THE SYNTHESIS, CHARACTERIZATION AND OPTICAL PROPERTIES OF
NOVEL DIACETYLENE-CONTAINING AROMATIC LIQUID
CRYSTALLINE POLYMERS

by

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in partial fulfillment of the requirements for the degree of

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The Synthesis, Characterization and Optical Properties of Novel Diacetylene-Containing Aromatic Liquid Crystalline Polymers

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Paula Therese Hammond

submitted to the Department of Chemical Engineering
on May 10, 1993 in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

New main chain, semi-rigid liquid crystalline polymers which contain reactive diacetylene groups within the repeat unit have been synthesized. These unique polymer systems have been designed to contain rigid aromatic mesogenic units separated by flexible diacetylene-containing methylene spacers alternating along the polymer backbone. Upon exposure to thermal and/or ultraviolet radiation, the polymers and the diacetylene monomers from which they are derived cross-polymerize to produce polydiacetylene conjugated backbones covalently bonded transverse to the mesogenic unit. These novel materials are of interest because they exhibit visible absorption spectra dependent on the molecular environment of the polydiacetylene chain. Variables affecting this environment include the degree of ordering within the host polymer or monomer system, and the structure of the crystalline or liquid crystalline phase. Changes in the ordering of these phases are indicated by dramatic color changes due to shifts in the visible absorption peaks observed using spectroscopy. The diacetylene reactivity of these new aromatic polymers as a function of the number of methylene spacers, the crystalline structure and the overall morphology within the solid, liquid crystalline, and isotropic phases is discussed. The effects of cross-polymerization on the resulting morphological and phase behavior of these novel polymers is also addressed. Diacetylene containing mesogenic polymers extend the range and nature of polydiacetylene thermo- and mechano-chromic behavior. Further development of main chain liquid crystalline diacetylene-containing polymers presents the potential to molecularly design highly oriented cross-polymerized materials with unique phase dependent optical properties.

Thesis Supervisor: Professor Michael F. Rubner
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Dedication

This thesis is dedicated to my daughter,
Therese Morgan Hammond
whose special smiles always keep me going
when nothing else works.
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Chapter 1.0

Introduction and Background

In the past twenty years since Wegner's initial investigations of the solid state topochemical polymerization of substituted diacetylenes, scientists and engineers have been investigating the varied and unique properties of polydiacetylenes. Some of these investigations have probed the solid state reactivity of different types of substituted diacetylenes, or the kinetics of the topochemical reaction. Others observed the unusual optical properties of polydiacetylenes, a result of the highly conjugated backbone of this class of polymers. Such studies have included third order nonlinear optical properties, as well as linear optical properties in the visible light range, such as thermo- and mechano-chromism.

In more recent years, attempts have been made to apply the properties of polydiacetylenes toward the solution of real world engineering problems. A great deal of this work has been concentrated on the area of nonlinear optics, a field in which organic materials are gaining more attention. Other researchers have taken advantage of the Raman-active polydiacetylene backbone, for which frequencies are quite sensitive to strain. These studies have utilized various types of substituted polydiacetylene single crystals as strain gauges of microscopic scale displacements; this technique has been especially useful as a measure of strain in fibers of composite systems. There have also been extensive studies on the effects of cross-polymerization on diacetylene macromonomers, particularly on the mechanical behavior in polyurethanes and polyamides.

For many of the above applications, however, very little effort has been centered on the actual engineering and design of diacetylenic materials to obtain or optimize specific optical properties. The research approach of most investigations has been to try new chemical structure variations, and then observe the resulting properties. This has been especially true of previous studies of the chromic behavior of polydiacetylenes. Although the color changes observed with temperature or strain application have been noted,
and the mechanisms that drive this novel behavior have been thoroughly investigated for many polydiacetylene materials, there have been no attempts to actually control the chromic nature of polydiacetylenes. Without the ability to in some way define and predict thermochoromatic behavior, useful engineering applications of these properties are not likely. However, by using the knowledge already available about the optical properties of this class of conjugated polymers, the chromic behavior of a given material may actually be designed by appropriate changes in the chemical structure of the material. The applications of a well controlled system such as this range from temperature sensors to temperature controlled optical filters. Highly oriented films and fibers can be obtained from liquid crystalline melts; increased orientation would take full advantage of the anisotropic nature of the polydiacetylene chains, resulting in highly dichroic optical properties, as well.

Polydiacetylenes absorb strongly in the visible light region due to their highly conjugated backbone. The wavelength of light absorbed, and the shape of the visible absorption spectrum of a polydiacetylene material is highly dependent on the conformation of the polydiacetylene chain. For this reason, small changes in the planarity of the polymer backbone can cause dramatic color changes. It has been found that these chromic changes often occur at first order transitions of the material of interest, such as melting transitions. It is therefore possible to tailor diacetylene-containing host monomers and polymers which, once converted to their polydiacetylene forms, would undergo chromic transitions at predetermined temperatures. Ideally, one would be able to design these materials to melt at a desired temperature using knowledge of the structure/property relationships of the host systems. The ideal system would allow the exhibition of more than one chromic change, and would be a relatively well-understood system in terms of its thermal behavior. Liquid crystals meet these requirements, and particularly liquid crystalline main chain thermotropic polyesters, which are a well-documented family of liquid crystalline polymers.

The objective of this thesis has been to design a new series of functionalized liquid crystalline diacetylene monomers, as well as a corresponding set of liquid crystalline main chain thermotropic polyesters derived from these monomers, which contain diacetylene groups in the repeat unit. The nature of the crystalline and liquid crystalline states of each material has been fully characterized to obtain a complete understanding of the effects of structure on mesogenic properties, as well as on the reactivity of the diacetylene groups. Finally, optical behavior was observed for each of the systems, to determine the correlation between the liquid crystalline phase transitions of these novel materials, and their thermochoromatic transitions. Further development of these novel materials presents the potential to molecularly design highly oriented cross-polymerized polymers with phase dependent optical properties.
1.2 Polydiacetylenes

The polymerization of diacetylene is a solid-state, topochemical process which was first characterized by G. Wegner. Diacetylene monomer, arranged in a crystal lattice, undergoes a 1,4 addition with its nearest neighbor to yield a conjugated polymer chain as shown:

![Polydiacetylene polymerization process](image)

Figure 1.1 The topochemical diacetylene polymerization process.

The process is diffusionless and involves rotation of the monomer units within the lattice. Generally, the substituents R remain in approximately the same positions throughout the reaction as the diacetylene groups rotate to attain contact with adjacent groups. This means that changes in crystallographic spacing and symmetry are relatively small. For a large number of monomers, this process occurs in one solid phase, thus yielding perfect polymer crystals. Methods such as optical spectroscopy and gel permeation chromatography have been used to observe degrees of polymerization ranging from 100 to 1000 in single crystals. The reactivity of diacetylene monomers is determined in large part by the packing of the monomer unit; the topochemical polymerization can only take place in an ordered lattice of monomer molecules stacked such that specific geometric constraints are satisfied. The two critical geometrical parameters are the stacking distance \(d\) along the polymer backbone and the angle \(\phi\) between the polymer chain axis and the diacetylene...
monomer. Baughman used crystal structure data derived from X-ray studies to produce the following model for diacetylene reactivity:

![Model of geometrical packing parameters for reactivity of diacetylene monomers](image)

Figure 1.2. Model of geometrical packing parameters for reactivity of diacetylene monomers (from ref. 9).

The range of values of phi and d that are conducive to photoreactivity lie within the shaded area of the plot shown above. The lattice parameters that involve the minimum amount of molecular motion and thus the maximum reactivity are $d = 5 \text{ Å}$ and $\phi = 45^\circ$. The values of $d$ and $\phi$ vary depending on the R substituent; factors such as the bulkiness of the side group and the bond angles involved affect the geometry of the monomer.

Diacetylene reactivity is also affected by the mobility of the side group. Even with the appropriate lattice parameters d and gamma, a diacetylene may not be reactive due to the lack of flexibility of the R group. It has been found in general that at least one methylene group spacer is necessary to obtain high reactivity. The issue of side group mobility becomes important especially when considering rigid, aromatic, liquid crystalline diacetylene monomers. A good example of the effect of mobility is seen in the work of Ozcayir and Blumstein on diphenyl diacetylene based diesters. Nematic mesophases were reported for several p,p'-diphenyl diacetylenedialkanoates; these materials contain a direct linkage between the diacetylene group and the phenyl groups, with no flexible spacer.
Although the compounds displayed interesting liquid crystalline behavior, the diacetylene moiety was relatively unreactive to thermal or light activation. Polyesters and copolyesters based on diphenyldiacetylene were reactive, but only at temperatures close to or lower than the liquid crystalline phase transition temperatures. In these cases, the degree of conversion was not reported. Ozcayir and Blumstein also investigated a group of liquid crystalline diesters derived from 10,12 docosadiyne 1,22 dioic acid. SAXS measurements indicated that the molecular conformation of the biphenyl diester of this series was an extended form, which resulted in a relatively small tilt angle of 30° in the formation of polydiacetylene. The diesters based on azoxybenzene were believed to take on a different molecular packing which not only enabled liquid crystallinity, but resulted in molecular packing undesirable for polymerization.

Lando and Day observed a dependence on even versus odd numbers of methylene spacers in hydrocarbon diacetylene monomers. It was found that there are two possible coplanar structures for monomers with an even number of methylene groups: one with favorable packing (all trans type about the diacetylene group) and one with unfavorable packing (alternating cis-trans packing). Odd numbers of methylene spacers yield only one coplanar, reactive structure. Schen synthesized a liquid crystalline diacetylene monomer which is not reactive in the crystalline state, but becomes reactive in the liquid crystalline state, indicating that the reactivity is phase dependent due to differences in either packing or reactant mobility in the mesophases. Finally, kinetic studies have also indicated a dependence on the symmetry of the diacetylene monomers and on the electronic nature of the substituents.

The conjugated, one dimensional backbone of polydiacetylene and its highly ordered state are the source of many interesting optical and electrical properties. Although polydiacetylenes cannot be doped to obtain metal-like conductivity, they have very large electronic carrier mobilities along the chain direction (> 10^3 cm^2 v^-1 sec^-1), making these materials of interest for electronic devices. It has been found that ion implantation of some polydiacetylene crystals using ion beam irradiation increases their conductivity by fifteen orders of magnitude. Optical properties of polydiacetylene include a large X(3) nonlinear susceptibility coefficient. This has sparked a large interest in the use of diacetylene materials in electro-optical devices.

The linear optical properties of polydiacetylenes are highly dependent on the effective conjugation length of the main chain. The conjugation length is defined as the distance in number of pi bonds along which electrons (mobile carriers) can travel. Changes in the effective conjugation length result in subsequent changes in the wavelength of absorption in the visible spectra. This effect is often seen as a color change due to changes
in temperature and is known as thermochromism. Chromism in polydiacetylenes will be addressed in detail in section 1.4.

The polydiacetylene backbone vibrations are Raman active; therefore, Raman spectroscopy has been used to characterize the vibrational modes in polydiacetylene crystals\(^{17,18}\). The use of Raman methods is especially effective because of the additional effect of Fermi resonance which greatly enhances the Raman signal. Because polydiacetylene vibrations change frequency with the application of stress, large single crystal "fibers" have been used to determine strain distributions of fibers imbedded in a composite matrix\(^{4,5}\). The stress state of the polydiacetylene backbone can be measured accurately even in thick or opaque samples using Raman spectroscopy. The Raman frequency change is found to vary linearly with tensile strain over a relatively wide range. The difference in frequency between the stressed sample and an unstressed control is used as a measure of strain. When subjected to stress, the frequency shifts to higher values under compressive strain, lower values for tensile strain. The resolution of frequency vs. strain plots is extremely high, and researchers have used polydiacetylene crystals as molecular "strain gauges" in composites\(^{5a}\).

### 1.3 Diacetylene Macromonomers

It was mentioned above that linear polymers containing diacetylene groups within the repeat unit have been synthesized and characterized. Such polymers are often referred to as macromonomers; when exposed to heat or light radiation, the diacetylene units react with neighboring macromonomers to produce a conjugated backbone transverse to the chain directions of the macromonomers. For the topochemical reaction to occur, the geometrical packing criteria discussed earlier must be met; therefore, well ordered semicrystalline polymer systems are often more reactive. However, amorphous polymers have also been found to react, particularly if some type of paracrystalline or semi-ordered state exists. The macromonomer reaction process, termed crosspolymerization to distinguish it from the more typical random polymer crosslinking is shown in Figure 1.4\(^{19}\).

Wegner\(^{1b}\) was the first to synthesize reactive macromonomers in the form of polyesters and polyurethanes. Thakur and Lando investigated polyethylene-based macromonomers, including poly (1,11-dodecadiyne)\(^{19b}\). This research team investigated the structure of the macromonomer and its crosspolymerized polydiacetylene, as well as the solvato- and thermochromic behavior of the product. Electron diffraction indicated that the cross-polymerization led to very few structural changes in the crystals. The same
crystallographic space group was maintained, and the only notable difference was a contraction of the unit cell volume. The fact that cross-polymerization yields little morphological change is a great advantage in that the mechanical and optical properties of a linear polymer may be enhanced by cross-polymerization, while maintaining the original morphology of the macromonomer.

Figure 1.3. A model of crosspolymerization in a macromonomer (from ref. 19).

Other macromonomers have been investigated, including various block copolymers and polyesters. Rubner developed segmented polyurethane-diacylenes containing diacetylene groups in the hard segments, and investigated the effects of cross-polymerization on the thermal, mechanical and optical properties these materials. He also studied thermochromism and mechanochromism of these materials using FTIR and visible absorption spectra. Recently, mechanical and detailed visible absorption studies of segmented polyurethanes containing diacetylene groups in the hard segment were produced by Rubner and associates. The thermochromism of these polyurethane-diacylenes was found to be due to changes in the planarity of the polydiacetylene backbone. When these materials were subjected to strain, color changes also took place, due to similar
conformational changes within the hard segments. This mechanochromism was studied in detail and led to a discussion on the orientation of hard segments during the deformation process. It was also found that crosspolymerization via UV or electron beam radiation was useful as a method of reinforcing material strength in polymers after processing. Liang, Weh-Yih and Reiser studied diacetylene-containing segmented polyurethanes and polyureas as well, and characterized the degree of phase separation and photoreactivity of these copolymers for potential photolithography purposes. Aliphatic polyester-diacetylenes were also synthesized by Patil et al.; the photoreactivity and absorption spectra of these materials were examined for different aliphatic lengths in the repeat unit. The interests in these materials have ranged from the possible development of a new highly sensitive, photoresistant to the potential of highly oriented nonlinear optical materials. The information from studies such as these include synthesis, spectroscopic results, photoreactivity, thermochromism, mechanical properties and phase behavior.

Aliphatic polyamides which contained diacetylene groups in the repeat unit were first characterized by Beckham and Rubner. These polymers were based on 10,12 docosadiyn-1,12-dioic acid or 4,6-decadiyn-1,10-dioic acid and hexamethylene diamine. Fiber and film samples of these polymers exhibited large increases in mechanical strength upon cross-polymerization. The effectiveness of the mechanical reinforcement was dependent on the degree of crystallinity and orientation in the samples. DSC and NMR data were used to determine the photoreactivity of the polyamides. The aliphatic polymer was found to be more reactive than an aromatic counterpart synthesized from the 10,12 docasadiynoic acid and p-phenylene diamine. T1 relaxation times obtained from NMR studies indicated that PADA 6,22 is more highly crystalline than PADA PPD, 22; thus crystallinity and packing are the factors affecting reactivity in this case, rather than chain mobility.

1.4 Chromism in Polydiacetylenes

Some of the first observations of thermochromism in a single crystal polydiacetylene were made by Exarhos, Risen and Baughman, when they discovered a phase transition in poly-ETCD (diacetylene R group = (CH2)4OCONHC2H5) single crystals at 130°C, accompanied by a frequency shift in the Raman spectra. Thermochromic effects were first attributed to a phase transition from the butatriene to the more electron localized acetylene electronic configuration states of polydiacetylenes based on similar shifts found in the Raman spectral results of TCDU (R = (CH2)4OCONHC6H5).
Chance et al. discovered what appeared to be further evidence of this transition by noting changes in the specular reflection spectra of TCDU crystals; spectral shifts to higher energies (shorter wavelengths) were clearly visible with increasing temperature, and the transition appeared to be completely reversible. Figure 1.5 shows the observed changes in the reflection spectrum of the polymer with temperature during the thermochromic transition. Because many of the polydiacetylenes originally investigated were not soluble in common organic solvents, the optical property measurements were generally made on single crystals of polydiacetylene. Not until the development of soluble urethane substituted polyurethanes were solvent effects on the optical properties realized. It was found, for example, that in certain soluble urethane substituted diacetylene polymers (alkoxy carbonyl methyl urethanes or ACMU's), color changes with solvent type occurred. The solutions varied in color from blue to red to yellow in order of increasing solubility of the polymer. Visible absorption spectra were correlated to conjugation length, and it was found that loss of planarity along the polymer backbone during the solvation process caused a decrease in conjugation length, and therefore a change in the observed color. It was subsequently found that a similar color change occurs in polymer gels at increasing temperatures. This information led to the realization that chromism is driven by conformational changes of the polydiacetylene chain, rather than changes in the electronic structure alone.
The loss of planarity in the soluble urethane monomers was attributed to a decrease in hydrogen bonding with increasing temperature or degree of solvation, as shown using differential scanning calorimetry and Fourier transform infrared measurements\textsuperscript{3}. It has since been noted that in other systems, thermochromism may be caused by conformational changes that do not involve hydrogen bonding. For example, in poly-ETCD, the interchain hydrogen bonding is not lost during the thermochromic transition; it was shown in FTIR studies\textsuperscript{31}, and later using solid state NMR techniques\textsuperscript{31} that a conformational transition of the alkyl side chains is responsible for the change in backbone planarity in poly-ETCD. Similar observations have been made with polyamide-diacetylenes\textsuperscript{32}. Utilizing NMR, it was found that hydrogen bonding was retained throughout the thermochromic transition. The transition observed was due to conformational changes of the methylene groups as torsional mobility increased with temperature.

Studies such as these indicate the diversity of causes for thermochromism in diacetylene materials. It is not uncommon for a substituted polydiacetylene to undergo dramatic color changes at first order phase transitions such as melting or solvation, as well as at second order transitions associated with molecular motions of the sidechains near the conjugated backbone. There are two fairly common types of chromic changes observed in these materials. In the first case, the thermochromism can occur through an order-disorder process, in which the original crystalline matrix of the polydiacetylene, or the monomeric matrix of a partially polymerized polydiacetylene, melts or is thermally disrupted, resulting in an isotropic phase in which the polydiacetylene chain exists in an unperturbed, random coil conformation. What is generally observed in visible absorption spectra of polydiacetylenes that undergo an order-disorder transition is the gradual loss of features such as the excitonic transition peak and its sidebands in the absorption curve. An example of such a transition is shown in Figure 1.6, in which a segmented polyurethane containing diacetylene functionalities in the hard domains (HDI-2,4-1000)\textsuperscript{3b}, which was synthesized and characterized by Rubner, was crosspolymerized to low levels, and then heated. At room temperature, an excitonic peak at 570 nm is visible, along with a broad second band representative of a large distribution of conjugation lengths present in the polydiacetylene. Upon heating, the excitonic peak gradually decreases in intensity as the absorption band shifts to higher energies, as the polymer undergoes thermal expansion, and finally begins to melt at higher temperatures. The peaks become broader with temperature, indicating a wide range of poorly organized polydiacetylene conformations present.
Rubner also investigated polyurethane films which exhibited a first order, crystallographic phase transition, in which the original ordered structure of the conjugated chain disappears, as a completely new peak appears with its own well-defined excitonic transition and secondary absorption bands. Figure 1.7 illustrates such a transition for HDI-5,7-1000 as a function of temperature\(^3\). The first excitonic transition slowly moves to lower wavelength due to thermal expansion. An entirely new peak appears at 90°C and continues to increase at the expense of the original peak until at 160°C.

Figure 1.5 Visible Absorption Spectra of HDI-2,4-1000 Polyurethane-Diacetylene copolymer as a function of temperature.

Figure 1.6 Visible Absorption Spectra of HDI-5,7-1000 as a function of temperature.
The polydiacetylene chains then exist in this second, well-ordered phase at 520 nm. In the case of a true thermochromic phase transition such as this, an ordered phase gives way to a second ordered phase, as opposed to a highly disordered phase. In general, the polydiacetylene chain is highly sensitive to molecular level changes in its environment. These changes include thermal expansion, motions of sidechains or of neighboring molecules, and thermally induced phase transitions. Other materials which have shown interesting chromic behavior include diacetylenic polyolefins studied by Butera et al. which undergo an order-disorder transition on melting. Many partially polymerized diacetylenes, including the BCMU series discussed earlier, undergo chromic transitions upon extraction of the monomer. The polydiacetylene double and triple bonds are believed to be placed under compressive (or, in some cases, tensile) stress while contained within the monomer lattice, thus changing the localization energy of the polydiacetylene bonds. Upon removal of the monomer, the polymer assumes its configuration within a polydiacetylene lattice, the strain is released, and the absorption wavelength is shifted accordingly.

Finally, very detailed studies of strain-induced mechanochromic behavior has been studied by Nallicheri et al. As mentioned above, the mechanochromic behavior of polydiacetylene containing polymers can be useful in determining information on their deformation behavior; when visible dichroism is measured with mechanochromism, the orientation and stress distribution of the conjugated backbone can be measured. These techniques have been utilized in the examination of strain induced orientation in the hard domains of polyurethane-diacetylene segmented copolymers.

One of the polyurethane-diacetylenes investigated was based on polytetramethylene oxide soft segments (PTMO) and hard segments formed from MDI and 2,4-hexadiyn-1,6-diol. (MDI-2,4-1000). The visible spectra recorded at 0% strain represent the initial state of the polydiacetylene backbone; the lowest energy peak appearing at 615 nm is the excitonic peak typically seen in polydiacetylenes. The blue color seen prior to straining is attributable to this strong absorbance. Figure 10(a) presents data of the vertically polarized stretched state; as the level of strain increases, the peaks gradually broaden and shift to higher energies (i.e. lower wavelengths). This is seen as a blue to red color change in the film. As stress is applied to the elastomer, much of it is transferred to the stiff hard segments, which contain conjugated polydiacetylene backbones. As these backbones become distorted due to the stress, planarity is lost and the conjugation length decreases. The broadening of the peaks is indicative of the widening distribution of conjugation lengths present in the sample. Note that at strains as low as 40%, a significant change in
Figure 1.7 Visible absorption spectra of MDI-2,4-1000 recorded in the stretch state during hysteresis cycling: a) vertical polarization; b) horizontal polarization.
the absorption peak has occurred; this implies that stress is transferred to the hard domains early in the deformation process. At high strains, only a broad, featureless peak remains.

The absorption spectra in horizontally polarized light (Figure 10(b)) indicates that there is very little shift in energy among conjugated backbones lateral to the strain direction, thus the level of stress is relatively low in this direction. Also note that the area under the curves decreases rapidly with increasing strain, indicating orientation of the polydiacetylene chains along the direction of stress.

It is apparent from vertically polarized spectra of the polymer in its relaxed state, following the application of strain, that the mechanochromic effect is highly reversible up to 350% strain. At higher strains, some permanent changes are noted; this is evidence of the disruption of hard domain ordering. Dichroic ratios were calculated by taking the ratio of vertical and horizontal polarized spectra at each strain level. This data indicated that a great deal of orientation takes place in the polymer upon stretching. It is proposed that during the deformation process, the hard segments are layered in stacks to form hard domains, and that these domains orient parallel to the stress direction, therefore causing the conjugated backbone connecting the hard segments to line up along the stress direction as well. There may be a maximum in the stretched state dichroic curve; if a true maximum exists at high strains, it is a sign that the original hard domain order is disrupted and hard segments are re-aligning into the direction of stress.

Investigations on the effect of increased cross-polymerization on the polyurethanes have recently been completed, and indicate that at low conversion levels, the orientation behavior of the hard domains is a function of the degree of conversion. More highly irradiated films exhibited higher dichroic ratios, and much lower degrees of reversibility. The fact that these differences were detectable even at very small degrees of cross-polymerization indicates the large effect of cross-polymerization on the hard domain rigidity.

Thus, it is clear that the high degree of sensitivity that the polydiacetylene backbone exhibits toward any alteration of its molecular environment is seen in the dramatic color changes and shapes of the visible absorption bands. The chromic behavior of many crystalline and paracrystalline materials has been reported in the literature. However, to date, no one has explored the thermochromic transitions that might be found in liquid crystalline phases. The multiphasic nature of liquid crystals provides a rich variety of ordered environments within which a polydiacetylene backbone may arrange itself. The presence of two or more first order thermal transitions should accommodate at least two corresponding color changes, and the abrupt thermal transitions of some liquid crystals
would provide for sharp and dramatic changes in the absorption spectra. For these reasons, liquid crystals provide the ideal host for the diacetylene moiety.

1.5 Liquid Crystals and Diacetylenic Liquid Crystalline Materials

Introduction to Liquid Crystals

The term "liquid crystal" is used to describe a state of matter intermediate between crystals, which possess nearly perfect positional and orientational order, and amorphous, isotropic liquids, which possess neither short nor long range order. The classification of liquid crystals therefore includes everything from highly disordered fluids with some orientational ordering to near-crystalline ordered melts, which some scientists debate are more crystalline than liquid crystalline. This broadly defined state of matter is separated into two classes. Lyotropic liquid crystals are typically amphiphilic compounds which form ordered structures in solution. Typical examples include soaps of fatty acids and other common surfactants. The second class of liquid crystals are thermotropic mesogens, which melt to produce ordered, birefringent fluids. This thesis will address thermotropic liquid crystalline materials.

Thermotropic liquid crystals are generally rigid or semi-rigid rod or disk shaped molecules with a large axial ratio. These molecules can arrange themselves in many different types of ordering to obtain a mesophase. The various types of mesophases are classified by the degree and type of order. The three basic types of thermotropic mesophases are nematic, cholesteric, and smectic. Figure 1.8 illustrates the types of ordering in nematic and smectic liquid crystals and main chain liquid crystalline polymers.

The nematic phase consists of the uniaxial orientation of rod-like mesogens along a common axis; for liquid crystals, this axis is termed the director. The alignment along this axis is not perfect, however, and there is no long range positional ordering. The nematic phase is the most disordered liquid crystalline phase obtainable. The cholesteric phase, which is not shown, consists of a nematic phase whose director is twisted along an axis perpendicular to the plane of the director, to form a twisted phase with a regular helical pitch. Such phases are exhibited by optically active compounds. Finally, three smectic mesophases are shown in Figure 1.9. All smectic phases have both positional and orientational ordering; generally, the mesogens are arranged in layers with varying amounts of order. Smectics A and C are two-dimensionally ordered phases; in smectic A the mesogens are aligned perpendicular to the layers, whereas in smectic C the mesogens are generally tilted at a characteristic angle from the normal to the layer planes. In both cases, the packing of molecules within each layer is not structured at all, and therefore these two
Schematic of Molecular Organization in Nematic and Smectic Phases

Figure 1.8 Examples of liquid crystalline ordering (from ref. 36)
smectic phases are termed "disordered smectics". In higher order smectic phases such as smectic B, the mesogens within each layer are arranged in a two-dimensional lattice, resulting in a mesophase with three dimensional ordering. For example, smectic B layers consist of mesogens aligned in an hexagonal array\(^{37}\). There are several different types of ordered smectic phases, some of which approach crystalline ordering. These types include smectics D, E, F, G, H, and I. More than one mesophase may be exhibited by a single compound. In many cases, a liquid crystalline compound will undergo phase transitions upon heating from one type of mesophase to another phase. When this happens, the order of appearance of mesophases is always such that the more ordered mesophase appears at lower temperatures. For example, a smectic C phase would exist at a temperature below that of smectic A.

All crystalline mesogenic compounds ideally exhibit at least two thermal transitions. The melting point of the crystalline form is, of course, a first order transition with an associated enthalpy and entropy. The liquid crystalline phase may usually be heated to a temperature at which all ordering in the melt phase is lost, and an isotropic, random melt is obtained. This transition is termed the isotropization or clearing point, named because the light scattering caused by the many oriented domains of the liquid crystal is eliminated, and a truly transparent melt is acquired. There are situations in which a melting point is observed in a liquid crystalline material, but the clearing point is actually higher than the temperature of degradation, and isotropization is never observed. When present, both transitions are generally reversible, and may be observed in both the heating and cooling cycles of a differential scanning calorimeter. Supercooling of these transitions on cooling from the isotropic melt is not unusual.

**Liquid Crystalline Polymers**

There are at least two ways in which to render a polymer mesomorphic. One may do this by incorporating a rigid mesogenic unit into the backbone of the polymer. This class of liquid crystalline polymers (LCP's) is termed main chain thermotropic polymers. A second approach is to attach the mesogenic units to the polymer backbone as side chains to produce side chain liquid crystalline polymers. Polymers which fit into both categories, containing both a semi-rigid backbone and mesogenic side chains have also been prepared. It has been found that many of the same design principles which have been used to vary transition temperatures and degree of ordering in the mesophase in small liquid crystals are applicable to LCP's as well. Because of the similarities between the structure/property relationships of LCP's and liquid crystals, only polymer structural effects will be discussed in this section.
To produce a main chain polymer which exhibits liquid crystallinity, rigid rod-like groups must be added to the repeat group; however, there are limits to how rigid the polymer chain may become before the transition temperatures are increased to values above the temperature of degradation. A fully rigid polymer structure, such as poly-p-phenylene terephthalamide (Kevlar) is completely intractable, and will not melt before its degradation temperature. It is only in solution as a lyotropic polymer that this aramid exhibits liquid crystalline behavior\(^{38}\). Other examples of rigid rod polymers include poly(p-hydroxy benzoic acid), which melts at close to 500°C, as it simultaneously degrades, and poly p-phenylene, which shows no melting transition \(^{39}\).

To lower the melting and clearing transitions below the degradation temperature, there are three basic approaches\(^{38}\). One may substitute the aromatic rings of the rigid polymer with a side group to obtain poorer crystalline packing, which will lower the melting point. This effect may be controlled by the size and shape of the substituent; generally, bulkier groups result in lower melt temperatures. A variation of this type of substitution is to attach long alkyl groups to the rings. By connecting mesogenic groups together with non-linear linkages, such as the meta versus the para linkage in an aromatic compound, one also affects packing, as well as increasing entropy effects on melting, both of which lower \(T_m\). Unfortunately, adding kinked linkages can also lower the stability of the liquid crystalline phase, due to the irregular shape of the resulting mesogen. Finally, flexible spacer groups may be placed between rigid, aromatic segments to increase the entropy of melting and lower the melting point. This approach leads to the semirigid aromatic polyesters discussed in this work. The structure/property relationships of this class of liquid crystalline polymers has been the subject of study for a number of years, and a great deal is known on the manipulation of transition temperatures in such materials.

Liquid crystalline side chain polymers are also of great interest in the polymer science community. These LCP’s are usually synthesized from a vinyl liquid crystalline monomer. For many years, researchers attempted to synthesize side chain LCP’s from liquid crystalline monomers, and failed. Finkelmann et. al.\(^{40}\) discovered that the motions of the polymer backbone must be decoupled from the mesogenic units. To accomplish this, he added flexible alkyl spacer groups between the mesogen and the polymer chain, and found that with two to six spacer groups, the polymers did exhibit liquid crystallinity.

**Diacetylene-containing Liquid Crystals and LCP’s**

The diacetylene group has been incorporated into small and polymeric liquid crystals for a number of different purposes. Many researchers have shown an interest in the diacetylene group as a connecting unit between two rigid components of a mesogenic
A good example of this is the investigations of para substituted diphenyl diacetylenes by a variety of researchers in the field of liquid crystals. Others have been primarily interested in the potential of optimizing the nonlinear optical properties of polydiacetylene. Due to the variety of reasons for interest in diacetylenic liquid crystals, this area is the most quickly growing area of diacetylene research, and a good deal of literature has appeared in the past ten years regarding this topic. The following is a brief review of some of the more significant studies of these materials. Table 1.1 includes the chemical structures of some of the compounds discussed below.

Plachetta reported the synthesis of diacetylenes derived from 10,12 dococadiyn-1,22 diol and several aromatic and aliphatic acids. The resulting monomers were polymerized in the solid state to produce colored polydiacetylenes which exhibited multiple melt endotherms. Although these materials were not described as liquid crystalline, birefringent melts were observed under the optical microscope. The first endotherm was described as a "melting of the side chains" and the second as the melting of the polydiacetylene backbone. Fibers were drawn from the melts of the fully polymerized polydiacetylenes to obtain highly oriented samples.

The first reactive diacetylenes reported as liquid crystals are the family of divinyl diacetylenes (DVDA's) investigated by Garito in 1984. An example of a typical substituted DVDA is shown in Table 1.1; the electronic structure of the compound is highly delocalized due to the connectivity of the conjugated bonds in the monomer. These materials were found to undergo a reversible melting transition to a nematic mesophase, followed by a large exotherm at approximately 180°C, which has been attributed to the thermally induced liquid crystal phase polymerization of the diacetylene groups. The resulting polydiacetylenes were either glassy, amorphous substances, or liquid crystalline state polymers, depending on the thermal treatments used to polymerize the DVDA monomers. The liquid crystal polydiacetylenes were yellow-orange in color, and optically transparent over a wide range of the visible and near-infrared range. Some of the excitement generated around these materials involved the potential to align the DVDA monomer in the nematic phase with applied electromagnetic fields, and then anneal the monomer to induce polymerization of highly aligned conjugated polymer. Such well oriented structures would then have quite high nonlinear optical coefficients, with high degrees of transparency above 500-600 nm.

Ozcayir, Asrar and Blumstein synthesized a series of diphenyl diacetylene based esters of the series shown in Table 1.1. Each of these compounds exhibited a nematic phase, as well as a great deal of crystalline polymorphism. In a later paper, Blumstein explains that these diesters were relatively nonreactive. However, the same group prepared
Table 1.1 Examples of Previously Synthesized Liquid Crystalline Diacetylenes

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<thead>
<tr>
<th>References:</th>
<th>Diacetylenic Compound</th>
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<tr>
<td>Plachetta et. al. [43]</td>
<td><img src="image1.png" alt="Diacetylenic Compound 1" /></td>
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<td>Garito et. al. [42]</td>
<td><img src="image2.png" alt="Diacetylenic Compound 2" /></td>
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<td>Ozcayir and Blumstein [10b]</td>
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<td>Ozcayir and Blumstein [11b]</td>
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<td>Schen [13]</td>
<td><img src="image5.png" alt="Diacetylenic Compound 5" /></td>
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<tr>
<td>Tsibouklis et. al. [46a]</td>
<td><img src="image6.png" alt="Diacetylenic Compound 6" /></td>
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main chain polyesters containing the diphenyl diacetylene group as a rigid mesogen, and acquired the first reported main chain mesogenic diacetylene macromonomers \(^{10}\). These polyesters were prepared by interfacial and solution polymerization from substituted diphenyldiacetylene diols and aliphatic diacid chlorides; the reduced viscosities ranged from 0.13 to 0.36 dl/g. Liquid crystalline textures were observed in several of the polymers when they were heated rapidly to the mesophase temperature. However, all of the polymers were thermally unstable above 175°C, at which point the diacetylene group began to undergo thermally induced polymerization. Substitution was used as a means of reducing the mesogenic transitions below that of thermal polymerization. This was relatively successful, but the liquid crystalline phases were de-stabilized, resulting in metastable monotropic phases that existed upon cooling over a very narrow temperature range.

More success was obtained when Blumstein and associates investigated liquid crystals in which the diacetylene group was placed within the flexible portion of the molecule in investigations of small molecule liquid crystals and polyesters derived from 10,12 docosadiyne 1,22 dioic acid \(^{11}\). Of the diesters synthesized, the liquid crystalline compounds, which contained azoxy groups, were not radiation sensitive. These two diesters exhibited nematic phases, but did not show any significant color change when exposed to ultraviolet light at room temperature, indicating little or no solid state reactivity of the diacetylene group. The third diester, based on a biphenyl ether group, was not liquid crystalline, although it did react upon exposure to UV light to form a deep blue polydiacetylene. The resulting partially polymerized polymer exhibited reversible thermochromism upon heating and cooling, undergoing a blue to red color change. The specific visible absorption behavior of this diester was not addressed in this paper.

Polyesters were synthesized from the 10,12 diacid and various mesogenic diols. Reduced viscosities ranged from 0.11 to 0.99; most of the polyesters were prepared using interfacial polymerization. In the case of the five polyesters synthesized, the two liquid crystalline polymers obtained also turned out to be the only two polyesters that were photo-reactive. Both the diphenyl and alpha-methyl stilbene based polyesters turned blue upon exposure to UV irradiation, and the diphenyl polyester apparently exhibited reversible thermochromism, although no further details are provided by the authors. In a later report on copolyesters made with dihydroxy alpha-methyl stilbene, 10,12 diacid, and azelaic acid it appears that the homopolyester crosslinks via both the diacetylene groups and the alpha-methyl stilbene moiety\(^{44}\). Each of the mesomorphic polyesters in the original paper exhibited a smectic H phase on heating to 122°C, and the alpha-methyl stilbene polyester exhibited solid state polymorphism as well.
A thermally polymerizable liquid crystalline monomer developed by Schen has been found to polymerize in the mesophase or the isotropic phase to produce amorphous polydiacetylene. This compound, in which the diacetylene sidegroups are 4-oxybenzylidene-4'-1-octyl-aniline (1OBOA) exhibits three different crystalline phases and two liquid crystalline phases - a highly ordered smectic G phase and a smectic C phase as well. When annealed in the smectic G phase, a polymer with a layered micromorphology was produced. If held in the smectic C or isotropic phase, the polymer formed was completely amorphous. The polydiacetylene produced was a dark red, transparent glass, which exhibited no transitions in its DSC thermogram.

Tsibouklis, Werninck, Shand and Milburn have synthesized several liquid crystalline diacetylenes with the aim of creating novel organic second order nonlinear optical materials. In a series of nitro-substituted unsymmetrical diacetylenes with a large variety of aromatic substituents, it was found that the diacetylene monomers exhibited a reversible smectic phase. When heated further, a large exotherm was encountered, which corresponded to the thermal polymerization of the diacetylene functionality to produce a nematic polymer. The polymers were orange-brown in color, and relatively insoluble in common solvents. The estimated molecular weight of these materials was 2500 g/mol, as determined using gel permeation chromatography.

The development of liquid crystalline diacetylene monomers and macromonomers has just begun in the last decade, and there are several unexplored areas in this field. The monomers synthesized in this work are new compounds containing functional hydroxyl and carboxylic acid groups. These functionalities allow the exploration of hydrogen-bonded liquid crystalline diacetylenes, as well as the opportunity for further functionalization of the monomers or their polymer counterparts. The diacetylene-containing aromatic polyesters introduce new chemical structures to the very limited area of liquid crystalline macromonomers, present the possibility of crosslinking within a liquid crystalline phase, and the potential for highly oriented structural or optical materials. Finally, chromism in liquid crystalline polydiacetylenes has not been the subject of any investigation to date. The optical studies presented here explore the ability to induce thermochromic transitions at mesogenic transition temperatures predetermined by the chemical structure of the polymer.


   b) Butera, R.J., Lando, J.B.; Simic-Glavaski, B.; Macromolecules 1987, 20, 1722.


21) Rubner, M.F.; Macromolecules 1986, 19, 2114.

22) a) Nallicheri, R.N.; Rubner, M.F.; Macromolecules, in press.


32) Beckham, H.W.; Rubner, M.F., to be published.

33) Butera, R.J.; Simic-Glavaski, B.; Lando, J.B. Macromolecules 1990, 23, 199 and 211.


2.1 Monomer Synthetic Procedures

A full description of the chemical structures of the diacetylene monomers, as well as an outline of their synthetic routes are included in Chapter 3.0, which discusses monomer synthesis and characterization. The detailed synthetic procedures used to make each monomer are included below. Each of the monomers was characterized using Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance spectroscopy (H\textsuperscript{1} NMR). The results of these analyses appear immediately following the paragraph describing the synthetic procedure. In cases where elemental analysis was performed, the results are also included. The last part of this section includes comments regarding the synthesis of these materials.

5,7 Dodecadiyn-1,12-diol (5,7 diol). This compound was prepared using the method of Hay\textsuperscript{1}. Tetramethylene ethylene diamine (2.4 ml, 0.015 mol) and CuCl (2.0 g, 0.02 mol) were dissolved in 100 ml of methanol contained in a 250 ml three neck round bottom flask fitted with an addition funnel, oxygen bubbler, and gooseneck. A magnetic stirrer was used to stir the solution as oxygen was bubbled into the methanol. The solution turned a dark blue color when the oxygen began bubbling. 5-hexyn-1-ol (20 g, 0.2 mol) was added dropwise to the solution over a period of 30 minutes. As the reaction progressed, a dramatic color change was observed in the solution from blue to green to opaque yellow, and finally the color changes reversed to the original deep blue color. The solution was allowed to stir at room temperature overnight. It was then acidified with 5 N HCl to a pH of 1, diluted with a small amount of water, extracted with diethyl ether.
repeatedly. The resulting organic phase was dried over MgSO\textsubscript{4}, filtered, concentrated using a Roto-evaporator, and vacuum dried to yield a white crystalline solid. The diol was recrystallized 1-2 times in diethyl ether in a freezer. Yields ranged from 75 to 90%.

\textbf{FTIR (cm}^{-1}): 3366 (str., OH), 2948 (str., CH\textsubscript{2}), 1485, 1462, 1429 (mod., C-0).

\textbf{1,12-dibromo-5,7-dodecadiyne (5,7 dibromo diacetylene).} Phosphorus tribromide (2.05 ml, 0.0216 mol) was added dropwise under nitrogen to a stirred slurry of 5,7-dodecadiyn-1,12-diol (3.5 g, 0.0180 mol) in 80 ml of benzene. An ice water bath was used to maintain the temperature at 0°C; the reaction mixture was allowed to warm to room temperature during the course of the reaction. Initially, upon addition of the phosphorus tribromide to the heterogeneous suspension of diol, the diol clumped together into large white lumps. After three to four hours, the lumps had dissolved, resulting in a clear amber solution with a small amount of immiscible dark brown oil at the bottom of the flask. The mixture was allowed to stir for three days to obtain optimal yield. The reaction solution was then decanted into a separatory funnel, diluted with diethyl ether, and washed several times with water. After drying the organic phase over MgSO\textsubscript{4} and concentrating the liquid with a rotary evaporator to obtain a clear yellow oil, the oil was re-dissolved in benzene, passed through a silica gel plug, and re-concentrated. The resulting pale amber oil was then dried under high vacuum overnight to remove residual solvent. Yield: 3.9 g, 67%.

\textbf{FTIR (cm}^{-1}): 2945 (str., CH\textsubscript{2}), 2200 (wk.), 1250, 1004, 510 (wk., C-Br).

\textbf{Diethyl 4,4'-(1,12-dioxy-5,7-dodecadiyn)bis(benzoate) (5,7 aromatic diester).} The potassium salt of ethyl 4-hydroxy benzoate was produced in large quantity by completely dissolving equimolar quantities of hydroxy benzoate with potassium hydroxide in dry ethanol. The salt was recovered and dried in vacuo to remove excess ethanol. The 1,12-dibromo-5,7-dodecadiyne oil (7.6 g, 0.02375 mol) was added under nitrogen to a round bottom flask with magnetic stir bar containing 100 ml of dry ethanol. The stirred mixture formed a partially immiscible solution. A small, catalytic amount of sodium iodide (<20 mg) was also added to the reaction mixture. A 10% molar excess of the phenoxide salt was then dissolved in 20 ml of dry ethanol and added dropwise to the reaction solution. A white precipitate (potassium bromide byproduct) began to form immediately upon adding the phenoxide solution. The reaction was allowed to stir for 3 days at room temperature to ensure complete reaction. The precipitate was then filtered out, and the clear pale yellow filtrate was extracted using diethyl ether and a 10% w/w KOH/water solution. The organic layer was washed several times with base to remove
residual phenoxide. The organic layer was dried over MgSO₄ and concentrated with a rotary evaporator, and finally dried under high vacuum to produce a pale amber liquid that solidifies when refrigerated (0°C). Yield: 3.8 g, 40%.

FTIR (cm⁻¹): 2945(s), 2200(w, 3 peaks), 1710(s), 1606(s), 1500(m), 1278(m), 1257(s), 1170(m), 1106(m), 1058(m), 647(m).

4,4'-(1,12-dioxy-5,7-dodecadiyn) dibenzoic acid (5,7 DODBA).
This monomer was prepared via two synthetic routes. Comments regarding each of these routes are included at the end of this section.

**Method A:** The aromatic diacetylene diester, diethyl 4,4'-(1,12-dioxy-5,7-dodecadiyn)bis(benzoate), was saponified to produce the diacid as follows. The diester (2.0 g, 0.0041 mol) was dissolved in 40 ml of ethanol contained in a round bottom flask. As the solution was stirred under nitrogen, a basic water solution (4 g NaOH and 8 ml water) was added dropwise at room temperature with stirring. A turbid mixture was formed upon adding the aqueous base. The reaction flask was fitted with a water cooled condenser, and the reaction was refluxed gently for 2-4 hours with stirring, and then allowed to cool to room temperature. The reaction solution was a cloudy brown color. The solution was stirred overnight, and then the solution was concentrated using a rotary evaporator to strip away some much of the ethanol. The solution was diluted with a basic aqueous solution (10% w/w NaOH in water), and then extracted with diethyl ether. After several washings, obtained a clear yellow-orange aqueous phase and a cloudy, deep orange organic phase. An intermediate phase of settled dark orange/red solid appeared as well. The aqueous phase was acidified with concentrated HCl to produce small quantities of a dark red/brown precipitate. The solid in the intermediate layer was soluble in basic water, and upon acidification, more of the dicarboxylic acid precipitate was formed. Yield: 0.3 g, 16.8%. This method repeatedly resulted in poor yields and large amounts of a diacetylene byproduct.

**Method B:** The 5,7 DODBA diacetylene diacid was synthesized by directly reacting the potassium salt of p-hydroxy benzoic acid with 1,12-dibromo-5,7-dodecadiyne. The dibromo diacetylene (4.0 g, 0.0125 mol) was dissolved in 80 ml of dimethyl formamide in a round bottom flask fitted with a water cooled condenser. An aqueous solution of hydroxybenzoic acid (3.09 g, 0.02750 mol - 10% molar excess) and potassium hydroxide (3.09 g, 0.0550 mol) was prepared using 40 ml of water to maintain a ratio of DMF:H₂O of 2:1; the pH of this aqueous solution was 11. The potassium salt was added dropwise to the DMF reaction solution. The reaction mixture remained clear, until approximately one
half to three fourths of the salt had been added, at which point it became slightly cloudy.
The solution was heated to a very light reflux for 8 hours, then allowed to stir overnight at
room temperature. At the reflux temperature, the solution became clear as apparently all
components of the mixture became miscible; at room temperature the cloudiness had
returned, along with some amount of white precipitate. The water/ethanol solvent was
stripped away using the rotary evaporator. The resulting white paste was dissolved in 120
ml of water to yield a solution of pH 9. This solution was then acidified using concentrated
HCl. The white product was too fine to filter, so the aqueous solution was placed in the
freezer to allow coagulation of some of the particles. The next day, the diacid was filtered.
This material was purified by recrystallization in chloroform. Method B was the primary
method utilized in this study. Purity of the 5,7 DODBA is estimated to be approximately
91-93%, based on elemental analysis, which indicated the presence of bromine. The
bromine is thought to come from approximately 3% residual potassium bromide salt; this
number was obtained from the percentage weight remaining after heating a sample of
DODBA to 1000°C in a thermogravimetric analyzer. The remainder of the impurity is
thought to be 5-7% mono-substituted byproduct. H1 NMR (d-THF) and FTIR verified
the structure of the diacid. Some of the impurity was visible in NMR, as well, and is
relatively consistent with the rough estimates given from elemental analysis. Impurities
were not visible in FTIR.
Yield: 2.9 g, 53%.
m.p.: 5,7 DODBA is polymorphic, and will melt in a range from 110-150°C, depending on
the crystallization solvent used. Upon melting, an opaque liquid is seen up to 190°C to
200°C, when melt becomes a clear liquid.
FTIR (cm-1): 2949.53(m), 2600(w), 2700 (w), 1682.14 (s), 1606.91(s), 1514(m), 1429,
1254, 1167, 1104.39(w), 850, 770.
H1 NMR:(d8-THF): 1.7(str., t of t, CH2-CH2-O, CH2-CH2-C=), 2.4(mod., t,CH2-C=),
3.5(wk.,s, CH2-Br), 4.0(mod., t, CH2-O), 6.9 and 7.9 (s, d, aryl-H), 8.0 (w, br., s,
acid-OH).
Elem. Analysis: Expected: % C: 71.89 Results: % C: 63.65
% H: 5.99 % H: 5.85
% Br: 0.00 % Br: 4.48
Estimated purity: 91-93%

4,4'-(1,12-dioxy-5,7-dodecadiyn) dibenzoic acid chloride (5,7 DODBA
chloride). Purified (recrystallized 2-3 times), vacuum dried 5,7 DODBA (1-3 g) was
weighed into a dry three neck round bottom flask under nitrogen. 20-30 ml of freshly
distilled thionyl chloride was added to the powder using an addition funnel as the solution was stirred. The diacid dissolved quickly in the thionyl chloride to give a clear solution. A small drop (catalytic amount) of dry dimethyl formamide was also added. The solution was stirred for 24 hours under a nitrogen blanket, to give a very pale amber solution. The thionyl chloride was removed under high vacuum for 4 to 6 hours, leaving an off-white to light brown colored pasty solid. Quantitative yield was assumed based on FTIR spectrum. The DODBA chloride was polymerized immediately to prevent hydrolysis from atmospheric water.

FTIR: 2949, 1768(s), 1739 (s), 1712 (w), 1600(s), 1575 (m), 1506 (s).

**Dihydroxydiphenoxo 5,7-dodecadiyne (5,7 DHDP).** 75 ml of dry, deaerated 95% ethanol (with 5% methanol, i.e., denatured alcohol) was added to a round bottom flask under nitrogen. A catalytic amount of sodium hydrosulfite (0.05 g) and 10 times molar excess of hydroquinone (10.3125 g, 0.094 mol) were added and dissolved by gently warming the solution and stirring using a magnetic stirrer. The 5,7 dibromo diacetylene (3.0 g, 0.0094 mol) was added using a pipette, and the solution was heated to reflux. Once the solution was at reflux conditions, a solution of potassium hydroxide (1.578g, 0.028 mol) in 20 ml of dry, deaerated 95% ethanol was added dropwise. The resulting cloudy solution was refluxed for 4 hours, then allowed to cool to room temperature. The reaction was stirred overnight to ensure complete reaction and then acidified with 33% sulfuric acid solution to a pH of 1.0. An off-white precipitate was formed upon acidification. The slurry was reheated to reflux temperature, and much of the precipitate dissolved, but some of the white powder remained insoluble. The reaction solution was hot filtered through a scinttered glass funnel connected to vacuum aspirator with a side arm and rinsed many times with hot 95% ethanol. The insoluble precipitate was mono-alkylated byproduct; the filtrate, which contained product, was concentrated to a thick white paste using the rotary evaporator. This paste was washed in a scinttered glass funnel with several aliquots of warm water (total volume of 1000 ml) to remove the excess hydroquinone and potassium bromide salt. The DHDP was then recrystallized in 95% ethanol to produce an off white powder. Yield: 0.95 g, 27%.

m.p. translucent liquid at 145-147°C, clear liquid at 159°C.

FTIR: 3345 (br.), 2952 (m), 1600(w),1514 (s), 1239 (s), 1103 (m), 1057 (m), 955 (m), 824 (m).

H¹ NMR(d₈-THF): 1.7 (tr,mod.,CH₂-CH₂-O), 1.85 (tr,mod. CH₂-CH₂-O, ), 2.3(tr.,mod.,CH₂-C≡), 3.9(tr.,mod.,CH₂-O), 6.8(str.,d, aryl-H)
**10,12-Docosadiyn-1,22-diol (10,12 diol).** 10-undecyn-1-ol (15 g, 0.089 mol) was coupled to produce a diol using the same Hay oxidative coupling procedure as that described for 5,7-dodecadiyn-1,12-diol. Much of the diol did not remain in solution during reaction and acidification; therefore, product recovery was facilitated for this compound by filtering out the already precipitated diol before the extraction with diethyl ether and washing this portion with water to remove excess CuCl. The filtrate was then extracted with diethyl ether as in the original procedure. The portions were combined and recrystallized two times in diethyl ether. A white crystalline powder is formed which turns light blue under UV irradiation. Yield: 13.08 g, 87%.

m.p. 80-82°C
FTIR: 3411, 3344 (br.), 2938 (s), 2851(s), 1468 (m), 1065 (m), 723.40 (m).

**1,22-dibromo-10,12-docosadiyne (10,12 dibromo diacetylene).** The 10,12 diol (6 g, 0.018 mol) was brominated using phosphorus tribromide in the same procedure as that described for 1,12-dibromo-5,7-dodecadiyne. The product was a waxy solid/viscous liquid at or near its melting point at room temperature. During the recovery filtration steps, several washes of both the Mg SO₄ drying agent and the silica gel column with benzene had to be used to completely recover product. Yield: 8 g, 97%.

FTIR (cm⁻¹): 2923(s), 2851(s), 1467(m), 1214(br.,m), 1007(m), 723(m), 647(w).

**Dihydroxydiphenox 10,12-docosadiyne (10,12 DHDP).** The 10,12 aromatic diol was synthesized from 10,12 dibromo diacetylene (5 g) and excess hydroquinone using the same procedure described for the 5,7 DHDP. A very light reflux was used due to the high diacetylene reactivity of the starting material and the product. The reflux was continued overnight (12 hrs.), and the reaction was allowed to stir at room temperature for another 24 hours. A white powder was produced after recrystallization in 95% ethanol. Yield: 3.6 g, 63.7%.

mp. 75°C-opaque liquid, 90°C, clear liquid.
FTIR(cm⁻¹): 3400 (br.), 2932 (s), 2851 (s), 1513(s), 1233(m, br.), 826(m), 768 (m).
H¹ NMR(d₈-THF): 1.3 - 1.6(str., br., sev.pks., CH₂-), 1.75 (mod., CH₂-CH₂-O, CH₂-CH₂C≡), 2.2(mod.,t, CH₂-C≡), 3.9(mod.,t, CH₂-O), 4.7(wk., br., OH), 6.8(aryl-H)

Elem. Analysis: Expected: % C: 78.76 % H: 8.88
Results: % C: 76.71 % H: 9.05

Estimated purity: 98%
Comments and Suggestions Regarding Monomer Synthesis

The most difficult of the three monomers to synthesize was the 5,7 DODBA diacid. The first synthetic method, described as Method A, involved the hydrolysis of an aromatic diacetylene diester in a solution of 95% w/w ethanol, 5% water. This technique consistently resulted in a small yield (3-20%) of diacid product, and a large quantity of an oily organic liquid which turned out to be a diacetylene diether resulting from the substitution of the dibromo compound with the ethoxy anions present in the reaction solution. The diacid product that was recovered had been exposed to heat from exposure to reflux at moderately high temperatures; therefore, the diacid was deeply colored red or orange, indicating a good deal of thermal polymerization of the diacetylene groups during the reaction. Should this method be attempted again, it is the suggestion of the author that the solvent used consist of 95% ethanol/5% methanol (denatured alcohol). This was the solvent used by Griffin and Havens to produce similar diacid compounds from aromatic diesters. A second primary difference in the method used here versus that of Havens is that a much larger proportion of base was used by Havens; this could have significant effects on the results of the synthesis.

Method B was ultimately chosen to synthesize the diacid monomer because it offered both higher yields and a more direct synthetic method. This technique worked quite well for the first six or seven batches of 5,7 DODBA. Unfortunately, some difficulty was experienced in attaining reasonable yields in the last few batches. This may be due to the introduction of a new impurity in the starting materials, a small change in one of the reaction variables, or some other experimental error. One source of problems was a variation in the solvent ratio; for example, only ester side-products were produced if the ratio of water to DMF was increased. It is believed that some of the difficulties with this procedure are due to the fact that it is a heterogeneous process, taking place in the presence of two incompatible phases. A suggestion is to utilize denatured alcohol or some other relatively non-reactive alcohol as a solvent. It should be noted that differences between the diacid products synthesized by both means were not detected by IR or NMR.

As described above, 5,7 DODBA was not easily purified. The major impurities were the reaction side products of potassium bromide (approx. 3%) and the mono-bromo (partially substituted) diacetylenic acid (approx. 5%), which were still present after three or four recrystallizations from chloroform. Ultimately, these impurities might be best removed using column chromatography techniques. The presence of impurities is anticipated to have lowered the melting point of the 5,7 DODBA monomer; however, it is believed that the overall thermodynamic behavior and diacetylene reactivity of 5,7 DODBA has not been greatly affected by its low purity level.
2.2 Polymer Synthetic Procedures

A full discussion of the design and synthesis of the liquid crystalline aromatic polyester-diacetylenes is presented at the beginning of Chapter 4.0. The following are detailed descriptions of the synthetic procedures used to make the polymers.

5,7 DODBA/PPD. The 5,7 DODBA chloride (derived from 1 g, 0.0023 mol of 5,7 DODBA) was dissolved in 10 ml of dry dimethylacetamide and stirred under nitrogen. An equimolar quantity of p-phenylene diamine (0.249 g, 0.0023 mol) was dissolved in 5 ml of hexamethylene phosphoramid in a separate flask also kept under nitrogen. The diacid chloride solution was cooled with a dry ice bath to approximately -20°C. The diamine solution was quickly poured into the diacid chloride solution as it was being stirred. The reaction mixture continued to be stirred as it warmed to room temperature. After allowing the reaction to continue overnight, had a brown solution. When poured into water, collected a brown precipitate. Following rinses in tetrahydrofuran and chloroform to remove starting materials, approximately 1 gram of polyamide that was insoluble in most common solvents was recovered; this polyamide was soluble in hexafluoroisopropanol. IR of this material indicates that there may be some free carboxylic acid present (peak at 1704 cm⁻¹), perhaps as polymer end groups, suggesting a relatively low molecular weight. Yield: 1.0 g, 80%.

FTIR (cm⁻¹): 3330(s), 2949 (s), 1704(m), 1645 (s), 1608(s), 1546 (m), 1515 (s), 1403(w), 1284, 1226, 1101, 841, 762, 685.

5,7 DODBA/HQ. Hydroquinone of 99+% purity (0.19 g, 0.0017 mol) was placed in a dry 50 ml round bottom flask under nitrogen, and 5 ml of 1,1,2,2 tetrachloroethane (TCE) was added to the flask, along with 2 ml of dry pyridine. This mixture was allowed to stir and dissolve under nitrogen. The 5,7 DODBA chloride (0.0017 mol) was dissolved in 10 ml of TCE in a separate dry flask under nitrogen to make a clear brown solution. Then an addition funnel was placed into a neck of the flask, and the hydroquinone mixture was added dropwise under nitrogen as the polymerization solution was stirred vigorously. During this addition, an ice bath was used to maintain a constant low temperature. The reaction mixture was slowly allowed to warm to room temperature. Upon addition of the hydroquinone solution, the reaction mixture became cloudy. To assure solubility of the reactants and oligomer, 5 ml of chloroform was also added. The solution then became clear. After stirring overnight, a brown precipitate was formed. The reaction solution
was poured into 200 ml of acetone and stirred at room temperature for two hours. The precipitate was then filtered and washed copiously with water and acetone to remove unreacted materials. The resulting light tan polyester was not soluble in most common solvents, but was soluble in hexafluoroisopropanol. The yield was relatively low, suggesting that soluble oligomers may have also been formed in quantitative amounts. Yield: 0.3 g, 33%.

FTIR (cm⁻¹): 2952 (m), 1724 (s), 1605 (s), 1512 (s), 1255 (s), 1166 (s), 1076 (w), 841, 761.

5,7 DODBA/MeHQ: Methylhydroquinone (0.13 g, 0.0010 mol) of high purity was dissolved in 5 ml of hexamethylene phosphoramidate and 2 ml of pyridine and reacted with an equimolar quantity of 5,7 DODBA chloride (from 0.43 g of diacid). The same procedure as that for 5,7 DODBA/HQ was used. Only a very small amount of red-brown polymer was recovered. Yield: 0.1 g, 17.8%.

FTIR (cm⁻¹): 2952 (m), 1728 (m), 1605 (s), 1511 (m), 1255 (s), 1165 (s), 1071 (m).

5,7 DHDP/TC The 5,7 DHDP diol (1 g, 0.0026 mol) was dissolved in 12.5 ml of dry TCE and 2.5 ml of dry pyridine, and stirred under nitrogen. Freshly recrystallized terephthaloyl chloride (0.543 g, 0.0026 mol) was dissolved in 12.5 ml in a separate flask, also under nitrogen. The terephthaloyl chloride solution was then added dropwise to the diol using an addition funnel. The solution was stirred for 24 hours at room temperature, and then poured into 100 ml of acetone, stirred for two more hours, and filtered to remove the polymer precipitate. An off-white solid that was relatively insoluble in most common solvents was produced. The polymer was soluble in m-cresol. Yield: 1.2 g, 93%.

FTIR (cm⁻¹): 2949.53, 1729.43 (s), 1509 (s), 1286, 1245, 1191, 1056, 720 (m).

10,12 DHDP/TC The polyester of 10,12 DHDP and terephthaloyl chloride was synthesized using the same procedure as that for 5,7 DHDP/TC. Yield: 1.69 g, 92%.

FTIR (cm⁻¹): 2932 (s), 2853 (s), 1789 (w), 1730 (s), 1508 (s), 1245 (s), 1075 (m), 721 (m).

2.3 Thermal Analysis Techniques
Differential scanning calorimetry experiments were conducted using a Perkin-Elmer DSC 7 thermal analyzer. A 20°C/min heating rate was generally used unless otherwise specified. Typically, materials were heated from 50 to 350°C in a single ramp experiment to determine the melt temperature, any potential liquid crystalline transitions,
and the temperature of the characteristic large exotherms indicative of polymerization/degradation transitions in diacetylene-containing materials. Once the melt behavior was determined, heat/cool cycles from 50°C to the clearing temperature of the material (the highest temperature endotherm) were executed to ascertain the stability and reproducibility of any mesogenic transition; two heat/cool cycles were generally used to determine repeatability of the thermal transitions. Samples of 5 to 10 mg of as prepared powder were placed in cramped cover aluminum sample pans, and a nitrogen purge was used throughout all experiments.

Thermogravimetric analysis was performed using a Sieko TG/DTA to obtain weight loss as a function of temperature for degradation and stability studies. Samples were heated from 50°C to 500°C.

2.4 Optical Microscopy

Optical microscopy studies were performed on a Zeiss optical microscope equipped with crossed polarizers and a Mettler FP-80 hot stage. Samples were prepared by placing thin films or solid powder sample onto a glass slide and adding a cover slip or a second glass slide.

2.5 X-Ray Diffraction Measurements

Wide angle X-ray diffractograms were obtained with a Rigaku 300 X-ray generator with rotating anode, adjustable pole figure goniometer and diffractometer. The generator was operated at 50 V and 60 mA or 200 mA unless otherwise specified. Ni filtered Cu K alpha radiation (1.54 Å) was used. The typical sampling interval was 0.05 degrees, and the scan rates varied from 2 to 5 degrees per minute. Powder samples were prepared with a small quantity of powder sample powder and a non-diffractive binder solution on glass slides; these samples were examined in X-ray reflection mode. Thin film samples were prepared from solutions of polymer cast onto glass slides; the films were carefully removed from the glass substrate and placed in a sample frame for WAXD in transmission mode. The liquid crystalline diffraction patterns were obtained by heating the sample to a temperature in the liquid crystalline range, and then rapidly cooling using an ice bath or dry ice bath to quench in the liquid crystalline structure. This technique was most effective in polymers and monomers with slow re-crystallization kinetics.

Most of the diacetylene-containing monomers and polyesters exhibited some color change when exposed to X-ray; however, substantial polymerization was not seen for the
standard exposure times of 15 to 30 minutes. The solubility of materials exposed to X-ray for these time periods did not change significantly, indicating less than significant levels of polymerization.

In-situ temperature variation studies were completed using a Rigaku furnace and a temperature controller attached to the Rigaku 200 X-ray generator, which was operated at 50 V and 200 mA. The accuracy of the furnace was approximately +/- 5°C. During this experiment, care was taken to take X-ray measurements over relatively fast time periods of 5 to 7 minutes to avoid cross-polymerization of the sample.

2.6 UV/Visible Spectroscopy

Visible absorption spectra were measured using an Oriel Instaspec System 250 multichannel analyzer with a quartz halogen light source and a continuous spectral wavelength range of 350 to 900 nm. The temperature of thin film samples cast onto potassium bromide plates was varied using a heated precision cell equipped with a Fenwal Model 550 temperature controller with a temperature range of 25 to 200°C. Spectra were recorded at each temperature after a two minute equilibration period.

Polymer and monomer samples for spectroscopy were prepared by casting from various solvents to obtain a uniform thin film on a potassium bromide cell. These films were then exposed to 250 nm UV light of 5 mW/cm² power density. The length of time required for UV exposure varied considerably, depending on the material, and sometimes on the solvent from which it was cast. For most cases, a series of films cast from different solvents were exposed for different time intervals. The samples which exhibited the lowest energy absorption peaks obtainable, as well as absorption strong enough to be easily detected, were those chosen for thermochromism studies. In the case of 10,12 DHDP/TC polyester, the films had to be annealed for a 48 to 72 hour period to obtain optimal absorption spectra.

2.7 Irradiation Methods

The as-synthesized powders of the monomers and polymers were irradiated with an electron beam from a Van de Graaff accelerator operated at 2.6 MeV. The accelerator is located at the M.I.T. High Voltage Research Laboratory. Dosages of up to 100 Mrad were administered in intervals of 10 to 20 Mrads to prevent overheating of the samples. The materials were contained in polyethylene containers during irradiation. Thin cast films of diacetylene monomer or polyester were irradiated with an ultraviolet lamp at 5 mW/cm² for varying amounts of time.
References


Chapter 3.0

Synthesis and Characterization of Aromatic Diacetylene Containing Monomers

Polydiacetylenes are of great interest to the polymer science community because of the unique electro-optical properties of their conjugated backbones. The unusual optical and nonlinear optical behavior of these materials has been thoroughly examined for a wide range of side groups. Of most recent interest is the incorporation of the polydiacetylene backbone into a liquid crystalline matrix, which can then be oriented in the mesophase to optimize the optical properties of the resulting system. The most direct method of accomplishing this feat is to synthesize liquid crystalline diacetylenic monomers, which can polymerize either in the solid or liquid crystalline state to form polydiacetylenes in an ordered matrix.

One interesting aspect of mesogenic diacetylene monomers is that when polymerized, it is possible to form side chain liquid crystalline polymers with a polydiacetylene backbone. Most of the polymeric backbones used for side chain liquid crystalline polymers are based on vinyl, acrylate, or siloxane monomers. Only in the past eight to ten years has the use of the polydiacetylene conjugated backbone in side chain LCP's been explored \(^1\text{-}^6\). Other side chain liquid crystalline polymers containing a conjugated backbone include the polymers based on metathesis polymerization of 1,6 heptadiyne derivatives \(^7\), and the ring-opening metathesis polymerization of substituted norbornenes \(^8\), both of which contain a polyacetylene backbone. All of the above-named materials are of interest because the anisotropic electro-optical properties of the conjugated backbone may be enhanced by orientation of the liquid crystalline phase. The linear optical properties of polydiacetylenes are highly dependent on the conformation of the backbone, thus liquid crystalline side chains introduce a new aspect to the chromic behavior of these novel materials.
Many of the diacetylenic liquid crystals previously synthesized have been diesters, substituted diaryl diacetylenes, or other aromatic compounds substituted to attain high nonlinear optical coefficients. The majority of these compounds only form a polydiacetylene when heated above the melting point\(^1\)\(^-\)\(^4\), and in some cases, above the isotropic clearing temperature\(^5\). Only a few of these liquid crystalline diacetylenes have been photo-polymerized in the solid state at room temperature\(^4\)\(^,\)\(^6\). This chapter discusses the synthesis and characterization of new aromatic diacetylene diols and an aromatic diacetylene diacid that are photo-sensitive. The liquid crystalline nature of the monomers and the polydiacetylenes that they form when irradiated at room temperature will also be discussed.

Because these monomers have alcohol or carboxylic acid end groups, they not only introduce a different chemical structure to the class of liquid crystalline diacetylenes, but they present the possibility of polycondensation with an aromatic comonomer to produce unique liquid crystalline polyesters, polyamides, and other classes of condensation polymers. Chapter 4.0 will discuss some of the polyesters synthesized using these monomers. The presence of the functional groups could also be utilized to functionalize the polydiacetylene monomer with surface active, nonlinear optical, or photochromic moieties. These possibilities suggest a number of potential applications for these unique monomeric diacetylenes.

### 3.1 Monomer Synthesis

The compounds synthesized in this study include 4,4'-(1,12-dioxy-5,7-dodecadiyn) dibenzoic acid (5,7 DODBA), 1,12-dihydroxydiphenoxy 5,7-dodecadiyne (5,7 DHDP), and 1,22-dihydroxydiphenoxy 10,12-docosadiyne (10,12 DHDP). The chemical structures of these monomers are shown below as structures I, II and III respectively. The aliphatic spacer groups surrounding the diacetylene group in these centrosymmetric molecules serve two functions. The flexibility of the spacer allows the mobility necessary for the diacetylene groups to order into a lattice which is conducive with solid state topochemical polymerization. This added mobility also lowers the transition temperatures, allowing the exhibition of liquid crystalline characteristics at temperatures below that of thermal degradation.
I. \( \text{HO} \text{C}_n \text{O} \text{(CH}_2\text{)_4 C} = \text{C} = \text{C} \text{(CH}_2\text{)_4 O} \text{COH} \)

II. \( \text{HO} \text{C}_n \text{O} \text{(CH}_2\text{)_4 C} = \text{C} = \text{C} \text{(CH}_2\text{)_4 O} \text{OH} \)

III. \( \text{HO} \text{C}_n \text{O} \text{(CH}_2\text{)_9 C} = \text{C} = \text{C} \text{(CH}_2\text{)_9 O} \text{OH} \)

Synthetic routes of the above compounds are shown in Figure 3.1. Alkyl diacetylene diols were produced by the oxidative coupling of acetylenic alcohols. The diols were brominated with phosphorus tribromide to create dibromo diacetylene compounds. The brominated diacetylene was then reacted with the potassium salt of hydroxybenzoic acid in a 2:1 solvent mixture of dimethylformamide and water to yield 5,7 DODBA, with the number of methylene spacers, \( n = 4 \). The DHDP monomers were synthesized by reacting a large excess of hydroquinone with the dibromo diacetylene compound in a basic ethanol solution. For this diphenoxy compound, two analogs were synthesized with four and with nine methylene spacers on either side of the diacetylene (\( n = 4, 9 \)) to examine the effects of spacer group length on liquid crystallinity and diacetylene reactivity. All monomers were purified by recrystallization in the appropriate solvents. The structures of the compounds were confirmed using NMR, FTIR and elemental analysis. The purity of 5,7 DODBA is estimated to be approximately 93%; the purities of 5,7 DHDP and 10,12 DHDP are estimated to be approximately 98%. A detailed description of the synthesis and analysis can be found in the Experimental Section.

3.2 Characterization of Monomers

*Thermal Analysis*

The thermodynamic melt behavior of the monomers was observed using differential scanning calorimetry. Transition temperatures and enthalpies were obtained from the peak positions and areas of the DSC thermograms. Entropies were calculated by dividing the molar enthalpy of each transition by the absolute temperature at which the transition occurs. Table 3.1 contains the transition temperatures of the three diacetylenic monomers discussed above. The transition enthalpies and entropies of each of these monomers may be found in

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Monomer Synthesis

\[ \text{HO(} \text{CH}_2)_n \text{C}==\text{C(} \text{CH}_2)_n \text{OH} \]

\[ \xrightarrow{\text{PBr}_3, \text{benzene}} \]

\[ \text{Br(} \text{CH}_2)_n \text{C}==\text{C(} \text{CH}_2)_n \text{Br} \]

\[ \text{DMF/} \text{H}_2\text{O} \]

\[ \text{H}^+ \]

\[ \text{K}^+ \]

\[ \text{HO} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{Dihydroxydiphenoxo dlyne (DHDP)} \]

\[ n = 4 \quad 5,7 \text{ DHDP} \]

\[ n = 9 \quad 10,12 \text{ DHDP} \]

Figure 3.1 Synthetic routes of functional diacetylenic compounds.
Table 3.2. The thermal behavior of each monomer is unique, and is discussed in detail below. Where relevant, thermal stability and thermally induced polymerization are also addressed.

5.7 DODBA

5,7 DODBA exhibits an enantiotropic liquid crystalline phase over a wide temperature range from approximately 110°C to 200°C. This range of liquid crystallinity was somewhat unexpected considering the length of the flexible segment, which contains 12 consecutively linked carbon atoms, including the diacetylene group, as well as the fact that only a single aromatic ring is attached to either side of the symmetrical molecule. The liquid crystallinity of 5,7 DODBA is probably due to hydrogen bonding of the carboxylic acid groups; for example, the 5,7 diacetylenic ethyl benzoate diester of similar structure (see Experimental Section) was a liquid at room temperature, and showed no evidence of liquid crystallinity. In fact, it is well known that the liquid crystallinity of the fairly simple p-n-alkoxybenzoic acids is due to the dimerization of the carboxylic acid groups to form a rigid mesogenic core. These compounds consist of a carboxylic acid group directly connected to a single aromatic ring, with an alkyl group of varying length attached para to the acid functionality. The structure of 5,7 DODBA is quite similar, although it contains two acid groups, with an alkyl-diacetylene spacer as the core. When the alkyl group of the alkoxy benzoic acids contain six or more methylene groups, a smectic phase is exhibited at melt temperatures ranging from 85 to 102°C. This value is quite close to the melting range of 5,7 DODBA, indicating consistency in the thermodynamic behavior of the mono- and diacid monomers. The clearing points of the benzoic acids were much lower than that of 5,7 DODBA. This is probably due to the additional stability gained with hydrogen bonding on both sides of the molecule.

The presence of the diacetylene group in the backbone also has a strong influence on the melt behavior of the diacid. A similar chemical compound with simply twelve methylene spacers in place of the tetramethylene/diacetylene/tetramethylene spacer is reported to melt at approximately 250°C, with no apparent indication of a liquid crystalline phase. The placement of a rigid group amidst the flexible aliphatic groups apparently disrupts the highly regular aliphatic crystalline lattice enough to lower the melting point, and a stable liquid crystalline phase results. (It should be noted that the presence of impurities may have also contributed somewhat to the lower melting point of the diacid - see Experimental Section - although this is not believed to qualitatively affect the thermodynamic behavior of the compound.) There is some question as to the role of the diacetylene group in increasing the rigid rod nature of the molecule; however, there are very
### Table 3.1: Transition Diagrams for Diacetylene Monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA</td>
<td>K (113°C) LC (196°C) I</td>
</tr>
<tr>
<td>5,7 DHDP</td>
<td>K (145°C) LC (165°C) I</td>
</tr>
<tr>
<td>10,12 DHDP</td>
<td>K1 (75°C) K2 or LC (90°C) I</td>
</tr>
</tbody>
</table>

K = crystal  
LC = liquid crystal  
I = isotropic

### Table 3.2: Diacetylene Monomer Enthalpy Information from DSC

<table>
<thead>
<tr>
<th>Monomer</th>
<th>T(K-LC) °C</th>
<th>Enthalpy, kJ/mol</th>
<th>Entropy, kJ/mol °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA</td>
<td>113</td>
<td>6.76</td>
<td>0.0175</td>
</tr>
<tr>
<td>5,7 DHDP</td>
<td>153</td>
<td>29</td>
<td>0.065</td>
</tr>
<tr>
<td>10,12 DHDP</td>
<td>69</td>
<td>6.13</td>
<td>0.0179</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Monomer</th>
<th>T(LC-I) °C</th>
<th>Enthalpy, kJ/mol</th>
<th>Entropy, kJ/mol °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA</td>
<td>196</td>
<td>11.41</td>
<td>0.024</td>
</tr>
<tr>
<td>5,7 DHDP</td>
<td>168</td>
<td>27</td>
<td>0.059</td>
</tr>
<tr>
<td>10,12 DHDP</td>
<td>85</td>
<td>0.57</td>
<td>0.002</td>
</tr>
</tbody>
</table>
many diacetylene containing molecules which do not exhibit liquid crystalline behavior, and no evidence exists which suggests that the diacetylene group alone can cause rod-like mesogenic behavior. On the other hand, alkan-2,4-dienoic acids, which are aliphatic acids with a pair of conjugated double bonds juxtaposed next to the acid moiety, do form liquid crystalline phases. This effect is thought to be due the increased polarizability of the compound, and the resulting increase in intermolecular forces. In the case of the diacetylenic monomers discussed here, the diacetylene group is well within the flexible portion of the molecules, where such effects may not affect the mesogenic nature of the compounds.

The DSC thermogram and thermogravimetric curve of 5,7 DODBA from 50 to 350°C is shown in Figure 3.2. The first broad endotherm at 113°C marks a transition from the crystalline to liquid crystalline state, which appears to be smectic A from optical microscopy and X-ray measurements to be discussed in following sections. The broadness of the melt endotherm may be due to the dissolution of, or decrease in the various hydrogen bonded environments present in the monomer crystalline lattice. Actually, the melt endotherms of each of these phenoxy and carboxy terminated monomers are broad relative to most small molecule diacetylenes, perhaps due to hydrogen bonding of the functional groups. The enthalpy of melting (Table 3.2) and the entropy change are within the range of typical small molecule liquid crystals. Above the melt temperature, there is a very small endotherm at 132°C. This peak appears to be the result of the melting of a second (minority) crystalline form of 5,7 DODBA; many of the diacetylenic monomers studied to date have exhibited multiple melting behavior and polymorphism. A large and broad isotropic clearing transition is observed at 196°C. The enthalpy change at the clearing point is rather large for a monomeric liquid crystal; typically ΔHiso is on the order of one tenth the size of ΔHm. Other liquid crystalline diacetylene monomers that exhibit large clearing enthalpies are the disubstituted 4-oxybenzylidene-4'-n-octylaniline diacetylenes (nOBOA) studied by Schen and coworkers. This material also exhibits a smectic to isotropic transition. Also, it is known that smectic A to isotropic transitions have very large enthalpies, on the order of 4-6 kJ/mol. An additional explanation for the size of this transition in the diacid is the dissolution of remaining hydrogen bonding, or some other type of intermolecular bonding which increases the enthalpy needed to obtain an isotropic melt. The enthalpy of 5,7 DODBA falls right within the range of isotropization enthalpies for the dimerized p-n-alkoxybenzoic acids, which vary from 8 to 12 kJ/g-mol.

The small endotherm seen at 250°C is believed to be due to an endothermic degradation process. Infrared spectroscopy of the 5,7 DODBA monomer indicates that no chemical changes or degradation occur within the liquid crystalline phase up to 200°C. As
Figure 3.2 DSC/TGA of 5,7 DODBA Monomer
can be seen from the weight loss curve in Figure 3.2, however, there is a slight 7-8% weight loss that occurs from 200°C to 300°C, suggesting that some amount of degradation occurs above the clearing point, in the isotropic liquid. Actually, decomposition has been observed upon continually heating alkoxybenzoic acids above their transition temperatures\(^9\), suggesting that this type of decomposition may involve a process that is specific to carboxylic acids. Finally, a large exotherm is found at 326 °C, with an enthalpy of 245 kJ/mol. This peak is due to a combination of thermally induced polymerization of the diacetylene groups and thermal degradation of the monomer. If the monomer is taken beyond 280 °C and consequently cooled and heated a second time, no thermal transitions are observed, suggesting polymerization or degradation of the material. At approximately 360°C, a large weight loss of greater than 50% occurs, indicating that thermal degradation takes place at temperatures just above that of large-scale thermally-induced polymerization of the diacetylenes in the isotropic liquid state. The 5,7 DODBA monomer turns dark brown in color when heated for prolonged periods above 200°C; this suggests a polymerization to produce highly disordered, low conjugation length polydiacetylene. There is also evidence that 5,7 DODBA will polymerize in the liquid crystalline state as well, although at a much slower rate. For example, when annealed at a liquid crystalline temperature of approximately 165 to 180°C under the optical microscope, a red polymer is gradually formed which is no longer soluble in acetone (a good solvent for the monomer).

Several other researchers have reported the liquid state polymerization of diacetylenes to produce colored polymers. Tsibouklis et al.\(^{13}\) studied crystalline substituted diphenyl diacetylenes that melted to form an isotropic liquid which exhibited a large exotherm at 275°C with an enthalpy of 140 kJ/mol. The resulting brown polymer from their study was insoluble in most organic solvents and had a low molecular weight of 2500g/mol. Liquid crystalline diacetylenes from the same research group were found to undergo this sort of large scale polymerization in the liquid crystalline state of the monomer, with an exothermic enthalpy of 240 kJ/mol\(^4\). Schen described similar exotherms in his 1OBOA diacetylene system, and performed an extensive study of the polymerization kinetics and X-ray diffraction behavior during the polymerization process; in this case, the monomer polymerized both in the liquid crystalline state and above the isotropic clearing temperature at 223 °C, with an enthalpy of polymerization of 247-273 kJ/mol\(^5\). Infrared spectroscopy was used by both researchers to ensure that degradation was not taking place. Garito also described similar thermal polymerization at elevated temperatures. In many of these cases, the enthalpy of thermal liquid state polymerization is much larger than the 150 kJ/mol enthalpy determined for solid state polymerization of crystalline diacetylenes\(^{14}\). This discrepancy might be explained in a few ways. There is a
good possibility that at such high temperatures, polymerization and degradation are coupled together. Rubner and associates have found this to be probable for the case of polyamides containing the diacetylene group\textsuperscript{15}. The fact that weight loss occurs at temperatures just higher than the polymerization temperature affirms this idea. However, there are cases of thermal polymerization in which the exotherm was relatively far removed from a separate degradation endotherm\textsuperscript{4}, or in which weight loss did not occur near the polymerization temperature. It appears that the role of degradation in the polymerization exotherm is highly dependent on the chemical structure and thermal stability of the monomer. Another possible reason for the discrepancy in $\Delta H$ between solid and liquid state reactions is that the diacetylenes may be polymerizing via 1,2 rather than 1,4 addition, as proposed by Berlin\textsuperscript{16} and recently studied by Blumstein\textsuperscript{17} in a comparison of thermally polymerized and UV polymerized polydiacetylenes. The first and second heating and cooling cycles of 5,7 DODBA are shown in Figure 3.3. The monomer was heated just beyond its clearing point and then immediately cooled down; the heating and cooling rates were 20°C/min, and each cycle was repeated promptly after the end of the first cycle. In general, slower rates were avoided due to the tendency of the diacid monomer to polymerize in the liquid crystalline state. The first cooling curve indicates an exothermic transition from the isotropic to the liquid crystalline state at 135°C. This transition is highly supercooled, suggesting a relatively high viscosity melt. Upon further cooling, no recrystallization endotherm is produced. Apparently, the liquid crystalline ordering becomes effectively quenched in at lower temperatures. When taken down to 15-20°C in DSC experiments, there is only a slight upward curve of the baseline at 20°C which might suggest the beginning of a transition. These observations are consistent with optical microscopy observations, in which the liquid crystalline texture appeared to remain even at room temperature. The difficulty in obtaining a clear recrystallization transition is probably due to the kinetic effects of recrystallization from the viscous smectic liquid crystalline melt as well as hydrogen bonding present in the melt, which may also inhibit the phase transition. An example of kinetic effects is a study by Schen, who made similar observations for a cyano-biphenyl substituted diacetylene which would not recrystallize unless re-heated from room temperature, at which point recrystallization occurred at 39°C\textsuperscript{18}.

During the heat/cool cycle process described above, the diacid did not completely recrystallize; the second heating therefore indicated a large decrease in the area of the original melting endotherm. However, it is notable that the small endotherm at 130°C has increased in size from about 1.2 to 2.6 kJ/mol, and that a shoulder from 145 to 180°C has also developed along the side of the clearing endotherm. The 5,7 DODBA monomer apparently exhibits many crystalline forms, and some amount of supercooled
Figure 3.3 Heat/Cool Thermal Cycles of 5,7 DODBA
Recrystallization does occur which results in more stable solid state forms that melt at these higher temperatures. It has actually been found that when the diacid is recrystallized from acetone as opposed to chloroform, these higher melting crystalline forms are more predominant, suggesting that the crystalline morphology is highly dependent on the recrystallization solvent as well as the thermal history. Note that the isotropic clearing temperature appears at the same temperature in the heating and cooling curves regardless of crystalline form. Another effect that influences the thermal behavior of 5,7 DODBA to a much smaller degree is its tendency to polymerize in the liquid crystalline state. Polymerization diminishes the size of the transition endotherms in general, and increases the melt viscosity, further exacerbating the problem of monomer recrystallization. The DSC samples turn a light orange-pink color upon heat cycling to 200°C at a rate of 20°C/minute, confirming that there is a small amount of polymerization in the liquid crystalline state. The second cool cycle indicates a slight decrease in the isotropic-liquid crystalline transition, another indication of some diacetylene polymerization. From the light color and the high solubility of heat cycled samples in acetone, the degree of conversion is thought to be low (<5%) during the thermal cycles, though perhaps enough to increase the viscosity of the melt.

5.7 DHDP

The DSC thermogram and superimposed thermogravimetric results for the 5,7 DHDP monomer are shown in Figure 3.4. In a single heat ramp, this monomer exhibits only one broad endotherm at 153°C and a slight shoulder at 130°C. The melting enthalpy is larger than average diacetylene monomeric crystal to isotropic transitions, and the broadness of the endotherm and the low temperature shoulder suggest that this monomer may exhibit a mesogenic melt over a short temperature range. Observation of the melt behavior in a capillary tube indicates the formation of an opaque liquid-like melt at 145°C; by 160°C, the monomer becomes an isotropic melt.

The second heating of 5,7 DHDP in a heat/cool cycle (Figure 3.5) reveals that it does, indeed, exhibit two large endotherms suggestive of a crystal to liquid crystal transition at 145°C and an isotropic clearing point at 160°C. The optical microscopy observations described below suggest that a highly ordered mesophase is present upon melting the monomer; wide angle X-ray results of a partially quenched sample indicate three dimensional ordering slightly different from the original monomer. This suggests either a liquid crystalline or a crystal-crystal transition. The clear observation of melting at 145°C implies that a highly ordered smectic phase is present, and, therefore 5,7 DHDP monomer is believed to be a liquid crystalline compound. The first endotherm was
Figure 3.4 DSC/TGA of 5,7 DHDP Monomer
Figure 3.5 Heat/Cool Thermal Cycles of 5,7 DHDP Monomer.
originally shouldered into the second peak on the first heating; recrystallization appeared to result in a slightly lower melting temperature and a more clearly defined transition. The smaller, low temperature endotherms could be due to solid state polymorphism. The cooling curve indicates a highly supercooled isotropic to liquid crystalline transition at 108°C. This peak is shouldered with a second peak at 95-100°C, which could be the transition to a second, metastable liquid crystalline phase. Finally, a small, broad exotherm at 80 to 85°C is visible, corresponding to recrystallization, as determined by optical microscopy. As in 5,7 DODDA, the kinetics of recrystallization are hindered by a highly viscous melt, and recrystallization is just barely perceptible in the DSC curves. The second cooling curve contains more well defined versions of each of these exothermic transitions.

It is interesting to note here that 5,7 DHDP has a melting point which is only slightly lower than the diphenoxy dihydroxy compounds containing aliphatic spacers in place of the diacetylene group 19. This is in contrast to 5,7 DODBA, for which the melting point was effectively lowered to a value much lower than its non-diacetylene counterpart, at least for its lowest melting crystalline form. The type of hydrogen-bonded crystalline lattice afforded by the diacids must therefore be in large part dependent on the flexibility and regularity of the spacer groups. With the addition of the diacetylene moiety, the original lattice and its network of hydrogen bonds must become destabilized, thus encouraging the formation of less stable crystalline forms. In the case of the 5,7 DHDP, however, the crystal stability seems hardly changed at all by the addition of the rigid diacetylene group. This suggests that quite a different type of crystalline packing should be expected in 5,7 DHDP versus 5,7 DODBA. This will be discussed in more detail with the X-ray diffraction results. Although 5,7 DHDP has a more stable crystalline structure, its liquid crystalline phase is less thermally stable, with only a 15 to 20°C range of mesogenic behavior exhibited; this may have to due with differences in the effect of hydrogen bonding in each of the two systems.

As shown by the DSC and TGA traces in Figure 3.4, the polymerization exotherm at 288°C has an enthalpy of 305 kJ/mol. This exotherm corresponds to a 50% weight loss, suggesting that it is highly associated with monomer degradation; this does not, however, rule out the possibility that some diacetylene polymerization also occurs at this temperature. A second broad exotherm at 390°C brings about further weight loss, resulting in 20% of the original weight remaining. The 5,7 DHDP monomer is quite thermally reactive at temperatures just below the melting point; thermal annealing produces a gold to brown colored polymer. In the liquid crystalline state, the monomer is even more
reactive, producing brown, non-birefringent polymer after holding at 150°C for thirty minutes to an hour.

10,12 DHDP

Two endotherms were found for the n = 9 DHDP analog (10,12 DHDP), as shown in Figure 3.6. These peaks are listed in Table 3.1 as possible melting and isotropic clearing endotherms. There is not enough evidence at this time to assert that this compound exhibits a true mesogenic phase. Like 5,7 DHDP, when the monomer is melted in a capillary tube, it melts to form an opaque liquid at 65°-75°C and then clears to become an isotropic liquid at 80°-90°C. The enthalpy of the first endotherm is relatively small for a crystal to isotropic transition, but would fit into the high range of crystal to smectic phase transition enthalpies. Heat/cool DSC thermal cycles, seen in Figure 3.7, show that the compound exhibits two clearly defined transitions. There is a third, smaller transition at 60°C, which is probably a solid-solid transition. Optical microscopy indicates a complex, ill-defined birefringence between the two primary endotherms, which exists for a brief 10 degree range; more detail regarding the optical texture of this monomer is found in the next section. In any case, if a liquid crystalline phase does exist for 10,12 DHDP, it is a relatively unstable one with a narrow temperature range. Heat/cool cycles of the monomer indicate that these transitions are repeatable when heated up to 100 and 150°C. The heat/cool thermograms of 10,12 DHDP up to 100°C is shown in Figure 3.7. The polymerization/degradation exotherm of this material occurs at 337°C. Below this temperature, the monomer is quite thermally stable, and heated samples maintain the white color of the original monomer or turn a very faint, pale blue color for time periods of two or three hours at 50 to 100°C.

Optical Microscopy

The optical textures of the liquid crystalline monomers were determined using an optical microscope with crossed polarizers at moderate to high magnifications (200-2000 magnification). Of the three monomers, 5,7 DODBA and 5,7 DHDP exhibit what appears to be liquid crystalline behavior in the melt. The mesogenic behavior of 10,12 DHDP has not been verified at this time, although it may also exhibit a liquid crystalline phase. A mesogenic phase for any of these monomers might be expected to be smectic because of the large numbers of aliphatic spacer groups in between the mesogenic phenylene units. Because smectic phases exhibit a very wide range of optical textures, classification of the liquid crystalline phases of these materials is determined using a combination of thermal analysis, optical microscopy, and X-ray diffraction. Even with the information from these
Figure 3.6 DSC/TGA of 10,12 DHDP
Figure 3.7 Heat/Cool of 10,12 DHDP
experimental techniques, the liquid crystalline phases were not always easily identifiable, and in these cases, only general statements are made concerning the nature of the mesophase.

5.7 DODBA

When the as prepared 5,7 DODBA monomer powder is placed between a glass slide and a coverslip and heated, optical birefringence is not noted until approximately 100°C. At this point, the powder begins to melt, forming a translucent, shearable, and highly viscous film between the glass substrates, and a complex, fine texture is observed. With further heating, more of this fine texture is seen, as well as some regions with a metallic, granular or sanded texture. Figure 3.8 a) shows a sanded metallic texture made up of this complex texture. The melt is sticky and gel-like, and can be sheared in the liquid crystalline state to produce aligned birefringent regions. When the monomer is held at liquid crystalline temperatures for several hours, a red polymer begins to form; this polymerization process seems to take place starting at 155-160°C. Figure 3.8 b) is an optical micrograph showing more detail of the birefringent melt, as well as the colored polymer produced in the melt (The photo shows coalesced droplets of the melted powder on a slide; large black regions are empty spaces.) The liquid crystalline melt clears from 190°C to 200°C. When cooled from 200°C, batonnets begin to form at approximately 140-135°C (see Figure 3.9a); this temperature coincides with the exotherm in the cooling curve of 5,7 DODBA. The thin needle-like liquid crystalline domains form rapidly and spontaneously, and begin to coalesce into larger domains with plate and fan-like regions as shown in Figures 3.9 (b) and (c). These textures look like focal conic textures, although the edges of the domains are smoother and more rounded than typical. The complexity of the patterns formed may be due to the introduction of a small amount of recrystallization which superimposes onto the liquid crystalline texture during cooling. Generally, smectic A and C liquid crystals exhibit the formation of batonnets when cooled from the isotropic phase and the formation of focal conic fan textures with further cooling. The texture described above persists to room temperature, without any large scale recrystallization of the original solid state crystal form. Although the film becomes more viscous with cooling, the 5,7 DODBA monomer remains somewhat shearable at temperatures as low as 80 or 90°C. The phase transitions described above are also observed in a heated capillary tube. The as-prepared monomer melts into a thick viscous, gel-like, translucent fluid at 110°C, and remains translucent until 200°C, when it becomes a low viscosity clear liquid.

Examination of the sample after twenty four hours suggests that the original very fine crystalline morphology had begun to re-appear, but not in the same amount as the fresh monomer. A second heating does not produce a true shearable birefringent melt until
165°C, and a third heating results in even less liquid crystalline behavior. This suggests that with subsequent heat/cool cycles, the higher melting crystalline forms are eventually produced. The highest melting form appears at approximately 180°C, leaving only a 10 to 15 °C window between melting and clearing, and possibly merging the two processes. This behavior is consistent with thermal analysis results discussed above.

Focal conic textures have also been reported by Milburn et al. for an asymmetric biphenyl diacetylene substituted with an aryl-CF3 group and a benzylidene-aniline long chain aryl ether. Smectic phases in other diacetylene monomers have been reported by Tsibouklis et al. for similar asymmetric diacetylenes, and by Schen et al. for an oxybenzylidene octylaniline diacetylene compound. Most of these materials consist of a rigid rod mesogen containing the diacetylene moiety and long alkyl ether or ester "tails". Blumstein's liquid crystalline diesters derived from 1,22 docosadiyn-10,12-dioic acid have an architecture not unlike 5,7 DODBA, although the mesogenic groups used in the Blumstein diesters were generally larger and stiffer. However, these diesters were found to display nematic phases. Smectic ordering in 5,7 DODBA may be encouraged by the presence of weak hydrogen bonds still present in the ordered melt; intermolecular interactions such as this could cause some positional ordering of the mesogens. Other examples in which hydrogen bonding has had similar ordering effects include gels consisting of urethane substituted polydiacetylene chains in a poor solvent system, and paracrystalline ordering in the hard domains of many segmented polyurethanes.

5.7 DHDP

Upon first heating 5,7 DHDP, melting is observed at 135-141°C. The resulting liquid has a bright metallic appearance with no very well defined detail or texture. The melt is shearable, but very viscous, and in fact, has the consistency of a slippery or oily wax. The birefringence disappears at 165°C-167°C as the monomer reaches its clearing point. Subsequent cooling brings about the growth of a highly birefringent phase at 134 to 129°C; this growth process has the appearance of crystal growth, with the nucleation and growth of fine needle-like threads that branch out to form large round branched shapes. These quickly coalesce, particularly in thicker drop regions, to form a complex patterned melt. There is no cooling exotherm in the 5,7 DHDP thermogram that corresponds to a phase transition at 135°C. The cooling process in the microscope hot stage may have cooled the sample at a slower rate, thus reducing the amount of supercooling seen in the DSC. At 90°C-80°C, the sharp needle-like texture slowly gives way to a complex rounded or swirled pattern. Also, some plate-like birefringent texture is seen in thinner areas at this temperature range. As the compound cooled to room temperature, dark, jagged fracture
Figure 3.8 a) Optical Micrograph of 5,7 DODBA, fine texture, heated to 165°C, 800 Mag.

Figure 3.8 b) 5,7 DODBA, partially polymerized in liquid crystalline phase, 160°C, 800 Mag.
Figure 3.9a) Batonets formed on cooling from isotropic phase of 5,7 DODBA, 120°C, 1600 Mag.

Figure 3.9 b) Coalescence of batonnets, 5,7 DODBA, cooled to 67°C, 800 Mag.
Figure 3.9 c) Smectic texture in thicker region of 5,7 DODBA, cooled to 80°C, 1600 Mag.

Figure 3.10a) Brush stroke patterns in 5,7 DHDP mesophase, heated to 145 °C, 800 Mag.
Figure 3.10b) Coalesced drops of 5,7 DHDP in mesophase, heated to 145°C, 160 Mag.

Figure 3.11 Threaded mosaic texture found in 5,7 DHDP, cooled to 110°C, 2000 Mag.
Figure 3.12  Melt phase of 10,12 DHDP, heated to 87°C, 800 Mag.
lines appear in both the thick, fine textured droplets, and the thin regions with plate-like texture, presumably induced by onsetting crystallization.

The second heating of 5,7 DHDP yielded more apparent liquid crystalline behavior. At 135-138°C, the droplets of monomer began to melt, and the fine, complex texture began to give way to fans or brush-stroke regions of bright birefringence. Figure 3.10(a) gives an example of this texture. The location of the bright fans changed with rotation of the sample. When the material was lightly sheared by moving the cover slip back and forth, individual drops of monomer began to coalesce, as shown in Figure 3.10(b).

Further heating to 153°C caused a decrease in the viscosity of the melt, and a great deal of flow was observed in the melt, which was still birefringent; however, at 155°C, the birefringence began to disappear. Eventually, only needle-like entities now recognizable as batonnets were visible, and these disappeared by 165°C. Microscopic observations of the second cooling of 5,7 DHDP were similar to those of the first; however, the growth of the fan-like phase took place at approximately 127-125°C, and once again, a plate-like texture much like the threaded nematic mosaic textures found in smectic F or I phases was found in thinner regions of the monomer film (see Figure 3.11). From these observations, it appears that the monomer exhibits a yet to be identified smectic phase I from 140 to 165°C upon heating; cooling produces the development of the same smectic I at 110°C (or higher), plus the development of a second monotropic smectic phase II with a mosaic texture at 95°C. Recrystallization is a slow process occurring at 70-80°C.

10.12 DHDP

The 10,12 DHDP monomer melts at 65°C to give a translucent liquid. From optical microscopy, one finds a complex, ill-defined texture upon heating from the solid state or cooling from temperatures above the isotropic temperature such as 100°C; the melt is relatively fluid above 75°C, when a great deal of birefringence is detected and the powder becomes a melt. A photo of this fine texture is shown in Figure 3.12. The monomer can be heat cycled several times to obtain relatively reversible results. With such a narrow temperature range, it is difficult to ascertain whether the birefringence is due to the melting of small crystals and subsequent recrystallization to a second crystalline form, or to the presence of a true liquid crystalline phase. Attempts at aligning the compound with surface treated glass slides to achieve a homeotropic melt were not successful21.
3.3 Diacetylene Polymerization of Monomers via Irradiation

Each of the three diacetylenic monomers is photoreactive, and thus undergoes a solid state topochemical polymerization of the diacetylene group upon exposure to ultraviolet light, electron beam irradiation, and/or thermal annealing below the melting point of the monomer. This polymerization can be initiated by ultraviolet light, electron beam irradiation, or thermal annealing below the melt temperature. Differences in reactivity among the three monomers are associated with the crystalline packing of the molecules. The crystalline packing in the less reactive systems may not be optimal for the diacetylene polymerization process; the tilt angle and spacing requirements for the topochemical process are described by Bloor, and reviewed in section 1.0. The degree and perfection of crystalline order are also factors in polymerizability and conversion in these systems. The diacetylene compounds were irradiated with electron beam in their powder forms to obtain varying levels of conversion. For example, the conversion of 10,12 DHDP after exposure to 50 Mrad of exposure, was found to be approximately 80% by extracting the monomer with hot 95% ethanol and measuring weight loss. Conversions varied from 20 to 80% in the monomers, depending on their respective reactivities.

Thermal Analysis of Irradiated Monomers

5,7 DODBA

The topochemical reaction of 5,7 DODBA is slow to moderate at room temperature. The monomer gradually turns pink in its as-prepared powder form when exposed to visible light for two or three days. Thin solvent cast films of 5,7 DODBA are transformed from white to a deep pink shade upon exposure to ultraviolet irradiation for six to eight hours. The monomer turns a very dark burgundy red color when electron beam irradiated at a dosage of 50 to 100 Mrads; the deep color obtained suggests a measurable degree of diacetylene conversion. The resulting partially polymerized solid is only partially soluble in tetrahydrofuran, both solvents which easily dissolve the monomer.

The effects of conversion due to electron beam initiated polymerization can be observed from the DSC thermograms shown in Figure 3.13. The thermal characteristics of 5,7 DODBA remained relatively unchanged at low electron beam dosages (< 5 Mrads), and significant differences were only detected at very high levels of irradiation. The monomer exposed to 50 Mrad of irradiation shows a slight increase in the melting point of the monomer from 113°C to 120°C, and from 120°C to 122°C in the 100 Mrad sample. Similar increases in the monomer melting point following partial polymerization have been reported by Patel for 2,4 hexadiyne-1,6-bis(p-toluene sulphonate) (PTS), as well as for a
Figure 3.13 DSC of irradiated 5,7 DODBA
rigid rod diacetylene synthesized by G. Hardy et al.\textsuperscript{24}. Although such increases do not always occur, the phenomenon is relatively well known. Conversely, the enthalpy of the melting endotherm has decreased relative to that of the fresh monomer; the decrease in enthalpy suggests a 20 to 25\% degree of conversion of the monomer at 100 Mrad. Such low levels of conversion at very high dosages suggest that the crystalline structure of 5,7 DODBA is not completely conducive to solid state polymerization. It is interesting that the smaller endotherm at 126°C seems to have decreased relatively rapidly; perhaps the crystalline forms that melt at these temperatures are more compatible with diacetylene polymerization.

The liquid crystalline to isotropic liquid transition is much more greatly affected by diacetylene polymerization. The clearing point shifts to slightly higher temperatures, and broadens to include a range from 175 to 210°C after exposure to 50 Mrads. At 100 Mrads, the clearing point is barely visible at all, and it appears that the remaining monomer maintains liquid crystallinity to much higher temperatures. This may be due to a stabilizing effect that the presence of polymer has on the liquid crystalline phase. It is possible that the increased viscosity due to the presence of polymer chains somehow decreases the ease with which the monomer can achieve isotropic ordering. Another possibility is that the monomer is slowly converting to liquid crystalline oligomer, which does not clear out until much higher temperatures are reached.

The size of the exotherm decreases with irradiation, introducing the possibility of two different causes for this decrease. One possible reason may be that the polydiacetylene is more thermally stable than the monomer within the 280-300°C temperature range; from observation of the thermogravimetric curve in Figure 3.14 of the 100 Mrad sample, however, it is clear that approximately 50\% weight loss occurs at 400°C, which is very similar to the weight loss observed in the unirradiated monomer. In fact, the irradiated monomer seems a little less thermally stable, with slight weight loss occurring as low as 120°C. It is therefore concluded that some portion of the exotherm is truly attributable to the polymerization of polydiacetylene, and it is for this reason that the exotherm shrinks slightly following polymerization. Finally, the combined polymerization/degradation exotherm shifts to lower temperature following irradiation. This drop in the exotherm temperature from 330°C to 310°C is similar to that cited in other aromatic diacetylenes; the polymerization exotherms of PTS\textsuperscript{22} and BDI (butadiyne-2,4-diol-1,6-bis(p-butoxybenzoyloxy) benzoate\textsuperscript{23} show similar drops following partial thermal polymerization, and Belina et al. found that the polymerization and degradation processes of a partially polymerized hexoxybenzoate diacetylene occurred at a temperature 25°C lower than in the original monomer\textsuperscript{25}. One explanation of this phenomenon could be that the
Figure 3.14 TGA of irradiated 5,7 DODBA
thermal stability of the partially polymerized monomer is decreased due to the exposure to high levels of electron beam irradiation.

It is notable that there are no apparent transitions visible that are characteristic of the poly-DODBA formed. From the wide angle X-ray diffraction data discussed in a following section, the lack of polydiacetylene thermal transitions is apparently due to the fact that the polymer formed is a glassy amorphous polydiacetylene, much like the polymers formed by Schen and Garito. There is very little information in the current literature on the melt or thermal behavior of polydiacetylenes with rigid rod or liquid crystalline side chains. In general, many polydiacetylenes with fewer than three methylene spacers in the side chain have been found to be infusible; those with more spacer groups tend to melt at lower temperatures. More specific examples include the thermally polymerized hexoxybenzoate polydiacetylenes investigated by Belina et al. A dark red partially polymerized product exhibited the original monomer melting endotherm at 57°C plus a second liquid crystalline or oligomeric melt endotherm at 83°C, followed by degradation. When the partially polymerized product was heated to induce thermal polymerization, the resulting polydiacetylene did not exhibit any endo- or exotherms below the degradation temperature. Hardy et. al. also report the polymerization of liquid crystalline diacetylenes, from which polydiacetylenes are formed that do not have any characteristic endotherms below the temperature of degradation. Presuming that the polydiacetylene formed is a glassy polymer, a glass transition may occur below degradation temperatures, but it would not necessarily be detectable in the presence of the original monomer transitions.

### 5.7 DHDP

The 5,7 DHDP monomer produced polymer of much lower conjugation length, and probably of lower molecular weight, than 5,7 DODBA. This compound turns pale yellow when exposed to ultraviolet irradiation for several hours. The yellow color is suggestive of a low conjugation length, and the formation of low molecular weight, highly disordered polydiacetylene chains. Electron beam irradiation to 100 Mrad yields a deep yellow-gold colored material. The DSC thermograms of 5,7 DHDP at various levels of electron beam irradiation are shown in Figure 3.15. After 20 Mrad and 50 Mrad dosages, the melt endotherm begins to decrease in total enthalpy, as in the case of 5,7 DODBA. It should be noted that the single broad endothermic peak of 5,7 DHDP is a convolution of a melting and a clearing transition. This should be considered if the relatively fast drop in enthalpy for 5,7 DHDP is compared to the diacid monomer. There is also a shift of the endotherm to somewhat lower temperatures. This behavior is not unusual, and has been found in a
Figure 3.15 DSC of irradiated 5,7 DHDP Monomer
few cases of polydiacetylene materials. This effect is probably due to the presence of polymer, which acts as an impurity and lowers the melting point of the monomer. The estimated conversion of the monomer is approximately 50%.

The exotherm of 5,7 DHDP decreases in size with irradiation; again, as in the DODBA monomer, this suggests that the exotherm is actually a composite of polymerization and degradation. A difference between these two monomers, however, is that the 5,7 DHDP exotherm position increases from 290°C to 325°C. Although this suggests an improved thermal stability, from the TGA of a sample irradiated with 100 Mrad, shown in Figure 3.16, it appears that the thermal stability of the partially polymerized monomer is actually a little worse than that of the original monomer. Weight loss occurs at approximately 175°C in this system, which indicates that the irradiation process may cause some amount of degradation itself. The increased temperature of the exotherm more than likely reflects changes in the structure of the material due to polymerization. Again, there is no indication of the development of new polymeric peaks in the irradiated version of 5,7 DHDP; wide angle X-ray data suggests an amorphous polymer.

10.12 DHDP

The most reactive monomer of the three discussed is 10,12 DHDP, which has nine flexible spacer units between the aromatic rings and the diacetylene groups. This compound turns light blue when exposed to visible light for ten to twelve hours. A thin cast film of the material will turn a deep purple-blue color following five minutes of UV light exposure. After more than ten minutes, the color shifts to a dark red color as the extent of conversion of monomer increases. Electron beam irradiated powder turns a dark reddish purple color at 50 Mrad dosages. This powder is not soluble in many organic solvents, and the monomer may be extracted out with 95% ethanol to obtain a burgundy colored polydiacetylene. The estimated conversion derived from this extraction experiment is 80%.

Figure 3.17 shows the effect of irradiation on 10,12 DHDP. The monomer endotherm broadens and is shifted to higher temperature after 10 Mrads of electron beam irradiation. This effect is something like that observed in 5,7 DODBA. However, the 20 Mrad dosage sample exhibits two separate endotherms, one that is partially visible at 60°C, and another at 90°C. The first partial endotherm is the melting point of unreacted monomer, and the second endotherm is due to the melting of polydiacetylene. At 50 Mrad, the polydiacetylene clearly exhibits two transitions independent of the melting endotherm: a broad peak at 100°C and a smaller, even broader transition centered at 180°C.
Figure 3.16 TGA of irradiated 5,7 DHDP Monomer.
Figure 3.17 DSC of irradiated 10,12 DHDP
From the inset, it is clear that the monomer is still present, and is melting at lower temperatures, probably due to the presence of polymer, which acts as an impurity. Heat/cool DSC experiments of this polydiacetylene indicate that its transitions are not reversible when heated to 200°C; the reasons for this irreversibility are unknown at this time. Optical microscopy confirms that a liquid crystalline phase is exhibited in the partially polymerized diacetylene. Thus, irradiation of the monomer has produced a side chain liquid crystalline polydiacetylene. The conversion estimated from the change in the melt endotherm enthalpy is 75% at 50 Mrad, which is quite consistent with the 80% estimate from extraction experiments. It appears that the 10,12 monomer will react quite readily to achieve appreciable yields of conjugated polydiacetylene, and the purple color of the polydiacetylene suggests that the polymer formed has a long effective conjugation length. The extracted polydiacetylene exhibits higher transition temperatures at 160 and 193°C, with a broad melt endotherm shouldered into the clearing transition. Optical observations indicate only a small amount of birefringent texture at these temperatures. A liquid crystalline transition is seen in the extracted polymer, but only within a very narrow temperature range. It appears that in the partially polymerized diacetylene, the monomer present acts as a diluent for the polydiacetylene, effectively lowering the transition temperatures.

The weight loss versus temperature curve of 10,12 DHDP at 50 Mrads is shown in Figure 3.18. As can be seen, a small amount of weight loss is seen at 170°C, indicating, as in the other monomers, that exposure to irradiation could cause a minimal amount of degradation or destabilization of the compounds. It is also notable that the temperature of the exotherm does not change much at all upon irradiation, although the size of the exotherm is decreased, as in 5,7 DODBA and 5,7 DHDP. Again, this suggests that the enthalpy of thermal polymerization is hidden in the degradation exotherm.

Optical Microscopy

Each of the irradiated compounds exhibits some liquid crystallinity when observed under crossed polarizers, although in 5,7 DODBA and 5,7 DHDP this is probably due to the presence of residual monomer. In these two cases, the liquid crystalline texture and stability seemed affected by the presence of the polymerized monomer. On the other hand, 10,12 DHDP, which has a questionable mesogenic nature, becomes a side-chain liquid crystalline polymer upon irradiation.

When the 100 Mrad irradiated sample of 5,7 DODBA is observed under the optical microscope, a dark red powder is seen at room temperature as a collection of featureless spherical powder particles or agglomerates. At 120°C, some birefringence appears within
Figure 3.18 TGA of irradiated 10,12 DHDP.
these particles, but no large scale flow is observed. The color of the powder changes from dark red to a lighter orange red color. The powder is difficult to shear; it acts more like a gel than a liquid, and the red polymeric material does not appear to melt until 200-230°C. At this point the powder particles begin to fuse together, and a little more birefringence is visible. The complex swirled pattern that was visible in the monomer during the first heating was visible here (see Figure 3.19). The birefringence begins to dim at 230°C, but does not disappear completely until 280°C. During this time, the compound appears to be slowly degrading; this is consistent with the weight loss curve of the irradiated monomer. Degradation is apparent at 300°C, when the film darkens considerably.

The fact that the irradiated monomer has no apparent clearing point is confirmed by the results of thermal analysis discussed above. The isotropic clearing transition broadens and decreases in size until it is barely visible in the DSC at 100 Mrad. Also, the material did not show any real sign of complete fusion until the temperature was greater than 200°C. This suggests that the polymer itself may undergo a glass transition at this point. Since the level of conversion is low, a second order transition is not perceptible in the DSC. Perhaps the glassy amorphous polydiacetylene formed by irradiation exhibits liquid crystalline behavior above its glass transition temperature, typical of most side chain liquid crystalline polymers. This would explain the observations described above, in which the monomer clearing transition is broadened due to the presence of oligomers, and the polymer begins to exhibit some liquid crystalline behavior at higher temperatures.

The 5,7 DHDP monomer exposed to 100 Mrad irradiation displayed birefringence when heated beyond 130°C, at which point the powder appears to melt. The texture is dim, and difficult to identify, and it finally clears out at 170-180°C. Upon cooling, dim texture is seen again from 140°C to 83°C, at which point recrystallization occurs. Figure 3.20 shows the sample after heating a second time to 123°C. A brighter texture appears as the irradiated monomer melts, and it is evident that this texture is quite different from the brush stroke texture of the fresh monomer. The bright texture grows to include most of the material present, then disappears at 136°C, leaving the dim ill-defined texture described above. The temperatures at which this texture appears corresponds to a shouldered transition in the DSC thermogram. The very dim liquid crystalline texture seen in the first heating from 130°C to 180°C could be due to the residual monomer, which originally exhibited liquid crystallinity from 140° to 165°C. It is possible, as in the case of 5,7 DODBA, that the polydiacetylene is a glassy side chain polymer, which undergoes a glass transition to exhibit liquid crystalline behavior. This might explain the appearance of a new, brighter texture.
Figure 3.19  Irradiated 5,7 DODBA heated to 238°C, 800 Mag.

Figure 3.20  Irradiated 5,7 DHDP, at 123°C, appearance of LC texture, 800 Mag.
Figure 3.21 a) Irradiated 10,12 DHDP, 145°C, sherulitic and focal conic regions. 800 Mag.

Figure 3.21 b) Irradiated 10,12 DHDP, 165°C, sheared region, 160 Mag.
In the cases of both 5,7 DHDP and 5,7 DODBA, only small conversions to polymer have been achieved. Because of this, the liquid crystalline range of these materials appears to have been expanded; this may be the effect of oligomer, or polymer, as mentioned earlier, resulting in broad transition endotherms and less identifiable liquid crystalline textures. In both cases, the transitions of the polymer may be obscured by the transitions of monomer and oligomer.

The irradiated 10,12 DHDP monomer, which was 80% converted, displayed more definite mesogenic transitions. At room temperature, the powder appeared as dark purple-red particles, much like the 5,7 DODBA described previously. However, upon heating to 50-60°C, a spherulitic crystalline structure becomes more evident as the residual monomer melts out. A gradual melting process from 100-130°C produces a birefringent melt with spherulitic forms coexistent with a broken focal conic fan texture (Figure 3.21 a). At higher temperatures, the maltese crosses in the spherulitic forms begin to fade away, leaving only dark centers. Shearing the melt causes coalescence of liquid crystalline regions, with some alignment of the LC domains (Figure 3.21b). The birefringence began to dim at 180°C, but some birefringence remained to 215°C.

3.4 Wide Angle X-Ray Diffraction

X-ray diffraction allows a further understanding of the structural characteristics of these monomers, and the polydiacetylenes that they form. This information is essential in determining the nature of the structural changes that the diacetylenes experience at phase transitions, and during solid state polymerization. Although the results of the wide angle X-ray studies alone cannot be used to fully determine the lattice parameters of the crystalline state, they can elucidate differences in the nature of crystalline packing for each material. In some cases, this data alone may provide insights into the differences in reactivities between the diacetylene compounds. Examination of the irradiated monomers can assist further in this means, and also provide an explanation for the thermal and optical observations of the partially polymerized diacetylenes. Finally, the liquid crystalline nature of each of these compounds can be further explored by examination of samples quenched from the melt. This section details the results of X-ray diffraction of unpolymerized and irradiated monomer and quenched monomer samples respectively.

X-ray diffraction samples were prepared from solid powder samples bound onto glass substrates, or very thick crystalline films cast from organic solvents such as acetone and chloroform. The data was collected from a wide angle diffractometer, as described in Chapter 2.0, the Experimental Section. Samples were not oriented. Quenched samples
were obtained by heating the sample on a hot stage to the temperature of interest, or, in some cases, slightly higher temperatures, and immediately dipping the sample in a liquid nitrogen, dry ice/isopropanol or ice water bath. A complete listing of the d-spacings derived from the diffractograms discussed below may be found in Table 3.3:

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Crystalline State</th>
<th>Quenched</th>
<th>Irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA</td>
<td>16.1, 5.6, 4.7, 3.8, 3.6, 3.2, 3.1</td>
<td>15.8, 4.6, 3.4</td>
<td>4.7, 3.8, 3.2</td>
</tr>
<tr>
<td>5,7 DHDP</td>
<td>20.7, 11.9, 7.8, 4.5, 4.1, 3.8, 3.7, 3.3, 3.1</td>
<td>23.2, 4.4, 4.0, 3.2</td>
<td>7.5, 4.4, 4.1, 3.8, 3.2</td>
</tr>
<tr>
<td>10,12 DHDP</td>
<td>32.1, 16.7, 11.2, 8.6, 6.7, 4.4, 4.3, 3.8, 3.1, 2.6, 2.5, 2.3, 2.2, 2.0</td>
<td>4.5, 3.8, 3.0, 2.4, 2.1, 2.0, 1.9, 1.6</td>
<td>18.8, 12.3, 7.1, 4.6, 4.4, 3.9, 3.2, 2.2</td>
</tr>
</tbody>
</table>

WAXD of Monomers and their Polydiacetylenes

The diffractogram of 5,7 DODBA, shown in Figure 3.22 a), contains several strong peaks situated atop a broad halo. The breadth of the peaks is relatively large, indicating that the size of the crystals themselves are quite small. This was found to be true for each of the three monomers, although 5, 7 DODBA appears to be an extreme case. There is apparently a large amount of disorder present in the crystals, judging from the indistinct nature of the peaks, and the diffuse halo at the base of the peaks. The DSC results for 5,7 DODBA indicate the melting of a slightly more stable crystalline form at 132°C; the size of the endotherm suggests that this second crystalline form is a minor one. The WAXD pattern of 5,7 DODBA may therefore be more complex due to the presence of more than one crystalline form. The peak at low angle corresponds to 16 Å, and is most probably an nth order reflection. The fully extended length of the DODBA is
approximately 30-32 Å; therefore it is possible that in its crystalline state, the diacid molecule is in its fully extended form. This cannot be confirmed without small angle X-ray analysis, but it seems a likely possibility, since the diacid can dimerize with itself on both ends of the molecule. The resulting hydrogen bonded lattice would be quite stable, due to the added strength of the intermolecular hydrogen bonds. The low melt temperature of 5,7 DODBA, however, is an indication that the crystalline structure is not stable. Perhaps the molecular organization of the crystalline structure is not optimal for the formation of strong hydrogen bonds, or the disorganization of the crystalline forms present is enough to lower the stability of the solid state.

When 5,7 DODBA is exposed to 100 Mrad of electron beam radiation, the crystalline peaks broaden to yield the pattern in Figure 3.22 b). The locations of the three peaks that remain have not changed from those in the non-irradiated pattern, but the shape of the pattern approaches that of an amorphous halo. It is apparent that solid state polymerization of 5,7 DODBA yields a polydiacetylene with low levels of crystallinity. At the estimated conversion of 25-30%, the crystalline features of the diacid are greatly diminished, and the small angle peak has disappeared altogether, suggesting a lack of long range dimensional ordering. Many of the diacetylene compounds found in the literature are reported to have a highly crystalline structure derived from the crystalline structure of the original monomer 26,27; however, some of the more recent reports of new diacetylenic monomers do not include information on the morphology, thermal behavior, or crystalline structure of the polymerized products. The low crystallinity observed in poly-DODBA is similar to that of 2,4 hexadiyn-1,6 diol. Researchers found that the diffraction pattern of this monomer developed an amorphous halo that increased with diacetylene conversion. During polymerization, a separate polymer phase segregated from the monomeric crystalline lattice. The resulting polymer was a brown amorphous solid that was relatively insoluble in organic solvents, with a low molecular weight. 5,7 DODBA does not maintain its crystalline form during the radiation process, yet produces a deeply colored purple-red polydiacetylene of moderate conjugation length. The polydiacetylene chains may exist in a relatively disordered lattice, but apparently, there is some sort of localized ordering present that allows the polymer chains to maintain a slightly planar conformation. Another red amorphous, highly conjugated polydiacetylene has been produced by Schen by thermal polymerization of a monomer in the isotropic phase 18. The fact that poly-DODBA is amorphous explains why new polydiacetylene melt transitions are not observed in the DSC thermograms of irradiated monomer in Figure 3.13.
Figure 3.22 Wide angle X-ray Diffractogram of 5,7 DODBA: a) 0 Mrad; b) 100 Mrad
The crystalline structure of 5,7 DHDP is quite different from that of 5,7 DODBA, as seen in Figure 3.23 a). The diffraction pattern consists of two primary peaks at 4.5 Å and 4.1 Å, and two strong, but slightly smaller doublets at 3.8 Å and 3.1 Å. The diffraction peaks are much sharper and narrower, a sign that the 5,7 DHDP sample contains larger crystallites, with more perfect crystalline ordering. As discussed in the thermal analysis section, 5,7 DHDP melts at a much higher temperature than 5,7 DODBA, despite the hydrogen bonding capability of the diacid groups. Some of the reasons for this anomaly is probably due to differences in crystalline lattice parameters, packing, and crystal size. The lower angle peaks indicate spacings of 20.3 Å, 11.9 Å, and 7.8 Å. It is clear that the lattice parameters of these two monomers are quite different.

Irradiation of 5,7 DHDP produces a decrease in crystalline diffraction peak intensity, as it does for 5,7 DODBA (see Figure 3.23 b). Here, again, the amorphous halo has grown significantly upon polymerization, indicating the production of amorphous polymer. The smaller angle peaks have also diminished in size, as crystalline ordering is lost. The locations of the diffraction peaks have not shifted significantly, although some of the peaks present in the monomeric crystal are not seen in the partially polymerized sample. It is clear that 5,7 DHDP reacts to form a non-crystalline polydiacetylene, as well.

The glass transition temperatures of poly-5,7 DODBA and poly-5,7 DHDP cannot be determined from the DSC data of the previous section. It is conceivable that either of these materials could be liquid crystalline side-chain polymers, which exhibit a liquid crystalline phase above the glass transition temperature. The optical microscopy observations of irradiated 5,7 DHDP indicate a higher temperature range of mesomorphic behavior, and the textures are different from those found in the original monomer. The observation of fluidity from 130°C suggests that the polydiacetylene is above its glass transition at temperatures at which liquid crystallinity is observed, and the unique texture suggests that the polydiacetylene is liquid crystalline. The DODBA polydiacetylene does not show signs of flow until above 200°C, at which point birefringence of the sample increases. From these observations, poly-5,7 DODBA may also show liquid crystallinity, though at much higher temperatures.

The 10,12 DHDP monomer has a relatively simple diffraction pattern compared to the other two monomers. As shown in Figure 3.24(a), strong peaks at 4.4 Å and 3.8 Å are the major features of the pattern. The crystalline peaks are somewhat broad, but well-defined, suggesting a well-organized crystalline structure. The locations of the dominant peaks correspond well to spacings in the triclinic cell of aromatic polyesters such as polyethylene terephthalate; in fact, as will be discussed in Chapter 4.0, the d-spacings correspond well to those of the polyester synthesized from 10,12 DHDP and terephthaloyl...
Figure 3.23 Wide Angle X-ray Diffraction of 5,7 DHDP: a) 0 Mrad; b) 100 Mrad
chloride. Considering the length of the flexible spacers in this monomer, it is not surprising that it assumes the crystalline structure of long chain crystalline polyesters. There are many peaks visible at low angle, including reflections corresponding to spacings of 32.1 Å, 16.7 Å, and 11.2 Å; these suggest crystalline spacings of approximately 33 Å, but the extended chain length of 10,12 DHDP is expected to be greater than 40 Å. The chain axis of the molecule might be tilted relative to the stacked layers of molecules in the crystalline lattice. The several weak peaks visible at much higher angles are second order reflections of the major diffraction peaks. The presence of higher order peaks for the small and wide angle reflections illustrates the excellent ordering of the crystalline phase.

10,12 DHDP is the most reactive of the monomers in the solid state. Its high level of reactivity may be due in part to its high degree of ordering, as well as the added flexibility of the long methylene sequences surrounding the diacetylene molecule. The irradiation of 10,12 DHDP yields a crystalline polydiacetylene at high conversions (estimated at 80%), as seen by the diffractogram in Figure 3.24b. The most noticeable change in the diffraction pattern is the increased relative intensity of the small angle peaks by two or three-fold. Improved long range ordering implies that the creation of the polydiacetylene backbone has enhanced the layer spacing of the monomer, which now exists as a mesogenic side chain connected to the polydiacetylene backbone. The d-spacing of the lowest order visible peak has shifted from 16.7 to 18.8 Å, and the 11.2 Å peak has shifted to 12.3 Å. These shifts indicate a change in lamellar spacing from approximately 33 to 38 Å, which is a sizable increase in lattice parameters. This information sheds light on the cross-polymerization process in the 10,12 DHDP monomer. Apparently, as the monomer converts to polymer, the mismatch in lattice spacings between monomer and polymer causes an adjustment in the arrangement of the side chains to allow expansion of the polydiacetylene chain. Changes in the intermolecular spacing included in this rearrangement are a shift from 3.8 to 3.9 Å, and the disappearance of the weak peak at 8.6 Å. This shift is probably facilitated by the rotation of methylene groups in the DHDP side chain, and the end result is a realignment of the side chains at an angle closer to the normal of the lamellar layers. The change in angle is seen as an increase in d-spacing, and the degree of tilt in the side chains is decreased from that in the original monomer lattice. The higher intensity of the peaks suggests that the registry between the polydiacetylene chains is more perfect than that in the monomer, as well. This effect might be further enhanced by improved hydrogen bonding opportunities between the side chain groups in the new arrangement. As discussed earlier, the resulting polydiacetylene is a side chain liquid crystalline polymer that melts from 100 to 120°, and clears above 160°C. The transitions of the polymer are easily seen in the DSC, even at low conversions, and because the
Figure 3.24 Wide Angle X-ray Diffraction of 10,12 DHDP: a) 0 Mrad; b) 100 Mrad.
monomeric transitions appear at much lower temperatures, it is easy to observe the optical texture of poly-10,12 DHDP. Examination of the differing effects of polymerization on monomer structure bring out trends in the effects of structure on reactivity. It appears that the monomers with four methylene spacers on either side of the diacetylene group were less reactive than the 10,12 monomer because of structural limitations. The crystalline lattices of 5,7 DHDP and 5,7 DODBA were not as conducive to the formation of polydiacetylene chains at high conversions because they lacked the flexibility to rearrange and thereby accommodate the polydiacetylene chains. Many diacetylenes exist in the literature that have just one, two, or four methylene spacers around the diacetylene, and are quite reactive. The increased spacer length therefore has some influence on reactivity in these systems, but other factors must also be accounted for. The distances between diacetylene groups, and the angles of the unit cell, have been found to be important parameters in diacetylene solid state reactivity \(^{24}\), and these values vary for each of the monomers. Finally, degree of conversion is undoubtedly affected by the perfection of the crystalline structure, which provides the alignment of diacetylene groups needed for solid state reactivity. 5,7 DODBA appears to have the least ordered crystalline structure, and it also displays the lowest conversion levels.

**Wide Angle X-ray Diffraction of Quenched Samples**

The X-ray diffraction pattern of 5,7 DODBA in the crystalline and liquid states are shown in Figures 3.25 a) and b). The liquid crystalline pattern was obtained by heating a sample to 145°C and quenching it in a dry ice/isopropanol bath. The resulting pattern is typical of a two-dimensional smectic phase such as smectic A or C. The amorphous halo indicates the loss of three dimensional short range ordering, although some very regular interplanar or intermolecular spacing remains, as seen by the two remaining peaks. The d-spacings of these peaks are 4.6 Å and 3.4 Å. The first peak corresponds to the location of a major peak in the crystalline state, and the second appears at an entirely new location, suggesting some rearrangement of the molecules from the crystalline to the smectic state. It should be noted that similar X-ray patterns were found for the smectic phases of polyester amides investigated by Aharoni \(^{28}\). This is especially interesting, because these polymers were also hydrogen bonding in nature, and the formation of batonnets is mentioned in this case, as is observed for 5,7 DODBA. The low angle diffraction peak remains, a definitive indication of a layered smectic phase. The spacing has shifted from 15.8 Å in the crystalline lattice to 16.1 Å between the smectic layers. This change is relatively small, and assuming that the reflection is a second order one, the spacing is approximately 32 Å. This corresponds relatively well to the extended length of the 5,7
Figure 3.25 Wide Angle X-ray Diffraction Pattern of 5,7 DODBA: a) crystalline; b) quenched state.
DODBA molecule, and the phase is therefore smectic A, with the molecular axis perpendicular to the smectic layers.

Quenching of the mesophase of 5,7 DHDP proved quite difficult, and even when cooled from temperatures well above the clearing point by quenching in liquid nitrogen, the same crystalline pattern was often obtained. However, partial quenching was achieved in some samples, as shown Figure 3.26. The weak reflections at 11.9 and 7.8 Å have disappeared, and the low angle peak corresponding to a long spacing of 20.7 Å has been replaced by a d-spacing of 23.2 Å, indicating some change in the arrangement of molecules in the new phase; the spacing is characteristic of a tilted molecular axis, as in the original monomer lattice. Also note that some of the diffraction peaks are moving to lower angles, and getting closer together. The doublet at two theta = 27° becomes a single, broad peak of lower intensity. A disordered halo at the base of the peaks has also developed, indicating disordering of the crystalline structure. This diffractogram may represent the DHDP monomer in mid-transition to a two or three-dimensional liquid crystalline structure. Most three dimensional smectic phases exhibit sharp Bragg peaks in the wide and small angle regions. Some potential smectic phase types with tilted molecular axes include smectics F, G, H and I. Smectic F phases are generally accompanied by smectic A or C mesophases, and no such phase has been observed for 5,7 DHDP. Smectic G and H phases have been reported for other diacetylenic liquid crystalline materials by Schen et al. and Ozcayir et al. Schen presents a diffractogram with several Bragg peaks, and reports a mosaic liquid crystalline texture. The textures described in section 3.2 included a schlieren mosaic texture seen in thinner regions, and a brushed texture seen at higher temperatures. There is a possibility that the phase change observed in 5,7 DHDP is really a crystal-crystal transition. However, the observation of melting, and the fact that this melt, though very viscous, was shearable, imply that an ordered liquid crystalline phase was present. At this time, no final conclusions can be made regarding the classification of this mesophase.

It was also difficult to quench the 10,12 DHDP monomer at a temperature between the two endotherms it exhibits at 75 and 90°C. By heating to higher temperatures and quenching, the diffractogram shown in Figure 3.27 was obtained. Again, this diffractogram appears to reflect the structure at mid-transition. The small angle peak and its reflections at low angle have nearly disappeared, perhaps to be replaced by a peak at an angle lower than the limits of the diffractometer. Peaks at high angles that were small and weak in the original monomer lattice appear to sharpen and increase in intensity, and one or two new peaks appear, as well. Like 5,7 DHDP, this monomer may exhibit a three-dimensional smectic phase or a crystal to crystal transition.
Figure 3.26 Wide angle X-ray diffractograms of 5,7 DHDP quenched from various temperatures.
Figure 3.27  Wide angle X-ray diffractograms of 10,12 DHDP: a) crystalline; b) partially quenched from liquid crystalline state.
Figure 3.28 Wide angle X-ray Diffractogram of irradiated 10,12 DHDP (100Mrad):
a) crystalline, b) quenched from LC state.
Finally, the 10,12 DHDP irradiated at 100 Mrad was heated to 150°C and then quenched, to yield the WAXD results in Figure 3.28. The small angle peak at 18 Å remains, although it has shifted to the right by a small amount. The major diffraction peaks have broadened and merged to form a split amorphous peak with some evidence of short range ordering. The focal conic regions seen under the optical microscope, as well as the d-spacing, which suggests tilted side chain configuration, lead to the assignment of a smectic C, or perhaps a three dimensional tilted smectic phase for this mesophase. Similar WAXD and optical microscopy observations were made for smectic C polyester amides by Aharoni.

3.5 Summary

A new series of reactive aromatic diacetylenes has been synthesized which contain dihydroxy or dicarboxylic acid functional end groups and long flexible alkyl spacer groups. Optical microscopy, thermal analysis, and wide angle X-ray diffraction were used to determine the solid state and mesogenic nature of each compound. Results indicate that the 5,7 DODBA monomer exhibits a highly stable smectic A liquid crystalline phase, which is quenched into the solid state upon cooling. The ordering of the mesophase is thought to consist of fully extended, dimerized diacid molecules. The diacetylene groups of 5,7 DODBA are moderately reactive in the liquid crystalline phase at temperatures near the clearing point. At these temperatures, a red-orange, nonbirefringent polymer is seen to appear after annealing times of a few hours. When held just above the clearing point, the diacid is highly reactive, forming a brown colored film. Finally, at higher temperatures, the monomer undergoes a combination of thermal polymerization and degradation. When irradiated in the solid state, 5,7 DODBA becomes pink or red. The solid state reactivity is relatively slow, but yields polymer of high conjugation length. The wide angle X-ray data of irradiated monomer suggest that despite this high degree of conjugation, the polymer formed is non-crystalline. It is possible that some sort of paracrystalline ordering is present in the poly-5,7 DODBA; perhaps residual ordering remains from the original crystalline or liquid crystalline lattice. Similar, dark red amorphous substituted polydiacetylenes have also been observed from isotropic and liquid crystal phase polymerizations by Schen and Werninck, as mentioned above. The partially polymerized monomer does exhibit birefringence, but does not flow until 200°C. The optical texture observed remains up to 230-240°C.
The 5,7 DHDP monomer exhibited an optically birefringent melt and liquid crystalline texture. Difficulties in quenching the dihydroxy compound prevent complete characterization of the phase observed between 145°C and 160°C. There is some possibility that this is a second crystalline phase, as diffraction peaks are seen in the partially quenched sample, but optical observations of a shearable melt suggest that a higher order smectic phase such as smectic G or H is present at these temperatures. Upon cooling, a second liquid crystalline texture is seen with a threaded mosaic pattern, suggesting the presence of a second monotropic (metastable) liquid crystalline phase at low temperatures. 5,7 DHDP is reactive in the liquid crystalline state, particularly at higher temperatures, and is highly reactive in the isotropic state. In both cases a gold-brown non-birefringent polydiacetylene of low conjugation length is obtained. The monomer is also fairly reactive in the solid state, producing gold, non-crystalline polydiacetylene, much like 5,7 DODBA. The irradiated monomer exhibited a different mesophase texture and temperature range than that of the fresh monomer, suggesting that the polydiacetylene may undergo a glass transition, followed by a mesomorphic phase, at these temperatures.

Finally the 10,12 DHDP monomer exhibits a narrow temperature range in which a birefringent melt is observed. It was difficult to verify the nature of this phase due to the narrow temperature span in which it is visible. Wide angle X-ray data of a partially quenched sample suggest the development of new Bragg peaks. This could be the development of a higher order smectic phase much like 5,7 DHDP, or a second crystalline form. 10,12 DHDP was relatively stable to thermal annealing in the solid and isotropic states. On the other hand, this was the most reactive monomer when irradiated with UV or electron beam irradiation; high conversions of polydiacetylene were obtained at 50 Mrad of electron beam irradiation. The partially polymerized 10,12 DHDP exhibited liquid crystalline behavior, indicating that a side-chain liquid crystalline polymer with a polydiacetylene conjugated backbone had been created. Only a few such polymers have been reported\textsuperscript{1-4}, and in this case the conjugation length of the purple-red polymer obtained is unusually high. It appears that the presence of unreacted monomer facilitates the exhibition of the mesophase.

The reactivity of each monomer varies a great deal. The 5,7 DODBA monomer, which has an imperfect, disordered crystalline structure at room temperature, was only moderately reactive to high dosages of radiation. Both of the DHDP monomers reacted to higher conversions, perhaps due to their well-ordered crystalline lattices. The 10,12 DHDP monomer was much more reactive than its 5,7 analog, indicating the important role that the number of flexible spacers appears to play in the solid state polymerization of these monomers.
The polydiacetylenes produced from each of the three monomers exhibit interesting and unique morphologies such as liquid crystalline and amorphous ordering, which are not common in polydiacetylenes. Amorphous polymers may be of interest in the development of optically transparent electro-optic devices. Liquid crystalline systems could be oriented in the mesophase to produce materials with highly anisotropic linear optical properties. In both cases, exciting new materials have been introduced to the class of polydiacetylenes.
References


21) Personal communication, C. Rosenblatt, Case Western Reserve University, Macromolecular Science Department, February, 1993.


Synthesis and Characterization of Polyester-Diacetylenes

Of the relatively small group of diacetylene containing polymers that have been investigated, most have been derivatives of relatively simple semi-crystalline linear polymers. The first diacetylene-containing aliphatic polyesters and polyurethanes were created and investigated by Wegner, and by Thakur and Lando. Rubner and associates have synthesized and extensively characterized a variety of diacetylene macromonomers, including segmented polyurethanes with diacetylenes in the hard segment repeat, as well as aliphatic and aromatic polyamides.

One of the most promising aspects of diacetylene macromonomers such as these has been the ability to induce a solid state cross-polymerization of the polymer without altering the morphology. These materials have been examined for their potential as post-processible structural materials, in which the mechanical properties may be altered simply by changing the dosage of irradiated energy. Another focus of these studies has been the exhibition of thermo- and mechanochromism in polymeric materials, optical properties which could be the basis of sensor or optical device applications.

A natural host polymer for the diacetylene moiety is the liquid crystalline polymer (LCP). The mechanical properties of many oriented LCP fibers or films could be enhanced by the cross-polymerization of diacetylenes in ordered regions of the polymer. Stiff polyaramids and rigid-rod polyesters exhibit poor transverse properties; the cross-polymerization process provides a way of increasing the intermolecular cohesion of highly oriented linear polymer chains such as those found in high strength, high modulus materials. However, the multi-phasic behavior of liquid crystalline polymers also provides an ideal host environment for the exhibition of conformationally induced thermochromic behavior. The opportunity to induce one or more chromic changes in a material at precise
temperature ranges determined by the liquid crystalline transitions of the host polymer is thus presented. Such polymers would provide the control needed to fully exploit the chromic behavior of polydiacetylenes for device applications. The optical characteristics of lightly cross-polymerized diacetylene liquid crystalline macromonomers is therefore of great interest. Finally, another interesting aspect of a diacetylene-containing LCP is the potential of locking in the liquid crystalline morphology of the linear aromatic polymer via liquid crystal state cross-polymerization. Previous attempts to permanently retain the liquid crystalline structure of polymers include the development of liquid crystalline side chain and main chain elastomers\textsuperscript{4,5}. Although the mesogenic nature of the polymer was preserved in most cases, the liquid crystalline phase itself was not permanently "locked-in" to the structure of the material.

To date, the only other diacetylenic liquid crystalline polyesters have been prepared by Blumstein and co-workers\textsuperscript{6}, who examined liquid crystalline polymers and copolymers based on dihydroxy diphenyldiacetylenes as well as 10,12 docosadiyne dioic acid. The diphenyl diacetylene polyesters were found to be thermally unstable above 175$^\circ$C due to the onset of cross-polymerization; this complication, combined with the high temperature transitions of the polymers, made it quite difficult to examine the liquid crystalline phases of these materials. Most of the polymers of this type exhibited nematic phases as well as multiple melting endotherms due to polymorphism. The solid state reactivity of these materials was not reported. For the second set of polyesters studied by Blumstein, the diacetylene group was placed in the flexible spacer portion of the polymer, and a variety of classical mesogenic groups were used. Out of five various mesogenic groups sampled, only polyesters incorporating a diphenyl or an alpha-methyl stilbene group exhibited mesomorphic behavior. These two polymers were also the only materials that were UV reactive in the solid state, probably due to a favorable crystalline structure. Neither of these polyesters were found to be thermally reactive.

Much of the potential for novel liquid crystalline diacetylenic polymers has yet to be explored. For example, little is known about the effect of the number of flexible spacers on the thermal or solid-state reactivity of liquid crystalline diacetylene macromonomers. Questions regarding the control of thermal stability of such materials also remain unanswered. The effects of crystalline and liquid crystalline structure on diacetylene reactivity and the effect of the diacetylene group on the mesomorphic behavior of the host polymer are also issues that must be addressed if the possibilities mentioned above for these novel materials are to be fully explored. In this chapter, these issues are discussed with respect to new diacetylenic polyesters based on dihydroxydiphenoxy or
dioxydibenzoic acid mesogens and flexible spacers of two different lengths, each containing the diacetylene group in the backbone.

4.1 Polymer Design and Synthesis

There is a large database of knowledge regarding the liquid crystalline nature and phase transitions of simple aromatic thermotropic semi-flexible polyesters\(^{7,12}\); this base of information is especially well-established for polyesters with mesogens based on phenoxy, oxybenzoic acid, and dicarboxy phenoxy groups. The chemical structures of these materials have been well correlated to their transition temperatures, mesogenic natures, and crystalline structures. For these reasons, these materials are excellent candidates to host the diacetylene moiety. It was also decided that the diacetylene group should be placed in the flexible portion of the polymer molecule to allow enough freedom of rotation to accommodate the packing favorable to the topochemical reaction of the diacetylenes. The structural requirements of the diacetylene polyesters described above are summarized in the following schematic:

![Schematic diagram of polymer structure]

The starting materials for these polymers are diacetylenic dioxy dibenzoic acid and dihydroxy diphenoxy aromatic diacetylenic monomers. The liquid crystalline behavior of these monomers, as well as their solid state and thermal reactivities, are discussed in detail in Chapter 3.0. The chemical structures of the monomers are as follows:

\[
\text{Diyne dioxydibenzoic acid (DODBA)} \quad \text{Dihydroxydiphenoxy diyne (DHDP)}
\]

\[
\begin{align*}
\text{Diyne dioxydibenzoic acid (DODBA)} & & \text{Dihydroxydiphenoxy diyne (DHDP)} \\
n &= 4 & n &= 4 \\
5,7 \text{ DODBA} & & 5,7 \text{ DHDP} \\
n &= 9 & n &= 9 \\
10,12 \text{ DODBA} & & 10,12 \text{ DHDP}
\end{align*}
\]

Each of the polyesters was synthesized using low temperature solution polycondensation of a diacid chloride with the appropriate diol. This method was chosen
to avoid high temperatures which might induce polymerization of the diacetylene groups of the monomer or the polymer product. A schematic of the polymerization route and the polyesters produced is given below:

\[
\begin{align*}
\text{HO} \quad \text{O} \quad \text{O} \quad \text{(CH}_2\text{)}_n \text{C} = \text{C} \quad \text{C} \quad \text{(CH}_2\text{)}_n \text{O} \quad \text{COH} \\
+ \quad \text{HO} \quad \text{OH} \\
\sim \text{C} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{(CH}_2\text{)}_4 \text{C} = \text{C} \quad \text{C} \quad \text{(CH}_2\text{)}_4 \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{DODBA/HQ}
\end{align*}
\]

\[
\begin{align*}
\text{HO} \quad \text{O} \quad \text{O} \quad \text{(CH}_2\text{)}_4 \text{C} = \text{C} \quad \text{C} \quad \text{(CH}_2\text{)}_4 \text{O} \quad \text{OH} \\
+ \quad \text{O} \quad \text{O} \quad \text{CCl} \\
\sim \text{O} \quad \text{O} \quad \text{(CH}_2\text{)}_4 \text{C} = \text{C} \quad \text{C} \quad \text{(CH}_2\text{)}_4 \text{O} \quad \text{O} \quad \text{O} \\
\text{DHDP/TC}
\end{align*}
\]

Details of the monomer and polymer synthetic methods are given in the Experimental Section (Chapter 2.0).

The solubilities of the 5,7 DHDP/TC and 5,7 DODBA/HQ polyesters were extremely low in all common organic solvents. 5,7 DODBA/HQ was found to dissolve in hexafluoro-isopropanol, and 5,7 DHDP/TC was only partially soluble in m-cresol.
Because of low solubilities, the molecular weights of these two polyesters could not be conveniently measured. However, the IR spectrum of both polyesters showed only small amounts of free acid and alcohol present in the polymer products, suggesting that true polymer, though of low molecular weight, had been formed. 10,12 DHDP/TC was soluble in several organic solvents, including warm acetone and chloroform. The inherent viscosity, which was measured at a concentration 0.5 g/dl in tetrachloroethane at 25°C, was found to be 0.36 dl/g. This value indicates a polyester of low molecular weight typical of many liquid crystalline polyesters synthesized in the same manner. Inherent viscosities of similar polyesters reported in the literature generally range from 0.2 to 0.6, although both higher and lower values can be found.

4.2 Thermal Analysis

All three of the polyesters synthesized exhibit a thermotropic liquid crystalline phase, and two undergo multiple melting behavior. The transition/temperature diagrams of each polymer are shown in Table 4.1. The enthalpies and calculated entropies of each transition are included in Table 4.2. The structures of these polyesters are quite similar to two series of polymers studied by Antoun, Lenz and Jin7. The first series of polyesters was based on dihydroxy diphenoxy alkanes and terephthalic acid, with structures like the DHDP/TC polymers, excluding the diacetylene groups. Series two included a polyester prepared from 1,10-bis(p-carboxyphenoxy) decane and hydroquinone, a material similar to the DODBA/HQ polymer, again with the exclusion of the diacetylene moiety. For both series, multiple melting endotherms were observed. This phenomenon is actually quite characteristic of aromatic polyesters, and in many cases, it is believed to be due to the melting and subsequent re-crystallization of smaller, less perfect polymer crystals8,9. A second possible cause of multiple melt endotherms or shouldered melt transitions is the presence of two distinguishable crystalline forms in a polymorphic material. Polymorphism is fairly common in both small molecule and polymeric liquid crystals, and is especially common in diacetylenic materials as well. For this reason, the true melting temperature of these polyesters has been designated as that of the endotherm corresponding to the melting of the solid phase and exhibition of the birefringent melt as indicated by optical microscopy. Lower temperature endotherms have been tentatively listed as crystal to crystal transitions, although they may be due to either polymorphism or the melting of less stable crystallites. Enthalpies of melting include both melt endotherms in these cases.
Table 4.1: Transition Diagram for Polyester-Diacetylenes

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA/HQ</td>
<td>K1 (105°C) K2 (141°C) LC (168°C) I</td>
</tr>
<tr>
<td>5,7 DHDP/TC</td>
<td>K (187°C) LC (227°C) I</td>
</tr>
<tr>
<td>10,12 DHDP/TC</td>
<td>K1 (110°C) K2 (129°C) LC (141°C) I</td>
</tr>
</tbody>
</table>

Table 4.2: Polyester-Diacetylene Enthalpy Information from DSC

<table>
<thead>
<tr>
<th>Polyester</th>
<th>T(K1-K2) °C</th>
<th>Enthalpy, kJ/mol</th>
<th>Entropy, kJ/mol °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA/HQ</td>
<td>105</td>
<td>1.48</td>
<td>0.0039</td>
</tr>
<tr>
<td>5,7 DHDP/TC</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>10,12 DHDP/TC</td>
<td>110</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polyester</th>
<th>T(K-LC) °C</th>
<th>Enthalpy, kJ/mol</th>
<th>Entropy, kJ/mol °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA/HQ</td>
<td>141</td>
<td>9.16</td>
<td>0.0221</td>
</tr>
<tr>
<td>5,7 DHDP/TC</td>
<td>187</td>
<td>6.19</td>
<td>0.0135</td>
</tr>
<tr>
<td>10,12 DHDP/TC</td>
<td>129</td>
<td>6.52</td>
<td>0.0162</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polyester</th>
<th>T(LC-I) °C</th>
<th>Enthalpy, kJ/mol</th>
<th>Entropy, kJ/mol °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA/HQ</td>
<td>168</td>
<td>5.15</td>
<td>0.0117</td>
</tr>
<tr>
<td>5,7 DHDP/TC</td>
<td>227</td>
<td>21.59</td>
<td>0.0431</td>
</tr>
<tr>
<td>10,12 DHDP/TC</td>
<td>141</td>
<td>7.78</td>
<td>0.0188</td>
</tr>
</tbody>
</table>
5,7 DODBA /HQ

At 141°C, the melting point of 5,7 DODBA/HQ is relatively low compared to the melt temperature of 5,7 DHDP/TC at 187 °C. The melt temperatures of these two polyesters might be expected to be close due to the similarities in their structures; both materials have the same number of methylene spacers, and differ only in the placement of the carboxy and phenoxy functionalities in the rigid mesogenic unit. In the aforementioned study by Lenz and associates, the non-diacylenic counterparts of these materials with 10 aliphatic spacer groups both melt at 237°C. On the other hand, Strezelecki and van Luyen synthesized polyesters with the same mesogenic core as DODBA/HQ and a varying number of flexible aliphatic segments. These researchers described the same polymer as that reported by Lenz as melting at 105°C to form an unidentified smectic phase; the final transition from nematic to isotropic is reported to occur at 270°C. The DODBA/HQ polymer contains eight aliphatic spacers plus four additional carbons in the form of the diacetylene group located in the middle of the flexible segment; similar melt and mesogenic behavior would be expected from this polymer as that of the polymers of Lenz and Strezelecki, though the differences in flexibility of the spacer groups might have some effect. The low melting point of 5,7 DODBA/HQ (at 141°C) better corresponds to the observations of Strezelecki and van Luyen than to those of Lenz. The clearing point of 5,7 DODBA/HQ is definitely lower than any of the values reported for the non-diacylenic polyester. In fact, Lenz found the mesogen of the polyester which is similar to DODBA/HQ to exhibit higher clearing points, and thus to have higher thermal stability, than the mesogen similar to that in DHDP/TC; the reason given for this observation was that the latter mesogenic group does not form a completely coplanar geometry. The opposite appears to be true in the case of the diacetylene-polyesters when the clearing points are compared to each other. Some reasons for the discrepancies between the melting and clearing temperatures found here versus those in the literature include the possibility that, despite the many structural similarities, the presence of the diacetylene group in the flexible spacer is more disruptive of the crystalline and liquid crystalline packing of 5,7 DODBA/HQ than of 5,7 DHDP/TC. Also, the melting point of DODBA/HQ may be low due to a highly disordered or imperfect crystalline structure. This possibility will be discussed with the wide angle X-ray results. Finally, there is the possibility that 5,7 DODBA/HQ is of considerably lower molecular weight than 5,7 DHDP/TC, thus causing an overall lowering of the transition temperatures.

The differential scanning calorimetry (DSC) results for 5,7 DODBA/HQ are shown in Figure 4.1. A liquid crystalline phase is observed between the large melt endotherm at 141°C, and the clearing point at 168°C. The smaller peak at 105°C is due to either a solid
Figure 4.1 DSC/TGA results for 5,7 DODBA/HQ.
Figure 4.2  DSC of 5,7 DODBA and 5,7 DODBA/HQ.
state transition, or the melting of less perfect polymer crystals, as discussed above. The large exotherm at 324°C is due to a combination of large scale thermal cross-polymerization and degradation. Thermogravimetric analysis confirms that some degradation does occur from 300 to 400 °C, with a corresponding weight loss of approximately 50%.

Figure 4.2 compares the thermal behavior of 5,7 DODBA/HQ with the diacid monomer 5,7 DODBA, from which it was polymerized. As expected, polyesterification has caused an increase in the melt temperature from 110°C to 141°C. However, it is interesting to note that the clearing point of the polyester is considerably lower than that of its monomer at 190°C. This effect is due to the fact that the liquid crystalline nature of the monomer is due in part to hydrogen bonding between the carboxylic acid moieties, as well as to the presence of rigid aromatic end groups. When the polyester is formed, this hydrogen bonded structure is eliminated, and the liquid crystalline behavior is determined by the rigidity of the mesogenic unit alone. In short, the strong intermolecular forces of the monomer are not present in the polymer to further stabilize the mesogenic melt. Note that the isotropization enthalpy of 5,7 DODBA monomer is also higher than that of the polymer, confirming that the breakup of the liquid crystalline phase of the diacid requires the breakup of greater stabilizing forces. Details on the thermal and optical properties of 5,7 DODBA are discussed in greater detail in Chapter 3.0.

The 5,7 DODBA/HQ polyester was heated in the DSC to temperatures above the clearing point and immediately cooled to produce the heat/cool cycles shown in Figures 4.3 to 4.5. When taken to 220°C, the polyester does not undergo any further transitions either during the cooling or the second heating and cooling scans (see Figure 4.3). When examined following this experiment, the 5,7 DODBA/HQ had turned a dark brown color, suggesting that thermally induced cross-polymerization had occurred. Degradation is ruled out as a possibility, as no weight loss occurs below 300°C. The brown color indicates that a low conjugation length network has been formed, with highly disordered polydiacetylene chains. To better determine at which point this reaction occurs, similar heat/cool cycles at 200°C and 180°C were performed; the first and second heatings for each case are shown in Figures 4.4 and 4.5 respectively. The endothermic transitions are partially recovered in each case, with the greatest recovery in the 180°C cycle. The melt enthalpies can be used to determine the extent of polymerization. At 220°C, the polyester undergoes close to 100% conversion. Heating to 200°C results in approximately 90% conversion, and cycling to 180°C produces only 42% conversion. These numbers suggest that the cross-polymerization takes place primarily in the isotropic phase during the time frame of this experiment, producing a network of amorphous polymer chains. The polymerization takes
Figure 4.3 Heat/Cool Cycles of 5,7 DODBA/HQ to 220°C
Figures 4.4 (top) and 4.5: First and Second Heatings of 5,7 DODBA/HQ to 200°C and 180°C.
place quite rapidly, without the need to hold the polymer at a fixed temperature for any given amount of time.

In Figure 4.5, one can see that generally the same transition endotherms are reproduced on the second heating, with a slight increase in temperature and some broadening of the peaks; however, it does appear that the low temperature melt endotherm at 105°C is no longer evident. It is not unusual that less stable crystalline forms or imperfect crystals do not reform during the second half of a cycling experiment, as the polymer recrystallizes into its more stable forms on cooling. The cooling curves of all of the heat/cool cycle experiments were relatively featureless down to 50°C. Recrystallization may proceed slowly, and at lower temperatures, due to the effect of the increased viscosity of the liquid crystalline melt on recrystallization kinetics.

Although thermal crosslinking proceeds relatively quickly in the isotropic melt, it is also possible to induce thermal cross-polymerization in the liquid crystalline state of 5,7 DODBA/HQ as well by holding the polymer at a temperature between $T_m$ and $T_i$ for a length of time. The polymer begins to turn light brown, and then dark brown over a period of two or three hours. The melt gradually becomes a dry, hard film that will no longer flow at the liquid crystalline temperature. This film is no longer birefringent, suggesting that the liquid crystalline texture is not maintained during thermal cross-polymerization in the liquid crystalline state. One reason that the thermally activated cross-polymerization process does not preserve the mesophase texture may be that the thermal polymerization mechanism is such that morphological characteristics are not retained, as they are in solid-state topochemical reactions. Thermal crosslinking of 5,7 DODBA/HQ probably involves the rearrangement of polymer segments in the liquid crystalline or isotropic melt to allow diacetylene groups the proximity needed for reaction.

5,7 DHDP/TC

The transition temperatures of the 5,7 DHDP/TC polyester are the highest of this group of liquid crystalline diacetylene-containing polyesters, with a melting point at 187°C and a clearing transition at 227°C. The DSC thermogram in Figure 4.6 as well as the enthalpy data in Table 4.2 also illustrate the fact that the temperature range of liquid crystallinity is wide, with a 40°C span of mesogenic behavior, and the relative size of the clearing endotherm is unusually large; both facts suggest that the liquid crystalline phase of 5,7 DHDP/TC is highly stable. Although typically the isotropization enthalpy of small molecule liquid crystals and many polymeric liquid crystals is lower than the melt enthalpy, in this case, the clearing enthalpy is over three times larger than the melt. This observation has been made for other main chain semi-rigid liquid crystalline polyesters as well; for
Figure 4.6 DSC/TGA results for 5,7 DHDP/TC
Figure 4.7 DSC of 5,7 DHDP and 5,7 DHDP/TC
example, the polyesters based on dicarboxy and dihydroxy diphenoxyl alkanes studied by Griffin and Havens\textsuperscript{9}, the azoxy and azo-based polymers of Iimura et. al.\textsuperscript{10}, and the polyesters based on dihydroxy benzophenone and sebacoyl chloride prepared by Makaruk et. al.\textsuperscript{11}. Griffin and Havens suggest that the imperfect semi-crystallinity of most polymers accounts for some of this discrepancy, since the melting enthalpies of polyesters cannot be as low as their model ester counterparts\textsuperscript{9}. Meurisse and coworkers discussed similar reasons for the enthalpic data of their aromatic-aliphatic terphenylene based polyesters\textsuperscript{12}. The isotropization process, on the other hand, involves the randomization of long polymer chains oriented in a melt, a process which requires considerably more energy than the randomizing of small liquid crystal molecules. Krigbaum and Salaris propose\textsuperscript{14} that the high levels of order found in polymeric liquid crystalline melts (particularly in the nematic phase) is due to the conformational energy needed to accommodate the correlation of chain bends needed to provide good packing of long chain molecules. The size of the liquid crystal to isotropic enthalpy may also indicate that this polymer exhibits a smectic rather than nematic phase; smectic phase transition enthalpies are generally quite a bit higher than nematic transitions\textsuperscript{15}. In any case, the mesogenic phase of 5,7 DHDP/TC is a highly stable, possibly well-ordered, melt.

The cross-polymerization/degradation exotherm reaches a minimum at 300°C, with an enthalpy of 260 kJ/gmol of repeat unit. This value is actually very close to the enthalpies found for thermal polymerization by several researchers\textsuperscript{16}; the value of approximately 250 to 300 kJ/gmol appears to be characteristic of the high temperature exotherms found in the majority of diacetylenic materials. The solid state polymerization enthalpy, on the other hand, is 150-160 kJ/gmol, and in many cases, the discrepancy is thought to be due to coincident degradation. For 5,7 DHDP/TC, the exotherm seems to be accompanied by only a 5% weight loss from 270°C to 350°C, and a subsequent weight loss of 45% corresponds to an exothermic shoulder at 400 to 475°C. This suggests that the initial degradation associated with small weight loss and the thermal polymerization processes are easily separated from the large scale second degradation process for this diacetylenic polyester, unlike 5,7 DODBA/HQ. Another potential explanation for the high value of the exotherm enthalpy is that the crosslinking is taking place via a different, thermally activated mechanism, as opposed to the solid-state radiation initiation mechanism. Blumstein studied the thermal and UV polymerization processes of various diacetylene monomers, and discovered that the structures of the isotropic melt-polymerized diacetylenes were products of 1,2 addition of the diacetylene linkage; those produced via UV irradiation were 1,4 polymerization products\textsuperscript{17}. 
Figure 4.7 includes the DSC of the 5,7 DHDP diphenoxy monomer and the 5,7 DHDP/TC polyester. The melt temperature increased from 145°C to 187°C with polycondensation, and the clearing temperature increased from 165°C (observed on the second heating of 5,7 DHDP monomer) to 227°C. These changes resulted in an increase in the temperature range of mesogenic behavior from 20°C to 40°C. Unlike 5,7 DODBA, the 5,7 DHDP monomer has less of a hydrogen bonded nature, and intermolecular forces do not play as key a role in stabilizing the monomeric liquid crystalline phase. Polymerization increases the number of rigid groups in the mesogenic unit from one to three, and therefore, the mesophase is further stabilized not only by macromolecular entropic effects, but by the increased axial ratio of the mesogenic unit. The effects of mesogen rigidity on the isotropic clearing transitions of polymers are discussed in great detail by Donald and Windle\textsuperscript{18}; the melting point of LCP's is affected by molecular weight, intermolecular forces, and crystalline structure, but the isotropic clearing point is most greatly affected by the rigidity and the aspect ratio of the mesogenic group.

The heat/cool cycling of 5,7 DHDP/TC presents some rather unusual thermal behavior, as shown in Figure 4.8. A single melting and a very large clearing endotherm are evident on heating in the first cycle. However, upon cooling, a much smaller exotherm appears at 215°C, which must correspond to the isotropic to mesogenic transition, although the size of the exotherm is much smaller than the original endotherm. An exothermic shoulder appears at 195°C, followed by the recrystallization exotherm at 180°C. The second heating indicates a shouldering of the original melt endotherm onto the isotropic clearing peak. The melt transition has increased to 215°C, and it appears that the clearing point has shifted to slightly lower temperatures. Finally, a second cooling reproduces the small exotherm seen in the first cooling at approximately 205°C along with a greatly supercooled recrystallization at 145°C. Note that the size of the recrystallization exotherm is much smaller in this second cycle. This heat/cycle experiment was found to be quite reproducible when repeated a second time. However, in a similar heat/cool experiment in which 5,7 DHDP/TC was taken to 250°C, just near the "tail" of the broad clearing endotherm, both the isotropic to liquid crystalline and the recrystallization exotherms were restored upon cooling, as shown in Figure 4.9; the size and shapes of the exotherms are more consistent with their corresponding endotherms in the heat cycle than in the higher temperature heat/cool series. A second cycle illustrates that the melt endotherm has merged into the clearing point; however, the second cooling curve is relatively similar to the first cooling curve, with both mesogenic transitions visible at approximately the same places.

The lack of complete reversibility found in the 270°C cycle is due to the high thermal reactivity of the diacetylene groups of 5,7 DHDP/TC, as well as the onset of
Figure 4.8 Heat/cool cycles of 5,7 DHDP/TC to 270°C
Figure 4.9 Heat/cool cycles of 5,7 DHDP/TC to 250°C.
degradation that occurs at 270°C. The polymer has a tendency to polymerize relatively quickly above the clearing point, turning a dark brown to black color in the process. In fact, when the polymer is heated to 270°C and held for 10 minutes, no further thermal transitions could be observed in subsequent cooling or heating experiments, suggesting complete thermal crosslinking to form an infusible network. Similar observations of irreproducible heat/cool cycles were made for one of the diphenyl diacetylene based polyesters studied by Ozcayir et. al. in which there were seven flexible spacers; in this case, the differences in subsequent cooling curves were also attributed to thermally activated cross-polymerization. Due to the effects of this cross-polymerization, as well as the annealing effects of the first heating cycle, the melting point of the polyester is increased, causing it to shoulder onto the clearing point. This shouldering is seen in both the 250 and 270 °C cycle, an indication that thermal annealing plays a large role in the increased $T_m$. Cross-polymerization also results in a reduction in the size of each of the polymeric transitions by restricting the mobility of the polymer chains. This explains the large decrease in the melting and clearing endo- and exotherms observed following the first heating to 270°C. Finally, the higher melt viscosity of the partially cross-polymerized network may have been sufficient to create a large supercooled effect on the recrystallization exotherm shown in Figure 4.8. The more reproducible results of the 250°C cycle indicate that the extremely high levels of reactivity experienced at the clearing point and isotropic liquid are not present in the mesophase.

10,12 DHDP/TC

The DSC and TGA results of 10,12 DHDP/TC are shown in Figure 4.10. This polymer is the analog of 5,7 DHDP/TC in which there are nine instead of four methylene spacers on either side of the diacetylene group. The result of lengthening the flexible spacer by a total of 10 more aliphatic spacer units is a polymer with much lower transition temperatures, and a very narrow window of mesogenic behavior. The polymer exhibits a broad melting endotherm centered at 129°C, and an isotropic clearing point at 141°C. The shoulder at 110°C is thought to be due to the melting of a less stable crystalline form of the polymer, which is present in very small quantity. Thermal annealing at 90 to 110°C generally results in a decrease in or disappearance of the shoulder. The exotherm at 320°C has an enthalpy of 147 kJ/mol, which is quite close to the values found for solid state 1,4 polymerization of the diacetylene groups. Unlike the 5,7 polyesters, 10,12 DHDP/TC appears to be thermally stable at the temperature of thermally induced polymerization; as seen from the thermogravimetric analysis, weight loss does not occur until 400°C, upon the appearance of a separate high temperature endotherm. This means that thermal cross-polymerization can take place in the isotropic state of this polymer without simultaneous
Figure 4.10 DSC/TGA results for 10,12 DHDP/TC.
degradation. A small minor exotherm is also observed at approximately 225°C; the cause of this slight dip in the baseline is unclear, but some possibilities include thermally activated cross-polymerization via a slightly different mechanism, or some barely detectable degradation; in fact, a minor (3-4%) weight loss is detected here; although no physical changes are observed in the material at this temperature. When compared to its starting material, 10,12 DHDP, it is clear that the 10,12 polyester has an increased melting temperature (see Figure 4.11). Both the monomer and its polyester are quite thermally stable, and both are UV reactive at room temperature, as will be discussed in the following section. Although the liquid crystalline nature of 10,12 DHDP was not very clear, the 10,12 DHDP/TC polyester exhibits definite liquid crystalline behavior. As was the case for 5,7 DHDP/TC, the resultant polyester has a much larger, more rigid mesogenic unit consisting of three aromatic rings.

As with the other diacetylenic polyesters, the heat/cool cycle results from DSC experiments differ with the temperature to which the polymer is taken. What is different about the 10,12 polyester is that its high thermal stability eliminates to a large extent the problem of cross-polymerization above the clearing point. The heat/cool cycle up to 200°C is shown in Figure 4.11. The cooling cycle exhibits a small and very broad exotherm at 130 to 135°C indicating the transition from the isotropic to the liquid crystalline state, and a large exotherm at 100°C indicates a supercooled recrystallization transition. The sizes of the exotherms correspond well to their respective endothermic counterparts, and the cycle is relatively reproducible, as seen by the second cycle. In fact, heat/cool cycles at temperatures from 200 to 275°C were highly reproducible, with the sizes of the endotherms decreasing significantly on the second heating only for the 275°C cycle. There were differences in the cooling curves collected from various start temperatures. Figure 4.13 contains the cooling curves of 10,12 DHDP/TC taken to each of four temperatures. As the polyester was heated to higher temperatures, the degree of supercooling of the recrystallization endotherm became greater, and the recrystallization exotherm broadened, until, when cooled from 275°C, the exotherm is no longer clearly visible above 50°C. In all of these cases, recrystallization is complete, as the second heating cycle is generally unchanged from the first. Cooling from higher temperatures simply affects the rate and temperature at which recrystallization occurs.

Examination of Figure 4.11 reveals the fact that the melt endotherm appears to have a shoulder at both 110°C and 120°C. The second shoulder, more evident in the second heating, indicates that the broad melting endotherm is actually a combination of two individual transitions. The shouldered peak could be another example of multiple melting behavior in polyesters. However, because melting is actually observed at approximately
Figure 4.11  DSC of 10,12 DHDP and 10,12 DHDP/TC
120°C, the second portion of the peak could be attributable to a liquid crystal to liquid crystal transition. This possibility is further discussed in the section on optical microscopy below.

Finally, the thermal stability of 10,12 DHDP/TC was further examined using an isothermal heating experiment in the DSC. The polyester was held at 135°C for 1 hour, then cooled to room temperature and thermally scanned from 50 to 200°C to determine changes in the thermal behavior. The isothermal experiment simply resulted in a very slow, monotonically increasing heat rate, with no clear sign of significant reaction of the diacetylene groups. The second thermal scan indicated the merging of the melting and clearing endotherms to form one large peak with close to the same total enthalpy of the original peaks. The merging of peaks is probably due to thermal annealing effects rather than the effects of cross-polymerization. Examination of the polymer sample after the annealing experiment indicated only a slight color change from white to pale blue. These results verify the fact that, unlike the 5,7 polyesters, 10,12 DHDP/TC is not prone to thermal cross-polymerization in the liquid crystalline state.

4.3 Optical Microscopy

The mesogenic nature of the diacetylene-polyesters and the correlation of their optical behavior with thermal transitions was examined using polarized light microscopy. All three of the polymers exhibited the ordered, birefringent melts characteristic of liquid crystalline phases. In all cases, the natural textures of the mesophases were observed from samples of the as-prepared powder pressed between a glass slide and a cover slip, and then heated to the melting point. In some cases, thin films of the polymers cast onto glass slides were used as well. The 5,7 DODBA/HQ and 5,7 DHDP/TC polyesters displayed the ill-defined textures often found to be characteristic of polymers, but the 10,12 DHDP/TC liquid crystalline texture was more easily identifiable. Details of the optical characterization follow.

5,7 DODBA/HQ

When the as-polymerized powder of 5,7 DODBA/HQ is heated, a dim, fine birefringent texture appears upon melting at approximately 140°C. Annealing the polymer in the molten state allows this texture to fully develop. The mesophase appears brighter, and its pattern somewhat better defined, when no cover slip is used. Thick regions of the polymer melt exhibited a sanded, granular, metallic texture which is often attributed to polymeric smectic mesophases, as seen in Figure 4.14 (a). Thinner regions had a dim, more complex pattern consisting of myriad tiny domains. When the polymer melt was
Figure 4.12 Heat/cool cycles of 10,12 DHDP/TC to 200°C
Figure 4.13 Cooling curves of 10,12 DHDP/TC from various temperatures
sheared, it flowed, producing bright regions of highly birefringent polymer (see Figure 4.14 (b)). The melt, though viscous, flowed with relative ease when sheared. There is no indication of the threaded or schlieren textures commonly seen in nematic main chain polymers; this fact, along with the sanded texture, suggest that DODBA/HQ exhibits a smectic phase. It is worth noting, however, that both nematic and smectic semi-rigid polyesters can potentially exhibit the kinds of ill-defined textures described above, and, particularly in this case, the mesophase texture alone cannot be used to determine the type of liquid crystalline phase observed. As discussed in the previous section, polyesters which have very similar structures, though without the diacetylenic group, were synthesized by both Lenz and co-workers and Strezelecki and van Luyen with a varying number of flexible aliphatic segments. Lenz characterized the polymer mesophase of the n = 10 analog as nematic. On the other hand, Strezelecki and van Luyen described the same polymer as exhibiting two consecutive smectic phases, followed by a nematic phase at high temperatures. The differences in the conclusions between the two groups illustrates the difficulty in identifying this type of polymeric mesophase. In any case, the mesophase appears to be a disordered smectic or possibly a nematic phase. X-ray diffraction at small angles is needed for any further elucidation on the nature of the phase.

The DODBA/HQ mesogenic behavior was reversible up to 170° or 180°C, but each subsequent heating cycle produced less birefringence, and by the third and fourth cycles, little or no birefringence was observed. The polyester turns a deep brown color after exposure to these temperatures, and there is a clear indication that some cross-polymerization occurs during the experiment while in the liquid crystalline state, and particularly when near the clearing point.

5,7 DHDP/TC

When heated to 190°C, melting is observed in 5,7 DHDP/TC, and it is accompanied by the appearance of a dim, complex birefringent pattern. The as-polymerized sample, which is in a powder form, does not fuse or flow easily at these temperatures, and only after pressing down on the cover slip does a bright, shearable melt become evident. This highly birefringent melt is colorful, and its patterns change with rotation of the polarizer, but it has no definable texture. Figure 4.15 contains a photograph of the highly birefringent sheared region as viewed with crossed polarizers. The mesophase is probably a nematic or disordered smectic phase, and appears to be similar in nature to the mesophase of 5,7 DODBA/HQ. Further heating to 270 - 280°C causes the unsheared, dim birefringent patches to clear out. Areas that were sheared by the coverslip tended to simply
become dimmer. At approximately 280°C, signs of degradation, such as blackening at the edges of the film, became evident.

This polyester, like the 5,7 DODBA/HQ sample, was prone to cross-polymerize when heated to its liquid crystalline state. In fact, the polyester turns a very dark orange to brown color when held between 200°C and 230°C for times as short as 10 minutes. Although liquid crystalline behavior is still observed after holding the material at this temperature range for short time periods, the viscosity of the melt appears to increase slightly, and the birefringent regions become somewhat dimmer.

10,12 DHDP/TC

The liquid crystalline textures of 10,12 DHDP/TC are more easily recognizable than those of the polyesters with n=4 methylene spacers on either side of the diacetylene group. Upon heating the as-polymerized powder, little or no change is observed until approximately 125 to 130 °C, when melting results in a threaded, fine schlieren texture. At 135 to 148°C, this texture clears out, but as it clears, isolated focal conic and batonnnet structures become evident. All birefringent texture disappears by 160°C. Upon cooling, the batonnets reappear at 140°C and quickly grow and coalesce to form a focal conic texture, as shown in Figure 4.16(a). Further cooling causes the disappearance of the needle-like focal conic texture at approximately 132 to 128°C, and a threaded schlieren texture much like that seen on heating is observed. The transition from the batonnet/focal conic texture to the threaded texture is shown in Figure 4.16(b), and the fully developed schlieren texture is shown in Figure 4.16 (c). Thus, there appear to be two distinct liquid crystalline textures that appear above the melting point of the polyester. These observations suggest that the polymer exhibits a smectic C phase at lower temperatures, which is characterized by fine schlieren textures; at higher temperatures, the batonnet/focal conic mesophase typical of either a smectic A or C phase appears. It is possible that only one mesophase, smectic C, exists for 10,12 DHDP/TC. However, it has been found that the polymer may be oriented into a homeotropic texture, which is possible for smectic A but not smectic C phases. This, plus the marked transition to different textures, leads to the conclusion that two phases may be present. The transition from smectic A to C appears to take place at approximately 130°C during cooling, and at 135°C upon heating. The DSC results for 10,12 DHDP/TC discussed in the previous section further corroborate the optical microscopy observations. The shoulder of the DSC melting endotherm at 120°C appears to be the true melting temperature from crystal to smectic C, and the shift in slope of the peak at 130 to 135°C might correspond to the smectic A to C transition. The fact that two individual exotherms are not seen on cooling is not surprising, as it is common for
Figure 4.14 a) Natural sanded metallic texture of 5,7 DODBA/HQ in LC state, cooled to 116°C, 800 Mag.

Figure 4.14 b) Sheared region of 5,7 DODBA/HQ in LC state, cooled to 130°C, 2000 Mag.
Figure 4.15  Liquid crystalline texture of 5,7 DHDP/TC, 220 °C, 800 Mag.

Figure 4.16 a) Batonets coalescing to form focal conic texture in 10,12 DHDP/TC, 141 °C, 800 Mag..
Figure 4.16 b) Transition to schlieren texture of 10,12 DHDP/TC, 130°C, 2000 Mag.

Figure 4.16 c) Schlieren texture of 10,12 DHDP/TC, 130°C, 2000 Mag.
smectic A to smectic C transitions to be relatively small and second order by nature, and there are even cases where such transitions do not yield any transitions in the DSC\textsuperscript{14}.

In general, the textures observed upon cooling were clearer and more easily identifiable than those observed on heating. The transitions were quite reversible, and could be cycled back and forth several times without a loss of mesogenic behavior. The polyester does not exhibit very much color change within the temperature range of these experiments; this is consistent with observations of its thermal stability discussed in the preceding section.

It is interesting to compare the mesogenic nature of the three polyesters. Both of the 5,7 polyesters, in which there are \( n=4 \) flexible spacers on either side of the diacetylene group, exhibit either a nematic or disordered smectic phase; in both cases, the texture is unclear and ill-defined. However, the 10,12 DHDP/TC polymer \((n=9)\) not only displays more definite smectic textures, but may exhibit two smectic mesophases. Several studies have connected the exhibition of smectic phases in main chain thermotropic polyesters to long flexible spacer sequences\textsuperscript{20}. Examples include a study by Lenz and Jin\textsuperscript{21} of polyesters based on oxybenzoic and dicarboxy phenoxy mesogenic groups, and aliphatic or ethylene oxy spacer units; for both types of spacers, increasing the number of flexible groups caused a change in the mesophase type from nematic to smectic. This transition occurred at nine spacer groups for the aliphatic flexible sequences. The extension of the flexible spacer length of the DHDP/TC polyester from a total of 8 to 18 methylene groups would explain the strong tendency toward the more ordered smectic phases exhibited in the 10,12 polymer. Also, the lower viscosity of the 10,12 polyester may allow the development of better defined textures. The overall decrease in rigidity of the polyester, however, also decreases both the melting and clearing points relative to the 5,7 polyesters, as well as the temperature range over which liquid crystallinity exists.

The liquid crystalline diacetylene-containing polyesters investigated by Blumstein et. al.\textsuperscript{6} were based on 10,12 docosadiyn-dioic acid and biphenyl or alpha-methyl stilbene mesogens; both of these polymers exhibited highly ordered smectic H phases at the relatively low melting temperature of 122°C. The biphenyl based polyester displayed liquid crystallinity up to 161°C, resulting in a mesophase temperature range of approximately 40°C. This mesophase therefore appears to be more stable than smectic phases present in 10,12 DHDP/TC, which exist over a 15 to 20 °C range. On the other hand, Blumstein's alpha-methyl stilbene polyester has a very brief temperature span of mesogenic behavior, from 122°C to 134°C, indicating that its mesophase is less thermodynamically stable. The fact that a smectic phase was found in all of the diacetylene-polyesters with \( n=9 \) spacer groups suggests that the length of the spacer does
directly influence the smectic characteristics of the polymer. The different types of mesogens used seemed to affect the type of smectic phase that is expressed, i.e., smectic H as opposed to smectic A or C.

4.4 Effects of Solid State Cross-polymerization

The solid state reactivity of the three polyesters varies not only with the polymer structure, but with the type of radiation source used to induce cross-polymerization. Certain polyesters were more receptive to crosslinking upon exposure to electron beam, ultraviolet irradiation, or thermal annealing below the melting point. Large differences were also found regarding the ordering of the resulting polydiacetylene backbone. Such differences may be assessed by the observation of the visible absorption spectrum of the cross-polymerized material. Detailed optical studies of these materials will be discussed in Chapter 5.0; however, a relatively quick assessment of the level of planarity of the conjugated system can be made by simply observing the color of the irradiated sample. Fairly low conjugation lengths and highly disordered polydiacetylene chains tend to appear yellow or brown in color; on the other hand, blue or purple colors indicate high conjugation lengths, and therefore a larger degree of planarity of the polydiacetylene backbone.

Thermal annealing of films cast from hexafluoro-isopropanol and of the as-polymerized 5,7 DODBA/HQ solid at 90-100°C overnight caused only a minor color change in the film from white to a pale beige color. Heating to slightly higher temperatures on a hot plate resulted in a light brown color visible in the polymer, whose natural color is off-white or beige. In fact, 5,7 DODBA/HQ was generally the least responsive polyester with regard to cross-polymerization in the solid state. This is in great contrast to the high thermal reactivity of the polymer in the liquid crystalline state, and the highly rapid cross-polymerization that occurs just beyond the isotropic clearing point. 5,7 DHDP/TC powder, however, does begin to turn a deep yellow to dark orange color when heated on a hot plate at temperatures below the melting point of the polyester for time periods ranging from several minutes to four or five hours. The moderate intensities of color obtained by annealing 5,7 DHDP/TC suggest that moderate to low degrees of cross-polymerization can be obtained using this method. Finally, 10,12 DHDP/TC films and solid powder turn a medium to light purple color when annealed at 90°C for several hours. In fact, a color change from clear to blue can be detected after annealing times as short as 30 to 40 minutes. The effects of thermal annealing are sufficient to produce lightly cross-polymerized films of 10,12 DHDP/TC. These results indicate that the DHDP/TC polyesters are more responsive
to thermal treatments below the melt temperature than the DODBA/HQ polyester. Possible reasons for these results include differences in the crystalline structure of the DHDP polyesters versus the DODBA polyester, or perhaps differences in the degree or perfection of crystalline order obtained in the polymers.

Ultraviolet irradiation yielded somewhat similar results. 5,7 DODBA/HQ exhibits little or no color change upon exposure to ultraviolet light, despite attempts to anneal polymer films and powders prior to irradiation. Exposure times as long as four days have given only slight color changes to tan or light brown. 5,7 DHDP/TC powder does cross-polymerize under the UV lamp, turning from white to a light yellow color; polymer "films" cast from partially dissolved polyester in tetrachloroethane or m-cresol turn slightly deeper yellow colors upon irradiation for several hours. These films turn yellow-orange upon annealing at relatively high temperatures, indicating further cross-polymerization. Finally, thermally annealed films of 10,12 DHDP/TC cast from toluene, benzene, and tetrachloroethane turn blue or purple under the UV lamp. A film annealed for 24 to 72 hours at 90°C will turn from light blue (from oven annealing) to a relatively darker shade of blue or purple in the UV lamp after one or two hours. UV exposures for long time periods result in a shift in absorption due to conformational changes in the polydiacetylene backbone as the conjugated network begins to predominate over the original crystalline lattice. The net result is a reddish color rather than the original blue or purple color. It was found that although 10,12 DHDP/TC is always UV-reactive, the color obtained is highly dependent on the thermal history of the sample; these colors range from yellow to red to purple depending on the degree of annealing. This reflects the different morphologies that may be found in 10,12 DHDP/TC, as discussed briefly in earlier sections. It appears that the degree of crystallinity, as well as the crystal structure, greatly influence the level of diacetylene reactivity and the conjugation length of the polydiacetylene product.

All of the polyesters exhibit some color change when exposed to electron beam irradiation. Thermal analysis of the irradiated materials has been performed to better quantify the degrees of conversion obtained for each polymer upon electron beam irradiation.

Irradiation of 5,7 DODBA/HQ produces a brown solid which remains relatively insoluble in most solvents. The DSC thermogram of the irradiated polyester is shown in Figure 4.17. Crosspolymerization results in the broadening of the endothermic transitions into one large peak centered at 156 °C, but extending from 60 to 180°C; the estimated enthalpy of this ill-defined transition is 4.76 kJ/g-mol per repeat unit. When compared with the total enthalpy represented by the original three transitions of the polyester, this suggests a 70% conversion of the polymer to a cross-polymerized network. This number,
Figure 4.17  DSC of irradiated 5,7 DODBA/HQ.
however, is based on the decreased enthalpies of the polymeric transitions of the polyester; the degree of suppression of the polymeric transitions is a measure of the effective crosslinking of the polymer network, but not a direct measure of diacetylene conversion. A more direct measure of diacetylene conversion can be made by comparing the change in enthalpy of the exotherm associated with cross-polymerization. Unfortunately, the degradation of 5,7 DODBA/HQ is coincident with its polymerization exotherm, and it is impossible to directly correlate changes in the exothermic enthalpy with the degree of cross-polymerization. Nonetheless, a quantitative idea of conversion levels is achieved by comparison of the exotherms, as well as the endotherms discussed above.

For 5,7 DHDP/TC, electron beam irradiation resulted in a deep yellow-gold insoluble powder. The DSC thermograms shown in Figure 4.18 indicate that large levels of diacetylene conversion were obtained. As discussed in the thermal analysis section, only a very small amount of degradative weight loss is detected over the temperature range of the exotherm at 300°C, and it may be assumed that this exotherm is predominantly due to cross-polymerization. After a 20 Mrad dosage of electron beam irradiation, the exothermic enthalpy is greatly reduced, representing a conversion of 82.6%. At 50 Mrad, the conversion is 87.1%. Upon irradiation, the exotherm shifts to a higher temperature at approximately 330°C; this is presumably due to the increased thermal stability of the cross-polymerized network, and perhaps to the decreased mobility of the polymer chains, which cannot accommodate the crosslinking of the polymer chains as easily as the original linear polymer system.

It is also apparent that the thermal transitions of the polyester are greatly reduced in size as the polyester becomes a crosslinked thermoset glass. Note that the large clearing enthalpy is reduced much more quickly than the melting endotherm. It appears that the generation of a cross-polymerized network does not inhibit the crystalline melting transition as much as it prevents the randomization of the melt in the isotropization process. With even a minimal amount of mobility, the breakup of the original crystalline lattice to form an ordered melt is possible, though the process is suppressed. However, the additional mobility necessary to arrange the polymer molecules as random coils in an isotropic melt decreases more rapidly with increased crosslinking density. Similar observations were made for the irradiated diacetylenic monomer precursors discussed in Chapter 3.0.

At 10 and 20 Mrad irradiation levels, 10,12 DHDP/TC as-polymerized powder turns a light purple color, higher radiation levels result in a brick red colored solid. The polyester turns much deeper shades of blue when thick films cast from benzene are exposed to just 5 Mrad of irradiation. This is evidence that the sensitivity to radiation of
Figure 4.18  DSC of irradiated 5,7 DHDP/TC
this polyester is highly dependent on its morphology. The DSC thermograms of the polyester in its as-polymerized form were taken as a function of radiation level, as shown in Figure 4.19. Because very little weight loss occurs at the temperature of the exothermic thermal cross-polymerization of 10,12 DHDP/TC, the exotherm at 330°C can again be used as a measure of degree of conversion. It appears that 10,12 DHDP/TC is not as reactive in its as-polymerized form as the 5,7 polyesters, and at 50 Mrad irradiation levels, only about 40 to 50% conversion is observed. These results reflect the reactivity of the polymer in its form immediately following synthesis. Because annealing effects strongly influence the polyester reactivity, it is likely that higher levels of conversion would be obtained from annealed powder or film samples. As in the case of 5,7 DHDP/TC, the polymer clearing point appears to decrease much more quickly than the melt endotherm, which remains intact even at 50 Mrads.

In summary, the electron beam irradiation of each of the three polyesters resulted in quantitative conversions estimated at 40 to 80%. The 5,7 DODBA/HQ polyester turned a medium shade of brown upon irradiation, whereas the DHDP/TC polymers each exhibited deeper, more intense shades of gold and purple/red for the 5,7 and 10,12 analogs respectively. Thermogravimetric analysis of the cross-polymerized polyesters indicates that there were no significant changes in the degradative weight loss versus temperature curves following the irradiation process, indicating that the thermal stability of these materials remains intact during the irradiation process. Examination of the cross-polymerized polyesters using a hot stage and optical microscope reveal that these polymers do not exhibit liquid-like flow behavior up to temperatures as high as 300°C. Some liquid crystalline texture is visible in 5,7 DHDP/TC and 5,7 DODBA/HQ at or near their original melting temperatures, but the polymeric material remained fixed, and appeared more as a crosslinked gel than a liquid. No texture reminiscent of the original polyester was found in 10,12 DHDP/TC.

An unusual aspect of many diacetylene-containing monomers and macromonomers is that often those materials that are quite reactive upon heating are sluggish or unreactive to UV light, and vice versa. This appears to be true with regard to the reactivity of the liquid crystalline diacetylene-polyesters. 5,7 DODBA/HQ is highly reactive in the liquid crystalline and isotropic states, in which molecular mobility is much greater, and the opportunity for diacetylene groups to line up and react is not as restricted by crystalline lattice constraints. However, in the solid state, reactivity is much lower, particularly with regard to ultraviolet radiation and attempts at thermal annealing. Electron beam radiation, however, is a much more effective method which can achieve measurable amounts of
Figure 4.19  DSC of irradiated 10,12 DHDP/TC
cross-polymerization, as illustrated by DSC. It is possible that the high levels of penetrative energy from the electron beam can overcome structural barriers to topochemical polymerization. 5,7 DHDP/TC is highly reactive in the isotropic and liquid crystalline state, and is also responsive to thermal annealing techniques at temperatures below the melting point. UV irradiation results in low levels of cross-polymerization produced at relatively slow rates, and electron beam irradiation yields high degrees of conversion.

Finally, 10,12 DHDP/TC shows little indication of reactivity in the liquid crystalline state, but it reacts at a moderate rate at temperatures below the melting point. The diacetylene groups contained in the longer flexible segments appear to prefer polymerizing in the solid state; this suggests that the crystalline structure is especially conducive to topochemical polymerization. UV and electron beam irradiation also result in quantitative amounts of cross-polymerization for the 10,12 polyester. To find out if topochemical polymerization can occur in the liquid crystalline state as well, a film of 10,12 DHDP/TC cast onto a glass slide was placed on a hot stage and exposed to UV light at 138°C for four hours. A control slide with a similar film was exposed at room temperature for the same length of time. The control slide had only started to turn a very light shade of reddish purple, but the irradiated film had turned a much deeper pink shade, indicating that the topochemical process can take place in the liquid crystalline state. The next step of investigation is to induce large scale topochemical polymerization while in the liquid crystalline state, and determine whether the mesogenic ordering can be locked in by the polydiacetylene backbone.

4.5 Wide Angle X-ray Diffraction Results

An understanding of the solid state structures of the diacetylene-polyesters is required for a thorough understanding of differences in the reactivities of these materials. For this reason, wide angle X-ray diffraction (WAXD) analysis has been used to elucidate the characteristic crystalline spacings of the polyesters before and after cross-polymerization. These studies can also be used to get a qualitative sense of the degree of crystallinity, and the perfection of crystalline ordering. By heating and quenching each polyester sample so as to preserve the ordering of its liquid crystalline state, WAXD has also been used to verify the presence of a liquid crystalline state, to confirm the type of mesophase observed, and to obtain a picture of the degree of ordering in the mesophase. All measurements were done on unoriented polymer films or powders; solid powders or thick films were placed on glass or quartz substrates, and the X-ray data was collected in reflection mode using a diffractometer. As a precautionary control, some free-standing
film samples were measured in transmission mode, to yield results similar to those taken in reflection. Because of the limitations of the WAXD equipment used, small angle information regarding d-spacings greater than approximately 15-30 Å is not available at the writing of this thesis; however, efforts are currently being made to obtain X-ray photographs using flat film methods, which should include the small angle diffraction data needed for quenched samples.

**WAXD of Cross-polymerized Polyesters**

The WAXD diffractograms of each of the polymers in both the non-irradiated and irradiated states are shown in Figures 4.20 through 4.22. For ease of reference, Table 4.3 contains the wide angle d-spacings derived from the WAXD traces. All three of the polyesters possess the same basic crystalline form. A very strong peak at 4.4 to 4.5 Å is followed by a second strong peak at 3.8 to 4.0 Å that is shorter and broader than the first. A second pair of much weaker peaks appears at higher angles, with d-spacings of 3.1 to 3.2 Å; in 10,12 DHDP/TC, only one of the two peaks is clearly visible. These peaks are so weak that it is not likely they are directly associated with the lattice spacings of the primary crystalline form. The small peaks could be due to the presence of a second, less predominant, crystalline phase; this possibility will be discussed in more detail in the following section. In all cases, the diffraction peaks lie atop a broad halo representative of the amorphous regions of the semi-crystalline polyesters. It appears that the degree of crystallinity does vary somewhat for each polymer. For example, 5,7 DODBA/HQ appears to have a much larger amorphous portion than 5,7 DHDP/TC, and therefore its peaks are less well defined.

**Table 4.3  WAXD d-spacings of polyester-diacetylenes before and after irradiation.**

<table>
<thead>
<tr>
<th>Polyester</th>
<th>d-spacings in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,7 DODBA/HQ</td>
<td>4.46 4.13 3.26 3.12 2.36</td>
</tr>
<tr>
<td>5, 7 DODBA/HQ, irrad.</td>
<td>4.47 4.16 3.28 3.10 1.89</td>
</tr>
<tr>
<td>5,7 DHDP/TC</td>
<td>4.49 4.04 3.23 3.12</td>
</tr>
<tr>
<td>5,7 DHDP/TC, irrad.</td>
<td>4.50 4.11 3.28</td>
</tr>
<tr>
<td>10,12 DHDP/TC</td>
<td>4.50 3.82 3.23</td>
</tr>
<tr>
<td>10,12 DHDP/TC, irrad</td>
<td>4.50 3.92 3.24 2.35</td>
</tr>
</tbody>
</table>
Figure 4.20 Wide angle diffractograms of 5,7 DODBA/HQ, 0 and 100 Mrad
Figure 4.21 Wide angle X-ray diffractograms of 5,7 DHDP/TC at 0 and 100 Mrad irradiation levels.
The two predominant peaks found in these diffractograms are very similar to the types of peaks found in aliphatic polyamides and aromatic/aliphatic polyesters such as polyethylene terephthalate (PET). In fact, the sizes and locations of the maxima nearly match those of a polyamide-diacetylene synthesized from 10,12 docosadiyn-dioic acid and hexamethylene diamine (PADA 6,22) which was extensively characterized by Beckham and Rubner 22. This comparison is especially convenient because the aliphatic spacer segment of PADA 6,22 is the identical 22-carbon diacetylene segment found in 10,12 DHDP/TC, and the d-spacings for the polyamide are 4.4 and 3.8 Å. The crystalline nature of PADA 6,22 is, of course, based in part on the hydrogen bonding nature of the polyamide; however, the aliphatic nature of the segments appear to greatly influence the crystalline lattice parameters.

It is good practice to look at the crystalline form of a typical aromatic polyester as well. Although both the aromatic and aliphatic segments of the 5,7 and 10,12 polyesters are much longer than those in PET, the similarities in their diffraction behavior suggest that the basic unit cell of PET might be used as a starting point to model the crystalline form of the diacetylene-polyesters. The unit cells of PET23 and PADA 6,22, shown in Figure 4.23, are both triclinic, and in both models, a fully extended repeat unit is presumed. Please note that the labelling of the a and b axes differs for each of the models. To facilitate future comparisons with PADA 6,22, the a axis will be used to refer to the direction along which the carbonyl groups lay, and the plane containing the aromatic rings of the polyester will be referred to as the ac or 010 plane. Based on this convention, a tentative model of the crystalline structure of 10,12 DHDP/TC is shown in Figure 4.24. The aromatic rings are highly planar, and the distance between these planes is \( b = d_{010} = 3.82 \text{ Å} \). The distances between the repeat units that lay within these planes is \( a = d_{100} = 4.5 \text{ Å} \). The angles alpha, beta, and gamma of the cell are unknown. This model assumes a fully extended repeat unit, with all trans conformations of the methylene spacers; however, small angle X-ray analysis is needed to confirm this assumption. This model is simply meant to determine basic characteristics of the cross-polymerization process, and therefore, an all-trans configuration of the methylene spacers is not necessarily essential to this discussion. It is important to point out that there are other potential configurations of the unit cell. For example, Ozcayir and co-workers found that the c unit lengths of the polyester-diacetylenes in their investigation were much shorter than the extended length of the repeat unit 6. These polyesters were also based on 10,12 docosadiyne dioic acid, and the proposed lattice structure for the liquid crystalline polyesters was a body centered triclinic cell. However, given the information from the wide angle X-ray data of the 10,12 DHDP/TC polyester, the unit cell proposed in Figure 4.24 is reasonable.
Figure 4.22  Wide angle X-ray diffractograms of 10,12 DHDP/TC at 0 to 100 Mrad.
With a rough model of the lattice structure of the aromatic polyesters, it is possible to examine changes in the lattice spacings with cross-polymerization. In general, cross-polymerization causes a decrease in intensity and a slight shift to lower angle of the second peak, which corresponds to the spacing between planes containing the aromatic rings. This is especially noticeable in 5,7 DODBA/HQ and 10,12 DHDP/TC; the intensity change in 5,7 DHDP/TC is not very great. From the data in Table 4.3, we can also see that the shift of the peak results in small increases in the spacings of the 010 parameter. The 5,7 polyesters increase spacing in this direction by 0.02 to 0.07 Å, and the 10,12 polyester increases its lattice distance by 0.1 Å, from 3.82 to 3.92 Å. Also note that the a spacing also increases minutely for the 5,7 polyesters by 0.011 and 0.015 Å, respectively. On the other hand, the 10,12 polyester experiences no change in the 100 spacing.

These findings correspond well to those of Beckham and Rubner; in their investigation, solid state NMR and WAXD were used to determine the nature of the cross-polymerization process in PADA 6,22. Cross-polymerization occurs between diacetylene groups within the ac (010) plane; the process causes the formation of gauche conformations within the originally all-trans sequence of methylene units. Because the gauche conformers take up more space, accommodations must be made in the crystalline lattice to provide the needed room. In PADA 6,22, the gauche methylene units are sandwiched between the hydrogen bonded ac planes, thus expanding the distance b between planes, and decreasing the regularity in 010 spacing. The net result is a decrease in the angle and the intensity of the second peak. Despite the fact that the polydiacetylene repeat unit is 4.9 Å, the a spacing within the plane of the hydrogen bonds of only 4.4 Å does not change. The reasons given for this discrepancy is that at the site of the diacetylene groups, in the middle of the flexible segment, neighboring methylene units assume conformations that will allow the local expansion of the lattice without disturbing the distances between hydrogen bonded groups near the ends of the unit cell. To accomplish this feat, the flexible region containing the diacetylene group must be reasonably long. In fact, it was found that a similar nylon, PADA 6,10, with a shorter methylene sequence, exhibited an expansion in all of its lattice parameters when cross-polymerized; this suggests an inability of the flexible spacer to fully accommodate the expansion induced by cross-polymerization.

The WAXD results of 10,12 DHDP/TC mentioned above indicate changes similar to the structural changes of PADA 6,22 upon irradiation; it is probable that the same types of accommodations of the polydiacetylene chain are made in the long flexible spacer of this polyester. The 5,7 polyesters, with flexible segments less than half the length of 10,12 DHDP/TC, show expansions in two directions, rather than a large accommodation along
Figure 4.23  Unit cells of polyethylene terephalate and PADA 6,22.
Figure 4.24  Proposed unit cell of 10,12 DHDP/TC
just the b axis. These differences explain in part why the reactivity of 10,12 DHDP/TC in the solid state is so much greater than that of the other two polyesters. The 5,7 polyesters must overcome the energy barrier of changing two major crystalline spacings to create polydiacetylene; the 10,12 polyester need only undergo a simple conformational change to do the same. Heating the 5,7 polyesters beyond the melting point destroys the crystalline lattice which inhibited cross-polymerization, and thermally induced polymerization is therefore favorable. The ability of the 10,12 polyester to fully accommodate the all trans polydiacetylene repeat unit also explains the high conjugation length of the polydiacetylene backbone that is created, as evidenced by the purple color. The conjugation length of all polydiacetylenes is dependent on the planarity of the conjugated backbone; therefore, the all trans conformation has a high conjugation length and absorbs light at 650 nm, yielding a blue colored material. The yellow and brown products of the 5,7 polymers are results of low conjugation length, poorly ordered polydiacetylene chains.

A second factor to consider regarding the solid state reactivity of the polyesters is degree of crystallinity. It has been observed that 5,7 DHDP/TC is considerably more reactive in the solid state than 5,7 DODBA/HQ. As mentioned earlier, the DODBA/HQ polyester seems to have a much lower degree of crystallinity. Diacetylenes generally require highly regular packing to polymerize in the solid state, and in semi-crystalline polymers, it has been found that diacetylenes in the crystalline regions are favored for cross-polymerization. It appears that DODBA/HQ has a smaller amount of crystalline material available for cross-polymerization. Of the crystalline portions of the polyester, it appears from the higher melting point of the structurally similar DHDP/TC that the DODBA/HQ polymer crystals are less stable, and are therefore probably less ordered.

WAXD of Liquid Crystalline Phases

Wide angle X-ray measurements were taken of each of the polyesters in their quenched states by heating a film or powder sample to a desired temperature, and then quenching in the mesophase using liquid nitrogen, or dry ice/isopropanol baths. This was done for temperatures within the range that the mesophase existed.

The results for 5,7 DODBA/HQ are shown in Figure 4.25. In heating from the crystalline to the liquid crystalline state at 155°C, the peak at approximately 22° two theta broadens until it is essentially a part of the large amorphous halo. The two smaller peaks at higher angles have also virtually disappeared. However, even in the molten LC state, the primary peak at 19.8° persists, although its intensity has decreased; this is an indication of some residual interplanar spacing present in the mesophase of DODBA/HQ. When quenched from 165°C, near the isotropic clearing point, the 19° (4.58 Å) peak decreases

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Figure 4.25 WAXD Quench Series of 5,7 DODBA/HQ
further as the sample approaches a true isotropic melt. Unfortunately, there are no first or higher order reflections evident at low angles in the WAXD data to indicate the degree of long range ordering in the mesophase. Although without small angle X-ray data, it is not possible to confirm whether the mesophase is nematic or smectic, the predominant amorphous halo indicates that three dimensional ordering is not present at the temperatures at which a birefringent melt was observed. This data, along with the optical microscopy and thermal analysis, verify the presence of a true liquid crystalline state with a low degree of ordering. From the WAXD pattern, the smectic A, C or nematic phase is present. The presence of a single sharp peak suggests the kind of retained intermolecular ordering that one might expect from a smectic phase. Diffraction patterns very similar to these were found for some of the smectic C liquid crystalline polyesteramides investigated by Aharoni. The DODBA/HQ patterns look particularly like those shown for a polyesteramide with a long 14 carbon aliphatic spacer, which exhibited a "birefringent" and a "batonnet" liquid crystalline phase\textsuperscript{24}. The micrograph of the birefringent phase is quite similar to the fine-grained speckled texture found in 5,7 DODBA/HQ as well. Other evidence of similar X-ray patterns exist in the literature, including the WAXD flat film photograph of one of the Lenz polyesters that resembles 5,7 DHDP/TC in structure, with 10 aliphatic spacers. The pattern is described as having an intense outer ring at 4.4 Å, and from the photograph, it appears this ring is superimposed on a more diffuse ring corresponding to an amorphous halo. This polyester is described as having a nematic phase, however. It is apparent that a final conclusion regarding the exact nature of the mesophase cannot be drawn without small angle data.

5,7 DHDP/TC melts to form the diffraction patterns shown in Figure 4.26. Like 5,7 DODBA/HQ, most of the crystalline peaks disappear, and an amorphous halo appears in the mesophase quenched from 200°C. What is different about DHDP/TC is that the original primary peak at 20° (4.485 Å) disappears completely, but the smaller peak at higher angle (3.23 Å) sharpens and increases in intensity. Also, a new, shorter peak also appears at an angle corresponding to 3.6 Å. The origin of these peaks is not known at this time, although the peak at higher angle could be due to an increased ordering involving interplanar or intermolecular spacing of 3.23 Å within the mesophase, as opposed to that in the original crystalline form. In any case, the pattern is like that of DODBA/HQ in that it consists primarily of the amorphous halo, but with two sharp characteristic peaks at wide angles. Again, this mesophase might be characterized as smectic A or C, or possibly nematic; there are no higher order reflections found at low angle to guide in differentiation between these three possibilities. In the cases of both of the 5,7 polyesters, if the mesophases are nematic, they must be somewhat more ordered nematic phases than typical,
Figure 4.26 WAXD quench series of 5,7 DHDP/TC.
with characteristic intermolecular spacings. Finally, as the 5,7 DHDP/TC polyester approaches its clearing point, the peaks shift to slightly higher angles as they disappear into the amorphous halo. The decrease in intensity of the last diffractogram is due to the fact that a different sample was used to collect this pattern.

The quenched series of diffractograms for 10,12 DHDP/TC, shown in Figure 4.27, indicate a slightly different type of melt behavior than that seen in the 5,7 polyesters. First, note that there is a small but visible peak at 10.9° two theta, corresponding to a d-spacing of 8.1 Å; it has been noted that this peak becomes somewhat larger and sharper with thermal annealing. From this information and the position and relative size of the peak, it is reasonable to assume that this peak is a higher order reflection of some characteristic long spacing, representative of the c axis unit length along the polymer chain repeat. Quenching from various temperatures in the melt causes a broadening and shortening of this low angle peak, but it does not disappear until the sample is quenched from 170°C, well into the isotropic melt range. The retention of long range ordering is characteristic of smectic phases, and the presence of the reflection in the diffractogram of the mesophase verifies the fact that a smectic phase is present. Also, preliminary X-ray photographs taken of the quenched polyester indicate diffraction rings at small angles, as well. A look at the wide angle peaks indicates that at 120°C, when liquid crystallinity first appears in the optical microscope, the peak at 23° two theta, corresponding to 3.8 Å, disappears, as does the very small peak at two theta = 27.5°. The primary peak shifts from 19.8° to approximately 21 degrees, and becomes an intense, sharp peak atop an amorphous halo. At 130°C, the peak sharpens further, and the pattern is cone shaped. This suggests a semi-ordered interplanar spacing within the mesophase. As the temperature is increased to 140°C, the peak becomes asymmetric, and a broad shoulder appears on the right half of the curve. It is not clear whether this slight change is an indication of a liquid crystal to liquid crystal transition, or just a sign of the approach of the isotropic phase. It was difficult to quench in the isotropic state of this polyester; the 170°C quench shown does indicate an elimination of the small angle peak, but the sharp pointed peak atop the amorphous halo remains. This may simply be due to the difficulty of quenching the melt quickly enough to avoid formation of the liquid crystalline state.

WAXD temperature studies were also performed in-situ using a temperature controlled furnace designed for use with the diffractometer. The detailed results of this study will be discussed in Chapter 5.0 to complement thermochromic measurements. These studies confirm the data found from the quenched series in Figure 4.26, and verify that data collected from quenched samples does provide an accurate picture of liquid crystalline structure. The in-situ experiments also proved the reversibility of the thermal
Figure 4.27 WAXD quench series of 10,12 DHDP/TC.
transitions with regard to the recovery of the original crystalline structure. The WAXD results, combined with the batonnet and focal conic textures of the mesophase, indicate that 10,12 DHDP/TC exhibits a smectic A phase. The exhibition of a second, threaded liquid crystalline texture just above the melting point, as well as a shoulder in the melt endotherm at the same temperature, suggests that a smectic C phase may be present at lower temperatures, although the WAXD results give no conclusive evidence of this possibility. The WAXD and optical microscopy results suggest that 10,12 DHDP/TC exhibits a more ordered smectic phase than the 5,7 polyesters, probably due to the flexibility that the long alkyl spacers provide in attaining well-aligned molecular order. The high degree of ordering may limit the mobility of the diacetylene chains within the melt. Presuming that the mechanism required for melt phase thermally induced polymerization such as that seen in the 5,7 polyesters requires some large scale molecular motion, this lack of mobility in a highly ordered melt may limit the ability of diacetylene groups in 10,12 DHDP/TC to undergo thermally induced cross-polymerization. This phenomenon may explain the low degree of cross-polymerization that occurs in the liquid crystalline state of the 10,12 polyester.

4.6 Chapter Summary

In conclusion, three new semi-rigid thermotropic liquid crystalline polyesters containing the diacetylene group in the flexible spacer have been synthesized. These polyesters are unique in that they contain mesogenic groups based on oxy- and carboxy-linked aromatic rings. The only other diacetylenic liquid crystalline polymers reported were those of Blumstein and associates, and of those materials, only two were reactive in the solid state. More importantly, the development of this series of polyesters gives a basis for comparison of the mesogenic properties of diacetylenic aromatic polyesters with the well-documented properties of their diacetylene-free analogs. Also, variations in the length of the flexible spacer groups and the structure of the mesogen present the opportunity to further understand the effects of these parameters on the liquid crystallinity, thermal characteristics, and diacetylene reactivity of this novel group of materials. This understanding may then be utilized to control the properties of these materials, and tailor them for uses such as thermochromic optical devices, enhancement of structural polymers, or retention of liquid crystalline order.

Liquid crystalline behavior is observed in all three of the diacetylenic polyesters, as confirmed by thermal analysis, optical microscopy, and wide angle X-ray diffraction. The mesogenic behavior of the 5,7 DODBA/HQ and 5,7 DHDP/TC, which contain four flexible
methylene spacers on each side of the diacetylene group, is characteristic of ordered nematic or smectic A or C phases. The 10,12 DHDP/TC polyester, with nine methylene spacers, is smectic A, and may also exhibit a smectic C phase as well. The structural differences between the three polyesters strongly affect the thermal stability of the crystalline and liquid crystalline phases, influencing both the melting and clearing temperatures. The 5,7 DODBA/HQ polyester exhibits a lower melting temperature than 5,7 DHDP/TC, indicating that the DHDP/TC crystalline structure is more stable than the DODBA/HQ structure; wide angle X-ray diffraction studies also suggest that the degree of ordering in the crystalline domains of 5,7 DHDP/TC are higher than in DODBA/HQ. Finally, the extended flexible segment of 10,12 DHDP/TC results in the lowering of the crystalline melting point, as expected, as well as a lower clearing point. The destabilization of the liquid crystalline phase, which is indicated by a narrow temperature range of mesomorphic behavior and low isotropization temperature, is due to the increased flexibility of the repeat unit. The smectic character of the mesophase was enhanced by the increased spacer length, resulting in the appearance of low angle diffraction peaks in the X-ray data and the exhibition of typical smectic textures under crossed polarizers with an optical microscope.

The reactivities of these polyesters varied, depending on the polyester, the source of activation energy, and the phase in which cross-polymerization was initiated. 5,7 DODBA/HQ and 5,7 DHDP/TC are both quite reactive when heated above their melting points in the liquid crystalline or the isotropic state. In both cases, a brown crosslinked network of low conjugation length is formed. The color suggests that unlike the deeply colored red or blue/black films reported in the literature for the isotropic and mesogenic polymerizations of some diacetylenic monomers, a relatively disordered, nonplanar assembly of polydiacetylene backbones is the product of these macromonomers when held at high temperatures. Although 5,7 DODBA/HQ is thermally reactive in the liquid crystalline state, particularly near the isotropic clearing point, much smaller quantities of thermally-induced cross-polymerization occur below the melt temperature. However, 5,7 DHDP/TC undergoes a color change from white to yellow or orange when heated below the melt temperature, indicating a moderate rate of solid state topochemical cross-polymerization by thermal annealing. Apparently, the crystalline structure or ordering of 5,7 DHDP/TC is more conducive to thermally induced solid state diacetylene polymerization than that of the DODBA/HQ analog. 10,12 DHDP/TC was relatively unreactive above its melting point; however, this polyester was also reactive to thermal annealing treatments below the melt temperature, turning a deep purple color when annealed for long times.
The most photo-reactive polyester was 10,12 DHDP/TC, followed by 5,7 DHDP/TC and 5,7 DODBA/HQ. For this series of polyesters, the solid state reactivity of the diacetylene group appears to be a function of the degree of crystallinity of the polymer and the flexibility of the sidechains surrounding the diacetylene moiety. Wide angle X-ray diffraction confirms these findings, illustrating that the diacetylene moieties in 10,12 DHDP are able to expand the crystalline lattice in a manner conducive to the creation of the polydiacetylene backbone. The ability of the side chains to accommodate the reaction may explain the fact that the cross-polymerized 10,12 polyester is purple, a color characteristic of the large conjugation lengths found in a relatively planar polydiacetylene backbone. The 5,7 polyesters, on the other hand, are yellow or brown, indicating highly disordered polydiacetylene chains in the cross-polymerized network. Indeed, the optical properties of these diacetylene-polyesters, and the monomers from which they are derived, can impart a great deal of information regarding the molecular environment of the polydiacetylene backbone. The optical characterization is discussed in Chapter 5.0.
References


19) Personal communication with C. Rosenblatt, Case Western Reserve University, 1993.


Chapter 5.0

Optical Properties of Liquid Crystalline Diacetylenes

General Comments

Perhaps the most unique characteristic of the class of macromolecules known as polydiacetylenes and its derivatives is that their optical properties are highly sensitive to changes in the surrounding molecular environment. The conjugated backbone absorbs strongly in the visible region, and the wavelength of that absorption is dependent on the polydiacetylene's effective conjugation length. This length, in turn, is affected by the degree of planarity and the level of stress of the pi orbitals in the system. It has been found that even the slightest conformational changes in the sidechains of some polydiacetylenes can cause significant chromic transitions. This is true for poly-ETCD; some of the first observations of thermochromism involved changes in the reflectance spectra of insoluble polydiacetylene single crystals, such as poly-ETCD, which has a diacetylene substituent R = (CH₂)₄OCONHC₂H₅₂. The cause of this transition was discovered to be due to the rearrangement of alkyl side chains, a change which disrupts the planarity of the polydiacetylene backbone. On the other hand, large scale changes in the conformation of the polymer chain will also trigger chromism. For example, chromic changes have been induced by the gradual loss of hydrogen bonding in soluble urethane substituted polydiacetylenes such as the ACMU (alkoxy carbonyl methyl urethane) series of polydiacetylenes; the thermo- and solvatochromic changes observed in the solutions of these polymers have been attributed to a rod-to-coil conformational transition.

More recent studies on the chromic behavior of polydiacetylenes has centered on diacetylene macromonomers, such as segmented diacetylene-polyurethanes and polyamides. The host polymers in such systems provide an environment rich in varied morphological and conformational behavior to which the polydiacetylene backbone may respond. In the segmented polyurethanes, the unique phenomenon of mechanochromism occurs when the elastomers are strained. These chromic transitions have been attributed to a disordering of polydiacetylene chains in the hard domains, and in certain cases, to a
mechanically induced phase transition\textsuperscript{9}. Solid state NMR studies of the aliphatic polyamides revealed that the thermochromic transition was due to the conformational changes of methylene spacers in the side chains from gauche to trans isomers. Studies such as these demonstrated the use of the visible absorption spectra of polydiacetylene systems as a means of determining physical changes that occur in these materials on a molecular level.

The degree of sensitivity of a polydiacetylene to its local molecular environment suggests that its optical behavior might be predicted, and perhaps controlled, if the host environment is well chosen. In other words, the chromic transitions of the conjugated backbone can be manipulated by controlling or changing the molecular environment of the polydiacetylene chain. For this purpose, the side chains of the diacetylene group may be chosen or designed to undergo phase or conformational transitions at desired temperatures to induce thermochromic behavior. The ideal hosts for this purpose are thermotropic liquid crystalline monomers and polymers, which are multi-phasic, and may undergo several types of ordering changes in both the solid and liquid states. The advantages of such systems include the fact that the temperatures at which mesophasic transitions occur in many liquid crystalline materials has been a subject of study for a number of years, and a large base of knowledge is available on the effects of chemical structure on thermal transitions and mesogenic behavior of liquid crystals. This database provides the capability of designing diacetylenic liquid crystals and liquid crystalline polymers which undergo phase transitions, and corresponding chromic changes, at pre-determined temperatures. Applications of such materials include thermo-optical sensors and thermal indicators, and perhaps even optical filters which automatically absorb or transmit the wavelength of a transmitted beam at a given temperature. The fact that some liquid crystals exhibit more than one mesogenic transition suggest that more than one chromic transition is possible for a single material. Other advantages of such systems include the ability to align the mesophase with a magnetic or electric field to obtain highly oriented thin films, enabling devices to take full advantage of the anisotropic nature of the polydiacetylene backbone.

Past studies of chromism in polydiacetylenes have focused on the causes of this interesting phenomenon. Included in these studies are examples of order-disorder transitions, which cause a gradual shift in color as the absorption band moves to higher energies. On the other hand, first order transitions typically induce chromic phase transitions, in which an abrupt color change is seen at a given temperature as new absorption bands appear in the spectrum. There have been no attempts, however, to design polydiacetylenes to undergo chromic transitions at certain points. In this investigation, first order thermochromic transitions are induced by the mesogenic behavior
of the liquid crystalline side chains of the polydiacetylene. Different mesogenic structures have been used to incur the transitions at different temperatures, and both small side chain mesogens and thermotropic polyester macromonomers serve as hosts to the polydiacetylene chain.

**Novel Diacetylenic Materials:**

The diacetylene monomers 5,7 DODBA, 5,7 DHDP and 10,12 DHDP, are small mesogenic molecules which can react upon exposure to UV or electron beam irradiation to produce polydiacetylene chains with mesogenic sidegroups. As discussed in Chapter 3.0, in the cases of the partially polymerized diacetylenes of 5,7 DODBA and 5,7 DHDP, there is no clear indication of the development of new, polymeric mesogenic transitions that occur before degradation temperatures. This is thought to be due to the amorphous nature of the polydiacetylenes formed in these cases. It is possible that glass transitions of the side chain polymers may be "hidden" by the transitions of residual monomer, and therefore are not readily observed. 10,12 DHDP monomer, on the other hand, cross-polymerizes to high conversions to yield a side chain liquid crystalline polydiacetylene with distinct melting and clearing transitions. In any case, all three of these monomers may be cross-polymerized to form highly colored samples, and two of these materials undergo thermochromic transitions induced by the mesogenic transitions of either the monomeric host lattice or the polydiacetylene itself.

The photo-reactivity and visible absorption behavior of the polyester-diacetylenes vary a great deal, depending on molecular structure. The two DHDP/TC polyesters are UV sensitive, and the 10,12 DHDP/TC polyester exhibits thermochromic behavior as well. Because of the wealth of morphological variations that a polyester may exhibit, particularly a mesogenic polyester, the semi-rigid diacetylenic polyester is a great candidate for the study of conformational effects in various types of ordered environments. The network structure of a cross-polymerized polymer should improve the reversibility of the thermochromic transition, in contrast to polydiacetylenes formed from small molecules. Other advantages to a polymeric system include increased thermal stability, which is essential in thermochromism applications, and mechanical integrity. The latter quality of polymers allows one to form films and fibers that exhibit unique optical properties.

The following sections describe the optical absorption and thermochromic behavior of each of the materials described above. Two different types of thermochromic behavior were observed. In 5,7 DODBA, the mesogenic transitions of the host monomer lattice drive the abrupt first order chromic changes observed; Section 5.1 includes results describing these transitions. The 10,12 DHDP monomer and polyester, on the other hand,
exhibit both order-disorder chromic changes and a first order thermochromic transition. In both cases, the chromic changes are driven by the liquid crystalline side chains, both monomeric and polymeric, that are directly connected to the polydiacetylene backbone. These two materials exhibit very similar absorption spectra due to the near-identical environments of the conjugated backbone, and therefore they appear together in Section 5.2. Finally, the optical properties of the non-thermochromic diacetylene systems are discussed in Section 5.3.

Details about synthesis and characterization of the monomers can be found in Chapter 3.0; information regarding the polyesters is found in Chapter 4.0. To observe their optical properties, thin films of the monomers and polyesters, generally a few tens of microns thick, were cast from the appropriate organic solvents onto glass slides. Films intended for thermochromic measurements were cast onto potassium bromide IR windows designed to be used with an IR temperature controller. The films were then irradiated under the UV lamp for lengths of time chosen to obtain films with the highest wavelength absorption attainable. This was done to enable observation of thermochromic behavior within the full visible light range in each material. In-situ visible and infrared absorption versus temperature measurements were made using a spectroscopic temperature controller with a temperature range of 25-200°C. Further information regarding the optical characterization procedures are provided in the Experimental Section, Chapter 2.0.

5.1 Optical Properties and Thermochromism in 5,7 DODBA

Figure 5.1 contains the visible absorption spectra of 5,7 DODBA taken at temperatures ranging from 30°C to 200°C in a single ramp mode. The UV/Visible absorption spectra of 5,7 DODBA at 30°C is shown in Figure 5.1. The shape of the absorption curve is typical of polydiacetylenes. The strongest peak at 572 nm corresponds to the excitonic transition of the conjugated polydiacetylene chains, and its position is dependent on the effective conjugation length of the polymer. The secondary peaks at 532 to 495 nm represent a broad distribution of conjugation lengths present in the DODBA polydiacetylene, overlaid on the vibronic sidebands of the polydiacetylene due to stretching frequencies associated with the double and triple carbon-carbon bonds. The primary and secondary bands are broadened by the presence of a distribution of conjugation lengths caused by slight differences in the local ordering of the chains; this results in a corresponding distribution of excitation energies, which is seen in the visible absorption
Figure 5.1 Visible Absorption Results of 5,7 DODBA, Single Ramp Heating Experiment.
The spectrum. The DODBA films, which were cast from acetone and chloroform, were a dark pink color in appearance. The films were UV irradiated for 4 to 8 hours, to obtain a conversion of polydiacetylene sufficient to obtain the intensity of absorption needed for visible spectroscopy. The degree of conversion in all samples was low enough to ensure that the thermal behavior of the monomer was not greatly affected by the presence of polydiacetylene (< 5 Mrad). All films were easily soluble in acetone, chloroform, and other organic solvents.

The DSC thermogram of the non-irradiated monomer is also shown in the inset of Figure 5.1, indicating the first transition from the crystalline to the smectic phase at 113°C, followed by a smaller endotherm at 132°C. As discussed in Chapter 3.0, this second transition is either due to the melting of a more stable crystalline form of 5,7 DODBA, which is present in a much smaller quantity than the first crystalline phase, or to a liquid crystal - liquid crystal transition. Optical microscopy does not indicate any change in the liquid crystalline texture at this temperature, although a slight increase in the intensity of the birefringent melt is observed; therefore, it is assumed that the small transition at 132°C is due to the further melting of more stable crystallites. Finally, the broad clearing transition at 195°C is observed, spanning from 180°C to 205°C.

When 5,7 DODBA is heated, its visible absorption spectra remains relatively unchanged up to temperatures as high as 90°C. However, at 110°C, the excitonic peak at 572 nm undergoes a sharp drop in intensity, and a second excitonic peak arises at 538 nm. Thus, it is at a temperature near the center of the melting endotherm that this new peak appears, representing a second population of polydiacetylene chains residing in the smectic mesophase. This liquid crystalline phase has a lower effective conjugation length than the crystalline phase that it replaces, and therefore the primary excitation appears at lower wavelength. At 120°C, just above the first endotherm, the vibronic sideband of this second phase becomes much more evident; however, some absorption is still present at 572 nm, indicating that not all of the crystalline material has disappeared. It is not until 130°C, as the second melt endotherm is reached, that the remainder of the crystalline excitonic transition and sidebands are eliminated. Here we see a classic ordered polydiacetylene spectrum, with a strong excitonic transition at 538 nm and a broad vibronic sideband at 490 nm; the shape is nearly the same as that of the crystalline phase, and, in fact, the bands are somewhat sharper and narrower, suggesting that the distribution of conjugation lengths in the smectic phase is not as broad as that in the polycrystalline state. This is compatible with the fact that the monomer exhibits more than one stable crystalline form, each of which melts to form a single smectic A mesophase. The layered structure of the smectic A phase involves a simple but regular spacing of the fully extended monomer, which may allow for
more uniformity in the ordering of polydiacetylene chains situated in the monomer lattice. Hydrogen bonding of the dimerized acid groups is in part responsible for this uniformity, as will be discussed presently.

Finally, at 200°C, the isotropic clearing point is reached, and the intensities of the liquid crystalline visible absorption peaks decrease as a high energy tail develops at 400 to 450 nm. Because the temperature device does not go beyond 200°C, it was not possible to obtain visible absorption data beyond the clearing transition. It is expected that the peaks at 538 and 490 nm will decrease as they are replaced by a broad, featureless peak at low wavelengths. In the isotropic phase, all ordering of the side chains is lost, and the polydiacetylene chains become free to assume nonplanar conformations in the randomized melt. Color changes are also observed during the heating experiment, corresponding to the changes in the visible absorption spectra. The dark pink color gives way to a lighter peach (orange-pink) color in the liquid crystalline phase. Films heated above the clearing point on a hot plate appear yellow, a color which generally corresponds to absorptions at 400 to 500 nm. The yellow color is observed in the highly disordered states of many polydiacetylene systems.

It is apparent that the conjugated polydiacetylene chains undergo conformational changes triggered by the phase changes of the non-polymerized diacetylene monomer. There exist two basic means by which polydiacetylene chains are produced within the solid monomer crystalline lattice. The diacetylene may polymerize homogeneously, in which case the polymer chains formed are evenly dispersed in a solid solution with the monomer. At low conversions, the monomer crystalline lattice acts as the solvent, surrounding the individual polydiacetylene chains. The alternative kinetic model involves nucleation of polydiacetylene at sites where pre-formed polymer already exists, thus resulting in a heterogeneous polymerization in which phase segregated monomer and polymer domains are formed. In this second case, the absorption wavelength of the polydiacetylene chains residing in the monomeric domains is generally different from that exhibited in the polymeric domains. The visible absorption spectrum of 5,7 DODBA has been observed to exhibit a single excitonic transition regardless of the length of irradiation exposure time. This suggests that, at least at the low conversion levels used for these experiments, no phase segregation occurs during solid state polymerization of 5,7 DODBA. Assuming homogeneous solid-state polymerization of the monomer, the poly-DODBA should be dispersed evenly throughout the monomer crystalline lattice. For this reason, at relatively low degrees of conversion, the polydiacetylene side chains are directly associated with surrounding monomer via hydrogen bonding of the carboxylic acid groups. The re-ordering of the three dimensional crystalline lattice to form a two dimensional
Smectic liquid phase involves changes in the conformations of the side chains, and consequently, adjustments in the planarity of the conjugated backbone. The high degree of ordering in the liquid crystalline phase suggests that these changes produce very periodic disturbances in the planar arrangement of the pi orbitals of the polymer. A further understanding of the conformational changes involved in the mesogenic transition requires more extensive information on the crystalline lattice parameters of 5,7 DODBA.

To observe the reversibility of the thermochromic transition, a 5,7 DODBA irradiated film was exposed to a series of heat/cool cycles, in which each cycle was taken to progressively higher temperatures. The UV/Visible spectrum was measured in-situ at the temperature of interest, then cooled to 50°C, where it was measured once again. The results of these experiments are shown in Figure 5.2a) and b). The heated states, shown in 5.2a), look fairly similar to those seen in the single ramp heating experiment of Figure 5.1. The film used was translucent and highly crystalline, and a large degree of scattering at low wavelengths is therefore seen in the spectra taken at temperatures below the melting point. At temperatures approaching the melting temperature, the first excitonic transition begins to decrease. Finally, a sharp melting transition is once again seen at 110°C, with complete disappearance of the shoulder at 572 nm occurring between 120 and 140°C. The spectrum of the liquid crystalline phase appears at 120°C as it did in Figure 5.1. A comparison of the low temperature spectrum and the liquid crystalline spectrum suggest that the new excitonic peak at 538 nm may have been present at room temperature in much smaller proportion; this is feasible, as it is possible to prepare samples of these materials which have a small amount of material quenched into the liquid crystalline state.

The sloping baseline seen at higher temperatures is the result of anomalies between the detector and the reference scan. The shape of the absorption curve remains relatively unchanged throughout the mesogenic range, and does not change significantly even at 200°C. Also, the spectrum at 200°C does not show the same high energy tail exhibited in the single heating experiment. This could be the result of very gradual increases in the degree of polymerization of the sample during the higher temperature cycles; data presented in Chapter 3.0 confirm that an increase and a broadening of the clearing endotherm occurs upon partial polymerization of the monomer. Perhaps enough polydiacetylene was formed during the thermal cycling experiment to increase the observed isotropization temperature beyond 200°C.

The absorption of 5,7 DODBA in its cooled state is shown in Figure 5.3 (b). The slight chromic changes at low temperature appear to be relatively reversible, but above the melting point at 110°C, the spectra in the cooled state look very much like their heated counterparts. It appears that once the material enters the liquid crystalline state, and the
Figure 5.2 Visible Absorption Results for the Heat/Cool Cycles of 5,7 DODBA
side-chains of the diacetylene backbone begin to reorder, the conformational changes of the backbone cannot be reversed. In fact, for the spectra taken at 80 to 110°C, the peak at 570 nm actually decreases in intensity from its heated to its cooled state. This strange phenomenon may be due to the prolonged time periods required to air-cool the sample back to 50°C for the cooled measurement; during this time, the sample was still exposed to temperatures high enough for the real time melting of the original crystalline phase of 5,7 DODBA to continue. Even annealing temperatures at 80°C and 90°C appear to be high enough to induce some melting behavior.

Now, for the case of 5,7 DODBA, recrystallization has been found to be slow and incomplete, at least within the time scale of DSC and optical microscopy experiments. From observations of heat/cool cycles in the DSC, the melting point is present, but greatly diminished upon a second heating. There is also an indication of some recrystallization to higher melting crystalline forms, as well. For these reasons, in the case of 5,7 DODBA, the lack of reversibility is a characteristic of the host monomer, rather than a characteristic of the polydiacetylene chain. Examination of the peach colored film soon following the cycling experiment revealed that both liquid crystalline and fine polycrystalline textures were present. Even a small amount of recrystallization should have been detected in the visible absorption spectra, unless the crystalline form produced upon recrystallization is one that does not require a significant rearrangement of spacer groups. The second heating of 5,7 DODBA in the DSC revealed a new shoulder at higher temperatures, as well as an increase in the size of the 132°C endotherm, suggesting that more stable crystalline phases are formed upon cooling from the melt (see Chapter 3.0). It is postulated that these new solid state forms have an ordering that is greatly influenced by the smectic layer ordering of the mesogenic melt. Therefore, it is likely that the irreversible structural changes of the polydiacetylene chain are inherent to the thermodynamic behavior of the monomer. This lack of reversibility is confirmed in the simple cooling experiment shown in Figure 5.3, in which the DODBA film was first taken to 200°C and then cooled to successively lower temperatures down to 50°C. At the clearing point, the relative size of the liquid crystalline phase excitonic transition is decreased, and the vibronic sideband has broadened significantly. As the film is cooled, the excitonic peak becomes more intense, and the sideband begins to narrow. However, there is no indication of the return of the original crystalline phase at low temperatures.

The role of hydrogen bonding is central to the smectic nature of the 5,7 DODBA diacid. Like all n-alkyloxybenzoic acids which show nematic and smectic liquid crystalline phases, this symmetrical carboxylic diacid is thought to be dimerized in the mesophase. The mesogenic stability is increased by the fact that the dimerization can take
Figure 5.3 Visible Absorption of 5,7 DODBA, Cooling from Isotropic Melt.
place on either end of the molecule, encouraging stacks of alternating rigid aromatic hydrogen bonded units with aliphatic spacer segments containing the diacetylene group. It is no wonder that the smectic phase is well ordered, or that it has such a high clearing point. Historically, analysis of the vibrational spectra of liquid crystals has been used as an additional means of characterization of many classic mesogens\textsuperscript{17}. Differences between crystalline and liquid crystalline spectra include decreases in the intensity of C-H stretches, broadening of peaks due to increased rotational and translational freedom of the molecules, and certain, more subtle differences unique to a given family of compounds. There is considerable data available on the IR spectra of the alkyloxybenzoic acids\textsuperscript{17,18} which are ideal for comparison with DODBA. To verify that hydrogen bonding does indeed persist in the liquid crystalline melt, and to observe potential structural differences in the mesophase, in-situ temperature variation infrared spectroscopy studies have been used to further characterize the mesogenic transition of 5,7 DODBA.

The FTIR spectra of 5,7 DODBA at 25 °C, 150°C and 200°C are shown in Figure 5.4. The hydrogen bonded carboxylic O-H stretch is the broad band from 2500 to 3000 cm\textsuperscript{-1}; the methylene stretches are superimposed on this band at 2980 and 2850 cm\textsuperscript{-1}. At room temperature, two clearly defined peaks that are also due to the hydrogen bonded OH are visible at 2500 and 2700 cm\textsuperscript{-1}. In the mesophase, at 150°C, the O-H stretch and the two smaller peaks remain present, although they have broadened considerably, suggesting an increasing number of variations of hydrogen bonding strengths present in the melt, as well as the effects of thermal expansion. The intensity of these peaks has also decreased somewhat, suggesting a decrease in hydrogen bonding. However, the O-H stretch is still very much intact in the liquid crystalline state. The melting of the crystalline structure apparently allows the retention of hydrogen bonding as stable dimerized structures are formed. The formation of an energetically favorable mesophase explains the thermodynamic reason for the relatively low melting point of 5,7 DODBA. As the isotropization point is reached at 200°C, the hydroxyl peaks spread into one continuous band of low intensity as the mesophase prepares to clear out. Again, at the limit of the temperature controller, the clearing point is reached, but not surpassed, and a truly isotropic melt cannot be observed using this technique. However, the observation of the carboxylic acid stretch at 1682 cm\textsuperscript{-1} proves useful at this point. This peak undergoes only a small drop in intensity in the mesophase, verifying the retention of hydrogen bonding in the mesophase. At 200°C, the intensity decreases further, and the band broadens as it prepares to split into two absorptions bands: one at the original 1682 cm\textsuperscript{-1} position, and the other at a non-hydrogen bonded acid position at approximately 1700 cm\textsuperscript{-1}. This is an
Figure 5.4  FTIR in-situ heating experiment for 5,7 DODBA Monomer.
indication that free acid is forming at the isotropization temperature, as the hydrogen bonding of the smectic liquid breaks up.

Other changes in the IR spectra are quite characteristic of liquid crystalline phase transitions. The decrease in intensity of the CH$_2$ bending vibrations at 1450 cm$^{-1}$ and the merging of CH$_2$ bands at 1250 to 1300 cm$^{-1}$ (two shouldered peaks along the edge of the C-O stretch at 1250 cm$^{-1}$) are especially characteristic of mesophases of n-alkoxy benzoic acids$^{17}$. The existence of many rotational isomers in the methylene spacer groups is the cause of this broadening. This is further evidence that the chromic transition occurring in 5,7 DODBA is activated by the increased mobility of side chains packed in the smectic phase. Other areas of change in the IR spectra also correspond to rearrangements or increased mobility of C-C and C-H bonds, including the single C-C stretch region at 950 to 1050 cm$^{-1}$, and the aromatic C-H deformations at 1165 and 1100 cm$^{-1}$.

Figure 5.5 contains the FTIR spectra obtained upon cooling. Most of the changes incurred on heating to the clearing point are reversed upon cooling to 130°C. The hydrogen bonded O-H peaks regain some of their definition upon re-entering the mesophase, and the free acid peak disappears from the carbonyl stretch as it regains its original shape and size. The bands attributed to C-H and C-C look similar to the way they appeared upon heating up to 150°C. Upon cooling to 30°C, however, only some of the original changes appear to be reversible to the crystalline phase. The smaller hydrogen bonded peaks have shifted back to the left again, although they are not quite back at their original spots, nor have they regained their original distinct shapes. On the other hand, the carbonyl peak resumes its former shape almost completely, and the CH$_2$ bending peaks between 1250 and 1300 are recovered, although they do not regain their former size. These subtle changes in the cooled 5,7 DODBA sample suggest that recrystallization has occurred to some extent, but that a slightly different crystalline form may have been recovered; there is also strong evidence that a large portion of the mesophase structure was quenched into the solid state, as well. These conclusions are consistent with the DSC and optical microscopy data presented in Chapter 3.0. Considering the apparent stability of the smectic mesophase, it is not surprising that its structure tends to be quenched in upon cooling.

The infrared spectroscopic data is quite consistent with the visible absorption spectra of lightly cross-polymerized 5,7 DODBA monomer. It appears that the solid solution produced undergoes changes which can be accurately followed by observing the thermochromic behavior of the conjugated polydiacetylene backbone. The fact that the absorption peaks of the liquid crystalline phase show high degrees of order are consistent with the increased hydrogen bonding found in the smectic mesophase. The high temperature stability of the hydrogen bonding is also corroborated by the retention of the
Figure 5.5 FTIR in-situ cooling experiment for 5,7 DODBA Monomer.
visible absorption peaks to 200°C. Finally, the fact that the infrared spectral changes upon cooling were subtler than those observed on heating suggest quenching of the mesophase, along with the possibility of the formation of more stable crystalline phases which retain some of the optimized hydrogen bonding and ordering of the smectic phase. This is reflected in the irreversibility of the poly-DODBA thermochromic transition.

5.2 Optical Properties and Thermochromism of 10,12 DHDP Derivatives

The 10,12 DHDP monomer, and its corresponding polyester, 10,12 DHDP/TC, exhibit nearly identical optical behavior when polymerized (or cross-polymerized). In both cases, the thermochromic transitions are driven by changes in the nine methylene spacer sequence positioned on either side of the polydiacetylene chain. These changes occur in the form of a first order transition at the temperature at which the side chains of the polydiacetylene backbone exhibit melt behavior. In the case of the irradiated 10,12 DHDP monomer, this occurs at the melting transition of the side chain liquid crystalline poly-DHDP itself. For cross-polymerized 10,12 DHDP/TC polyester, this happens at the melt temperature of the host polyester.

To fully explain the similarities between the monomer and the polyester, a schematic of the two materials before and after polymerization of the diacetylene groups is shown in Figure 5.6. Wide angle X-ray diffraction results discussed in Chapter 3.0 reveal that upon solid state polymerization, the long range ordering of 10,12 DHDP is greatly improved. It is believed that the introduction of the conjugated backbone somehow causes a re-alignment of the DHDP aromatic rings. The result is an improved registry of the DHDP monomeric units with neighboring molecules; the hydrogen bonding between units, though not as strong as that in 5,7 DODBA, no doubt plays some role in maintaining this highly regular ordering. With the added degree of ordering, and the associative effects of hydrogen bonding, the 10,12 DHDP in its polymerized form looks and acts very much like the cross-polymerized polyester. The rigid mesogenic portion of the semi-flexible polyester consists of three covalently bonded aromatic rings. The corresponding rigid portion of the small monomeric side chain is made up of a phenoxy group, hydrogen bonded to a neighboring phenoxy as part of a crystalline lattice. Even the crystalline structures of the monomer and polymer are quite similar, each exhibiting two major diffraction peaks at approximately 4.5 and 3.8 Å.

The spectral changes that each material undergoes are also similar. These changes are thought to involve basically the same conformational changes of the neighboring
Figure 5.6 Schematic of polydiacetylene backbone in 10,12 DHDP monomer and 10,12 DHDP/TC polyester.
methylene spacers; therefore, the spectral shifts are the same, but the temperatures at which they occur differ, depending on the melting point of the side chains, as mentioned earlier.

**10,12 DHDP**

The 10,12 DHDP monomer was highly reactive to UV light, and turned deep, dark colors upon exposure to the UV lamp. At very short exposure times of up to 5 minutes, blue-purple films were formed; however, further cross-polymerization resulted in a gradual shift to a violet-red color. The visible absorption spectra of 10,12 DHDP taken at two different irradiation times are shown in Figure 5.7. At very short irradiation times, two excitonic transitions are visible at 650 and 580 nm; the vibronic side bands of the smaller 650 nm peak are shouldered into the transition at higher energy. Observation of the sample irradiated for 15 minutes shows that the red-shifted peak at 650 nm is no longer present after longer exposure times. The disappearance of this peak, as well as the color change with further irradiation, have been observed in other polydiacetylenes, including PTS-12 (dodeca-5,7-diyin-1,12-diyl-bis-p-toluene sulphonate) and 12-8 PDA (substituents R = C₁₂H₂₅, R' = (CH₂)₈COOH))¹⁹,²⁰. In both of these examples, two absorption peaks appear at low conversions, and the peak at higher energy gradually increases at the expense of the lower energy transition. For PTS-12, Siegel et al. label these peaks P₁ and P₀ respectively. The authors explain that the peaks are due to the differences between the monomer lattice in a solid solution of polydiacetylene at low conversions, and the polymer lattice which exists at higher conversions (greater than 2-5% conversion). Unlike the gradual shifts to higher or lower energies exhibited by polydiacetylenes formed in single-phase reactions, monomers such as PTS-12 and 12-8 PDA undergo a polymerization-induced phase transition at a given level of conversion, at which point regions of polydiacetylene chains rearrange, shifting the monomeric lattice spacings so as to better accommodate the packing requirements of the polymer, and thus creating a new polymeric crystalline lattice with a different characteristic conjugation length. The presence of both peaks in the visible absorption spectra illustrate the fact that the polymerization is taking place in two different regimes: the monomer with polydiacetylene dispersed in a solid solution, and domains consisting predominantly of growing polydiacetylene chains in a polymer lattice. Therefore, when examining thermochromic changes in 10,12 DHDP, it must be kept in mind that the first transition at 650 nm is representative of polydiacetylenes in a monomeric matrix, but the second, much stronger peak at 580 nm corresponds to poly-10,12 DHDP in its own polymeric lattice. For this reason, the thermochromic shifts exhibited by this peak are expected to correspond to the phase transitions of the polydiacetylene chains themselves, and not necessarily to those of the monomer.
Figure 5.7 Visible absorption spectra of 10,12 DHDP monomer samples at two irradiation times.
Figure 5.8 Visible absorption spectra of 10,12 DHDP, single ramp heating experiment.
Figure 5.8 shows the visible absorption spectra of irradiated 10,12 DHDP films taken during a single ramp heating experiment. To extend the range of thermochromic effect observed, samples irradiated at short times were used for all thermochromic experiments, so that both peaks at 650 and 580 nm were present. For convenience, the DSC thermogram of the polymerized monomer (50 Mrad e-beam irrad., 80% conversion) is shown in the inset. Also note that the original DHDP monomer has two transitions at 70° and 90°C respectively. Due to light scattering of crystals in the monomer film, a large degree of scattered intensity is visible at lower wavelengths in the spectra taken below the melting point of the polydiacetylene. From 70 to 90°C, the peak at 650 nm begins to decrease in intensity, disappearing completely at about 100°C. Because the polydiacetylene chains represented by this peak are surrounded by monomer units, it is not surprising that they undergo a chromic transition fairly early in the heating process, corresponding more directly with the transitions found in the monomer. The gradual disappearance of this peak appears to be an order-disorder transition that occurs as flexible methylene spacers of the monomeric lattice gain rotational freedom. The polydiacetylene chains, now free from the strain of the original lattice, are presumed to gradually take on the preferred conformations of the polymeric phase. The 580 nm peak remains unchanged at temperatures up to 100°C, at which point this peak, too, slowly decreases in intensity, as a new, broad band appears at about 540 nm. The 580 nm peak, which is representative of polydiacetylene chains immersed in a polydiacetylene host environment, continues to decrease at 110°C, and is gone by 120°C. This very broad transition is quite reflective of the breadth of the DSC endotherm from 90 to 120°C that marks the melting range of the polydiacetylene. What remains is a fully developed, broad excitonic transition at 545 nm, with an equally broad secondary band. The spectra is somewhat better defined at 140°C, well into the mesogenic region of poly-DHDP. This spectra is representative of the liquid crystalline phase of polymerized 10,12 DHDP, which has been characterized in Chapter 3.0 as a smectic phase. The appearance of a distinct transition suggests that at least a moderate degree of ordering exists in the mesophase, although the ordering of polydiacetylene chains in this phase does not appear to be as good as that in the crystalline phase. This is in contrast to the observations of a very well-defined, relatively narrow absorption band for 5,7 DODBA at its liquid crystalline temperature. The lower degree of order in this mesophase is due to two effects. The fact that the poly-DHDP mesophase is that of a side chain liquid crystalline polymeric material means that less precise layering, and a larger number of defects, are expected in the smectic phase. This results in a wider range of conformational possibilities for the liquid crystalline side chains, and thus, for the polydiacetylene backbone. Also, the hydroxyl groups of the DHDP monomers are not as
strongly hydrogen bonding as the acid groups of DODBA. For this reason, the efficiency of packing and the perfection of the ordering between the layers is expected to be better in the diacid monomer.

Finally, as the clearing transition from 160°C to 180°C is approached, the features of the peaks go away, and a wide band indicating a very large distribution of conjugation lengths in relatively disordered polydiacetylene chains is left in the isotropic melt. Abrupt color changes accompany each of the transitions described above. At the disappearance of the 650 nm peak, the film turns from blue-purple to violet-red, as described before. Upon entering the mesophase, the color becomes bright orange, and on entering the isotropic state, it turns yellow-orange or peach.

Figures 5.9 a) and b) contain the results of heat/cool cycles on the optical properties of partially polymerized 10,12 DHDP. The results in the heated state exactly parallel the results shown in Figure 5.8 for the single ramp experiment. The cooled state spectra indicate that the crystalline spectra are recovered up to 100 to 110°C, which is the melting range of poly-DHDP. The 650 nm peak appears to be almost fully recoverable below this temperature, indicating that the disappearance of this peak is a reversible thermochromic transition. However, once the mesophase is entered, the polydiacetylene chains seem to quench into the conformational state of the mesophase. This quenched in structure is much more well-defined at room temperature, and indicates a well-ordered polydiacetylene environment. When cooled from the isotropic state, the liquid crystalline spectra is also obtained. This means that the isotropic to liquid crystalline transition is reversible in the UV/visible spectra, but not the liquid crystalline to solid state transition. The cooling experiment shown in Figure 5.10 confirms that the polydiacetylene structural changes incurred upon heating to the mesophase are not thermally reversible. DSC results indicate that the melting transition of irradiated 10,12 DHDP is not reversible; therefore, as in the case of 5,7 DODBA, the polydiacetylene absorption spectra simply reflect the irreversible thermodynamic behavior of the crystalline to liquid crystalline phase transition.

10,12 DHDP/TC

The optical properties of cross-polymerized 10,12 DHDP/TC are highly dependent on the morphology of the polyester prior to irradiation in the solid state. This fact is made clear upon observation of annealing effects on the visible absorption spectrum of 10,12 DHDP/TC. Thin films of the polymer were cast from toluene onto glass slides, and annealed in an oven at 90°C for varied amounts of time. These films were then exposed to ultraviolet radiation for exactly five hours. The visible absorption spectra of these films is
Figure 5.9 Visible absorption spectra of 10,12 DHDP from Heat/Cool Experiment
a) heated state; b) cooled state.
Figure 5.10 Visible absorption spectra of 10,12 DHDP, as cooled from 160°C.
shown in Figure 5.11. The overall intensity of the bands increases with annealing time, in part due to cross-polymerization induced in the annealing process. However, ordering of the crystalline structure of the films also seems to have a strong effect on the shapes of the absorption curves. When a film is not annealed at all, cross-polymerization produces a light yellow clear film with a broad absorption band at 420 nm and a tail seen as a sloping baseline traversing the visible range, with intensity increasing with decreasing wavelength. The degree of crystallinity is quite low in toluene cast films prior to annealing, as evidenced by the transparency of the film. The reactivity of the diacetylene groups is lowered in a predominantly amorphous environment, without the ordering needed to facilitate a solid state topochemical reaction. Those polydiacetylene chains which are produced have a low degree of polymerization, and tend to exist in a broad distribution of highly non-planar conformations, resulting in the observed "yellow" spectrum shown. Just one hour of annealing time facilitates the development of an ordered semi-crystalline structure in these films, and the polydiacetylene chains are readily formed in the crystalline regions of the film, as seen by bands absorbing at 650 nm and 570 nm, respectively. There is still a peak at 420 nm, indicating that a good deal of amorphous material is present, as well. Continued annealing tends to reduce the amorphous "yellow" peak and increase the size of the low energy peaks. Film samples appear blue to purple in appearance after such long annealing times, and the films become translucent as crystallinity is increased and crystallites become bigger and more perfect. After three days of annealing, the two primary peaks are large and well-defined; a secondary sideband can be seen clearly for the 570 nm peak. The amorphous peak at 420 nm is decreased and now background scattering from the semi-crystalline film is seen at low wavelength.

The shape of the 10,12 DHDP/TC is also highly dependent on the solvent from which it was cast. Figure 5.12 contains the absorption spectra of films cast from three different solvents using various techniques. Each of the films received some sort of thermal treatment such as annealing before irradiation. It is clear that m-cresol, a highly polar solvent, renders the film highly disordered, probably due to strong polymer-solvent interactions. The purple-pink film cast from tetrachloroethane has an absorption maximum of 580 and 550 nm, and appears relatively well-ordered. When the TCE solution is cast onto a heated slide to form a film through fast solvent evaporation, the shape of the spectra is significantly changed, and the film appears red in color. The toluene cast film appears to yield the best optical films in terms of ordering and low energy absorption. As in the annealing study, it is clear that the polymeric qualities of variable morphology and ordering are superimposable on the sensitive optical spectra of the polydiacetylene backbone in these materials.
(Top) Figure 5.11 Visible absorption vs. annealing times for 10,12 DHDP/TC.
(Bottom) Figure 5.12 Solvent Effects on spectra of 10,12 DHDP/TC cast films.

(Annealing Temperature = 90°C; All samples UV exposed for 5 hours)
Given similarities in their room temperature spectra, it is safe to assume that the polymerization process discussed for 10, 12 DHDP is applicable to the 10,12 polyester. In fact, the peak at 650 nm, indicative of homogeneously dispersed polydiacetylene chains in the original polyester lattice, does indeed disappear at longer irradiation times (e.g. 24 hrs.). For the case of lightly cross-polymerized monomer, the peak at 570 nm represents domains of cross-polymerized polyester. At low levels of conversion, here thought to be 5% or less, the phase transitions of 10,12 DHDP/TC should not be greatly inhibited by cross-polymerization at all. Therefore, thermochromic transitions involving the 570 nm transition are expected to follow the phase transitions of the host polyester.

Figure 5.13 a) contains the heated states of a heat/cool cycling experiment on an irradiated 10,12 DHDP/TC polyester film. Included in the inset is the DSC of the polyester, which indicates a shoulder at 110°C, a broad melting endotherm centered at 129°C, followed by a clearing point from 140 to 155°C. The first spectrum at 50°C illustrates the initial state of the polyester, and is similar to the peaks of annealed films described above. Upon heating to 90°C, the 650 nm peak quickly drops off. It is interesting that the same effect was seen in the 10,12 DHDP monomer, where it corresponded well to the melt transition of the monomeric lattice. It seems quite likely that, although the ends of the original monomer are now tied down as part of a polymer repeat unit, the methylene spacer groups near the diacetylene monomer are so far away from the rigid mesogenic units that their local motions remain uninhibited. The relaxations and increased rotational freedoms gained at 70 to 90°C by the spacer units in the monomer due to melting are gained by the identical spacer groups in the polyester repeat. This sort of "localized melting" is made possibly solely by the extremely long flexible spacers of the 10,12 DHDP/TC polyester. As in 10,12 DHDP, the thermochromism at low temperatures possibly involves the rearrangement of the original polymer lattice (absorption at 650 nm) to the more stable expanded lattice form predominant in the cross-polymerized phase at higher conversion (i.e., the 570 nm phase).

At 110°C, the peak at 570 remains, but a new absorption at 538 nm has just begun to rise out of the vibronic sidebands of the first transition. This transition corresponds to the shoulder at 110°C in the DSC. It is at this point that melting of the polyester begins, and the peak at 570 nm gradually drops off from 110 to 130°C. In the meantime, the absorption which first appeared at 110°C is visible as a disordered, but not featureless, broad absorption at 130 to 140°C. These temperatures are in the midst of the liquid crystalline phase of 10,12 DHDP/TC, which is smectic, and from optical microscopy results, may exhibit both a smectic A and smectic C phase. Examination of the broad endotherm indicates that there are three peaks present, buried beneath a broad distribution.
Figure 5.13 a) Heated state of heat/cool cycle for 10,12 DHDP/TC.
Figure 5.13 b) Cooled state of heat/cool cycle for 10,12 DHDP/TC.
of polydiacetylene conjugation lengths. The relative sizes of these peaks seem to change with temperature from 130° to 140°C and finally 150°C, near the clearing point. This broad absorption corresponds to the relatively disordered polydiacetylene chains in the mesophase. The ill-defined appearance of the spectra is due to the more disordered nature of polymeric mesophases, particularly in cases where there is a broad molecular weight distribution. It is possible that the presence of more than one excitonic peak may be accounted for by the multiple nature of the liquid crystalline phase. If so, the changes in the relative sizes of peaks at 530, 475 and 445 nm might be related to a smectic to smectic phase transition. Optical microscopy indicates the coexistence of two different optical textures in the mesophase, as the smectic A phase coalesces into what is proposed to be the smectic C phase on cooling. Evidence of such a correlation with the absorption spectra shown is not currently available; further examination of the optical properties of similar liquid crystalline diacetylenes having more well defined transitions would be necessary to verify that observations such as this are due to a true liquid crystal to liquid crystal transition, rather than to other anomalies of the polydiacetylene backbone absorption. For example, another explanation may be that the peak at the lowest wavelength is due to the introduction of the isotropic phase. In any case, the absorption spectrum becomes completely featureless between 180°C and 200°C, way above the clearing point for the polyester. The higher apparent clearing point is probably due to the effects of small levels of cross-polymerization on the clearing point. DSC data from the previous chapters illustrates that cross-polymerization suppresses the clearing point of these materials, often pushing the transition to slightly higher temperatures.

Color changes were observed during the heating experiments which corresponded to the thermochromic observations found in the visible spectrophotometer. Before heating, the polyester films were generally a light to medium purple color. Heating to 90°C resulted in a bright red color, corresponding to the disappearance of the peak at 650 nm, and the color then changed once more to a peach color in the mesogenic temperature range. At very high temperatures, the color was light yellow.

The cooled states of the visible absorption spectra, corresponding to the heated states discussed above, are shown in Figure 5.13 b). It appears that the thermochromism of 10,12 DHDP/TC is fairly reversible up to 130°C, which is just beyond the melting point. From 140°C, some of the liquid crystalline phase begins to get quenched in as well. Unlike the monomeric diacetylenes, the crystalline peak is recovered up to temperatures as high as 150°C, where only a small shoulder in the cooled state absorption spectra indicates where the 570 nm crystalline phase peak should be. When the isotropic melt was cooled from 180 and 200°C, the liquid crystalline phase absorption bands are completely quenched in,
and it is possible to see details in the cooled sample that were not visible at the actual mesophase temperatures due to molecular thermal vibrations. The middle peak at 475 nm is broad, and could be the convolution of a vibronic sideband corresponding to the excitonic transition at 530 nm, and a second excitonic transition. The presence of multiple bands suggests the presence of more than one type of ordering.

These spectra verify the presence of three distinct peaks from the mesophase. The new peaks were not at all present in the original, unheated state, and they coexist with the original 570 nm peak at 130°C in the heated state, and in the cooled state quenched from 150°C. These facts indicate that the thermochromic behavior of 10,12 DHDP/TC corresponds to a first order phase transition at approximately 125 to 130°C; of course, this transition is the melting point of the polyester. There is a similar, though very gradual, transition to the isotropic melt, characterized by the complete disordering of the polydiacetylene chain. It is known from DSC data that the transitions of 10,12 DHDP/TC are reversible when cooled at 20°C/min. For these experiments, the films were cooled in air at room temperature. Generally the initial temperature decrease was fast, slowing as the temperature approached lower values. For this reason, it is highly likely that conditions were favorable for quenching in the mesophase, and it is not surprising that the higher temperature cooled state spectra show evidence of freezing in the liquid crystalline mesophase. The fact that some of the peaks from the crystalline phase returned even after traversing the melting point is a sign that reversibility is possible in these thermochromic, liquid crystalline systems. Under more controlled circumstances, it may be possible to optimize the reversibility. It does appear that the polyester is much more reversible than the monomers, which were irreversible immediately upon reaching the melting point. This may be due to the constraints imposed on the system by the cross-polymerized polydiacetylene network, as well as the irreversible nature of the 5,7 DODBA and 10,12 DHDP monomers.

To complement the thermochromic observations of Figure 5.13, in-situ temperature variation wide angle X-ray diffraction measurements were made with a thick, annealed film of 10,12 DHDP/TC. The results of the heating experiment are shown in Figure 5.14 (a). At room temperature, the crystalline Bragg diffraction peaks of the polyester at two theta values of 19.8° and 23.3° are the dominant features of the diffractogram. There is also a small, nth order reflection at 10.9° two theta which is indicative of long range ordering, and a very small diffraction peak at 27.6°, which, as discussed in Chapter 4.0, is thought to be due to a minor crystalline form. All of these peaks are superimposed on an amorphous halo due to the unordered regions of the polymer. The diffraction pattern remains unchanged upon heating up to 110°C. At this temperature, the amorphous halo broadens, and the
Figure 5.14 In-situ WAXD with temperature variation: a) heating from 25°C
b) cooling from 190°C.
peaks at 23.3° and 27.6° decrease in intensity, indicating the onset of melting. In Figure 5.13 (a), this onset is indicated by a noticeable drop in the intensity of the 570 nm crystalline phase peak. At 120°C, the minor crystalline form has completely disappeared; this seems to correspond to the shoulder at 110°C found in the DSC, suggesting that the shoulder is due to a separate, less stable crystalline form. The two primary diffraction peaks remain, but the 23.3° peak is quickly waning. It is at this point that some birefringence is first detected under the optical microscope. The new, broad peaks at lower wavelength begin to appear between 110° and 130°C in the visible absorption spectra, corresponding to the relatively disordered mesophase. At 135°C, the diffraction pattern has changed dramatically. The crystalline diffraction peaks have gone, indicating that the temperature is that of the liquid crystalline melt. A broad amorphous halo with a peaked top is present, similar to the diffraction patterns of quenched samples of 10,12 DHDP/TC shown in Figure 4.27. This triangular halo, along with the presence of the peak at low angles, indicates a smectic mesophase. As mentioned in Chapter 4.0, an X-ray photograph of the quenched polymer indicates a small angle peak, verifying the presence of a smectic phase. AT 150°C, the peaked cap of the amorphous halo rounds off, but the small angle peak remains. This may be an indication of a second, less ordered smectic phase, which appears near the clearing point at 140 to 145°C in the optical microscope. The visible absorption spectra at 140°C and 150°C exhibit the multiply peaked, broad absorption band described earlier. Again, it is not clear at this time whether the shifting of the broad peaks from 130 to 150°C are an indication of a liquid crystalline-liquid crystalline transition. Finally, at 190°C, the small angle peak begins to decrease in size, and the amorphous halo broadens, as the isotropic melt is approached. It is interesting that in both the visible absorption spectra and the WAXD experiment, the clearing point is elevated to temperatures much higher than those given in the DSC thermograms. Note that low degrees of cross-polymerization do occur in the X-ray diffractometer. Scans were limited to 4.5 minutes for this experiment to avoid any extensive crosslinking; the sample did not show signs of large amounts of cross-polymerization following this experiment.

Figure 5.14 (b) illustrates the reversibility of the thermal transitions as the X-ray sample is cooled. The liquid crystalline pattern re-appears at 107°, and recrystallization is seen as the original diffraction peaks re-appear at 90° to 60°C. The super cooling observed in the diffractometer corresponds to DSC cooling results, as well. The reversibility of the cooled state absorption spectra corroborate the fact that these transitions are quite stable and reversible under controlled conditions. However, attempts to cool the mesophase from the isotropic melt, and measure the visible absorption spectra with decreasing temperature
simply resulted in the quenching of the mesophase, as it did for the diacetylene monomers. These effects are probably due to the uncontrolled cooling rate of the heating device used.

5.3 Optical Properties of Other Diacetylenic Materials

5,7 DHDP

The 5,7 DHDP monomer turned pale yellow to orange in color upon exposure to ultraviolet irradiation. The UV/Visible absorption spectrum of this monomer at room temperature is shown in Figure 5.15. The featureless absorption at 400 to 500 nm is indicative of a highly non-planar diacetylene backbone\(^1\), which is present in the original form of the polymerized monomer. Unfortunately, when the polydiacetylene backbone is this disordered upon its formation, it is not likely to acquire a more ordered state through thermal annealing, orientation of films, or other attempts to increase the planarity of the polydiacetylene chain. The fact that a yellow, disordered polydiacetylene backbone is formed is due to the parameters of the crystalline lattice of 5,7 DHDP. Detailed discussion of the solid state packing of the diacetylene monomers and their respective polydiacetylenes is found in Chapter 3.0. Due to the fact that the highest energy visible absorption edge attainable is already present in the 5,7 DHDP polydiacetylene, thermochromic changes are not observable.

5,7 DHDP/TC

Much like its monomeric precursor, 5,7 DHDP/TC also turns yellow upon irradiation. The UV/Visible absorption spectra of a film of this polyester cast from a very dilute m-cresol solution, indicates a broad absorption centered at 450 nm, as shown in Figure 5.16. Attempts to anneal the polymer to improve its ordering failed to produce a material that, when irradiated, would absorb at higher wavelengths. Heating only increased the degree of polymerization, turning the film from yellow to amber or orange-yellow. Electron beam irradiation of the solid polymer in its as-polymerized form also turns yellow, suggesting that the crystalline form of 5,7 DHDP/TC polyester is not conducive to the formation of long chain, high conjugation length, planar polydiacetylene chains. The lack of features in the absorption indicate that a broad array of low conjugation length, disordered polydiacetylene is produced, instead.

5,7 DODBA/HQ

The DODBA/HQ polyester is quite unreactive to UV radiation, and films cast from hexafluoroisopropanol turn a faint brown color after a few days of UV exposure. Thermal annealing promotes cross-polymerization at a much faster rate, but the same brown color results. Like the 5,7 DHDP/TC polyester, attempts at improving the order of the polyester
(top) Figure 5.15 Visible absorption spectrum of 5,7 DHDP.

Figure 5.16 Visible absorption spectrum of 5,7 DHDP/TC
did not work; only shades of brown were obtainable with this polymer. Electron irradiation produces a dark amber colored powder. Attempts at obtaining a film of good optical quality for 5,7 DODBA were unsuccessful due to large amounts of scattering present in hexafluoroisopropanol cast films.

5.4 Discussion

It is apparent that the thermochromic behavior of 5,7 DODBA corresponds with great precision to the thermal transitions of 5,7 DODBA. In the case of this monomer, even the lack of reversibility is consistent with the cooling behavior of the monomer itself. The shapes of the original absorption band and the spectrum in the liquid crystalline state suggest that a well-ordered, stable liquid crystalline phase is formed. These findings confirm earlier observations made of the 5,7 diacid. Infrared spectroscopy proved to be a good complementary technique to visible spectroscopy, and it was established that hydrogen bonding is increased, rather than lost, upon melting. It was shown that, in fact, that hydrogen bonding remains intact up to the clearing point. This provides further support to the idea that the diacid dimerizes in the melt, forming a layered smectic A phase.

The striking similarities between 10,12 DHDP and 10,12 DHDP/TC warrant further discussion. It appears that the chromic nature of the 10,12 DHDP unit is strongly influenced by its long length of methylene spacers, and its characteristic packing parameters. However, measurements consistently place the disappearance of the 570 nm peak at 110°C for 10,12 DHDP, and at 130°C for the polyester. Despite this, the melting points are so close, and the melting endotherms so broad for both materials, that there is a great deal of overlap in their melting regions. The fact is that the melting range of materials based on 10,12 docosadiyn-1,22 diacids and diols tends to vary from 100°C to 130°C. Examples include the liquid crystalline polyesters based on the 1,22 diacid synthesized by Ozcyir, Blumstein and associates21. The polyester that incorporated a biphenyl ring mesogen melted at 122°C, and the polymer with an alpha methyl stilbene group melted at 122°C as well. The polyester with an azoxy group melted at 132°C. It appears that the flexible spacers in these polyesters play a large part in determining thermal behavior, which is not surprising, considering the size of the aliphatic group.

Ultimately, the thermochromic transition is attributed to the added flexibility of methylene spacer groups in the side chain of the polydiacetylene backbone. In both cases, this added flexibility does coincide with the melting transitions of those side chains, whether they are the side chains of the liquid crystalline polydiacetylene, or the main chain liquid crystalline polyester. In both cases, the melting transition brings about a second
absorption band with its own excitonic transition(s); this is evidence of a first order transition, rather than an order-disorder process. The shape of the new absorption band seems highly dependent on the degree of order present in the mesophase. 10,12 DHDP yields a much cleaner optical transition than the broad, ill-defined transitions of the polyester mesophase. This reflects differences in the degree of order in the well-aligned smectic phase of the side chain polydiacetylene, and the less ordered smectic state of the main chain polyester. These differences are confirmed in the X-ray data of Chapter 3.0.

Finally, it is of interest that the characteristic absorption peaks for the liquid crystalline phases of all three mesogens appear at approximately 540 and 480 nm. Apparently, although the shapes of the spectra depend on the degree of ordering in the phase, the actual absorption wavelengths did not vary much for different materials. This is due to a characteristic packing of the polydiacetylene chain or its side-chains in layered smectic mesophases.

5.5 Chapter Summary
This study illustrates two ways in which the diacetylene backbone can be designed to undergo chromic changes at specific points. One can begin with a liquid crystalline monomer which, when cross-polymerized at low levels, produces polydiacetylene chains immersed in a monomeric crystalline lattice. An alternative approach is to choose a monomer which forms a mesogenic liquid crystalline polydiacetylene with transitions in the temperature range of interest, and allow the thermochromic transitions to be driven by the liquid crystalline nature of the polydiacetylene itself. The use of a main chain liquid crystalline polymer with the diacetylene incorporated in the backbone is actually a combination of these two approaches. The polyester is a host to the polydiacetylene chain, as in the first case; however it is also covalently bonded to the backbone as a macromonomer side chain.

Examination of the thermochromic data presented in this chapter confirm that each of these concepts is quite successful. A polydiacetylenic first order transition occurs at the melting points of all three materials, resulting in a well defined color change, and the appearance of a second absorption band characteristic of the mesophase. A second transition to the isotropic state was also observed in the 10,12 derivatives, marked by an order-disorder transition in which the absorption peaks become featureless. The transitions of the 5,7 DODBA monomer corresponded quite well to the DSC trace of the material, as well as to its infrared spectral changes with temperature, and the visible absorption spectra remained relatively unchanged within the mesogenic region, illustrating the ability to design a material to transmit a certain wavelength over a given temperature range. The color
changes exhibited by the 10,12 DHDP and 10,12 DHDP/TC occurred at a low temperature order-disorder thermochromic transition, the melting point, and the clearing point. The colors of 10,12 DHDP were especially deep and bright, which could prove important for some applications of this novel material.

Future directions for this study might include an examination of polyesters with a shorter methylene spacer group (between 5 and 8 units). These materials would introduce a broader range of melting points and colors with which to experiment. Other chemical structural changes might increase or depress the melting points of these materials. It is possible, for example, to create a material which undergoes mesogenic phase transitions near room temperature. Finally, further investigations of diacetylenic monomers would be worthwhile, considering the optical results from 5,7 DODBA. A liquid crystalline material that undergoes sharper transitions, and perhaps more than one transition, would prove especially interesting. An important factor to consider is the reversibility of the thermochromic transitions, and therefore, of the mesogenic transitions, themselves. It appears that the polyester was much more reversible than the monomer, and this increased the thermochromic reversibility as well.

In summary, the design of optical transitions in liquid crystalline diacetylenes is a viable means of manipulating the unique chromic behavior of these materials for new engineering applications.
References


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Diacetylene-containing compounds have been actively researched for the past twenty five years. These materials undergo a solid state, topochemical reaction upon exposure to ultraviolet or electron beam irradiation and heating to form highly conjugated polydiacetylenes with variety of side chain substituents. The unique properties of these polymeric materials include a high nonlinear optical coefficient, and a strong absorption in the visible light range. The wavelength of absorption in the visible spectrum is highly dependent on the molecular environment of the polydiacetylene chain. Small changes in the conformation of the chain can result in dramatic color changes; often these changes take place upon heating the polymer. The resulting thermochromic behavior is well-documented in the literature. Recently, researchers have been searching for ways to take advantage of the novel properties of these materials. Although great emphasis has been placed on the optimization of the nonlinear optical properties of polydiacetylenes, very little has been done to take advantage of the unusual linear optical properties of these materials. Once given the ability to tailor polydiacetylenes to exhibit changes in color at specific temperatures, however, the possibilities for the development of thermal sensors, thermally controlled optical filters, and other "smart materials" are opened.

It is known that the polydiacetylene backbone will often undergo chromic transitions that correspond to a first or second order transition of its host environment. Given this knowledge, it is possible to design diacetylenic materials to exhibit a transition at a desired temperature range, and thus induce a thermochromic transition in the polydiacetylene chain. The ideal host materials for the tailoring of the chromic response are liquid crystalline monomers and polymers. Due to the multi-phasic nature of these materials, significant changes in ordering are exhibited at two or more mesogenic
transitions; in the simplest case these transitions are the melting point and isotropization
temperatures present in most liquid crystals. Because the relationships between chemical
structure and thermal behavior of liquid crystals and liquid crystalline polymers are well
understood, these materials are natural choices for the concept of controlling
thermochromic behavior.

To examine the potential for this concept, a series of small molecule functionalized
diacetylene-containing liquid crystals were designed, as well as a corresponding group of
aromatic diacetylene-containing polyesters derived from these monomers. In this way it
was possible to examine the differences in the thermal and optical behavior of
polydiacetylenes obtained from monomers and macromonomers. The diacetylene group in
each case was located in the flexible spacer portion of the molecule to allow mobility near
the diacetylene reaction site. The structures were varied by increasing the length of the
flexible spacer in which the diacetylene group was located, and by varying the functional
groups of the monomers, or the structure of the mesogenic segment in the polyesters.
Thermal analysis, optical microscopy, and wide angle X-ray diffraction methods were used
to determine the nature of the crystalline and liquid crystalline states of each material.
These materials were electron beam irradiated to induce polymerization of the diacetylene
groups. This resulted in the formation of polydiacetylenes in the case of the monomers; the
polyesters were cross-polymerized to form a network consisting of conjugated
polydiacetylene backbones. Each of the resulting polydiacetylene systems were then
examined to determine extent of conversion, morphology, and thermal behavior of the
products. Finally, optical characterization was used to examine thermochromism and
optical absorption characteristics of these novel materials.

Summary of Results

Three aromatic monomers were synthesized. The first, 1,12 dodecadiyn-5,7-dioxy
dibenzoic acid (5,7 DODBA), was prepared from 1,12 dibromo-5,7- dodecadiyne and
hydroxy benzoic acid. 1,12-dihydroxy diphenoxy 5,7 dodecadiyne (5,7 DHDP) was
synthesized from the 1,12 dibromo compound and excess hydroquinone, and 1,22-
dihydroxy diphenoxy 10,12 docosadiyne (10,12 DHDP) was synthesized from 1,22
dibromo docosadiyne and excess hydroquinone. 5,7 DODBA consists of a diacetylene
with four methylene spacers on either side, followed by an oxybenzoic acid group. 5,7
DHDP has a similar structure, with the carboxylic acid groups replaced by hydroxy
groups. The 10,12 DHDP monomer is, in turn, similar to 5,7 DHDP, except that it has
nine methylene spacers on either side of the diacetylene group.
5,7 DODBA exhibited a highly stable mesophase from 113°C to 200°C. The high stability of the mesophase was attributed to dimerization of the diacid groups to form a hydrogen bonded smectic phase. Wide angle X-ray results, along with optical microscopy, indicate that this mesophase is smectic A. The 5,7 DHDP monomer appeared to exhibit at least one smectic phase of three dimensional order, and optical microscopy and thermal analysis suggest that a second, metastable smectic phase exists as well. Conclusions could not be made about the mesogenic nature of 10,12 DHDP, although it does exhibit what appears to be a liquid crystalline phase over a very narrow temperature range.

The 5,7 DODBA and 5,7 DHDP monomers were thermally reactive in the liquid crystalline and isotropic phase, but were only moderately reactive when annealed in the solid state. The opposite was true of the 10,12 DHDP monomer, which was polymerized to high conversions using electron beam irradiation, but was relatively stable to heat in the solid, liquid crystalline, and isotropic states. Differences in solid state reactivity varied as a factor of the degree of ordering in the crystalline state of the monomer, and the length of the flexible spacer. It was found from wide angle diffraction studies that the 10,12 DHDP monomer was able to better accommodate the growing polydiacetylene chain during the polymerization reaction, thus allowing the production of a highly conjugated, well-ordered polydiacetylene chain.

All three of the monomers were reactive to electron beam irradiation in the solid state. 5,7 DODBA was converted to a red, conjugated polydiacetylene with aromatic acid sidechains. The degree of conversion at 100 Mrad of irradiation was approximately 25% based on thermal analysis. The partially polymerized diacetylene of 5,7 DODBA exhibits no new transitions in the DSC, although the transitions of the original monomer moved to higher temperatures, and diminished in size. The DODBA polymer is relatively non-crystalline, as determined by X-ray measurements. It is postulated that this polymer is a glassy, amorphous side chain polymer which undergoes a glass transition to a mesophase at higher temperatures. Similarly, irradiation of 5,7 DHDP produced an amorphous brown or yellow-gold colored partially polymerized diacetylene of approximately 50% conversion. As was the case for 5,7 DODBA, the resulting polymer was amorphous, and no new transitions were visible in the melt. New liquid crystalline texture was observed at temperatures higher than those of the original monomer, suggesting that the 5,7 DHDP polydiacetylene may undergo a glass transition to a liquid crystalline state as well. The presence of the residual monomer in each case made further characterization of the polydiacetylenes difficult.
The 10,12 DHDP monomer was polymerized to form a crystalline polymer that melted at temperatures above that of the original monomer to form a liquid crystalline melt. The new melting and clearing endotherms of the 10,12 DHDP polydiacetylene were visible in DSC thermograms, and wide angle X-ray indicated the crystalline nature of the product. Above the melting point of the 10,12 DHDP polydiacetylene, a smectic phase is observed using optical microscopy, which resembles a smectic C mesophase. These polymerized materials are unique examples of functionalized polydiacetylenes with liquid crystalline side chains. Highly oriented, anisotropic optical materials might be made by processing these materials in the mesophase. The breadth of morphological changes that the polydiacetylenes in this study undergo illustrate the versatility of polydiacetylenes as a class of polymers; the existence of such different morphologies provides the framework for thermochromism studies at the phase transitions of these materials.

The monomers were used to synthesize three polyesters from either hydroquinone (HQ) or terephthaloyl chloride (TC). The three resulting polymers all exhibited enantiotropic liquid crystalline behavior. The mesophases of 5,7 DODBA/HQ and 5,7 DHDP/TC were identified as either nematic or disordered smectic phases. 10,12 DHDP/TC appears to have a smectic A phase, with a possible transition to smectic C at lower temperatures.

Like the monomers from which they were derived, the 5,7 DODBA/HQ and 5,7 DHDP/TC polymers were quite thermally reactive at temperatures near the clearing point, and in the isotropic liquid state. On the other hand, the 10,12 DHDP/TC polyester was relatively stable in the liquid crystalline and isotropic melts, and for this reason, its thermal transitions were much more reversible than those of the 5,7 polymers. Annealing in the solid state to induce cross-polymerization did not have very much effect on 5,7 DODBA/HQ, but 5,7 DHDP/TC and 10,12 DHDP/TC both turned deep colors following annealing treatments below the polyesters' melt temperatures, indicating a high degree of solid state thermal reactivity.

Exposure to UV irradiation resulted in cross-polymerization in the 5,7 and 10,12 DHDP/TC polyesters as well; 10,12 DHDP/TC was especially sensitive to UV light, forming a highly conjugated, blue or purple polymer network. The color of cross-polymerized 5,7 DHDP/TC was yellow to gold-orange, indicating a lower conjugation length. The 5,7 DODBA/HQ exhibited minimal change when exposed to UV light. Only electron beam irradiation successfully induced cross-polymerization of 5,7 DODBA/HQ. The 5,7 DHDP/TC and 10,12 DHDP/TC were also responsive to electron beam irradiation. In short, the 5,7 DODBA/HQ polyester generally was not very reactive in the solid state, whereas the DHDP based polyesters were solid state reactive, particularly the 10,12
polyester. The overall effect of cross-polymerization was the gradual loss of thermal transitions of the polymers with increasing levels of irradiation. At very high levels of cross-polymerization, the polyesters exhibited very little or no liquid crystalline behavior or other thermodynamic transitions below the degradation temperature. However, small levels of cross-polymerization had only minimal effects on the mesomorphic nature of the polymers.

The differences in solid state reactivity appear to be due in part to differences in the crystalline structures of the polyesters. The 5,7 DODBA/HQ polyester, which was quite unreactive in the solid state, had a poorly ordered crystalline phase, and a large amorphous fraction. 5,7 DHDP/ITC and 10,12 DHDP/TC both appeared to have more ordered crystalline phases. Upon exposure to irradiation, the changes in d-spacings of these two analogs is quite different, suggesting that the flexible spacers in the 10,12 polyester changed their conformations to better accommodate the polydiacetylene backbone into the lattice structure of the original polymer. These adjustments allowed the development of a highly conjugated, and therefore highly planar, polydiacetylene backbone in 10,12 DHDP/ITC. The low conjugation length (yellow color) and lower reactivity of the 5,7 DHDP/TC is an indication that a much less efficient process is involved in the cross-polymerization of 5,7 DHDP/TC.

Finally, the optical properties of the polymerized monomers and cross-polymerized polyesters were studied to determine thermochromic effects. Three of the materials synthesized in this study were thermochromic: the 5,7 DODBA and 10,12 DHDP monomers, and 10,12 DHDP/TC polyester. In each of these cases, visible absorption spectroscopy indicated a change in the absorption wavelength upon entering the liquid crystalline state; changes in the absorption spectra were accompanied by dramatic color changes at the melting point.

The thermochromic behavior was driven by the liquid crystalline transitions of the monomer in 5,7 DODBA. In this case, the polydiacetylene chain itself exhibited no transitions within the temperature range of the thermochromism experiments, and at low levels of conversion, the unreacted monomer served as the local molecular environment for the polymer; the partially polymerized monomer was a solid solution containing the polydiacetylene. Upon heating irradiated films of this monomer, the original excitonic transition at 572 nm decreased in intensity at the crystal-liquid crystal transition of 5,7 DODBA monomer. This sharp drop was accompanied by the appearance of a second excitonic transition at 538 nm. This new peak represented a relatively narrow distribution of polydiacetylene conjugation lengths; the well-defined shape of the peak indicated the high degree of order present in the mesophase. A color change from pink to orange is also
observed with the melting point. At 200°C, some disordering is seen in the absorption spectrum, but the clearing point was not exceeded in this set of experiments. The thermochromic transition of 5,7 DODBA was not reversible; the absorption spectra observed above the melting point remained unchanged upon cooling. This is consistent with the fact that the liquid crystalline texture is quenched in, as noted in the discussion of the thermodynamic behavior of the monomer in Chapter 3.0.

A very different mechanism was the root of the thermochromic behavior of polymerized 10,12 DHDP; in this case, the liquid crystalline transitions of the polymerized monomer rather than the original monomer most greatly affected thermochromism. The monomer experienced a phase transition from a monomeric to a polymeric lattice during solid state polymerization. The resulting absorption spectrum at room temperature contained two excitonic transitions: a peak at 650 nm, representative of the polydiacetylene chains in a monomeric lattice, and a second peak at 580 nm, indicative of the polymer chains residing in a polydiacetylene lattice. Upon heating, a gradual color change from blue to red or purple occurred at 50 to 90°C, coincident with the melting of residual monomer. Coincident with this color change, the 650 nm peak gradually disappeared. At the melting point of the polymerized 10,12 DHDP monomer, which was 90 to 110°C, the peak at 580 nm began to drop off, as a new absorption peak at 540 nm appeared. This was accompanied by a change of color from purple-red to orange. This first order transition resulted in a well-developed absorption spectra, as it did in 5,7 DODBA, indicating that a mesogenic phase is present. At 180 to 200°C, the ordered spectra of the liquid crystalline phase changed once more at the clearing point. A broad absorption band was visible for the isotropic liquid, which was yellow in color. This transition was typical of order-disorder transitions, resulting in the broadening of peaks, and the disappearance of order in the absorption curves.

The absorption spectra of lightly cross-polymerized films of 10,12 DHDP/TC were extremely dependent on factors affecting the overall morphology of the polymer, such as casting solvent and thermal treatments. Well-annealed polyester films exhibited two peaks at 650 and 570 nm, much like the polymerized 10,12 DHDP monomer. Upon heating, the peak at 650 nm gradually decreased in intensity, disappearing at 90°C. This effect is thought to be related to rearrangements of methylene spacer groups in the repeat unit of the polyester; these motions paralleled those observed in the monomer. The peak at 570 nm decreased in intensity from 120 to 130°C, and was completely gone at 140°C. At this point, a color change from red-purple to light orange occurred, and a new absorption band characteristic of a less ordered mesogenic phase became predominant. At the clearing
point, this band became a broad, featureless peak, indicative of the highly disordered isotropic state.

**Recommendations**

To obtain a greater understanding of the polymerization process in the novel mesogenic diacetylenic monomers discussed in this thesis, further studies of the polymerization kinetics and mechanism in the crystalline, liquid crystalline and isotropic states of the original monomers would prove useful. Any differences in the morphology of polydiacetylenes formed in each of the different phases might prove interesting. Also, the method of polymerization may prove an interesting parameter. There may be major differences in the conjugation length or degree of polymerization of polydiacetylenes formed by thermal annealing versus electron beam initiation, for example. Further examination of the thermodynamic behavior of the polydiacetylenes produced from these monomers is also needed to better understand the causes of potential problems such as irreversibility and broad transition ranges. Because the liquid crystallinity found in partially polymerized diacetylenes seems to be affected to some degree by the presence of monomer, systems polymerized to different conversion levels should be examined for mesogenic behavior. The development of side chain liquid crystalline polydiacetylenes could prove quite useful in the development of oriented optical materials.

A wide range of polyesters may be studied to determine the variety of temperature ranges over which thermochromism can be expressed. Systems with longer, more rigid mesogens should provide thermochromic transitions at higher temperatures, and lower transitions can be attained by substituting the aromatic rings of the mesogen, or using a meta-rather than a para-linkage in the rigid segment. Because the thermochromic effects are highly associated with motions of the flexible methylene spacers, different temperature ranges, and perhaps, different types of thermochromic behavior may be possible by changing the length of the flexible segment. Finally, an important advantage to the polyester systems is that they exhibit thermodynamic and thermochromic reversibility. Because a network is formed in the process of cross-polymerization, the thermochromic reversibility might be optimized at certain degrees of cross-polymerization.

Finally, although diacetylene macromonomers result in greater reversibility, sharper melting and clearing transitions, with correspondingly sharp thermochromic changes, are probably best obtained by examining monomeric systems. Diacetylenic monomers with narrow melting ranges, and perhaps with the ability to exhibit more than one liquid crystalline phase, would be ideal for a second generation of these diacetylenic materials.
**Final Conclusions**

Novel liquid crystalline diacetylene containing monomers and polymers have been designed successfully to undergo thermochromic transitions at the melting points of the mesogens present in each system. Effects of chemical structure have been addressed, and recommendations have been made based on these results. Two different types of chromic behavior have been observed: one case in which the polydiacetylene chain conforms to the liquid crystalline transitions of its host monomeric lattice, and two cases in which the sidechains covalently bonded to the polydiacetylene chain undergo mesogenic transitions which drive the thermochromic transition. Also, an interesting new class of hydrogen bonding, liquid crystalline diacetylenes, and their polydiacetylene products, have been synthesized and characterized. The polydiacetylenes produced have mesogenic side chains, and at least one of these materials appears to exhibit liquid crystallinity in its partially polymerized form. Finally, a unique class of liquid crystalline diacetylene-containing semi-rigid polyesters with aromatic mesogenic units has been developed. These materials show promise in the areas of solid state mechanical reinforcement of oriented fibers and films, the potential preservation of liquid crystalline ordering in polymers, and the development of oriented optical materials.