell, G.R., 1982, 1985a], we have analyzed the non-periodic (i.e. non-crystalline) portion of our 3-D WAXS traces using spherical harmonics. A separation of variables is implicit in the applicability of this method to analyzing any data. This allows the contributions of each independent variable to be analyzed individually. Mathematically, this may be expressed as:
In Equation 4.8, n, m, and l are indices whose ranges are shown in the summations. $A'_{nm}(s)$ is the coefficient for a given spherical harmonic term and $\Psi'_{nm}(\cos \alpha, \beta)$ is a spherical harmonic of the first kind. [Hobson, E., 1955] The spherical harmonics of the first kind have the following functional forms:

$$\Psi'_{nm}(\cos \alpha, \beta) = \sin \phi A'_{nm}(s) \cdot \Psi'_{nm}(\cos \alpha, \beta)$$

Equation 4.8 shows that the experimental data trace may be viewed as a series of spherical harmonic terms of the first kind and their coefficient traces. In theory, any function may be reproduced by this basis set of functions. One should also note that in Equation 4.8 only the coefficient traces of the series $A'_{nm}(s)$, are functions of scattering vector magnitude (and therefore of the local structure of the material in the sample). This highlights one of the advantages of this method: the ready deconvolution of a multidimensional WAXS trace into a (hopefully small) number of 1-D coefficient traces.

Practically speaking, the coefficient traces are derived from the numerical integration of the experimental trace:

$$A'_{nm}(s) = \int_{\alpha} \int_{\beta} I_{ex}(s, \alpha, \beta) \cdot \Psi'_{nm}(\cos \alpha, \beta) \sin \phi \sin \alpha d\alpha d\beta$$

The series is terminated when one reaches a specified level of comparison to the experimental data. As previously indicated, the noise level in the data becomes
significant once we have accounted for 85% of the total intensity, implying that this percentage is then the natural upper limit to the applicability of the series expansion analysis. The termination criterion for the series was that the sum of squared deviations of the series reconstruction of the data subtracted from the experimental data over the entire pattern must match to within 15% of the total squared deviations of the experimental trace from zero. The total deviations of the data to zero would be equivalent to a volumetric integration, if we did not have negative values in the data.

4.4.2.2 The Role of Symmetry
When dealing with the spherical harmonics analysis, it behooves us to consider the various symmetries of the situation. In the case of even-ordered spherical harmonics of the first kind, there are always 2 mirror planes in the $\beta$-part ($\cos m \beta$ or $\sin m \beta$) of the harmonic. From the definitions of our axes conventions, these planes fall on the $xz$- and $yz$-planes. Given this, the patterns contain four-fold symmetry. Spherical harmonics of the first kind are also symmetric about $\cos \alpha$. Of the 8 octants of possible data to be taken, only one of these needs to be taken in reality. We have done studies to ensure this fact, by taking data from over the entire sphere and comparing the level of symmetry exhibited. For comparison, we measured the scattering over an entire hemisphere of spatial orientations ($\text{range}_{\alpha L} = 0^\circ - 90^\circ$ and $\text{range}_{\beta L} = 0^\circ - 360^\circ$). The values at each equivalent site of the hemisphere in the $\beta$-range, for example $\pm 40^\circ$ and $\pm 140^\circ$. The averages and the standard deviations were than calculated. The standard deviations were all within $\pm 5\%$ of their respective average values. These studies verified our assumption that symmetry exists in the sample and that taking data in only one of the octants was enough to ensure proper sampling of the spatial orientations.

The overall effect of symmetry on the analysis is a reduction in the number of indices used in to characterize the spherical harmonics in the series. We no longer need to account for any of the $\sin m \beta$ terms, as their coefficients are all zero. Since, we are only using a subset of the spherical harmonics of the first kind, Equations 4.8, 4.9, and 4.10
become:

\[ I(s, \alpha, \beta) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} A_{nm}(s) \cdot \Psi_{nm}(\cos \alpha, \beta) \]  \hspace{1cm} (4.11)

and

\[ \Psi_{nm}(\cos \alpha, \beta) = P_{nm}(\cos \alpha) \cdot \cos m\beta \]  \hspace{1cm} (4.12)

and

\[ A_{nm}(s) = \int_{\alpha} \int_{\beta} I_{ex}(s, \alpha, \beta) \cdot \Psi_{nm}(\cos \alpha, \beta) \sin \alpha d\alpha d\beta \]  \hspace{1cm} (4.13)

respectively. All of these equation are merely reduced in the number of indices. The semi-quantitative discussions of the various terms and their relevances still hold. From this point on in the thesis, we will be dealing with only two indices, \( n \) and \( m \), with the last index \( I \), implicitly understood to be \( \cos \phi \) for all non-zero terms.

4.4.2.3 The Orientation Distribution Function (ODF)

The experimental coefficients can be compared to those that are known elsewhere (generally from theoretical structure factor calculations). The calculated and experimental coefficients are related to the each other in the following manner:

\[ A_{nm}(s) = D_{nm} \cdot A_{nm}^{\text{calc}}(s) \]  \hspace{1cm} (4.14)

That is, the experimental scattering coefficient, \( A_{nm}(s) \), on the left hand side is proportional to the structure factor calculation coefficient, \( A_{nm}^{\text{calc}}(s) \), on the right-hand side by the scaling coefficient, \( D_{nm} \). Note that only the scattering coefficients are functions of the scattering vector and thus features between the two must correspond. The better the feature agreement between experimental observation and structure factor calculation, the more appropriate the use of the scaling coefficient. \( D_{nm} \) is then the coefficient for the relevant spherical harmonic in a series reconstruction of the ODF.
in three dimensions:

\[ D(\alpha, \beta) = \sum_{n=0}^{N} D_{n0} \Psi_{n0}(\cos \alpha, \beta) + 2 \sum_{n=0}^{N} \sum_{m=0}^{n} D_{nm} \Psi_{nm}(\cos \alpha, \beta) \] (4.15)

One of the major advantages of the spherical harmonic series analysis is that the overall pattern is broken down into its components which are easier to handle separately. The different contributions to the pattern, which are due to the various atomic spacings, may be studied and explicitly quantified given molecular model. That is, a particular "scattering unit" is chosen and the scattering properties of that unit are encompassed in the radial or magnitude component of the separation of variables. The orientation of that particular scattering unit is then completely reflected in the ODF of the 3-D WAXS pattern.

Therefore, one of the keys to the spherical harmonic series analysis is determination of the "proper" scattering unit whose scattering characteristics match those of the experimental data. The model is discussed in Chapter 2, and here it is sufficient to say that there is no general model or technique that will always give you the explicit atomic coordinates that produce the desired calculated structure factor coefficient traces. One must build up such a model via a certain amount of experience and intuition. The proper scattering unit could be as simple as a monomer or as complex as a multichain structure, but for the purposes of the structure factor calculation must have explicit atomic coordinates.

4.4.2.4 Semi-Quantitative Interpretations of the \( A_{nm}(s) \) traces
Appendix 8.2 gives the formula, and graphically shows the functional forms for both the even-ordered spherical harmonics of the first kind up to \( n = 4 \). In the appendix, we discuss the rigorous definitions and forms of the spherical harmonics of the first kind. However, for our purposes, we restrict the discussion to highlighting certain, semi-quantitative trend behavior.
Understanding the qualitative trends of the spherical harmonics of the first kind enables one to gain a better understanding of how the features in our coefficient traces are reflections and refinements of features that are present in the overall scattering pattern. The $\Psi_{00}(\cos \alpha, \beta)$ trace is an orientationally averaged representation of the data. It is averaged over both of the orientation angles (also sometimes referred to as the polar angles or Euler angles). Thus, it is the isotropic component to a multidimensional trace.

The higher order harmonics do not \textit{a priori} correspond to a given molecular-level feature or spacing. They represent anisotropic contributions to a material’s scattering behavior of a certain angular distribution. The more a spatial distribution of interatomic spacings correlates to the form of $\Psi_{nm}(\cos \alpha, \beta)$, the larger the respective coefficient term of that spherical harmonic in the structure factor calculation. For example Figure 4.10 shows a representation of $\Psi_{22}(\cos \alpha, \beta)$.

![Stereographic projection of $\Psi_{22}(\cos \alpha, \beta)$ spherical harmonic of the first kind.](image)

The function may be broken up into two contributions, the radial, $\cos \alpha$-dependent part, and the polar, $\beta$-dependent, part. Note that for $m \neq 0$, the spherical terms must be 0 in the center due to symmetry. The $\cos \alpha$-dependent part of the function is very much like the equivalent Legendre polynomial, displaying a similar number of maxima and...
minima. In fact, \( \Psi_{n0}(\cos \alpha, \beta) = P_n(\cos \alpha) \) (that is all of the \( m = 0 \) spherical harmonics are axisymmetric). Thus, our discussion in section 2.2.1 in Chapter 2 aids our intuition here in thinking about form of the spherical harmonics. The \( \beta \)-dependent part of the spherical harmonic only influences the polar symmetry of plot in the figure. At \( m = 2 \), two mirror planes appear. Similarly, one can envision that, for \( m = 4 \), an eight-point pattern (with 4 mirror planes) would appear. For \( m = 4 \), the pattern would contain four positive and four negative spots on the periphery.

4.4.3 Results of Experimental Leg of Analysis

Figure 4.11 shows the experimental coefficient traces for PET190SC. The figure displays the 6 experimental coefficient traces up to \( n = 4 \). The sum of squared deviations over the entire pattern between the experimental data and the series reconstruction was within 17\% of the sum of squared deviations over the entire pattern of the experimental data relative to zero through the first 6 terms. The ratio of squared deviations was less than 10\% when the next 15 terms (up to \( n = 10 \)) were included. The magnitudes of the higher order traces were small, implying that the ODF would be primarily described by the matching the first six traces.

![Figure 4.11: Experimental structure factor coefficients for PET190SC (A_{00}(s) - A_{44}(s))]
$A_{00}(s)$ and $A_{20}(s)$ traces are largest in magnitude implying a pseudo-axisymmetric modeling of the system would not be a gross error. However, the $A_{4m}(s)$ traces are also significant, indicating that a spherical harmonic series would be more appropriate to analyze the data.

The $A_{00}(s)$ trace for PET190SC is the largest coefficient trace in absolute magnitude and it has two features, one interchain at $s \sim 1.6\text{Å}^{-1}$, the other intrachain at $s \sim 3.1\text{Å}^{-1}$. The higher order coefficients for the PET190SC sample, however, only show one feature, either a minimum or maximum at $s \sim 1.6\text{Å}^{-1}$. The coefficient traces indicate that the interchain feature is localized to the LD-CD plane and that further, that more scattered intensity is coming from the LD preferentially over the CD. This conclusion is based upon the fact that the $A_{20}(s)$ is negative. Since $P_{20}(\cos \alpha, \beta)$ only becomes negative as it approaches $\alpha = 90^\circ$, we infer that intensity is localized on the LD-CD plane. We infer that the azimuthal ($\alpha$) distribution of the intensity is fairly narrow, since $A_{40}(s)$ is positive and $P_{40}(\cos \alpha, \beta)$ is negative off-axes, positive on axes and has a feature FWHM of $\sim 50^\circ$. We can infer from the positive values in the $A_{22}(s)$ trace that the intensity in the LD-CD plane is localized in the LD ($\beta = 0^\circ$) direction.

The large absolute magnitudes of the $A_{00}(s)$ values indicate that it will likely contribute the most significantly to the ODF. It is the only trace which features the intrachain feature at $s \sim 3.0\text{Å}^{-1}$. This implies that the intrachain spacing of the non-crystalline portion of the sample is evenly distributed. This is not surprising, since wide breadth of the feature indicates that it is likely due to a short number of repeats in the chain direction. Additionally, a very diffuse feature in the higher order coefficient traces would be difficult to resolve. Note that this does not preclude a larger number of repeats lateral to the chain direction. The interchain feature (as delineated above) does show orientation.

The PET190SC coefficient traces show distinct oscillations in them due to the
crystalline peak subtraction. These artifacts are most prevalent in PET190SC due to its high degree of crystallinity. We saw such subtraction artifacts in the annealed HIQ-40 fibers samples (which had degrees of crystallinity comparable to PET190SC). Such peak artifacts could be dealt with in two ways: 1) the peak could be modified or 2) after subtraction that data could be smoothed using a filter. In the first case, it had been reported that the Pearson VII [Murthy, N., 1997] or a combination of Cauchy and Gaussian forms [Hindeleh, A., 1984] could be used for better peak shape agreement. Filtering the data is possible using a low-pass or Fourier filter. [Press, W., 1992] It should be noted that filtering the data can lead to other artifacts, such as the removal or introduction of features in the trace.

4.5 Discussion of Experimental WAXS Results

Figure 4.12 parts a) and b) display the experimental data for PET190SC and its series reconstruction using the spherical harmonics terms and their respective coefficient traces. Note that by and large the salient features of the experimental pattern are captured in the series reconstruction. The annular ring of intensity about the LD-CD plane is captured as well as the localization of some intensity along the LD axis. As previously noted, the series reconstruction via the first 6 terms (up to n = 4) accounts for over 83% of the experimental data. Visually, one can see that agreement between traces is quite good. The plots display contours of iso-intensity. As such, the contours wrap around each other.
Figure 4.12: Comparison of experimental data and spherical harmonic series expansion reconstruction for PET190SC sample. a) Experimental 3-D WAXS pattern b) Spherical harmonic series expansion reconstruction
Table 4.2 displays a comparison of WAXS and DSC crystallinities determined for PET190SC:

<table>
<thead>
<tr>
<th></th>
<th>( \chi_{\text{WAXS}} )</th>
<th>( \chi_{\text{DSC}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET190SC</td>
<td>25.9%</td>
<td>38.0%</td>
</tr>
</tbody>
</table>

Table 4.2: Comparison of Degrees of Crystallinity: WAXS and DSC

As with the HIQ-40 fibers, the degree of crystallinity measured by DSC is higher than that of WAXS. This is understandable, since WAXS is very sensitive to distortions and defects in periodic structures, whereas the DSC is not. Additionally, since the DSC peak analysis incorporated the long leading tail of the melting peak, it was counted in the enthalpy measurement. Thus, the smaller and imperfect crystalline material was integrated into the \( \chi_{\text{DSC}} \) calculation, but was purposefully removed from the \( \chi_{\text{WAXS}} \) calculation.

4.6 Quantitative Interpretations: PET Simulations

4.6.1 The Molecular Model

Our computer modeling code is a variation of the aromatic polyester modeling code used by Rutledge. [Rutledge, G., 1992] In brief, it uses a Rotational Isomeric States (RIS) algorithm to build realistic oligomer chains, then places those chains on a 2-D lattice through a Monte Carlo (MC) sampling routine.

4.6.1.1 Alterations from 2-D Aromatic Polyester Code

For our purposes, the code has been modified in order to determine if the output ensemble is realistic. The list in section 2.3.3 (p. 20) in Chapter 2 applies to this version of the code as well. That is, we do not use the energetics subroutines and the acceptance criteria are based on the hard-sphere overlaps and the \( \beta_\chi \) ("measure of merit") criteria. The latter requires that we use a three-dimensional structure factor calculation, instead of the two-dimensional calculation used in Chapter 2. Therefore,
on top of that list of changes in Chapter 2 to Rutledge's aromatic polyester code, there are two other major changes:

1) The RIS scheme required the integration of ethylene units into the chain building library
2) The scattering equation was in 3-D, i.e. using spherical harmonics

4.6.1.2 Incorporation of Ethylene into Mesogen Library

Because we are modeling PET, the base monomer units library of Rutledge's code needed modifications since it contained information on ester linkages and aromatic moieties only. While we use only esters as our mesogen connectors, the mesogen library contained only aromatic groups which were not suitable to generate ethylene groups to be placed in our PET chains. In Rutledge's nomenclature, all of the moieties placed between esters were described as a maximum of four "virtual" bonds between the two esters. [Rutledge, G., 1992]

Fortunately for us, ethylene is a simple molecule. The geometric data for ethylene is as follows. We required only 3 bonds to describe the polymer backbone of ethylene. All of those bonds correspond to real bonds in the polymer backbone. Table 4.3 lists the bond types and parameters. [Streitwieser, A., 1985]

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Length, $l_i$ (Å)</th>
<th>Bond Angle, $\theta_i$ (°)</th>
<th>Bond Torsion, $\phi_i$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O - C</td>
<td>1.37</td>
<td>109.2</td>
<td>180</td>
</tr>
<tr>
<td>C - C</td>
<td>1.54</td>
<td>109.2</td>
<td>180</td>
</tr>
<tr>
<td>C - O</td>
<td>1.37</td>
<td>110.9</td>
<td>180</td>
</tr>
</tbody>
</table>

Table 4.3: RIS Bond Parameters for Ethylene Moieties

The bond lengths and bond angles are of constant values. We have chosen to use only the fully extended, planar version of the molecule since we are primarily interested in modeling the anisotropic extended chain conformations. The ethylene monomer and its various bond lengths, bond angles, and bond torsions are diagramed in Figure 4.12.
The use of only trans conformers for the ethylene in our simulations implies that we are really only using 1 state in RIS for the ethylene. Torsions about the C-O ester bond are still allowed to vary, such that the entire chain is not fully extended in conformation.

![Figure 4.13: Schematic description of the bond lengths, angles, and torsions associated with an ethylene moiety](image)

4.6.2 Three-Dimensional Structure Factor Calculation
Given a molecular ensemble, a structure factor can be calculated as a function of the scattering angle. By assuming the separation of variables implicit in the spherical harmonic analysis, the intensity, which is a function of the scattering vector, may be broken up into individual components, which are functions of single variables only. This decomposition of the various contributions to the scattering may be viewed as a simplification of an otherwise mathematically complex problem. This separation then attributes the scattering vector magnitude part of the scattering to a coefficient and the angular part to the orientation distribution. To enable us to compare the model with the experimental data, we require an equation to determine the molecular ensemble's structure factor.

Conceptually, the difference between two- and three-dimensional modeling is relatively minor. The two-dimensional case is simpler mathematically, since it is merely a subset of the three-dimensional case. From a general scattering equation, such as one from Guinier [Guinier, A., 1963] (see section 1.1.3.1), we can derive an explicit expression which describes the scattering coefficient as a function of the scattering vector:
Equation 4.16 is a summation of contributions by all of the atom pairs in a given structure. For proper use of the equation, all atom types and relative distances must be known. In analogy to Equation 2.8, Equation 4.16 has four main parts: a prefactor, the atomic scattering factors for a given atom pair, an integer-order spherical Bessel function, and a weighting distribution. The prefactor is an outgrowth of the spherical harmonics orthogonality constraint and ensures proper scaling between coefficient traces. It is also derived on a per atom basis. $f_j$ and $f_k$ are the atomic scattering factors for each of the atoms (and the summations denote that we calculate the structure factor over all atom pairs). The spherical Bessel function is derived from the symmetry of the system. Note that spherical Bessel functions are $(n+1/2)$-order Bessel functions (see Appendix 8.5 for more details). The spherical harmonic is a weighting function based on the distribution function (and the analysis in general).

Note, that the structure factor calculation makes no mention nor assumption about the connectivity or relationship of the spacings relative to one another. It is not meant to, since it is only a structure factor calculation. As is generally the case with such calculations, only information about the pair-wise distances is relevant. How those spacings are related to each other is a matter of interpretation. This is where a molecular model comes in. The ensemble generated by the molecular model is built to fulfill the constraints of the system incorporating information pertaining to the connectivities and compositions of the constituent molecules. The "proper" ensemble satisfies both sets of constraints, the macroscopic (experimental observations) and microscopic (bond connectivities and relative compositions).

4.6.3 Structure Acceptance Criteria

Once we have the ability to calculate a comparison to the experimental data, we have
to determine proper conditions for acceptance of a model generated structure into the molecular ensemble. We have two means available and utilize both within the simulation. The first is the steric constraint of non-overlapping atoms (often referred to hard-sphere interactions) and the second is a "measure of merit" criterion which accepts a particular structure based on whether its structure factor improves the comparison (i.e. reduces the total squared deviations) between the experimental and theoretical structure factor coefficient traces. Because we are using a 3-D model in Chapter 2 as well as here, both of the criteria for structure acceptance are unchanged in the simulation between Chapter 2 and here in Chapter 4.

4.6.4 Parameter inputs
The parameter inputs into the model are the same as the 2-D case, only the structure factor calculation and the extension of the RIS library to include ethylene moieties were required changes between the two- and three-dimensional cases. To summarize the code statistics from Chapter 2, we assumed a planar chain backbone for the fairly rigid aromatic polyesters. The torsion of ester C-O bond was allowed to randomly vary between values of ±30° out of the plane of the chain backbone. The aromatic moieties were allowed 4 states (±45° or ±135°) if bonded to an ester oxygen, otherwise they were planar with carbonyl due to π-orbital conjugation. The lattice unit cell parameters, a and b, were allowed to randomly vary by ±50% about a fixed mean value. The angle between a and b, γ, was fixed and not allowed to vary. The structure acceptance criteria parameters were set at $K_{vdw} = 0.6$ and $\beta_X = 200$. The former criterion indicates that some overlaps are likely. The latter criterion indicates that a minimum of 40% of the structures that pass the steric constraint would be accepted into the molecular ensemble even if they did not improve the fit. 40% is based on the total integrated area under the 6 experimental coefficient traces being approximately 200. As with the 2-D case, we used the crystalline unit cell and the hexagonal close packed (HCP) cells as reasonable starting points for the iterative ensemble search.
4.6.5 Modeling Results

Table 4.4 shows the results for a sample set of parameter inputs to the model. It represents our best results dealing with our PET190SC sample.

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Unit Cell Parameters</th>
<th>$K_{vdw}$</th>
<th>$\beta_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET190SC</td>
<td>4x4x2mer</td>
<td>4.00Å</td>
<td>3.75Å</td>
</tr>
</tbody>
</table>

Table 4.4: Model Simulation Parameters for PET190SC

Based on these parameters we calculate an average simulation density, $\rho$, of 2.16 g/cm$^3$. This density is quite high compared to the reported literature value of the crystalline density of 1.49 g/cm$^3$. We can think of a number of reasons for the high density of the simulation cell. First, the ±30° ester torsions should lead to a slight compaction of the unit cell in the chain direction. However, since we are dealing with only dimers in this simulation, this effect should be minimal. Second, we are matching specific spacings in our simulations. The spacings being matched are the dominant ones in the experimental data. Our structures are generated randomly and are accepted based on their ability to match the positions of the experimental features. However, due to the hard-core potential being used, the average parameters may not accurately reflect the density of the accepted simulations. In other words, since the accepted structures must be free of overlaps, they may contain a set of randomly generated lattice site distances which correspond to a less dense system. It was noted in our simulations that decreasing the unit cell parameters $a$ and $b$ to values of 3.5Å or lower, while keeping $K_{vdw}$ fixed at 0.6, drastically reduced the acceptance rate of new structures and that the accepted structures did not show features in their structure factor calculations corresponding to spacings of 3.5Å ($s \approx 1.75Å^{-1}$) in them. Instead, the structure factors peaks were found predominantly at spacings of approximately 4.0Å ($s \approx 1.5Å^{-1}$). Given this, the simulations as presented may be lacking in one respect. They do not take into account cooperative events between adjacent chains,
but instead generates the setting angle of each chain randomly. By cooperative events, we mean that the system does not take into account, for example, edge-to-face effects or the placement of a less bulky ethylene unit adjacent to a phenylene ring in the lattice. This implies that the simulation relies on the random generation of these cooperative events and that the simulation is relatively inefficient in its sampling of parameters space with respect to such events.

Our simulation results also show that we required very short “chains” in the simulation, only dimers. The diffuse intrachain feature in the experimental data required that a low number of repeats in the chain direction were necessary to obtain the desired peak breadth (see section 4.4.3 for discussion on the intrachain feature in Figure 4.11 (a)).

Figure 4.14 shows a sample structure from the structural ensemble deduced for PET190SC and the structure factors calculated from the average ensemble using the parameters used in Table 4.4. Once we see the sample ensemble from in an “overhead view,” the distorted nature of the lattice is readily apparent.
Figure 4.14: Outputs from the simulation, a) Sample structure from our total ensemble. b) \( A_{00}(s) - A_{22}(s) \) structure factor coefficients c) \( A_{40}(s) - A_{44}(s) \) structure factor coefficients.

Figure 4.15(a-c) shows the coefficient trace comparisons for the model output using the parameters in Table 4.4. Figure 4.15(a) shows the combination of both the oriented \((A_{00,\text{calc}}(s))\) and unoriented \(A_{00,\text{am}}(s)\) non-crystalline material.
Figure 4.15: Comparison of experimental and calculated structure factor coefficient traces, $A_{nm}(s)$. a) $A_{00}(s)$ traces, b) $A_{20}(s)$ traces, c) $A_{22}(s)$ traces. Experimental traces are of PET190SC.

The unoriented non-crystalline portion of the $A_{00}(s)$ is derived from the series expansion of the amorphous reference trace (see section 4.3.3). Given that the sample was completely isotropic, its scattering properties could then be used to model the unoriented non-crystalline portion of the $A_{00}(s)$ trace. In order to use the amorphous reference merely needed to account for the self- and Compton scatter and renormalize the data. The $A_{00}(s)$ term in spherical harmonic series expansion completely describes the amorphous reference’s scattering pattern, since it is completely isotropic.
We can see the scaling coefficients capture a number of the features of the experimental traces. The fit is reasonable. All of the features in the experimental data are reflected in some way in the model structure factor calculations. The peak positions are well represented in all three of the traces. The model could undergo some additional refinement to enhance the matching of the peak breadths for the all three traces.

The n = 4 traces are shown in Figure 4.16.

![Graphs comparing experimental and calculated structure factor coefficient traces, $A_n(s)$](image)

Figure 4.16: Comparison of experimental and calculated structure factor coefficient traces, $A_{nm}(s)$. a) $A_{40}(s)$ traces, b) $A_{42}(s)$ traces, c) $A_{44}(s)$ traces. Experimental traces are of PET190SC.

Here the agreement is not as good as the previous three coefficient traces, but we can
see that the approximate positions of the peaks at $s \sim 1.6\text{Å}^{-1}$ are well represented. Further refinement of the model parameters are required for better agreement. A larger number of accepted structures may also be required since, our current simulations only accepted 50 structures out of 11,000 generated.

Once we are satisfied that the features of the coefficient traces have been properly represented, the scaling coefficients, $D_{nm}$'s, may be derived. In this case, $D_{nm}$'s are obtained by comparing the maximum values of feature between traces. That is:

$$D_{nm} = \frac{(A_{nm}(s))_{\text{feature, max}}}{(A_{nm}^{\text{calc}}(s))_{\text{feature, max}}}$$

(4.17)

While, the positions of some of the model features are off (for example, the peak in $A_{22}(s)$ traces), their presence in the field of measured values represents that the spacings represented in the model are reasonably accurate. Table 4.5 lists the scaling coefficients for the ensemble derived from the parameters listed previously (and whose structure factor coefficients are shown in comparison to experiment in Figures 4.15 and 4.16).

<table>
<thead>
<tr>
<th>n,m</th>
<th>0.0</th>
<th>2.0</th>
<th>2.2</th>
<th>4.0</th>
<th>4.2</th>
<th>4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET190SC</td>
<td>2.0</td>
<td>1.2</td>
<td>1.5</td>
<td>0.025</td>
<td>-0.21</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 4.5: Scaling Coefficients, $D_{nm}$, for PET190SC

From the scaling coefficients, we can deduce the orientation distribution function (ODF) for the ensemble relative to the sample. Figure 4.17 shows the resultant ODF from the $D_{nm}$ values given in Table 4.5.
Figure 4.17: ODF for PET190SC based on the $D_{nm}$ values listed in Table 4.5

Figure 4.17 is a stereographic projection of the ODF information, analogous to one quadrant of a pole figure. The dark contours are lower population, the lighter contours denote higher populations. One should not confuse Figure 4.17 with a pole figure diagram, however. Whereas the pole figure plots the scattered intensity as a function of spatial orientation, Figure 4.17 is a plot of the population density of structure ensemble as a function of spatial orientation. The ODF for PET190SC shows some interesting behavior. The figure indicates that a significant population of chains in the PET sample orient in a distribution centered about the FD. However, there is also a distinct chain population that is centered also about the LD. The majority of chains distribute themselves in the LD-FD plane. This is also what Bellare, et al, saw in their studies of orientation development of PET crystallites in their plane-strain deformed specimens. [Bellare, A., 1993] It appears that the chains of both the crystalline and non-crystalline phases are aligning themselves preferentially in the FD and to a lesser extent in the LD. The CD shows a near negligible population of monomers pointing in that direction.

The reconstruction of the ODF shows some aphysical values. The problem is small
(and limited to values off of the 3 axes) These result from inaccuracies in the scaling coefficient estimations necessary between the experimental and calculated structure factors. Better refinement of the model ensemble and an improved algorithm for the comparison of the experimental and calculated structure factor coefficients would result in the elimination of the negative values in the ODF.

As noted earlier, as well as in Chapters 2 and 3, the $A_{00}(s)$ trace is a function of the two factors, the oriented non-crystalline (ONC) material and the unoriented non-crystalline material (UNC). As such we derive the relative percentages of each phase in addition to the scaling factor, $D_{00}$. That is, we deduce the degree of oriented non-crystalline material, $\chi_{\text{ONC}}$, and unoriented material, $\chi_{\text{UNC}}$. Since we have the reference sample (section 4.3.3), which is purely amorphous, we need merely scale this data appropriately (and remove the Compton and electron-gas contributions) to derive a measure of the structure factor of the unoriented non-crystalline material. Doing so, yields that $\chi_{\text{ONC}}$ is 60% of the non-crystalline material. The relative percentage breakdown of the three phases present in the PET190SC sample are summarized in Table 4.6:

<table>
<thead>
<tr>
<th></th>
<th>$\chi_{\text{xxtal}}$</th>
<th>$\chi_{\text{ONC}}$</th>
<th>$\chi_{\text{UNC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET190SC</td>
<td>25.9%</td>
<td>44.4%</td>
<td>29.6%</td>
</tr>
</tbody>
</table>

Table 4.6: Relative Breakdown of Material Phases for PET190SC sample

These relative percentages indicate that like HIQ-40 fibers, the PET190SC sample displays a significant amount of oriented non-crystalline material. In PET, this non-crystalline material is likely tied to the crystalline phase. [Bellare, A., 1993] From the processing route, we can infer that the crystallites which were known to be produced during the thermal equilibration step are likely to act as anchors to the non-crystalline material. We infer that as the crystallites align, so does a portion of the non-crystalline material. The total percentage of oriented material is over 70% for the PET190SC sample.
Our simulation densities are consistently high, implying that our ensemble has many structures with slightly unrealistic distances. As with the HIQ-40 fiber simulations, the high density also implies that atom pairs maybe in the repulsive region of their interactions (consistent with the fact that we used \( K_{vdw}=0.6 \)). The fact that we do not included any optimization or energetic minimization leads to some of the unrealistic overlaps in the ensemble. Because the distances of these “overlaps” are small (< 1.2Å) they do not affect the structure factor calculations since they are well outside the s-range (0.710Å\(^{-1}\) to 3.44Å\(^{-1}\)) which corresponds to d-spacing range of 8.84Å - 1.82Å.

4.7 Summary and Conclusions

The PET190SC sample shows a degree of orientation which is arrayed between the load and flow directions in the sample. The degree of orientation is relatively low requiring only the first 6 terms (up to index \( n =4 \) terms) in a spherical harmonic series to describe over 83% of the total scattered intensity. The rest of the 3-D WAXS pattern was found to contain primarily noise and crystalline artifacts with the next 15 terms in the series giving only a marginally better agreement with the experiment data. The ensemble which best describes the PET190SC sample consists of 16 dimers placed on a 4x4 non-rectangular lattice. The simulation density was too high, placing some uncertainty on the model parameters used.

The amount of oriented material in the plane-strain deformed PET sample is significant, encompassing over 70% of the total material. The ODF derived from the comparison of the model calculation and the experimental data showed that the oriented non-crystalline phase (like the crystallites in the material) concentrates primarily in the FD and LD directions (the two directions which experience the macroscopic deformation in a channel die) in the sample. These results correlate well with the observations of the localization of chain orientation between the FD and LD seen by Bellare, et al. [Bellare, A., 1993]
4.8 Overall Summary and Conclusions

We have shown the versatility of the 3-D spherical harmonic series analysis by demonstrating its use on PET plane-strain deformed samples. The degree of orientation in the sample is moderate, which limits the number of terms needed to characterize the system. The use of the spherical harmonic series deconvolution of the experimental data coupled with the introduction of a structure factor calculation from a molecular-scale ensemble allows us to derive the relative amounts of the oriented and unoriented phases in the material.

Since a three-dimensional pattern was analyzed, the applicability of this methodology is readily apparent to other systems. One must remain cognizant of the assumptions that went into this particular analysis (primarily those of symmetry, which enables one to use a subset of the spherical harmonics of the first kind), but the general case is conceptually very similar. This has been one of the major points of the past three chapters, in which we have shown the applicability of the method in two-dimensions and its extension to three-dimensions. The primary changes in extending the method from two- to three-dimensions were making the experimental deconvolution and the structure factor calculations appropriate for a more general three-dimensional case. Additional extensions can be easily envisioned; for example, the molecular model could be expanded to encompass a larger library of polymer compositions instead of just polyarylates.

Now, we turn to a study where we utilize the spherical harmonic series expansion analysis as one of a number of techniques used to analyze a sequence of processing histories.
3-D Case Study: Study of Plane-Strain Deformed PET

Rule I: We are to admit no more causes of natural things than such as are both true and sufficient to explain their appearances.

To this purpose the philosophers say that Nature does nothing in vain, and more is in vain when less will serve; for Nature is pleased with simplicity, and affects not the pomp of superfluous causes.

- Sir Isaac Newton, *Principia*, Bk 3, p. 398

5.1 Introduction

Figure 5.1 shows a typical curve of stress as a function of time for a poly(ethylene terephthalate) (PET) sample annealed under load after plane-strain deformation in a channel die. The load was applied at time = 0 min. The platen displacement after the initial deformation and the processing temperature of the sample are held constant for the duration of the experiment.

Figure 5.1: Stress normal to the load direction as a function of time for plane-strain deformed PET sample: $T_{proc} = 190^\circ$C, $CR = 2.6$

The sample was annealed after deformation under load at $190^\circ$C for 5 hours. The final
compression ratio of the sample (the ratio of the initial to final thickness as measured in the LD) was 2.6. One should note that the curve shows a recovery of stress at "long" times (on the order of hours) direction of the load direction. The experiment was repeated to ensure that the observation was reproducible.

What follows is a report of application of analyses described in previous chapters on a series of samples produced to investigate this stress recovery phenomena. The techniques used to investigate these samples include: Differential Scanning Calorimetry (DSC), Carbon-13 Slow Magic Angle Spinning with Direct Exchange Correlation of Orientation Distribution for Evaluation and Reconstruction Nuclear Magnetic Resonance ($^{13}$C SMAS-DECODER NMR), Small Angle and Wide Angle X-ray Scattering (SAXS and WAXS, respectively).

While extensive effort has been expended in elucidating two-dimensional orientation in PET samples (such as fibers [Hristov, H., 1991] or films [Clauss, B., 1987]) and in the crystalline phase of plane strain deformed samples [Bellare, A., 1993], there has been less effort focused on the study of orientation of the non-crystalline phases of such materials. The non-crystalline portion of these samples seems especially important since 1) they are a majority phase of the material and 2) any study of orientation in the material should encompass the majority phase.

5.1.1 PET processing
We are interested in the role of two factors in PET processing: the temperature and mechanical histories. Both factors can have extensive effects on the molecular level structure of the material. Stresses introduced arise during processing in any given sample geometry. These stresses have a tendency to align chain backbones in the direction of extension. [Bellare, A., 1993, Fu, Y., 1993] Clauss and Salem have looked at a number of effects that the strain rate has upon crystallization. [Clauss, B., 1987] A number of additional studies on strain-induced crystallization have been done. Hristov and Schultz characterized the orientation in moderately oriented PET fibers. They postulate that the PET fibers contain a highly oriented, load-bearing, non-crystalline
phase. They do not explicitly link this highly-oriented non-crystalline phase to interface of the crystalline-amorphous region. [Hristov, H., 1990] Lee and Schultz investigated the effect of annealing on the mechanical properties of PET fibers via WAXS and SAXS. They noted that as PET fibers anneal, the non-crystalline mobility decreases and the fiber stiffness and modulus increase. Their annealing times ranged in the millisecond to second range. [Lee, K.-G., 1993] Fischer and Fakirov looked at the accuracy of a two-phased model in describing PET WAXS and density data of oriented films. They noted that the two-phase model of crystalline and amorphous phases was not sufficient to describe the system. [Fischer, E., 1976] Asano and Seto studied PET samples drawn at room temperature and subsequently annealed. They found that strain-induced crystallization progressed though a steady evolution from an oriented non-crystalline phase to an intermediate monoclinic cell and finally to the triclinic cell reported in the literature [Asano, T., 1973] Misra and Stein looked at amorphous PET films deformed above and below $T_g$ and noted that a deformed ellipsoidal spherulitic "super-structure" developed. [Misra, A., 1979] Gupta, et al., studied the effects of draw ratio and annealing on the shrinkage behavior of PET films and fibers. They observed that higher degrees of orientation had a tendency to inhibit chain mobility leading to higher residual stress in such materials and less stress relaxation over time. [Gupta, V., 1994] All of these studies in strain-induced crystallization imply that it plays an important role in the development of morphology in PET. The studies also find that oriented and strain induced crystallization occurs on a much shorter time scale than unoriented, quiescent crystallization.

The effect of the processing temperature on crystallization has been touched upon elsewhere in this thesis. Refer to Chapters 1 and 4 for a more detailed discussion on the relevance of crystallization and its kinetics on this particular polymeric system. Suffice it to say here, that the processing temperature ($T_{proc}$) that we have chosen, $190^\circ$C, is at (or near) the maximum rate of crystallization reported in the literature. Thus, it is likely that any samples produced for this study will have a high degree of crystallinity (whether measured by WAXS or DSC or whether it is strain-induced or
unoriented crystallization). Generally, the main effect of annealing in a PET sample is to increase the crystalline perfection. [Lee, K.-G., 1993]

5.2 Experimental

5.2.1 Sample Production

A series of three samples underwent the following procedure. A rectangular plaque of amorphous (~5% residual crystallinity as measured by DSC) PET, measuring 25mm x 12mm x 6mm, was placed in a stainless-steel channel die with a 12mm wide channel. A plunger of the same material as the die was placed in the channel on top of the sample. All metal parts were coated with teflon lubricant to ensure that a no-slip condition applied to the surfaces of the channel die. Thus, the PET sample was deformed in plane-strain compression. The reader is referred to Figure 1.1 for a schematic of the channel die and its geometry.

A Carver manual hot press Model C (no. 2086) with heated platens was used to produce the PET sample for the study. The samples were created in the channel die under uniaxial compression, yielding plane-strain deformed specimens with varying degrees of anisotropic molecular orientation (see Chapters 1 and 4 for a more detailed description on the use of the channel die). This series of samples was created by using the following protocol. All times are expressed relative to the time of initial loading.

1) \( t \sim -3600 \text{ sec} = -60 \text{ min} \): The die and plunger were heated for a minimum of 1 hour the target temperature of 190°C (463 K). This was to ensure that when the sample was placed in the die, 15 minutes would be enough time for the sample alone to reach the processing temperature. The sample is not within the die at this time.

2) \( t = -15 \text{ min} = 900 \text{ sec} \): The sample is placed in the die, with the plunger on top and allowed to thermally equilibrate for 15 minutes. Calculations of the thermal response of PET indicate two things. First, because of the short half-time of crystallization of PET (~ 90 sec at 190°C), we anticipate the sample has a significant (and non-uniform, since the center reaches
190°C later then the edges) degree of crystallization in it previous to deformation. Second, 15 minutes should be enough time to achieve thermal equilibration of the sample of 6 mm thickness or less. At this point we created reference sample, which underwent the thermal equilibration step, but no load:

Sample 0: \( t_{\text{anneal}} = 0 \) sec, load = 0Klbs

3) \( t = 0 \): The deformation of the sample occurs. The time of this step is on the order of 5 seconds (0.08 min) to achieve the desired displacement (which corresponds to a certain compression ratio (CR). The reaction of the sample to the mechanical stress is a function of the strain rate, as a well-known phenomena in PET is strain induced crystallization. [Fischer, E., 1976, Clauss, B., 1978, le Bourvellec, G., 1987]. Studies by various groups have indicated that strain induced crystallization occurs very quickly, on the order of seconds. [Adams, A., 1997, Blundell, D., 1996]

4) \( t > 0 \): The sample is then held at the processing temperature (190 °C for the purposes of this study) for a set period of time, \( t_{\text{anneal}} \). This step is a thermal anneal under stress. For the three samples that we looked at:

Sample 1: \( t_{\text{anneal}} = 0 \) sec
Sample 2: \( t_{\text{anneal}} = 2700 \) sec
Sample 3: \( t_{\text{anneal}} = 18,000 \) sec

5) Lastly, the sample is quenched to room temperature. To do this, the heating coils in the press platens are turned off and the platen coils are flooded with cooling water at ~20°C. Cooling water circulated for a minimum of 15 minutes. Approximately 3 minutes is needed for the cooling platens to drop below \( T_g \) (= -65°C). Practically speaking, this method of cooling is a moderately slow quenching process.

Table 5.1 shows the nomenclature for the 4 PET samples that will be used hereafter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing Time</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 sec (no load)</td>
<td>PET190NL</td>
</tr>
<tr>
<td>1</td>
<td>0 sec</td>
<td>PET190Q</td>
</tr>
<tr>
<td>2</td>
<td>2700 sec</td>
<td>PET190T1hr</td>
</tr>
<tr>
<td>3</td>
<td>18,000 sec</td>
<td>PET190T5hr</td>
</tr>
</tbody>
</table>

Table 5.1: Nomenclature Designations for PET Plane-Strain Deformed Samples
Figure 5.2 shows schematically the temperature cycle history for the three samples produced for this study.

The figure shows the temperature of the sample as a function of time, where $t = 0$ is point at which the load is applied and the sample deformed. Note that for each of the samples the only difference is in the time at which it is held at the processing temperature after the initial load has been applied.

5.2.2 Characterization Methods

What follows are brief descriptions of the four analytical techniques (DSC, $^{13}$C SMAS-DECODER NMR, WAXS, and SAXS) used to study this series of samples. The sections themselves will only contain short general discussions of the techniques and some of the specific details dealing with our application of such techniques. The following sections will contain the specific parameters and notes that pertain to this study. All of these methods were used to help characterize various aspects of the sample. From these observations, a more cohesive picture of any molecular-scale mechanisms involved with this stress recovery phenomena may be gained.

5.2.2.1 Differential Scanning Calorimetry (DSC)
Differential Scanning Calorimetry (DSC) is used to measure thermodynamic properties and transitions of a material. By comparing the thermal input into a sample relative to a reference material of known heat capacity, thermal properties and weight, an unknown material's thermodynamic properties can be investigated and quantified.

PET has a glass transition, $T_g$, reported between 67°C (for the amorphous phase) and 81°C (for PET at its maximum degree of crystallinity). [Kolb., H., 1949] The melting point of PET, $T_m$, is reported as 265°C. [Bellare, A., 1993, Kolb., H., 1949]. The maximum degree of crystallinity, $X_{DSC}$, for PET is generally reported to be about 40%. Mehta et al., derive a value of $\Delta H^0_f = 140 \pm 20$ J/g for the heat of fusion in surveying literature and experimental values from a number of different sources. [Mehta, A., 1978] Under very high strain rates at moderate to low temperatures, strain induced crystallinity becomes a significant factor though rarely does it increase the maximum degree of crystallinity. [Clauss, B., 1992, le Bourvellec, G., 1987]

We used a Perkin-Elmer DSC-7 with the following experimental parameters in our DSC runs: a heating rate of 20°C/min and a temperature range of 50°C (323.16 K) to 300°C (573.16 K). Sample weights were measured on a microbalance. They ranged from 5.000mg to 20.000mg. The Perkin-Elmer DSC-7 used is located in the Center for Material Science and Engineering (CMSE). This work made use of MRSEC Shared Facilities supported by the National Science Foundation under Award Number DMR-9400334.

5.2.2.2 Nuclear Magnetic Resonance (NMR)
Nuclear Magnetic Resonance (NMR) is used to probe the electronic environment of an atom. It relies on the principle that nuclei in a material placed in a magnetic field will resonate preferentially with that field at a characteristic frequency. This characteristic frequency is indicative of the nucleus' magnetic (and thus, electronic) environment. That is, the electronic environment of a molecule can shield or expose a particular nucleus, producing a characteristic shift in the resonant frequency response of that
nucleus. This chemical shift is measurable and is generally reported in terms of parts per million (ppm) shift in frequency. The chemical shift can vary in each of the 3-D spatial directions and is most generally expressed as the chemical shift anisotropy (CSA) tensor.

Carbon-13 Slow Magic Angle Spinning with Direct Exchange Correlation for Orientation Distribution Evaluation and Reconstruction (\(^{13}\text{C}\) SMAS-DECODER) NMR is a multi-dimensional (2-D) NMR correlation technique. As a 2-D NMR correlation technique, \(^{13}\text{C}\) SMAS-DECODER enables one to measure the local orientation of a given nucleus (in our case the \(^{13}\text{C}\)) by determining the orientation dependence of the CST (or of higher order interactions as well, such as the quadrupolar interaction tensor). [Liao, M.-Y., 1997] For more details on the theory of \(^{13}\text{C}\) SMAS-DECODER and the specific experimental setup, the reader is directed to Appendix 8.1. [Schmidt-Rohr, K., 1994]

5.2.2.3 Wide-Angle X-ray Scattering (WAXS)

PET processed in a channel die shows "pseudo-single crystal" order, a type of three-dimensional orientation. [Bellare, A., 1993] Given that we have three-dimensional orientation in our sample, we were required to analyze the sample with a technique that would measure a sample's three-dimensional structural morphology. Wide Angle X-ray Scattering (WAXS) techniques fit the bill perfectly. The use of the pole figure attachment on a standard \(\theta/2\theta\) goniometer enabled us to measure the orientation dependency of the scattered intensity from a sample at various \(2\theta\) values.

The following data collection mesh was used for obtaining WAXS data from the three samples. Due to symmetry, we were required to measure the scattering from only one octant of the great sphere. We chose our polar angle ranges as \(\alpha = 0^\circ\) to \(90^\circ\) and \(\beta = 0^\circ\) to \(90^\circ\) in steps of \(10^\circ\) (i.e. \(\Delta\alpha = \Delta\beta = 10^\circ\)). The \(2\theta\) data range was between \(2\theta = 10^\circ\) to \(50^\circ\) in steps of \(0.5^\circ\) (i.e. \(\Delta2\theta = 0.5^\circ\)). A finer mesh in \(2\theta\) was not required since our main focus in the study was to measure the oriented non-crystalline material, whose features were very broad in \(2\theta\). The crystalline peaks which were to be subtracted out
from the trace required only a few points to characterize. With $\Delta \theta = 0.5^\circ$ and crystalline peak Full Width at Half-Maxiums (FWHM) on the order of $2.0^\circ$ or more, we were assured of at least four (4) points with which to fit the crystal peaks, ensuring that our statistics for the peak subtractions were reasonable.

The experimental data analysis for the 3-D PET samples was the same as delineated in Chapter 4. In brief, we subtract off the crystalline portion of the sample, which allows us to derive the WAXS degree of crystallinity, $\chi_{\text{WAXS}}$. The data is then normalized into atomic scattering units and the incoherent (Compton) and free electron-gas (self-)scattering subtracted from the trace. The 3-D WAXS pattern is then a representation of the reallocation of intensity based on the local (i.e. molecular-level) structural details of the material.

The data is then analyzed using a spherical harmonic series deconvolution. The reader is directed to Chapters 2 and 4 for a more detailed account of the series deconvolution method. Using a series of spherical harmonics to describe the 3-D WAXS pattern, we accomplish two things. First, we separate out the individual contributions of the various spatial components of the system. In effect, we divide the pattern into features that are solely due to local structure and those that are due to the orientation of that local structure (whatever it may be). Second, the series deconvolution has the effect of acting like a low-pass filter. Noise in the trace is attenuated in the lower terms since we integrate in the angular variable directions and the low index spherical harmonics contain terms that have broad, smoothly varying features. Higher order terms do have narrower features, but are generally not needed unless we are dealing with highly ordered systems. The desired output from the series deconvolution are the experimental structure factor coefficients, $A_{nm}(s)$.

The series coefficients are then compared to calculated theoretical structure factor coefficients, $A_{nm,\text{calc}}(s)$, which are derived from an explicit atomic coordinate structure generated as part of a molecular ensemble. The ensemble is generated from a
computer simulation which utilizes a Rotational Isomeric States (RIS) algorithm to generate polyarylate chains and places those chains upon a two-dimensional lattice using a Monte Carlo (MC) sampling technique. The outputs from the model are the molecular ensemble and the calculated theoretical structure factor coefficients.

5.2.2.4 Small Angle X-ray Scattering (SAXS)
Like WAXS, Small Angle X-ray Scattering (SAXS) depends on differences in electron density to differentiate between scattering or diffracting bodies. Unlike WAXS, however, SAXS spans a size scale which is orders of magnitude larger than WAXS. Whereas WAXS deals with atomic-scale distances (~1 Å - 10 Å), SAXS is primarily sensitive to spacings on the order of 100's to 1000's of angstroms. This size scale allows one to see the “fine” structure of a material. In polymers, lamellae, particulates, some phase separations, and domain and grains structures occur on this size scale, making SAXS an appropriate tool for analysis of these phenomena.

We use a Rigaku rotating copper anode with a tungsten filament running at 40kV and 30mA to probe our samples. The rotating anode generated CuKα radiation (λ_{CuKα} = 1.5425 Å). The scattered radiation from the sample traveled though an evacuated path to two-dimensional Siemens detector placed 60cm (0.6 m) from the sample. This enabled us to collect data in the 2θ range of 0.2° to 2.0°.

5.3 Results
We now present the results of our studies on the three stress relaxation and recovery systems. There are 5 sections. The first is stress behavior of the samples as a function of time (primarily to motivate the discussion). The other four report results from the four analytical techniques: DSC, NMR, WAXS and SAXS. These results should give us a good idea of the structural details at many different size scales as well as the thermal behavior of the system.
5.3.1 Stress as a Function of Time

Figure 5.3 shows the stress normal to the LD as a function of time for the samples PET190Q, PET190T1hr, and PET190T5hr.

![Graph showing stress as a function of time](image)

Figure 5.3: $\sigma$ as a function of time for PET190Q, PET190T1hr and PET190T5hr samples

Figure 5.3 shows that the normal stress increases dramatically at $t = 0$, when the initial deformation occurs. After $t = 0$, PET190Q is quenched at constant displacement. During the cooling of the material, the normal stress drops dramatically (off the scale of the graph depicted in Figure 5.3). This is due to the decrease in volume from the corresponding reduction in the molar volume at the lower temperature. The PET190T1hr and PET190T5hr samples show similar stress reduction due to sample contraction upon cooling at 45 minutes and 300 minutes, respectively. However, since both PET190T1hr and PET190T5hr are annealed at 190°C at constant displacement for extended periods of time, we also observe some stress relaxation after the initial deformation. In addition, we observe that the stress in the LD of the PET190T5hr sample begins to increase after 60 minutes of annealing time. The stress then levels off at a new, higher level. Note that one can also see that there is a slight upturn in the PET190T1hr data, which reproduces what was seen in the PET190T5hr up to that point.
We note a couple of experimental observations. First, the final CR for all of the samples was ~2.7 and the deformation loads were all similar (21,000 pounds of force, which corresponds to 51.0 MPa in our channel die configuration), indicating that the processing history of our samples through the initial deformation process should all be the same. Second, we applied the stress “instantaneously” and therefore, are at a constant strain (i.e. displacement). Thus, the stress as a function of strain curve of these samples does not appear here. This compression ratio is smaller than expected based on the compressive stress as a function of CR reported by Bellare [Bellare A., 1993]. While Bellare reports no strain rates for the deformation, we believe the discrepancy in CR at an given applied load to be due to different strain rates in our deformation steps. Our deformation occurred over a 3 second period, implying an average strain rate of 0.8 s⁻¹. It should also be noted here than the PET190T5hr sample showed brittleness upon removal from the channel die. In contrast, the PET190Q and PET190T1hr samples both remained pliable after quenching and removal from the channel die.

5.3.2 DSC

Figure 5.4 shows the DSC traces for the series of three samples analyzed in this study.

![DSC Results for the PET samples](image)

Figure 5.4: DSC Results for the PET samples: a) PET190Q, b) PET190hr1, c) PET190hr5
The traces are very similar in appearance. The small peak in the PET190Q sample at \( \sim 290^\circ C \) is an artifact produced by the DSC for all runs on that particular day. All samples analyzed on that day displayed that peak. Neither PET190T1hr nor PET190T5hr which were analyzed on a different day reproduced that peak. The spurious peak is likely trace contamination in the pans. The melting peak data for each sample is summarized in Table 5.2.

<table>
<thead>
<tr>
<th></th>
<th>PET190NL</th>
<th>PET190Q</th>
<th>PET190hr1</th>
<th>PET190hr5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset (°C)</td>
<td>239.71</td>
<td>245.84</td>
<td>246.40</td>
<td>250.16</td>
</tr>
<tr>
<td>( T_m ) (°C)</td>
<td>253.55</td>
<td>259.95</td>
<td>259.05</td>
<td>256.82</td>
</tr>
<tr>
<td>( \Delta H_f ) (J/g)</td>
<td>42.18</td>
<td>47.13</td>
<td>50.27</td>
<td>48.91</td>
</tr>
<tr>
<td>( \chi_{DSC} )</td>
<td>30.1%</td>
<td>33.7%</td>
<td>36.6%</td>
<td>35.7%</td>
</tr>
</tbody>
</table>

Table 5.2: DSC Melting Peak Results for Stress Recovery Study

The table contains the peak onset, temperature at maximum (\( T_m \)) and enthalpy (\( \Delta H_f \)) for the 4 PET samples. The degree of crystallinity is calculated using a value of \( \Delta H^0_f \) of 140 J/g (\( \pm 20 \) J/g) from Mehta and Wunderlich [Mehta, A., 1978]. Comparison of the three samples shows that \( \chi_{DSC} \) does not vary much between samples. All 35% (\( \pm 2\% \)), which is close to the maximum degree of crystallinity seen in PET (\( (\chi_{DSC})_{max} \sim 40\% \)). However, DSC alone does not account for the state of orientation of the crystals (or crystallites). The PET190NL sample shows a lower degree of crystallinity than the plane-strain deformed samples indicating that approximately 3.5% - 5.5% of the crystallinity in the plane-strain deformed samples is due to strain-induced crystallization.

5.3.3 NMR

In order to present a basis for comparison in the \(^{13}\text{C SMAS-DECODER} \) NMR results, we show in Figure 5.5 an unoriented sample of PET. The main features to be noticed are the triangular shape in the lower left hand corner of the two-dimensional frequency
spectrum and the circular peak in the upper right hand corner. The circular peak in the upper right hand corner is due to the methylene groups in the ethylene and varies little with processing. The other lower-left triangle displays a strong dependence on carbonyl carbons of the ester. Thus, this feature is intimately tied to the orientation of the chain backbone. The triangular shape is present primarily in an unoriented morphology (such as with a powder). This triangular feature is present in $^{13}$C SMAS-DECODER spectra of other polyarylates such as HIQ-x. [Liao, M.-Y., 1997] The ellipsoidal diffuse background is due to the phenylene ring carbons. It varies very little with processing.

Figure 5.5: $^{13}$C SMAS-DECODER spectrum for unoriented PET powder

Figures 5.6 - 5.9 show the carbonyl orientations for the PET190NL, PET190Q, PET190T1hr, and PET190T5hr samples. One can see that the $^{13}$C SMAS-DECODER spectrum for PET190NL is very similar in appearance to the unoriented powder pattern. This implies that the material before deformation is unoriented. Therefore, the crystallites within the PET before plane-strain deformation are also unoriented.
The $^{13}$C-SMAS DECODER NMR spectrum displayed in Figure 5.7 for PET190Q shows the characteristic features of a polyarylate: the circular pattern in the upper right and a
distorted triangular form in the lower left hand side. The triangular feature in the PET190Q sample displays more intensity on the diagonal portion of the feature as opposed to the horizontal and vertical edges of the triangle. In contrast, the horizontal and vertical edges of the triangular feature are accentuated in the unoriented powder sample. The vertical band of intensity at 90ppm in Figure 5.7 is an artifact due to a zero frequency pickup by the detector. It is not indicative of a feature within the PET sample itself.

Figure 5.8: $^{13}$C SMAS-DECORDER spectrum for PET190T1hr

This concentration of orientation on the diagonal of the triangular feature of Figure 5.8 is starkly apparent in the $^{13}$C SMAS-DECORDER NMR spectrum for PET190T1hr. In fact, PET190T1hr shows the highest degree of carbonyl orientation of the three samples studied. The triangular feature becomes crescent-like in its contours. This indicates a high degree of localization of intensity on the diagonal, and hence a high degree of preferential orientation of the chain backbone.
Figure 5.9: $^{13}$C SMAS-DECODER spectrum for PET190T5hr

Figure 5.9 shows that the degree of orientation seen in the PET190T1hr spectrum (in Figure 5.8) has begun to disappear on the local scale. The diagonal of the PET190T5hr spectrum in Figure 5.9 is no longer the most intense on the triangular feature. From Figure 5.8, we see that the vertical and horizontal sides of the triangle again contain a number of features. These results indicate that the overall orientation of the material is greatest after an hour then decreases after five hours. Since PET190T5hr has the most evenly contoured triangular shape (in PET190Q the diagonal is accentuated and in PET190T1hr the vertical and horizontal legs of the triangle are negligible), we conclude that the PET190T5hr sample has the most "powder-like", that is unoriented, local structure.

In all of the NMR spectra displayed, the number of contours plotted remained the same. It is this fact which causes the diffuse background to seemingly vary between samples. In truth, this is an artifact of varying the range of the contour levels while leaving the number of levels constant.
5.3.4 WAXS

5.3.4.1 Crystalline Orientation

Since we must subtract out the crystalline reflections from our 3-D WAXS patterns, it is straightforward to results of the crystalline subtraction first. Figures 5.10 -5.12 show the spatial orientation of the 105 (FD), 100 (LD), and 010 (CD) crystalline reflections in the three oriented samples in this study. The pole figures indicate, First, the crystallites are aligned with their chain axes in the free directions (FD). The LD and CD show less order in the crystallite orientation. This is understandable. First, the CR we are at is slightly below the shearing transition that is espoused in Lin and Argon. They note that the Galeski, et al. introduce the idea that in PE, at CR ~ 3.13, the deformed spherulitic in PE become begin a process of reorganization through a mechanism of shearing of lamellae and slippage along the chain axes and subsequent annealing of lamellae and reduction of their interfacial surfaces. Bellare, et al., [Bellare, A., 1993] noted a similar mechanism in PET and also noted that the critical CR was approximately 2.6 in PET.

Figure 5.10: Pole Figure Diagrams of the 105 reflection of the Stress Recovery Samples

Figure 5.11: Pole Figure Diagrams of the 100 reflection of the Stress Recovery Samples
One should note that with our high shear rates the processes that Galeski et al., postulate are likely continuing for sometime after the initial deformation. One should also note from Figures 5.10 - 5.12 that the crystallite orientation displays a maximum at the intermediate times. This corresponds well with the results from NMR which note a maximum carbonyl orientation at intermediate times, which is subsequently lost.

5.3.4.2 Non-crystalline Orientation

Figure 5.13 show the results of the spherical harmonic series expansion coefficients for the PET190Q sample.

Figure 5.13: Experimental structure factor coefficients for PET190Q: $A_{00}(s) - A_{44}(s)$
One can readily see that the trace is dominated by the $A_{00}(s)$ coefficient, whose absolute magnitude is much higher than any of the other $A_{nm}(s)$ traces. The series was terminated at the $n = 4$ terms, which accounted for 80% of the total integrated intensity in the 3-D WAXS pattern. That is:

$$Residual = \frac{\sum \sum \sum |I_{calc}(s, \alpha, \beta) - I_{ex}(s, \alpha, \beta)|}{\sum \sum \sum |I_{ex}(s, \alpha, \beta)|}$$

(5.1)

Where $I_{ex}(s, \alpha, \beta)$ is the experimental data and $I_{calc}(s, \alpha, \beta)$ is the series reconstruction of the experimental data. A higher number of terms could have been used to capture more of the intensity in the 3-D WAXS pattern, but for the purposes of the comparison between samples the first six spherical harmonic terms were found to be sufficient.

Figure 5.14 show the resultant experimental structure factor coefficient traces, $A_{nm}(s)$ from the spherical harmonic series deconvolution of PET190T1hr.

![Figure 5.14: Experimental structure factor coefficients for PET190T1hr: $A_{00}(s) - A_{44}(s)$](image)

Like the series deconvolution used for PET190Q, the series was truncated after the sixth term (i.e. after $n = 4$, $m = 4$). For this sample, the first six terms of the series accounted for more than 84% of the total intensity in the 3-D WAXS pattern.
Figure 5.15 show the resultant experimental structure factor coefficient traces, $A_{nm}(s)$ from the spherical harmonic series deconvolution of PET190T5hr.

For PET190T5hr, the spherical harmonic series deconvolution was truncated at $n = 4$. The first six terms of the series accounted for more than 87% of the total scattered intensity in the 3-D WAXS pattern. This fact indicates that broad features (i.e. ones that are well-characterized by the low index spherical harmonics) seemingly dominate the pattern.

The residuals for each of the three samples as a function of spherical harmonic index $n$ is listed below in Table 5.3.:

<table>
<thead>
<tr>
<th></th>
<th>$n = 0$</th>
<th>$n = 2$</th>
<th>$n = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET190Q</td>
<td>37%</td>
<td>32%</td>
<td>20%</td>
</tr>
<tr>
<td>PET190T1hr</td>
<td>49%</td>
<td>29%</td>
<td>16%</td>
</tr>
<tr>
<td>PET190T5hr</td>
<td>48%</td>
<td>23%</td>
<td>13%</td>
</tr>
</tbody>
</table>

Table 5.3: Residuals for PET190Q, PET190T1hr and PET190T5hr as a Function of the Index $n$. 

Figure 5.15: Experimental structure factor coefficients for PET190T5hr: $A_{00}(s) - A_{44}(s)$
The residuals reflect the degree to which the functional form of the spherical harmonic terms match the distribution of intensity in the experimental data. PET190Q has a significant isotropic contribution and the higher order terms contribute far less to the data fit. In contrast, both the PET190T1hr and PET190T5hr samples show significant residual reduction by the higher order terms. This implies that the PET190Q sample contains a lesser degree of orientation than the longer annealed samples. However, one must be wary of drawing conclusions about the orientation based solely on the residuals, as the residual do not tell the entire story. There are two reasons for this: 1) the higher order residuals contain multiple traces since the m-index depends on the n-index, and 2) the residuals do not account for features in the trace, they are a sum over all of the data points in the pattern.

Therefore, we need to view and compare all of the coefficient traces. Figure 5.16 shows the comparison between all of the $A_{nm}(s)$ traces calculated for each of the PET samples.
From Figure 5.16, we note a couple of things. First, the traces for the series of data are all very similar in shape. The only real differences between traces are the magnitudes of the various coefficients. This makes this set of samples prime for analysis via a spherical harmonic series deconvolution using a single ensemble model validation. It is very likely that all three of the samples have a similar enough local (re: molecular-scale) structure that a single ensemble will be able to describe them accurately enough. This immensely simplifies the number of simulations necessary to determine the appropriate molecular-scale structural ensemble.
Second, each of the coefficient traces displays a dominant feature, an interchain peak at $s \sim 1.6\,\text{Å}^{-1}$. The $A_{00}(s)$ coefficient traces also display the characteristic intrachain peak at $s \sim 3.0\,\text{Å}^{-1}$. For the three samples shown here, the $A_{00}(s)$ traces are completely negative. The reason for this the subtraction of the zero-point scattering during the renormalization. As noted in Chapter 4 section 4.4.1.3, we do not shift the pattern to be centered about zero, but a slightly negative number. The redistribution of intensity brought about by orientation of local structures may not be enough to produce an average positive value at a given $s$. The $A_{00}(s)$ is just the orientational average of the scattering at a given $s$-value. The fact that we have only negative values in our $A_{00}(s)$ implies that the degree of orientation in our three samples is moderate.

One might also note, that these results are very similar to those seen previously in Chapter 4 for the PET190SC sample. This is not surprising, since the processing conditions (plane-strain deformation to a CR of $\sim 2.6$ at 190°C) between these samples and PET190SC are quite similar.

Lastly, in comparing the series of coefficient traces for the WAXS data, we can see that the PET190hr1 sample shows the greatest degree of orientation. We can infer this from the fact that for every coefficient trace except the first ($A_{00}(s)$, the isotropic scattering), the PET190hr1 sample has the highest magnitude. The fact that the PET190hr1 sample shows the highest degree of orientation (even in the non-crystalline portion) is consistent with the NMR results. From the individual coefficient traces, PET190T5hr has the smallest coefficient values for all of the traces, implying that it would display the least orientation. This seems at odds with our assessment based on the residuals. This highlights the shortcoming of using either of these as a measure of orientation. From the experimental coefficient traces and the residuals alone it is difficult to determine which of our three samples has the “least” orientation. The function that pulls the data from both of these together is the ODF, a “true” measure of orientation.
5.3.4.3 Molecular Simulations and ODF Determination
The calculation of the theoretical structure factor coefficient traces were carried out in
the methodology delineated in Chapter 4. The simulation code requires no additional
modifications since the monomer library was modified to incorporate ethylene moieties
in Chapter 4. To refresh our memories, the simulation consists of the generation of an
ensemble of molecular-scale structures with explicit atomic coordinates. The chains in
this simulation are generated with an RIS algorithm and then placed on a two-
dimensional lattice of average lattice positions. A Monte Carlo sampling algorithm is
used to place the chains on the lattice. The main inputs into the lattice generation
portion of the simulation are the average lattice dimensions and the degree by which
these lattice parameters may vary. For the chain building steps, we are constrained in
our backbone compositions (we must alternate ethylene and terephthalate moieties),
but did allow the ester torsions to vary randomly up to ±30°. In PET, because the
phenylene rings in the terephthalate moiety are always bonded to 2 carbonyl carbons,
the ring is always assumed to be in a planar configuration. Additionally, only the trans-
conformer of the ethylene moiety was considered, since we are primarily interested in
extended chain conformations.

The $A_{nm(s)}$ traces present for the three samples here are very similar to those seen in
Chapter 4 for the PET190SC plane-strain deformed sample. We can therefore assume
that the model parameters which reasonably satisfy the experimental coefficient traces
in Chapter 4 will also apply here. The similarity of the experimental traces between the
PET190Q, PET190T1hr, and PET190T5hr samples allows us to use a single ensemble
validation. Using the same model parameters and structure factor calculations enables
us to derive ODFs for the three samples. Table 5.4 shows the molecular simulation
input parameters.
Table 5.4: Model Simulation Parameters for PET190Q, PET190T1hr, and PET190T5hr

Table 5.5 shows the scaling coefficients, $D_{nm}$'s, for each of the three samples for the simulation ensemble.

<table>
<thead>
<tr>
<th>Sample, n,m</th>
<th>0,0</th>
<th>2,0</th>
<th>2,2</th>
<th>4,0</th>
<th>4,2</th>
<th>4,4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET190Q</td>
<td>1.93</td>
<td>0.74</td>
<td>1.05</td>
<td>0.31</td>
<td>-0.27</td>
<td>1.85</td>
</tr>
<tr>
<td>PET190T1hr</td>
<td>1.85</td>
<td>1.02</td>
<td>2.16</td>
<td>0.050</td>
<td>-0.42</td>
<td>1.59</td>
</tr>
<tr>
<td>PET190T5hr</td>
<td>1.90</td>
<td>0.55</td>
<td>1.81</td>
<td>0.018</td>
<td>-0.21</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 5.4: Model Simulation Parameters for PET190Q, PET190T1hr, and PET190T5hr

Table 5.5: Scaling Coefficients, $D_{nm}$, for PET190SC

Using the values in Table 5.5, the corresponding oriented non-crystalline phase ODFs for the structural ensemble relative to the three samples are shown in Figure 5.17.
The ODFs for this series of samples indicates that all of the systems still display a significant degree of chain orientation. As with Chapter 4, the series reconstruction of the ODF for these samples show negative portions of the trace. These aphysical values are due to the uncertainty in the large values of the higher \((n = 4, \text{ both } m = 2 \text{ and } m = 4)\) coefficients. One should also note that the negative values of the traces are localized to the very edge of the ODF \((\alpha = 90^\circ)\) and are off axes \((\beta = 50^\circ - 80^\circ)\).
most of the molecular level reorganization occurs in the LD-FD plane (these two axes being the focus of the compressive and extensional forces in the sample [Bellare, A., 1993]), it is reasonable that the series reconstruction in the area where chain alignment is least will have values near 0. One can also note that the ODFs indicate that the LD has the highest concentration of aligned chains. Like the negative values off-axis, the higher order spherical harmonic terms also account for some aspect of this feature in the ODF reconstruction. The large values (in absolute terms) of the $D_{42}$ and $D_{44}$ coefficients in the ODF reconstruction will both have negative contributions to the ODF off-axes between the LD and CD and positive contributions in the direction of the LD. Although we must be wary of a quantitative comparison between samples, we can still do a relative comparison between samples. As noted previously, the negative values in the ODF are localized and their magnitude small; thus, even if the numerical values of the $D_{nm}$'s are refined such that these artifacts no longer appear, the altered ODF values will not change the overall shape (or trend behavior) nor any conclusions which we draw based on comparisons between samples based on those trends.

The ODFs indicate that in all three samples there is significant chain orientation. This orientation is broad in its features. For example, in PET190Q, the ODF shows significant population over almost the entire pattern. In PET190T1hr, where the orientation is strongest, chain orientation is concentrated on the LD-FD plane and primarily on the two axes. In the PET190T5hr sample, the orientation is still concentrated in the FD-LD plane, but is no longer strongly associated with only the axes. Thus, the polymer chains in the samples seemingly reorganize over time. Ostensibly, the oriented material first crystallizes, relaxing to an oriented state whose distribution is centered on the FD. Subsequent reorganization of the non-crystalline material places it into a more disordered state that is arrayed at all values in the LD-FD plane. Coupled with the NMR results, this seems to indicate a more randomly coiled (i.e. disoriented) configuration for the chain, which distributes itself between the tensile (in the FD) and compressive (in the LD) stresses in the system. The concentration of aligned chains in the LD-FD plane is not unusual, having been postulated by Bellare when looking at the crystalline material and noting that the non-crystalline should follow
suit. [Bellare, A., 1993]

As discussed in Chapter 4 sections 4.3.3 and 4.6.5, the $A_{00}(s)$ coefficient has two contributions: oriented and unoriented non-crystalline contributions. An amorphous reference sample coupled with the spherical harmonic series deconvolution analysis also allows us to determine the relative percentages of oriented ($\chi_{\text{ONC}}$) and unoriented non-crystalline contributions ($\chi_{\text{UNC}}$) to the $A_{00}(s)$ coefficient trace. We determine the $\chi_{\text{ONC}}$ and $\chi_{\text{UNC}}$ by minimizing the following equation with respect to $D_{00}$ and $\chi'_{\text{ONC}}$:

$$OBJF = \sum_{s}^{N_s} D_{00}(\chi'_{\text{ONC}}A_{00,\text{calc}}(s) + (1 - \chi'_{\text{ONC}})A_{00,\text{am}}(s))$$ (5.2)

$D_{00}$ is the scaling coefficient for the isotropic portion. $\chi'_{\text{ONC}}$ is the relative fraction of oriented non-crystalline material with respect to all non-crystalline material only. $A_{00,\text{calc}}(s)$ and $A_{00,\text{am}}(s)$ are the calculated structure factor coefficient and the amorphous coefficient for $n = 0, m = 0$, respectively. The non-crystalline relative fractions coupled with WAXS degree of crystallinity ($\chi_{\text{xtal}}$) allows us to elucidate the relative fractions of the three phases in each sample. Table 5.6 shows the breakdown of the relative percentages of the three phases present in the PET190Q, PET190T1hr, and PET190T5hr samples.

<table>
<thead>
<tr>
<th></th>
<th>PET190Q</th>
<th>PET190Thr1</th>
<th>PET190Thr5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{\text{xtal}}$</td>
<td>19.5%</td>
<td>22.0%</td>
<td>22.1%</td>
</tr>
<tr>
<td>$\chi_{\text{ONC}}$</td>
<td>48.3%</td>
<td>46.8%</td>
<td>46.7%</td>
</tr>
<tr>
<td>$\chi_{\text{UNC}}$</td>
<td>32.2%</td>
<td>31.2%</td>
<td>31.2%</td>
</tr>
</tbody>
</table>

Table 5.6: Relative Fractions of Phases in PET190Q, PET190T1hr, and PET190T5hr. $\chi_{\text{xtal}}$, $\chi_{\text{ONC}}$ and $\chi_{\text{UNC}}$ are the relative fractions of the crystalline, oriented non-crystalline, and unoriented non-crystalline phases, respectively.

Given that the degrees of crystallinity for each of the samples showed very little variance between them and we used the same molecular ensemble for comparison to
all of the $A_{nm}(s)$ traces for each sample, we anticipate that the relative percentages of phases will not vary by that much. All three samples contain around 70% oriented material.

Table 5.7 compares the degree of crystallinity via DSC ($\chi_{DSC}$) and WAXS ($\chi_{xtal}$) for the three samples.

<table>
<thead>
<tr>
<th></th>
<th>$\chi_{DSC}$</th>
<th>$\chi_{xtal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET190Q</td>
<td>33.7%</td>
<td>19.8%</td>
</tr>
<tr>
<td>PET190T1hr</td>
<td>36.6%</td>
<td>22.0%</td>
</tr>
<tr>
<td>PET190T5hr</td>
<td>35.7%</td>
<td>22.1%</td>
</tr>
</tbody>
</table>

Table 5.7: Comparison of $\chi_{DSC}$ and $\chi_{xtal}$

As we have seen previously in Chapters 2 and 4, the degree of crystallinity as measured by WAXS is less than that measured by DSC. The same reasons that applied previously (that WAXS is more sensitive to crystalline defects and disruptions and that our DSC calculations include the long tail preceding the melting peak in the peak enthalpies) still hold.

5.3.5 SAXS
Small Angle X-ray Scattering (SAXS) affords us the chance to take a look at the fine structure of a material. The length scale generally viewed are on the order of 100’s to 1000’s of angstroms. These size scales are generally large enough to capture lamellae and other “fine” structures.

For our purposes, this study required the determination of the shearing angle and the long period of the samples. The shearing angle is the average angle at which the sheared lamellae lie and the long period is the bulk mean spacing between lamellae layers. Figure 5.18 displays the SAXS patterns for the three samples in this study. The figure also denotes the orientation of the sample relative to the beam (which
entered the sample perpendicular to the page):

Figure 5.18: 2-D SAXS scans of a) PET190Q, b) PET190T1hr, and c) PET190T5hr showing four-point patterns. The axes systems are shown above the pattern. The incident X-ray beam was parallel to the CD.

Figure 5.19 shows the SAXS pattern integrated over $2\theta$, which displays the azimuthal dependence of the scattered intensity for each of the samples.

Figure 5.19: $2\theta$ integrations of the SAXS data from the three PET samples showing the azimuthal dependence of the SAXS pattern. The arrows indicate the approximate positions of the peaks in the four-point pattern.
This method of visualization of the pattern gives a better representation of the four point pattern in the various data sets. From the azimuthal integrations, we can derive the shearing angle of the lamellae in each sample. Bellare, et al., noted that in PET under plane-strain deformation the spherulitic lamellae shear into a herring-bone pattern. The characteristic angle of that herring-bone structure is the shearing angle seen in the SAXS pattern. In plane-strain deformed PET, the quiescent spherulites before deformation have randomly oriented lamellae. Upon deformation, any lamellae tied to chains not already aligned in the flow direction undergo a distortion as the chains in the sample are forced to align. The shearing angle is taken relative to the FD (i.e. shearing angle is 0° when parallel to the FD). [Bellare, A., 1993] This is schematically diagramed in Figure 5.20:

![Diagram of herring-bone arrangement](image)

Figure 5.20: Schematic of the herring-bone arrangement of the lamellae in plane-strain deformed PET

Table 5.8 shows the shearing angles derived for our samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shearing Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET190Q</td>
<td>69° (± 6°)</td>
</tr>
<tr>
<td>PET190T1hr</td>
<td>55° (± 5°)</td>
</tr>
<tr>
<td>PET190T5hr</td>
<td>62° (± 4°)</td>
</tr>
</tbody>
</table>

Table 5.8: The Average Shearing Angle for the Plane-Strain Deformed PET Samples

One can see that the shearing angle varies between samples fairly significantly. As
with our WAXS and NMR results, the PET190T1hr shows the greatest degree of average lamellae alignment with the FD. The fact that the average shearing angle begins to rise again with the PET190T5hr sample implies that disorientation is again taking place. Thus, NMR, WAXS and SAXS all offer a consistent picture of chain orientation and subsequent disorientation through annealing. All three methods show consistent results implying that a “short-time” process, one with a time constant on the order of 10’s of minutes, and a “long-time” process, one with a time constant on the order of 100’s of minutes, are occurring within this series of samples.

If we incline the sample at an angle equal to the shearing angle, we can deduce the average long spacing between lamellae centers for the majority of the sheared lamellae. Bragg’s Law can be applied to analyze the scattering vector dependence of the SAXS pattern, once we have accounted for the Lorentz factor. By plotting \( s^2 I(s) \) as a function of the scattering vector, \( s \), we effectively take a volumetric filter (the \( s^2 \) portion) to the data. In effect, this analysis assumes that the lamellae are stacked in a 1-D array of planes. The plot of \( s^2 I(s) \) as a function of \( s \) is then a measure of the periodicity in the direction of the normal to the lamellae planes. Figure 5.21 shows the azimuthal integration of intensity as a function of the scattering vector for each of the PET samples inclined near their shearing angle. The intensity has the Lorentz factor accounted for and thus is plotted on a semilog scale as \( s^2 I(s) \).
Figure 5.21: Azimuthal angle integrations of SAXS patterns for PET190Q, PET190T1hr, and PET190T5hr, showing the $2\theta$ dependence of the SAXS pattern.

From Figure 5.21, we can see that the series of azimuthal integrations for the samples shows decreasing lamellae spacings with time. The maximum of the PET190Q distribution is at $s = 0.066\text{Å}^{-1}$ ($2\theta = 0.93^\circ$), which corresponds to a long period of 95.0Å. The maximum of the PET190T1hr distribution is at $s = 0.069\text{Å}^{-1}$ ($2\theta = 0.97^\circ$), which corresponds to a long period of 91.1Å. The maximum of the PET190T5hr sample is too broad to get an accurate measure of the average lamellae spacing. These long periods in the PET190Q and PET190T1hr samples correspond to about 8-10 trans configured ethylene-terephthalate units. As we have noted before in Chapter 4, the viscosity-average molecular weight ($MW_v$) of our PET chains is 18,000 amu which corresponds to approximately 95 - 100 ethylene-terephthalate units. Thus, we can envision that any given polymer chain will participate in one or more lamellae with the potential to act as a tie molecule in a taut-tie mechanism. The fact that the lamellae long periods are decreasing with time indicates that there may be a melting and recrystallization phenomena occurring over time.
5.4 Discussion: Stress Relaxation and Recovery Mechanisms

5.4.1 Summary of Analyses Results

To summarize our results and collect our thoughts relevant to this study, we have collated the following list of results for the four analytical techniques used in this study:

1) DSC:
   a) From $\chi_{DSC}$, we deduce that the similar degrees of crystallinity in the samples are quite similar

2) NMR:
   a) The carbonyl orientation greatest at intermediate times.
   b) The carbonyl orientation essentially axisymmetric.
   c) Currently, our NMR technique does not distinguish between crystalline and non-crystalline phases.

3) WAXS:
   a) Both crystalline and non-crystalline orientation is maximum at intermediate times.
   b) Crystalline orientation: aligned chains, primarily axisymmetric (about FD).
   c) Non-crystalline orientation: bundles align in FD consistently, but there is broad variation about that alignment. There is a significant population of bundles in the LD and LD-FD plane.
   d) From $\chi_{WAXS}$ and $\chi_{ONC}$, we deduce that the relative amount of oriented material remains quite similar between samples.

4) SAXS:
   a) Shearing angle shows a maximum at intermediate times. This implies that the short time mechanism improves orientation of lamellae and is consistent with the stress relaxation mode of shearing and annealing lamellae.
   b) The long period decreases over time (no minimum or maximum in series of samples). Again, consistent with shearing and regrowing lamellae. Since long period does not remain the same, the implication is that rotation of lamellae stacks is less likely.
Thus, there appears to be two competing mechanisms, one which orients and the other which does not. The orientation and disorientation observations are consistently seen on 3 different size scales, atomic, molecular and lamellar. The fact that the long period continues to decrease implies that lamellae stacks are being continually melted and recrystallized in the samples, rather than the lamellae stacks merely being reoriented. However, WAXS indicates that the extended chains are disorienting. From this result we conclude that some lamellae stacks may be rotating, since both crystalline and non-crystalline material show similar behavior.

5.4.2 The Overall Picture
Since the change in crystallinity between samples is not significant, we must infer that the crystallites in the material are either concertedly reorienting or being destroyed and recrystallizing in a new orientation. DSC alone does not allow us to infer which of these possibilities is happening. The literature suggests that both are occurring to varying degrees. It seems reasonable that the reorientation of an entire crystallite would be possible for smaller crystallites, but exceedingly difficult for larger ones. Therefore, the former mechanism is likely favored by the smaller crystallites and the latter (or some variation thereof) favored by larger crystals. At 190°C for PET, the combination of nucleation and growth is maximized (hence the maximum rate of crystallization), but in addition to nucleation and growth, there are also mechanisms dealing with crystalline perfection and thickening as well as melting and regrowth possibly occurring as well. [Dennis, L., 1987]

The fact there is a minimum in the stress as a function of time implies that there are two different, competing mechanisms involved that have different characteristic time constants. Stress recovery in oriented materials has been seen for a number of different polymeric systems. Kawai et al., studied polyethylene films under tension and looked at crystallization as a function of draw ratio as observed in X-ray scattering and electron microscopy. [Kawai, T., 1967] Dennis and Buchanan looked at the thermo-mechanical response of Nylon 6 carpet fibers under tension. [Dennis, L., 1987] Gupta
et al., studied stress shrinkage in PET fibers and films. They measured the shrinkage stress of a number of different types of fibers as a function of annealing temperature. [Gupta, V., 1994] All of the morphologies that show the strain recovery are oriented (as our system is). All of these studies have postulated a two-mechanism model which consists of the following:

1) The standard stress relaxation phenomena which is driven by crystallization (and recrystallization) of the oriented material.

2) A mechanism which is entropically driven. This mechanism is often associated with the non-crystalline portion of the material. The less-extended conformations of the non-crystalline chains assert themselves more slowly under stress, thus their relaxation occurs on a longer time scale.

Galeski et al., describe a mechanism of lamellae shearing at moderate to high plane-strain deformation rates. They also use a strain rate of 0.0025 sec\(^{-1}\). [Galeski, A., 1992] This strain rate is much lower than ours. While this is inconclusive, the process of perfection of orientation continuing after the initial deformation, but is consistent with our observations and a variation or extension of the theory. Mandelkern [Mandelkern, L., 1964] discusses in depth the role of the extended chain and its increased propensity to crystallize when aligned with similar chains. He discusses the thermodynamics of the system being more facile in light of the extended chain having already overcome a significant portion of the barrier to crystallization by assuming an extended chain conformation under stress. The second mechanism originally proposed by Kawai et al., states that crystallization, and especially oriented crystallization, can lead to residual stresses being formed on the molecular-level in the non-crystalline regions of the material. The residual stresses are transmitted through (or concentrated in) tie-molecules between the two phases.

The above arguments can be extended to our system as well. While all of the above studies dealt with samples under tension, for plane-strain deformed samples (such as ours) the applicability of these mechanisms is reasonable. We have merely decided to deform the sample geometry in a compressive mode as opposed to a tensile one. One
should note that only the normal stress to the compression direction (i.e. in the LD) is shown in this study. Our experimental setup did not allow direct measurement of the stresses on either the CD or FD directions. It may well be that in the other two directions (the CD and FD), we continue to see a reduction in either stress or strain. We do not see any visible retraction of material back into the die.

Our studies agree with the two mechanisms espoused above. If we diagram the processing histories of our three PET samples (as shown in Figure 5.22), we can breakdown the process into five distinct parts (labelled [I] through [V] in Figure 5.22):

![Figure 5.22: Schematic of processing histories for stress recovery series: (1) PET190Q, (2) PET190hr1, (3) PET190hr5](image)

**Part I)** Thermal Equilibration: In this step, we begin to produce unoriented crystallites. This material is evenly distributed and oriented throughout the material. As noted in Chapter 1, after 15 minutes at 190°C, the PET sample should have obtained a degree of crystallinity which approaches the maximum degree of crystallinity, 40%.

**Part II)** Plane-Strain Deformation: Immediately before introducing the plane-strain deformation the crystallites are unoriented. However, immediately following the deformation the unoriented crystallites and lamellae are sheared as the chains begin to align preferentially in the FD.

**Part III)** PET190Q: Via WAXS, the immediately quenched PET sample shows an oriented chain morphology which is locked into a number of sheared lamellae. It is likely that there is a large amount of residual stresses in the material which can be reduced by annealing.

**Part IV)** PET190T1hr: After an hour the reorganization of oriented material into
oriented crystallites has apparently run its course. The Mandelkern's stress relaxation mechanism dealing with an oriented semi-crystalline system is complete. From our WAXS results, not all of the oriented non-crystalline material has been consumed (in fact the proportion is nearly the same as when this mechanism started). This implies that the material is simultaneously melting and recrystallizing. The new crystallites are in a less stressed orientation, which presumably is the driving force. This process continues until the degree of residual stresses involved in the non-crystalline material have reached the point where it is no longer favorable to continue to orient additional material. Thus, the maximum degree of orientation in the sample has been reached (on all levels), which is in agreement with the NMR, WAXS and SAXS measurements in this study.

Part V) PET190T5hr: The non-crystalline phases of the PET now undergo an entropically driven relaxation. Some of the "looser" tie-molecules are pulled from their respective oriented crystallites and their chains relax into more relaxed (i.e. stable) conformations. From the SAXS and WAXS data, we can see that this disorientation of chains and reorientation of crystalline and non-crystalline material is concentrated in the FD-CD plane. Relaxations of residual stresses in the non-crystalline regions of the sample account for the driving force for this mechanism.

This series of events highlights the fact that the time scales for these two mechanisms are not the same. As discussed at the beginning of this chapter, the oriented and strain-induced crystallization processes are faster than their unoriented counterparts. [Mandelkern, L., 1964, Adams, A., 1997] Our results are consistent with this assertion. The process with the long-time mechanism is localized to the non-crystalline phase and acts on the order of hours. The short-term mechanism is concentrated in the oriented phases of the sample and has run its course within tens of minutes.

We may ask the question is: what is the mechanism that explains the stress recovery that we see in the LD direction of the sample? To get at this topic, we make a couple of notes about the second mechanism. We have already noted previously, that strain recovery behavior in long chain molecules is not uncommon (see section 5.4.1). Additionally, Bergstrom and Boyce have reported recently about the mechanical behavior of elastomeric chloroprene rubbers, that if the strain deformation is staged, the rubber displays a stress recovery mechanism on the unloading stage of the strain
deformation cycle. [Bergstrom, in press] Bergstrom and Boyce note that the stress recovered asymptotically approaches an “equilibrium” value. They use a coupled two-network model to explain their results. The first network is the equilibrium response of the material. The second network is a function of the time-dependent entropically-driven elastic response of the non-crystalline phase of the material under the constraint of the strain deformation at that stage. When the two models are coupled, the behavior of the time-dependent behavior of the system causes an “overshoot” in the stress-strain behavior of the sample. On a molecular level, the coupling of the two networks implies that the faster network dissipates energy (or stress) at the expense of the slower network. Thus, whereas the faster network can minimize its energy separately, the slower network must minimize the total energy of the system (both the slow and fast networks). A similar entropically-driven elastic response could also be at play with our plane-strain deformed PET sample.

Strain recovery is a common phenomena seen in many studies of deformation of semi-crystalline polymers. [Zaroulis, J., 1997, Galeski, A., 1992] The strain recovery occurs upon annealing of samples which have undergone elastic, affine deformation. In these samples, the annealing occurs with no load and temperatures approaching the melting point. Strain recovery is often cited as a phenomena indicative of polymer “memory,” as the specimen attempts to return to its original shape. In our case, the stress recovery, could be seen a variation on the strain recovery phenomena. We hold the temperature of the system at a high temperature (over 100°C above T_g and only 70°C below T_m), for an extended period of time, while keeping the shape of the sample distorted. Given that the material cannot return to its original shape, the resultant strain field may appear as a corresponding increase in stress measured. Presumably, this response to the induced strain is entropic.

In addition to the elastic response of the non-crystalline phase, PET undergoes hydrolytic degradation effects at temperatures above 100°C. [Zimmerman, H., 1984, Allen, N., 1991] Above 100°C, hydrolytic degradation of PET is auto-catalytic and only
0.01% H2O by weight is required. We did not guard our sample from atmospheric moisture before or during processing, implying that the moisture content could have been high enough to cause considerable chain scission by hydrolytic degradation in the sample. Although the studies at 100°C noted hydrolytic degradation processes taking on the order of 10's to 100's of hours, it is quite possible that at our higher processing temperature the rate of hydrolytic degradation could be accelerated by one to two orders of magnitude. Hydrolytic degradation causes an increase in the number of free chain ends in the material. In turn, the number of chain ends causes an increase in molar volume. The higher molar volume would imply that at a constant strain, the stress on any surface of the sample would increase.

With the current data at hand, we are unable to determine which (if either) of these mechanisms is the more probable. It is likely that both the non-crystalline elastic response and hydrolytic degradation mechanisms are active in the samples to some degree. Ultimately, the two mechanisms are not mutually exclusive, but can be complimentary. For example, while longer chains have a higher entropically-driven response to extensional bias, once chain scission occurs the number of chains doubles. Both scissioned chains are then free to assume more entropically favored conformations. This situation may be made even more favorable if the shorter chains are no longer tied to a crystallite or otherwise freed of disentanglements within the polymer matrix.

5.5 Conclusions and Chapter Summary

We have investigated the observation that in PET annealing for periods on the order of hours leads to a stress recovery phenomena in the direction normal to the LD. This behavior may be explained by the use of model in which there are two competing mechanisms. Using 13C SMAS-DECORDER NMR, we showed that the orientation of the chain backbone shows its greatest degree of orientation about an hour into the anneal. Subsequent to that maximum in chain orientation, additional annealing leads to a
disorientation. We showed with WAXS that the local structure of the material oriented preferentially in the FD-CD plane. This is reasonable, since the FD and LD are the two directions which experience the largest tensile and compressive biases, respectively. Short-term annealing (on the order of 10's of minutes) leads to preferential chain alignments in the FD, but longer annealing times (on the order of 100's of minutes) subsequently leads to disorientation of the chains in the FD-LD plane. We showed with SAXS that the shearing angle varied in our samples. The results showed that initially the lamellae are sheared and with time they align towards the FD, but subsequently disorient after longer annealing periods. All of these techniques built a cohesive picture of polymer chains orienting then disorienting in some manner at long annealing times.

Coupled together all of these techniques aid us in understanding some of the dynamics of the reorganization of the chains and fine structure in the material. This allowed us to deduce mechanisms and to couple chain orientation to the fine structure as well as the processing history of the sample. Our results indicate that the two mechanisms have different times scales. The chain reconfiguration to a more entropically favored conformation in the non-crystalline phase happens on a longer time scale than the crystalline perfection and orientation mechanism. We also postulate that hydrolytic degradation may be occurring within the sample and that the relaxation of the non-crystalline chains may require some disentanglement by chain scission before becoming the dominant mechanism.

One of the main points of this chapter was to demonstrate the potential of the spherical harmonic series deconvolution analysis as an additional technique to probe the local scale structure of a material. This chapter highlighted the information that could be obtained from the experimental and calculated structure factors. We showed that the technique is sensitive enough to give useful information about comparisons between samples in a series of processing steps. This information was in the form of a local structural ensemble and its corresponding ODF. The combination of the analytical techniques on different size scales allowed us to make inferences about the overall mechanisms driving the development and destruction of chain orientation in PET.
Chapter 6

Conclusion

“And now, as I think, I have discharged my debt with the completion, by God's help, of this huge work. It my be too much for some, too little for others. Of both these groups I ask forgiveness. But of those for whom it is enough I make this request: that they do not thank me, but join with me in rendering thanks to God. Amen. Amen.”
- St. Augustine, City of God, Bk XXII, Ch. 30.

6.1 Summary

The point of this thesis work has been to develop a method by which the non-crystalline portion of polymer material may be quantitatively evaluated. In specific, we looked at two polyarylate systems: PET and HIQ-x. The results of this study are summarized as follows:

A complete methodology was developed for the analysis of multi-dimensional WAXS patterns. There is both an experimental and a theoretical branch to the analysis. The experimental methodology developed the systematic separation of the instrumental, geometric, crystalline and non-crystalline contributions to the WAXS pattern of an experimental sample. The remaining non-crystalline portion of the pattern is then separated into orientation and structural contributions in a series expansion which uses a set of basis functions appropriate to the symmetry of the system. We have detailed the series expansion analysis for two aromatic polyesters; one an axisymmetric two-dimensional case, which requires the use of Legendre polynomials terms and the other a general three-dimensional case requiring spherical harmonics terms.

The simulations developed consist of an algorithm which utilizes a MC sampling method to populate a two-dimensional paracrystalline lattice with perfectly aligned chains generated by RIS. The acceptance criteria of this algorithm varies from conventional Metropolis Monte Carlo in that, in addition to energetic considerations weighting the acceptance probability, a “measure of merit” criterion (which compared the theoretical...
and experimental structure factors as a basis for structure acceptance) was also utilized. The output from the model consisted of the molecular ensemble generated and the structure factor of that ensemble, allowing comparison to the experimental data. Comparison between the experimental and theoretical structure factors yields an ODF, which when coupled with the molecular ensemble can be used in further simulations. This analytical methodology is not limited to the polymer chemistries used here. The overall methodology (i.e. both experimental and theoretical branches) is general, except for the model structure generation. If a suitable molecular model for any given system can be generated, the series expansion analysis may be applied to any two- or three-dimensional WAXS pattern without modification.

The analysis was demonstrated by studying two polyarylate samples. In the two-dimensional case, unannealed HIQ-40 solution-spun fibers were looked at. In the three-dimensional case, plane-strain deformed PET samples were analyzed. These examples showed the details of the analysis, as well as its versatility. The examples also indicate that the analysis works best on materials that display only moderate amounts of orientation, in order to limit the number of terms in series expansion.

The analysis invokes the use of a 3-phase model, which was required to describe all of the features in the structure factor coefficients determined in the analysis. For HIQ-40 fibers, the analysis yields the result that over 70% of the chains in the fibers are oriented locally (i.e. aligned with respect to its nearest neighbors). The molecular ensembles for the fibers display local packing, but the corresponding ODFs contain significant isotropic portions implying macroscopic disorientation. Similarly, for PET samples, a significant proportion (> 65%) of the material is in the oriented state. In the plane-strain deformed PET samples, the ODFs of the structural ensembles indicates that most of the chains line up in the plane containing the load and flow directions.

Processing studies on two sets of polyarylate samples were performed. The Legendre polynomial series expansion analysis was completed on a set of polyarylate fibers both
solution- and melt-spun. A 3-D orientation study, requiring the spherical harmonic series expansion analysis was performed on a set of plane-strain deformed PET samples processed with the same initial deformation, but with varying post-deformation annealing times. Both studies produced similar results concerning the role of mechanical and thermal processing. It was determined that annealing of the materials increases only the perfection of orientation already present within the sample. The initial orientation of chains in the material is highly dependent on the deformation history. In both HIQ-40 and PET samples, it was found that the initial deformation history of the sample induces similar local packing structures within sets of comparable samples. The orientation of that local structure changes, but the structure itself is retained through the annealing process. This highlights the fact that the mechanical bias used to induce orientation has a lasting effect on the properties of the system.

6.2 Recommendations of Future Work

From the work presented in this document, a number of recommendations can be proposed:

1) Given some of the limitations of the molecular ensembles generated, further refinement of the molecular model should be sought. In particular, the assumptions and details of the lattice generation and the MC acceptance criteria should be investigated in more depth. Also, with respect to chain generation in the model, the number of RIS states used can be increased; this is particularly germane in the case of PET, where the use of only the trans conformer of the ethylene moiety requires further study.

In terms of the lattice generation, we focus on three areas: the alignment of the generated chains, the size and nature of the lattice, and long-range interactions. We assumed that the radius of gyration \( R_{\text{gyra}} \) of each chain is aligned perfectly parallel to the z-axis of the reference frame. In principle, the use of \( R_{\text{gyra}} \) implies that the director of any given monomer is not necessarily aligned with the z-axis. However, in our
simulations, where the short oligomer lengths were used, the variation of the monomer director about \( R_{\text{gyra}} \) is small. Allowing for a distribution of \( R_{\text{gyra}} \) about the z-axis would lead to a more physically realistic picture, especially with low oligomer chains.

The nature of lattices generated in the simulation may be varied. We currently use a variation on a crystalline lattice. One could envision additional variations to the crystalline methodology, such as using the lattice size as the mean value with a distribution about it. More radical changes such as removing chains from a lattice to simulate a completely non-periodic lattice or allowing chain placement that incorporates a distribution of average spacings describing Type II paracrystalline distortions could also be considered to make the system. Such changes would ultimately generate structures which are more realistic and responsive to features in the structure factor.

We have neglected the long-range interactions of material outside the boundaries of our simulated chains. A more physically realistic picture could be obtained by introducing long-range interactions either through a mean-field approximation or periodic boundary conditions. The introduction of long-range interactions will not necessarily alter the structure factor, except to force the size of structures in the simulation to be maintained at the average cell size. This would allow a density based on the input parameters to be a more accurate reflection of the ensemble generated.

For the acceptance criteria, a more physically realistic interaction potential, a standard 12-6 (Lennard-Jones) potential or a 9-6 (such as used in Biosym\textsuperscript{TM}), could be used instead of the hard-core potential currently in the simulation. This would allow more efficient MC sampling. Also, a more sophisticated sampling routine could be initiated. The current model regenerates an entire structure at each Monte Carlo step. Substitution of one or more chains within a given generated structure could make the MC sampling routine more efficient.
2) Additional processing conditions for the two polyarylate systems (HIQ-x and PET) may be investigated. The analysis is general enough that it can be adapted for use in describing any two- or three-dimensional WAXS pattern of polyarylates. We have only demonstrated the qualitative trend behavior of mechanical and thermal bias in processing. Further studies to quantify this relationship would likely prove invaluable.

Studies of more complex processing geometries can be also readily characterized using the series expansion analysis. Since one of the main motivations of this research was to investigate the melt processing potential of HIQ-x, it would be particularly interesting to study the role of processing on orientation in extruded geometries and its variations within a sample.

3) Additional chemistries may be investigated. We have only looked at two particular polyarylate systems in this work. As it stands, neither the experimental nor simulation branches of the analysis would require modification, if one were to extend the analysis look at a number of other polyarylate chemistries containing m-phenylene, p-phenylene, naphthalenic, or bi-phenyl aromatic moieties. It might be particularly interesting to study a commercial material such as Vectra™, which is composed solely of 1,4-phenylene and 2,6-naphthalene moieties.

4) As an ambitious undertaking, studies of moieties and linkages (that were not aromatic and esters, respectively) could be undertaken. Such investigations would require extensive redevelopment of a molecular model in order to produce realistic chain structures and packing for such systems. However, the principles of the series expansion analysis would hold, allowing it to be applied to any new system under investigation.

5) In principle, the methodology delineated in this thesis can be extended to materials with a lower degree of symmetry. The overall methodology would remain the same. However, one would be required the use of a more generalized basis set of the spherical harmonics. Use of a generalized three Euler angle rotation matrix, i.e. a Wigner
rotation matrix, is uncalled for since the scattering vector is a cylindrically symmetric object. In principle, a material which displayed macroscopic orientation without a mirror plane about its center would require a larger data set to be taken and odd-order index spherical harmonic terms to be included in the series expansion. Conceptually, such materials are possible (for example, a set of chains displaying a "handedness"). Processing of such chains would require special care to ensure that microscopic order translates to the macroscopic scale.
Chapter 7

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Chapter 8

Appendices

8.1 $^{13}$C SMAS-DECODER

For decades, molecular orientation in polymers has been determined by wide-line NMR lineshape analysis of the dipolar interaction. [McBrierty, V., 1991] This method has also been applied previously to the investigation of aromatic polyesters by Ward and coworkers. [Allen, R., 1991, Rutledge, G., 1993] However, due to the restrictions on acquisition of the FID at short times, where the technique is most sensitive to higher order moments of the orientation distribution, only the first few moments are reliably obtained by broadline NMR lineshape measurements. One dimensional lineshape analysis has also been employed successfully by Spiess and coworkers to extract orientation information in polymer solids from the angular dependence of the quadrupolar interaction ($^2$H) [Hentschel, R., 1978, 1981, Spiess, H., 1982] and anisotropic chemical shift ($^{13}$C) frequencies. [Kulik, A., 1994, Utz, M., 1996] However, for most polymers these methods require isotopic enrichment in order to attain adequate sensitivity and to avoid problems of spectral overlap (in the case of anisotropic chemical shift spectra). More recently, advancements in multidimensional solid-state NMR techniques have permitted the extraction of molecular order information based on either the calculation of the intensities of 2-D side bands using rotor synchronization CPMAS, as described by Harbison, [Harbison, G., 1986, 1987] or the simulation of 2D lineshapes obtained by macroscopic reorientation and detection during two different time periods, as described by Henrichs. [Henrichs, P., 1987] The later technique has been elaborated for polymers by Spiess and coworkers, [Schmidt-Rohr, K., 1992, Chmelka, B., 1993] who proposed the acronym DECODER (Direction Exchange with Correlation for Orientation Distribution Evaluation and Reconstruction) NMR. The 2-D correlation technique has been applied to the lineshapes arising from the orientation dependence of the anisotropic chemical shift tensor, [Chmelka, B., 1993] the quadrupolar tensor, [Schmidt-Rohr, K., 1992] and in the case of selectively $^{13}$C labelled samples, the dipolar coupling tensor. [Utz, M., in press] In its original implementation, reorientation was achieved by mechanically flipping the sample between two discrete orientations with re-
spect to the magnetic field. Recently, Lewis et al [Lewis, R., 1995] demonstrated a variant of DECODER using slow continuous rotation of the sample about the magic angle using a conventional CPMAS probe; this variant is simpler to implement than the static mechanical flip. This new method, which for the sake of brevity we denote here as SMAS-DECODER (Slow Magic Angle Spinning DECODER), has the advantages of simplicity of probe construction and capability for fast reorientation to avoid problems in materials exhibiting short longitudinal relaxation times and spin diffusion. Here, we describe our use of the SMAS-DECODER method to measure the molecular orientation of different samples of PET with different process histories.

8.1.1 General Theory: Slow-Magic-Angle-Spinning DECODER
The DECODER experiment correlates the resonance frequency measured before and after a macroscopic reorientation of the sample, which allows one to determine the orientation distribution of the chemical shift tensors (the so-called principal axis frame of reference) with respect to the magnetic field. Knowing the orientation of the sample itself in the magnetic field and the orientation of the principal axes of the interaction tensor with respect to the structure of the molecule, or same short architectural subunit of the polymer chain (e.g. repeat unit), one can determine the orientation distribution of the architectural subunits within the sample. The important coordinate systems involved in the SMAS-DECODER experiment are illustrated schematically in Figure 1 and have been described in detail previously. [Schmidt-Rohr, K., 1992, 1994, Chmelka, B., 1993, Lewis, R., 1995]
The Laboratory Frame (LF) refers to the direction of the static magnetic field and the Rotor Frame (RF) refers to the direction of the rotor axis, both of which are selected during the experimental setup. The Director Frame (DF) is chosen to correspond to the axes of orientational symmetry in the sample, based on knowledge of the deformation and flow history of the material. The Molecular Frame (MF) refers to a user-defined reference direction in the architectural subunits chosen to describe the molecular orientation. The Principal Axis System (PAS) denotes the reference frame of the interaction tensor, which in our case corresponds to the chemical shift anisotropy (CSA) tensors of each carbon site, with respect to the architectural subunit.
Molecular Frame Rotation Frame
(MF) \( Z_M \)

\[ \Omega_4(\Psi_m, \Theta_m, \Phi_m) \]

\[ \Omega_5(\theta_n) \]

Rotation Frame
(RF) \( Z_R \)

Director Frame
(DF) \( Z_D \)

\[ \Omega_4(\Psi, \Theta, \Phi) \]

\[ \Omega_1(\alpha, \beta) \]

Principal Axes System
(PAS) \( Z_P \)

\[ \Omega_0(\theta, \phi) \]

Laboratory Frame
(LF) \( Z_L \)

Figure 8.1: Relative orientation (Euler Angles) between different reference frames involved in the SMAS-DECODER experiment.

In the \(^{13}\text{C}\) CSA version of the DECODER experiment, the 2D-NMR lineshapes are based on the orientation distribution function \( P(\theta, \phi) \) of the PAS in the LF and the orientation dependent frequency \( \omega(\theta, \phi) \) for each carbon site, where \( \theta \) and \( \phi \) are the polar angles of the magnetic field \( B_0 \) with respect to the anisotropic chemical shift tensors in the PAS.

\[
\omega(\theta, \phi) = \omega_{iso} + \frac{\Delta}{2} \left[ 3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos(2\phi) \right]
\] (8.1)

\( \omega_{iso} = \omega_0\sigma_{iso} \) is the isotropic chemical shift, where \( \sigma_{iso} = (\sigma_x + \sigma_y + \sigma_z)/3 \) is a function of the principal values \( \sigma_{i=x,y,z} \) of the chemical shift tensor, and \( \omega_0 = \omega_0\sigma_i \). \( \omega_0 \) is the Larmor frequency. The chemical shift anisotropy parameter \( \Delta \) and the asymmetry parameter \( \eta \) are functions of the principal values and are defined as \( \Delta = \omega_z - \omega_{iso} \) and \( \eta = (\omega_y - \omega_x)/\Delta \). [Schmidt-Rohr, K., 1994, Haeberlen, U., 1976, Mehring, M., 1983, Veeman, W., 1984]

8.1.2 Experimental \(^{13}\text{C}\) SMAS-DECODER NMR Procedure

The experiments were performed on PET (Aldrich Catalog No.: 20,025-5) pellets. These pellets were ground into powder to obtain the powder spectrum. The PET plaques were cut into strip approximately 10mm x 1mm x 1mm. Talc (Aldrich) was used to pack the samples in the rotor and to ensure proper balancing during spinning. The initial orientation
\(\alpha_0\) of the sample must be estimated from the position of the sample director relative to the mark of the rotor. All of the samples were packed in the rotor with the FD parallel to the rotor axes and the LD in line with the rotor timing mark on the casing.

The experiments were conducted on a home-built spectrometer designed for solid state measurements. The \(^{13}\text{C}\) and \(^1\text{H}\) resonance frequencies on this system are 67.906 MHz and 270.024 MHz, respectively. Pulse sequence and data acquisition were controlled using the Tecmag LIBRA system. The probe is a standard Chemagnetics 7.5 mm double-resonance magic-angle-spinning probe. The 90 degree pulse length for both channels is 4 \(\mu\text{s}\). Spinning speed was controlled by the Chemagnetics MAS spin controller unit, which provides a rotor trigger signal to the LIBRA system to achieve rotor-synchronization. The spinning rate was closely monitored and was stable at 100 Hz with fluctuations of less than 1 Hz during each experiment. The SMAS-DECORDER pulse sequence is shown in Figure 8.2. The reorientation angle \(\omega_\tau\tau_m\) was held constant so that the mixing time \((\tau_m - \tau_1)\) varied with the \(\tau_1\) increment. An echo pulse with delay \(\tau\) was applied before acquisition to avoid the receiver dead time. The FIDs were collected with a cross-polarization time of 2 ms and a recycle delay of 3 s. Most of the 2-D data sets were measured using a dwell time of 20 s in both dimensions, 60\(\tau_1\) increments and 256 points during acquisition. Two hypercomplex 2D data sets were recorded separately and processed using the method described by States. [States, D., 1982] In order to confirm that spin diffusion and molecular reorientation due to the thermal motion are insignificant during sample reorientation, the SMAS-DECORDER spectrum of melt-spun fibers with a reorientation angle of 360° at the spin rate of 100 Hz was measured. All the signal falls along the diagonal in this case, indicating that both effects may be neglected for mixing times up to 10 ms. In addition, measurements on each sample were repeated with different reorientation angles to confirm the experimental and calculated results.
Figure 8.2: Rotor synchronization pulse sequence of the two-dimensional SMAS-DECODER NMR experiment. $\tau_r$ is the cycle of the rotor period, and $\omega_r$ is the spinning rate. The initial magnetization is created by cross-polarization (CP) and evolves under the proton dipolar decoupling (DD) during the $t_1$ period. The magnetization is stored along the z direction during the mixing time to get a total rotation angle of $\omega_r \tau_m$ with respect to the initial angle. A final spin echo with delay $\tau$ is applied to detect the signal during the $t_2$ acquisition (ACQ) period.

8.1.3 $^{13}$C Chemical Shift Tensor for PET

Both the magnitude of the principle values and the relative orientation with respect to the molecular structure of the chemical shift tensor of each carbon site in PET are required.
for 2-D NMR line shape calculation. There are five types of carbons designated in the ethylene terephthalate structure: the ester carbonyl carbon, the methylene carbon, the unprotonated phenylene ring carbons, and two types of protonated phenylene ring carbons. The two types of protonated phenylene ring carbons differ only in their Euler angles relating their PAS to the MF. Table 8.1 lists the principal values of the chemical shift tensor and the Euler angles for the PAS to MF transformation for each of the carbon types in PET. The principal values used are derived from Chmelka et al. [Chmelka, B., 1993] The Euler angles for the five carbon types are derived from the geometry of an all-trans ethylene terephthalate unit.

<table>
<thead>
<tr>
<th>PET</th>
<th>$\omega_x$</th>
<th>$\omega_y$</th>
<th>$\omega_z$</th>
<th>$(\alpha_p, \beta_p, \gamma_p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>COO</td>
<td>113</td>
<td>126</td>
<td>252</td>
<td>(-90°, 18°, 90°)</td>
</tr>
<tr>
<td>OCH$_2$</td>
<td>87</td>
<td>76</td>
<td>22</td>
<td>(0°, 8°, 90°)</td>
</tr>
<tr>
<td>protonated $\Phi_1$</td>
<td>223</td>
<td>158</td>
<td>13</td>
<td>(138°, 90°, 180°)</td>
</tr>
<tr>
<td>protonated $\Phi_2$</td>
<td>223</td>
<td>158</td>
<td>13</td>
<td>(78°, 90°, 180°)</td>
</tr>
<tr>
<td>unprotonated $\Phi$</td>
<td>228</td>
<td>146</td>
<td>31</td>
<td>(18°, 90°, 180°)</td>
</tr>
</tbody>
</table>

Table 8.1: Listing of the Principal Values of the Chemical Shift Tensor and Euler Angles for the Principal Axes System Relative to the Molecular Frame

Figure 8.3 shows the geometry of the all-trans PET monomer. The figure also shows the convention for the PAS for the different carbon types relative to the molecular frame. In all cases, the PAS axes shown are in the plane of the molecule.
8.1.4 Interpretation of the $^{13}$C SMAS-DECORDER Spectra

Now that we know the chemical shift information, we may have a better idea of how to interpret a typical $^{13}$C SMAS-DECORDER spectrum. We reproduce Figure 5.5 to demonstrate the typical features found in a $^{13}$C SMAS-DECORDER spectrum of PET. The circular peak in the upper-right hand corner is due to the methylene carbons, it shows very little dependence on the orientation of the molecular frame relative to the laboratory frame. The diffuse elliptical background is due to the six phenylene ring carbons, it also displays very little dependence on the orientation of the carbons within the sample. The triangular
shape in the lower left hand corner is due to the two carbonyl carbons. This feature displays the most dependence upon the orientation of the molecular frame relative to the laboratory.

**Figure 5.5:** $^{13}$C SMAS-DECODER spectrum for unoriented PET powder

8.1.5 References:
8.2 Spherical Harmonics of the First Kind

The spherical harmonics of the first kind, \( Y_{nm}(\cos \alpha, \beta) \), are the solution which satisfy the following differential equation:

\[
(1 - x^2) \frac{d^2 w}{dx^2} - 2x \frac{dw}{dx} + \left[ \nu(\nu + 1) - \frac{\mu^2}{1 - x^2} \right] w = 0 \tag{8.2}
\]

\( \nu, \mu \) are arbitrary constants. \( n, m, l \) are indices. \( n \) ranges from 0 to \( \infty \), \( m \) ranges from \( -n \) to \( n \), and \( l \) connotes either \( \cos \phi \) or \( \sin \phi \). \( Y_{nm}(\cos \alpha, \beta) \) is separable into two parts dependent on only one of the given variables:

\[
Y_{nm}(\cos \alpha, \beta) = P_{nm}(\cos \alpha)[\cos m\phi + \sin \phi] \tag{8.3}
\]

\( P_{nm}(\cos \alpha) \) is an associated Legendre function.

8.2.1 Closed Form Expressions for Some Associated Legendre Functions

The first few associated Legendre functions are as follows:

\[
P_{00}(\cos \alpha) = 1 \tag{8.4}
\]

\[
P_{10}(\cos \alpha) = \cos \alpha \tag{8.5}
\]

\[
P_{11}(\cos \alpha) = -\sin \alpha \tag{8.6}
\]

\[
P_{20}(\cos \alpha) = 1/2(3\cos^2 \alpha - 1) \tag{8.7}
\]

\[
P_{21}(\cos \alpha) = -3/2(\sin 2\alpha) \tag{8.8}
\]

\[
P_{22}(\cos \alpha) = 3/2(1 - \cos 2\alpha) \tag{8.9}
\]

8.2.2 Recursion Formulas for the Associated Legendre Functions

The following recursion formulas were used:

\[
P_{n,m+2}(x) + 2(m+1) \frac{x}{\sqrt{1-x^2}} P_{n,m+1}(x) + (n-m)(n+m+1) P_{nm}(x) = 0 \tag{8.10}
\]
8.2.3 Graphical Representations

Figures 8.4 and 8.5 show the spherical harmonics of the first kind for $n = 2$ and $n = 4$, all $m$-values.

Figure 8.4: Spherical harmonics of the first kind for $n = 0$, a) $m = 0$, b) $m = 2$. 
Figure 8.5: Spherical harmonics of the first kind, $n = 4$. a) $m = 0$, b) $m = 2$, c) $m = 4$.

8.2.4 References


8.2.5 Fortran Code for Generating spherical harmonics
SUBROUTINE FUNC(N,M,L,A,B,OUT)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
REAL*8 A,B,X,Y,PI,PLGNDR,OUT,PARTA,PARTB,PARTC
REAL*8 FACSUB,FACADD
INTEGER N,M,L

PI = 3.1459265359D0
X = COS(PI*A/180.DO)
Y = COS(PI*B/180.DO)
OUT = 0.DO

C Part A: The Associated Legendre Part (Azimuthal Angle)
C
PARTA = PLGNDR(N,M,X)

C Part B: The Other Angle Part (Polar Angle)
C
PARTB = SIN(REAL(M)*PI*B/180.DO)
IF(L.EQ.0)THEN
    PARTB = COS(REAL(M)*PI*B/180.DO)
ENDIF
C Part C: Prefactor
C
FACSUB = 1.D0
IF ((N-M).GT.0) THEN
    DO 10, I=1,(N-M)
        FACSUB=FACSUB*REAL(I)
    CONTINUE
10 CONTINUE
ENDIF
FACADD = 1.D0
IF ((N+M).GT.0) THEN
    DO 20 I=1,(N+M)
        FACADD=FACADD*REAL(I)
    CONTINUE
20 CONTINUE
ENDIF
C
PARTC = SQRT((2.DO*N+1)*(FACSUB/FACADD))
C
Combining Parts A, B, and C...
C
OUT = PARTC*PARTA*PARTB
C
RETURN
END
C
C--------------------------------------

FUNCTION PLGNDR(L,M,X)
INTEGER L,M
REAL*8 PLGNDR,X
INTEGER I,LL
REAL*8 FACT,PLL,PM,PMMP1,SOMX2
if(M.lt.0.or.M.gt.L.or.abs(X).gt.1.)pause
+ 'bad argument in plgndr'

259
PMM=1.D0
if(M.gt.0) then
  SOMX2=sqrt((1.-x)*(1.+x))
  FACT=1.D0
  do 11 I=1,M
    PMM=PMM*FACT*SOMX2
    FACT=FACT+2.D0
  11 continue
endif
if(L.eq.M) then
  PLGNDR=PMM
else
  PMMP1=x*(2*M+1)*PMM
  if(L.eq.M+1) then
    PLGNDR=PMMP1
  else
    do 12 LL=M+2,L
      PLL=(X*(2*LL-1)*PMMP1-(LL+M-1)*PMM)/(LL-M)
      PMM=PMMP1
      PMMP1=PLL
    12 continue
  endif
  PLGNDR=PLL
endif
return
END
8.3 Legendre Polynomials

The Legendre polynomials are the solutions to the following differential equation:

\[
(1 - x^2) \frac{d^2 w}{dx^2} - 2x \frac{dw}{dx} + [n(n + 1)]w = 0
\]  

(8.13)

where, \( x \) is our independent variable with limits \([-1,1]\). \( w \) is the solution to the 2nd order differential equation, and \( n \) is a constant.

8.3.1 Closed Form Expressions for the First Few Legendre Polynomials

The first 3 Legendre polynomials are as follows:

\[
P_0(\cos \alpha) = 1
\]  

(8.14)

\[
P_1(\cos \alpha) = \cos \alpha
\]  

(8.15)

\[
P_2(\cos \alpha) = \frac{1}{2}(3\cos^2 \alpha - 1)
\]  

(8.16)

8.3.2 Recursion Formula for Legendre Polynomials

The recursion formula for the Legendre polynomial is as follows:

\[
P_n(x) = \frac{1}{n}[(2n - 1)xP_{n-1}(x) - (n - 1)P_{n-2}(x))]
\]  

(8.17)

8.3.3 Graphical Representation of the Legendre Polynomials

Figure 8.6 diagrams first 6 even-ordered of Legendre polynomials \((2n = 0 - 10)\).
Figure 8.6: Even-ordered Legendre polynomials, \( P_{2n}(\cos \alpha) \), \( 2n = 0, 10 \)

8.3.4 References


8.3.5 Fortran Code for Generating Legendre polynomials

```
c--------------------------------------------------------------------------------
c Subroutine to calculate the Legendre Polynomial of Order TWON
C
FUNCTION LEGPOLY (X, TWON)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
REAL*8 X,P0,P1,P2,LEGPOLY
INTEGER TWON,I

c
P0 = 1.D0
P1 = X
P2 = 0.5D0*(3.D0*X*P1-1.D0)
IF (TWON.GT.3) THEN
   DO 1000, I = 3, TWON
      P0 = P1
      P1 = P2
      P2 = (1/REAL(I))*((2.D0*REAL(I)-1.D0)*X*P1-(REAL(I)-1.D0)*P0)
   CONTINUE
1000 CONTINUE
ENDIF
```

ENDIF
LEGPOLY = P2
C
RETURN
END
C
C---------------------------------------------------------------------
8.4 Integer Bessel Functions

The integer Bessel functions are the solution to the following differential equation:

\[ x^2 \frac{d^2 w}{dx^2} + x \frac{dw}{dx} + [x^2 - n^2] w = 0 \]  

(8.18)

The Bessel functions are generally generated numerically, as there are no succinct closed forms for them.

8.4.1 Recursion Formula for Bessel Functions

\[ J_{n-1}(x) + J_{n+1}(x) = \frac{2n}{x} J_n(x) \]  

(8.19)

8.4.2 References


8.4.3 Fortran Code for Generating Bessel polynomials

Taken from *Numerical Recipes* [Press, W., 1992]

```
C Functions to calculate the Bessel function of order NN

FUNCTION bessj(n,x)
INTEGER n, IACC
REAL*8 bessj, x,BIGNO,BIGNI
PARAMETER (IACC=40,BIGNO=1.e10,BIGNI=1.e-10)
USES bessj0,bessjl
INTEGER j, jsum, m
REAL*8 ax, bj, bjm, bjp, sum, tox, bessj0, bessjl
if(n.lt.2)pause 'bad argument n in bessj'
ax=abs (x)
if(ax.eq.0.)then
  bessj=0.
else if(ax.gt.float(n))then
  tox=2./ax
  bjm=bessj0(ax)
  bj=bessjl(ax)
  do 11 j=1,n-1
```
bjp = j * tox * bj - bjm
bjm = bj
bj = bjp

11 continue
bessj = bj
else
  tox = 2. / ax
  m = 2 * (n + int(sqrt(float(IACC * n)))) / 2
  bessj = 0.
  jsum = 0
  sum = 0.
  bjp = 0.
  bj = 1.
  do 12 j = m, 1, -1
      bjm = j * tox * bj - bjp
      bjp = bj
      bj = bjm
      if (abs(bj) .gt. BIGNO) then
          bj = bj * BIGNI
          bjp = bjp * BIGNI
          bessj = bessj * BIGNI
          sum = sum * BIGNI
      endif
      if (jsum .ne. 0) sum = sum + bj
      jsum = 1 - jsum
      if (j .eq. n) bessj = bjp
  12 continue
  sum = 2 * sum - bj
  bessj = bessj / sum
endif
if (x .lt. 0. and .mod(n, 2) .eq. 1) bessj = -bessj
return
END

C-----------------------------------------------------------------
FUNCTION bessj0(x)
REAL*8 bessj0, x
REAL*8 ax, xx, z
DOUBLE PRECISION p1, p2, p3, p4, p5, q1, q2, q3, q4, q5, r1, r2, r3, r4, r5, r6,
* s1, s2, s3, s4, s5, s6, y
SAVE p1, p2, p3, p4, p5, q1, q2, q3, q4, q5, r1, r2, r3, r4, r5, r6,
* s1, s2, s3, s4, s5, s6
DATA p1, p2, p3, p4, p5, p1/1.d0, -.1098628627d-2, .2734510473d-4,
* -.2073370639d-5, .2093887211d-6, q1, q2, q3, q4, q5, r1, r2, r3, r4, r5, r6,
* s1, s2, s3, s4, s5, s6, y
SAVE p1, p2, p3, p4, p5, q1, q2, q3, q4, q5, r1, r2, r3, r4, r5, r6, s1, s2, s3, s4,
* s5, s6
DATA p1, p2, p3, p4, p5, p1/1.d0, -.1098628627d-2, .2734510473d-4,
* -.2073370639d-5, .2093887211d-6, q1, q2, q3, q4, q5, r1, r2, r3, r4, r5, r6,
* s1, s2, s3, s4, s5, s6
DATA r1, r2, r3, r4, r5, r6/57568490574.d0, -13362590354.d0,
* 57568490411.d0, 1029532985.d0, 9494680.718d0,
* 59272.64853d0, 267.8532712d0, 1.d0/
if (abs(x) .lt. 0.8 .and. .not. abs(x) .lt. 1.e-3) then
    y = x**2
    bessj0 = (r1 + y**2 / r3 * y**2 / r4 / r5 / r6) / (s1 + y**2 / s2 / s3 / s4 / s5 / s6)
ENDIF
else
    ax=abs(x)
    z=8./ax
    y=z**2
    xx=ax-.785398164
    bessj0=sqrt(.636619772/ax)*(cos(xx)*(p1+y*(p2+y*(p3+y*(p4+y*
*p5))))-z*sin(xx)*(q1+y*(q2+y*(q3+y*(q4+y*q5))))))
endif
return
END

C------------------------------------------------------------------
FUNCTION bessj0(x)
REAL*8 bessj0,x
REAL*8 ax,xx,z
DOUBLE PRECISION p1,p2,p3,p4,p5,q1,q2,q3,q4,q5,r1,r2,r3,r4,r5,r6,
*s1,s2,s3,s4,s5,s6,y
SAVE p1,p2,p3,p4,p5,q1,q2,q3,q4,q5,r1,r2,r3,r4,r5,r6,s1,s2,s3,s4,
*s5,s6
DATA r1,r2,r3,r4,r5,r6/72362614232.d0,-7895059235.d0,
*242396853.1d0,-2972611.439d0,15704.48260d0,-30.160366606d0/,s1,s2,
*s3,s4,s5,s6/144725228442.d0,2300535178.d0,18583304.74d0,
*99447.43394d0,376.9991397d0,1.d0/
DATA p1,p2,p3,p4,p5/1.d0,.04687499995d0,
*.183105d-2,-.3516396496d-4,
*.2457520174d-6,-.240337019d-6/,q1,q2,q3,q4,q5/.04687499995d0,
*-.2002690873d-3,8449199096d-5,-.88228987d-6,.105787412d-6/
if(abs(x).lt.8.)then
    y=x**2
    bessj0=x*(r1+y*(r2+y*(r3+y*(r4+y*(r5+y*r6))))))/(s1+y*(s2+y*(s3+
*y*(s4+y*(s5+y*s6)))))
else
    ax=abs(x)
    z=8./ax
    y=z**2
    xx=ax-.356194491
    bessj0=sqrt(.636619772/ax)*(cos(xx)*(p1+y*(p2+y*(p3+y*(p4+y*
*p5))))-z*sin(xx)*(q1+y*(q2+y*(q3+y*(q4+y*q5))))))
endif
return
END

C------------------------------------------------------------------
8.5 Spherical Bessel Functions (Modified Bessel Functions), \( j_n(x) \)

Differential Equation

\[
\frac{d^2}{dx^2} \left( x^2 \frac{dw}{dx} \right) - 2x \frac{dw}{dx} + \left[ x^2 - n(n+1) \right] w = 0
\]  

(8.20)

The spherical Bessel functions are related to Bessel functions as follows:

\[
j_n(x) = \sqrt{\frac{\pi}{2x}} J_{n + \frac{1}{2}}(x)
\]  

(8.21)

8.5.1 Closed Form Expressions for the First Few Spherical Bessel Functions

The first 3 spherical Bessel functions are shown below:

\[
j_0(x) = \frac{\sin x}{x}
\]  

(8.22)

\[
j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}
\]  

(8.23)

\[
j_2(x) = \left( \frac{3}{x^3} - \frac{1}{x} \right) \sin x - \frac{3}{x^2} \cos x
\]  

(8.24)

8.5.2 Recursion Formula for Spherical Bessel Functions

The spherical Bessel functions have the following recursion formula:

\[
j_n(x) = \frac{x j_{n-1}(x) + j_{n+1}(x)}{2n + 1}
\]  

(8.25)

8.5.3 Graphical Representations of Spherical Bessel Functions

As examples of the spherical Bessel Functions, Figure 8.7 shows the first four spherical Bessel functions \((n = 0 \text{ to } 3)\): [Abramowitz, M., 1965]
Figure 8.7: The first four spherical Bessel functions (n = 0, 3) [Abramowitz, M., 1965]

8.5.4 References


8.5.5 Fortran Code for Generating Modified Bessel Functions

C-----------------------------------------
C Subroutine to calculate the Spherical Bessel Function (Abramowitz & Stegun)
C
FUNCTION SPHBESSJ(N,X)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
REAL*8 X,P0,P1,P2,SPHBESSJ
INTEGER N,I

C IF(N.LT.2)THEN
   WRITE(*,*), 'Illegal Index in Sph. Bessel Func.'
   GO TO 20
ENDIF
IF(X.LE.0.D0)THEN
   WRITE(*,*), 'Illegal Argument in Sph Bessel Func.'
   GO TO 20
ENDIF
P0 = SIN(X)/X
P1 = (SIN(X)/(X**3.D0))-(COS(X)/X)
P2 = (3.D0/(X**3.D0)-1/X)*SIN(X)-(3.D0/(X**2.D0))*COS(X)
IF(N.GT.3)THEN
   DO 10, I=3,N
   ENDIF
P0 = P1
P1 = P2
P2 = ((2.DO*REAL(I)+1.DO)/X)*P1 - P0
10 CONTINUE
ENDIF
SPHBESSJ = P2
20 RETURN
END

C
C-----------------------------------------
8.6 Code for Structure Factor Calculations

8.6.1 2-D Structure Factor Calculation

C-----------------------------
C Added subroutines by DCO:
 SUBROUTINE SCATT(NATOM,NN,NS,SMIN,SSTEP,X,Y,Z,ATYPE,A2N)
 IMPLICIT DOUBLE PRECISION (A-H,O-Z)
 INTEGER NATOM,NS,NN,M,I,J,K,L,ATYPE(500)
 CHARACTER*1 GARB,ATYPE(500)
 REAL*8 X(500),Y(500),Z(500),TEMP3(20,500),S(500)
 REAL*8 FJ, FK, TEMP, TEMP2, P2N, J2N, RJK, COSAJK, LEGPOLY
 REAL*8 PI,LAMBDA,A2N(20,500),TTHA, COMPMIN,COMPMAX
 C
 C Initial Parameters
 PI = 3.14159265359D0
 LAMBDA = 1.542508D0
 C
 C Calculate the s-values based on input data
 DO 10, I=1,NS
 TTHA = SMIN+SSTEP*REAL(I-1)
 S(I) = 4.DO*PI*SIN(TTHA*PI/360.DO)/LAMBDA
 10 CONTINUE
 C
 C Initialize TEMP3 and A2N matricies
 DO 30, I=1,20
 DO 32, J=1,NS
 TEMP3(I,J) = 0.DO
 A2N(I,J) = 0.DO
 32 CONTINUE
 30 CONTINUE
 C
 C Ready to begin calculation of scattering pattern. For each s-value
 C we cycle over all indices, and atom pairs.
 DO 35, L=1,NS
 WRITE(*,*) 'Starting s-value: ',S(L)
 WRITE(64,*) 'Starting s-value: ',S(L)
 DO 40, I=0,NN,2
 COMPMIN=0.DO
 COMPMAX=0.DO
 TEMP=0.DO
 M=INT(I/2+1)
 TEMP3(M,L)=TEM
 DO 50, J=1,NATOM
 IF (ATYPE(J).EQ.3) GO TO 50
 FJ=FATOM(ATYPE(J),S(L))
 DO 60, K=J+1,NATOM
 IF (ATYPE(K).EQ.3) GO TO 60
 FK=FATOM(ATYPE(K),S(L))
 270
RJK = SQRT((X(J) - X(K))**2.0) + ((Y(J) - Y(K))**2.0) + ((Z(J) - Z(K))**2.0)

COSAJK = ABS(Z(J) - Z(K)) / RJK

IF (RJK.EQ.0) GO TO 60

J2N = bessj0((RJK*S(L)))

IF (I.GT.1) THEN
    J2N = bessj(I, (RJK*S(L)))
ENDIF

P2N = 1.0

IF (I.GT.1) THEN
    P2N = LEGPOLY(COSAJK, I)
ENDIF

TEMP2 = (FJ*FK*J2N*P2N) / REAL(NATOM)

TEMP3(M,L) = TEMP3(M,L) + TEMP2

C-------- Added 10/11/97 -------

IF (TEMP2.GT.COMPMAX) THEN
    WRITE(64,995) I,J,K,INT(ATYPE(J)), INT(ATYPE(K)), RJK, TEMP2
    COMPMAX = TEMP2
    GOTO 60
ELSEIF (TEMP2.GE.(0.9DO*COMPMAX)) THEN
    WRITE(64,995) I,J,K,INT(ATYPE(J)), INT(ATYPE(K)), RJK, TEMP2
    GOTO 60
ELSEIF (TEMP2.LT.COMPMIN) THEN
    WRITE(64,995) I,J,K,INT(ATYPE(J)), INT(ATYPE(K)), RJK, TEMP2
    COMPMIN = TEMP2
    GOTO 60
ELSEIF (TEMP2.LE.(0.9DO*COMPMIN)) THEN
    WRITE(64,995) I,J,K,INT(ATYPE(J)), INT(ATYPE(K)), RJK, TEMP2
    GOTO 60
ENDIF

C-------------------------

60 CONTINUE
50 CONTINUE

TEMP3(M,L) = (-1)**REAL(I/2)*(4.DO*REAL(I)+.DO)/REAL(NATOM)
    * TEMP3(M,L)

A2N(M,L) = TEMP3(M,L)

40 CONTINUE
35 CONTINUE

CLOSE(64)

995 FORMAT(1X,I3,1X,I4,1X,I4,1X,I2,1X,I2,1X,F8.3,1X,E16.5)

C
C Outputting data to output file
C
WRITE(*,*) 'Scattering Coefficients'
WRITE(*,990) NN,NS
DO 100, J=1,NS
  WRITE(*,1000) S(J), (A2N(I,J), I=1,(NN/2+1))
100 CONTINUE
990 FORMAT(1X,'Max. No. of Coeff.: ',I3,' No. of. S-values: ',I4)
1000 FORMAT(1X,F6.3,20(1X,F10.3))
C
WRITE(*,*) 'Leaving SCATT'
RETURN
END
8.6.2 3-D Structure Factor Calculation

C Added subroutines by DCO:

SUBROUTINE SCATT(NATOM,NN,NS,SMIN,SSTEP,X,Y,Z,ATYPE,ANM)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER NATOM,NS,NN,M,I,J,K,L,ATYPE(500)
CHARACTER*1 GARB,ATYP(500)
REAL*8 X(500),Y(500),Z(500),TEMP3(20,20,500),S(500)
REAL*8 FJ, FK, TEMP, TEMP2, PNM, J2N, RJK, COSAJK, LEGPOLY
REAL*8 PI,LAMBDA,ANM(20,20,500),TTHA, COMPMIN,COMPMAX

C Initial Parameters
PI = 3.14159265359D0
LAMBDA = 1.542508D0

C Calculate the s-values based on input data
WRITE(*,*) 'Calculating S-values'
DO 10, I=1,NS
   TTHA = SMIN+SSTEP*REAL(I-1)
   S(I) = 4.DO*PI*SIN(TTHA*PI/360.DO)/LAMBDA
10 CONTINUE

C Initialize TEMP3 and ANM matrices
WRITE(*,*) 'Initializing Coeff. Matrices'
DO 30, I=1,20
   DO 31, J=1,20
      DO 32, K=1,NS
         TEMP3(I,J,K) = 0.DO
         ANM(I,J,K) = 0.DO
32 CONTINUE
31 CONTINUE
30 CONTINUE

C Ready to begin calculation of scattering pattern. For each s-value
C we cycle over all indices, and atom pairs.
WRITE(*,*) 'Starting Scattering Calculation'
OPEN(64,FILE='contrib.a2n')
DO 35, L=1,NS
   WRITE(64,*) 'Starting s-value: ',S(L)
   DO 40, I=0,NN,2
      IN=INT(I/2+1)
      DO 45, M=0,I,2
         IM=INT(M/2+1)
         TEMP3(I,M,L)=TEMP
         ANM(I,J,K)=ANM(I,J,K)+TEMP3(I,M,L)/S(L)
45 CONTINUE
40 CONTINUE
35 CONTINUE
FJ=FATOM(ATYPE(J),S(L))
FK=FATOM(ATYPE(K),S(L))
RJK=SQRT(((X(J)-X(K))**2.DO)+((Y(J)-
Y(K))**2.DO)+((Z(J)-Z(K))**2.DO))
AJK=ASIN(ABS(Z(J)-Z(K))/RJK)*(180.DO/PI)
BJK=ASIN(ABS(X(J)-X(K))/SQRT((X(J)-X(K))**2.DO+
(Y(J)-Y(K))**2.DO))*(180.DO/PI)
IF (RJK.EQ.0) GO TO 60
J2N=1.DO
IF((I.EQ.0).AND.((RJK*S(L).GT.0)))THEN
 J2N=(SIN(RJK*S(L)))/(RJK*S(L))
ENDIF
IF (I.GT.1) THEN
 J2N=SPHBESSJ(I,(RJK*S(L)))
ENDIF
PNM = 1.D0
NL=0
IF (I.GT.1) THEN
 CALL FUNC(I,M,NL,AJK,BJK,PVAL)
 PNM = PVAL
ENDIF
TEMP2=(FJ*FK*J2N*PNM)/REAL(NATOM)
TEMP3(IN,IM,L)=TEMP3(IN,IM,L)+TEMP2
60 CONTINUE
50 CONTINUE
 ANM(IN,IM,L) = TEMP3(IN,IM,L)
45 CONTINUE
40 CONTINUE
35 CONTINUE
CLOSE(64)
995 FORMAT(1X,I3,1X,I4,1X,I4,1X,I2,1X,I2,1X,F8.3,1X,E16.5)
C
C Outputting data to output file
 DO 60, K=J+1,NATOM
   IF (ATYPE(K).EQ.3)GO TO 60
   WRITE(*,*) 'Exiting Scatt'
   WRITE(*,990) NN,NS
   DO 100, J=1,NS
   WRITE(*,1000) S(J),(A2N(I,J),I=1,(NN/2+1))
100 CONTINUE
990 FORMAT(1X,'Max. No. of Coeff.: ',I3,' No. of. S-values: ',I4)
1000 FORMAT(1X,F6.3,20(1X,F10.3))
C
RETURN
END
C
C---------------------------------------