BLENDs OF CRYSTALLIZABLE POLYBUTADIENE ISOMERS: COMPATIBILIZATION BY ADDITION OF AMORPHOUS DIBLOCK COPOLYMER

by

MOIRA MARX NIR

BSChE, University of Pennsylvania (1985)

MSCEP, Massachusetts Institute of Technology (1986)

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

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in Chemical Engineering

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Signature of Author

Department of Chemical Engineering
July 30, 1991

Certified by

Robert E. Cohen, Bayer Professor of Chemical Engineering
Thesis Supervisor

Accepted by

William M. Deen
Chairman, Committee for Graduate Students

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Abstract

Precipitated blends of two crystallizable polybutadiene (PBD) isomers
were characterized in terms of crystallization and phase behavior,
morphology, and tensile mechanical properties. The isomers are syndiotactic
1,2 PBD (Mv=32.5k g/mol) and trans 1,4 PBD (Mv=425k g/mol). As predicted by
Flory-Huggins theory, the blends exhibit heterogeneous behavior over the
full range of composition.

Degree of heterogeneity due to precipitation is on the order of 5μ or less,
whereas spin-cast blends of amorphous (atactic 1,2 PBD/mixed cis+trans 1,4
PBD) homopolymers give macromdomains up to 50μ in diameter. Tensile
properties of the crystalline blends are intermediate between those of the
corresponding crystalline homopolymers, while tensile properties of the
amorphous blends are generally worse than either of the amorphous
homopolymers. But in both cases, property enhancement is evident at
approximately 10% 1,2 PBD content.

Additionally, mechanical properties at break of the s-1,2 PBD/trans 1,4
PBD crystalline blends are improved by addition of 5-10% amorphous 1,2
PBD/1,4 PBD diblock copolymer. The effect of block molecular weight and
micro-phase behavior on compatibilization of the crystalline homopolymers
was also investigated. Heterogeneous diblocks enhance blend properties to a
greater extent than homogeneous diblocks. In blends with enhanced
properties, percent coverage of interfacial surface area by diblock is on the
order of 10%.

Thesis Supervisor: Robert E. Cohen, Bayer Professor of Chemical Engineering
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Chapter I
INTRODUCTION

IA. INTRODUCTION AND MOTIVATION

To satisfy the need for new materials with specified properties, new polymers can be designed or compatible polymers whose properties are already known can be blended to combine their properties. Blending is more feasible than developing and testing new polymers.

Most homopolymer blends, however, are thermodynamically immiscible. Equilibrated phase-separated layers are not achieved in immiscible polymer systems, rather islands or macrodomains of one polymer typically form in a matrix of another. Interfacial adhesion between the phases is usually poor. As a result, the properties of these incompatible blends are often much poorer than those of either homopolymer.

Some incompatible homopolymer blends can be advantageously manipulated by the addition of an appropriate copolymer. Various types of copolymers include graft, random, and block copolymers, as illustrated in Table I.1. In ternary blends of two homopolymers with the corresponding copolymer, the copolymer may reduce the domain size of the dispersed phases, decrease interfacial tension, and enhance adhesion across the homopolymer phase boundaries. The altered morphology leads to improved properties [1]. For example, graft copolymers improved the compatibility of polystyrene/polyethylene blends [2, 3]. At low concentrations, the graft copolymers improved interfacial bonding between the homopolymer phases. At higher concentrations, the phase-separated (heterogeneous) homopolymer macrodomains became progressively smaller so that the copolymer acted as an emulsifier.

As early as 1967, Reiss et al. [4] reported that block copolymers are more effective compatibilizing agents than graft or random copolymers in polystyrene/polymethylmethacrylate and polystyrene/polyisoprene (PS/PI) systems. The A portion of an A-B diblock incorporates into the A phase of the homopolymer blend and the B block extends into the B phase. Reiss et al. also found that

1) Emulsification is most often observed when the majority of the ternary blend is diblock copolymer and the MWs of the blocks are larger than the corresponding homopolymers.
2) Diblocks of equal segment lengths are the most efficient emulsifying agents, and
3) If the MWs of the two blocks are unequal, the homopolymer corresponding to the larger block is preferentially solubilized into the diblock copolymer.

Kohler et al. [5] and Inoue et al. [6] confirmed these observations in additional blends of PS, PI, and PS/PI diblock. The added diblock copolymers, in addition to the binary homopolymer blends, were heterogeneous in all of these cases.

Ramos and Cohen [7] later showed that single-phase (homogeneous) 1,4 polybutadiene/cis 1,4 polyisoprene diblocks are capable of compatibilizing heterogeneous blends of their two homopolymers to the extent that the ternary blends exhibit only one glass transition. This condition is referred to as "homogenization" of the blends. They studied three homogeneous PBD/PI diblocks with differing block length ratios but a total MW close to that of both homopolymers together [8]. The relationships between MW, diblock content, and compatibilization in these blends are similar to those of the PS/PI blends:

1) Homogenization occurs when diblock content is approximately 80% or more of the blend,
2) Diblocks of equal segment lengths are the most efficient homogenizing agents, and
2) When the MWs of the blocks are unequal, the homopolymer corresponding to the larger block is preferentially solubilized into the diblock copolymer.

When the lengths of the two blocks are identical, the diblock is soluble in either of the homopolymers. Since heterogeneous diblocks lead to blend emulsification but homogeneous diblocks lead to blend homogenization, this work suggests that homogeneous diblocks have more potential than heterogeneous diblocks to compatibilize homopolymer blends.

Until the 1980's, noncrystalline (amorphous) polymers were most often the focus of blend research. All of the blends discussed so far are completely amorphous. But approximately one-half to two-thirds of all commercially significant polymers are crystalline or crystallizable [9]. Crystalline polymers, often referred to as "semi-crystalline", are important because they often form hard, tough materials and have high melting points, enhanced mechanical strength, and chemical resistance [10]. "Semi-crystalline" refers to the fact that for any polymer that crystallizes, some portion of the polymer
remains in the uncrystallized, amorphous state. The majority of the material often remains amorphous, and crystallinity contents of 40-50% can constitute highly crystalline materials.

There are a number of compatible blends where one polymer is amorphous and one is semi-crystalline [11, 12]. There is also abundant information on block copolymers where at least one block is crystalline. Many polymers that crystallize have stereoregular structures and are obtained primarily by difficult Zeigler-Natta (ZN) synthesis methods compared to the relatively straight-forward anionic synthesis techniques typically employed to obtain amorphous polymers. Creating a diblock copolymer with one semi-crystalline block can be difficult, but synthesis of diblock copolymers with two semi-crystalline blocks is even more problematic. As a result, little has been published on blends of crystallizable polymers in the presence of the corresponding diblock copolymers.

Anionic-to-ZN sequential polymerizations of 1,4 polybutadiene with isotactic polypropylene [13] and ZN-to-anionic sequential polymerizations of polybutylene with polystyrene [14] have been achieved. Dzrewinski [13] found that just 5 wt% iPP/PBD diblock emulsified the corresponding homopolymer blend. He also reconfirmed that molecular weight of the block components relative to the homopolymers is a major factor in determining the nature and extent of the emulsification. In his work, the $M_w$s of the blocks were less than those of the corresponding homopolymers: The homopolymer weight-average molecular weights ($M_w$s) were 450k-500k g/mol each while the blocks $M_w$s were approximately 225k g/mol each.

In a ternary blend of isotactic polypropylene/isotactic polystyrene diblock with its homopolymers, again only 5 wt% copolymer brought changes in blend morphology [15]. The blend and block $M_w$s of this system were nearly identical to those of Drzewinski's system. Yet in this case, both homopolymers and both blocks of the diblock copolymer were crystallizable. These ternary blends gave better dispersion than without diblock, had reduced domain size and improved adhesion between phases, and showed a synergistic effect in impact resistance. The diblock was synthesized by sequential ZN polymerization. Outside of this example, sequential ZN polymerization is virtually undocumented. ZN catalysis gives polymers with short lifetimes, making sequential polymerization difficult or impossible [14]. Endcapping of
ZN synthesized blocks to allow further linkage may be the most feasible route to producing novel diblocks where both blocks can crystallize.

As an alternative to emulsifying two crystallizable homopolymers with the difficult-to-synthesize corresponding semi-crystalline/semi-crystalline diblock copolymer, we suggest altering the blend morphology by manipulating the amorphous portions of the semi-crystalline homopolymers. The effects of adding amorphous diblock to crystallizable homopolymer blends, where the blocks correspond to amorphous isomers of the homopolymers, are not reported in the literature. Compared to synthesizing semi-crystalline diblocks, synthesizing amorphous diblocks is relatively easy via anionic-to-anionic transformations or coupling of blocks previously synthesized. If crystalline homopolymer blends can be compatibilized by amorphous diblocks, the commercial implications are much greater than if these blends can only be compatibilized by semi-crystalline diblocks.

Intimate mixing of crystallizable polymers can be accomplished in solution or in a bulk melt state. The crystallizable portions become amorphous in solution or in a melt, and polymer chains from two materials that differ only in tacticity or cis/trans structure become less distinguishable from each other. Thus in a melt or solution, polymer blocks with a given atactic structure may mix with homopolymer that is syndiotactic or isotactic but otherwise structurally identical to the atactic blocks; and similarly, blocks with a mixed cis+trans structure are expected to mix with homopolymer that is primarily all-cis or all-trans but otherwise structurally identical to the cis+trans block.

A number of scenarios are possible regarding the interplay between phase separation and crystallization as a binary blend of two crystallizable homopolymers is cooled from the melt. For example, assuming an upper critical solution temperature (UCST), consider the following cases:

Case 1: The homopolymers form a homogeneous melt. As the temperature is lowered,

Case 1a: Crystallization of both homopolymers occurs prior to or significantly faster than phase separation, or phase separation doesn't occur at all.

Case 1b: Phase separation of the two homopolymers occurs prior to or significantly faster than crystallization.

Case 1c: Crystallization and phase separation are cocurrent.
Case 2: The homopolymers form a heterogeneous melt. When the temperature is lowered, the materials are already phase separated upon crystallization.

In case A, eutectic or isomorphic behavior may occur. For any of the other cases, the presence of an appropriate diblock may alter the degree of phase separation that occurs. If phase separation can be totally prevented by the addition of the diblock, then eutectic or isomorphic behavior can possibly result. UCST, eutecticity, and isomorphism are defined and discussed more fully in Chapter II.

IB. PROJECT GOALS

In light of the discussion above, the objectives of our research program were as follows:

1) Characterize binary blends of crystallizable syndiotactic 1,2 and trans 1,4 polybutadienes (PBD) in terms of crystallization and phase behavior, morphology, and mechanical properties.

2) Investigate the effects of amorphous (atactic 1,2 PBD)/(mixed cis+trans 1,4 PBD) diblocks on the above-mentioned properties in blends of syndiotactic 1,2 PBD and trans 1,4 PBD homopolymers.

The second goal initially involved determining whether or not amorphous diblock copolymer played any role at all in such a system. Then we analyzed the effects of diblock content, block MWs, and phase-behavior of the added diblocks.

IC. SELECTION OF BLEND COMPONENTS

Previous work in this laboratory led to extensive characterization of amorphous polymer blends and diblocks [16], especially amorphous blends involving PBD homopolymers and diblocks [17-21]. Considering the present commercial desire to understand and develop semi-crystalline polymer systems, research on blends of semi-crystalline polybutadienes progressed logically from these earlier studies. The research described in this thesis allowed us to study the relatively unexplored field of blends of two semi-crystalline materials, as well as extend our general knowledge of PBD blends and diblocks.
Since similar polymers are more likely than dissimilar polymers to form homogeneous blends, pairs of homopolymers with similar chemical structures are the best candidates for eutectic or isomorphic systems. We considered the possibility of discovering such a system due to the isomeric nature of our two homopolymers.

The concept of tacticity is illustrated in Figure 1.1. In isotactic polymers, a given monomer side group is always aligned on the same side of the polymer backbone, and in syndiotactic polymers, the pendant group alternates from side-to-side along the backbone. The inherent stereo-regularity in polymers synthesized via isotactic or syndiotactic 1,2 addition or via cis or trans 1,4 addition of alpha-olephin and diene monomers allows them to crystallize, as long as they do not contain overly bulky side groups [22]. In atactic polymers, the pendant group is aligned in a random manner, thus the polymers are not stereo-regular and typically do not crystallize.

The monomeric units for 1,2 PBD and 1,4 PBD are given in Figure 1.2, and the chain conformations of the four stereoisomers of PBD - trans 1,4 PBD, cis 1,4 PBD, syndiotactic 1,2 PBD and isotactic 1,2 PBD - are shown in Figure 1.3. We chose to investigate syndiotactic 1,2 PBD (s-1,2 PBD) over isotactic 1,2 PBD due to commercial interest in and availability of the syndiotactic material. S-1,2 PBD has high crystallinity, a high melting point, and excellent solvent resistance. The rubber industry is presently developing s-1,2 PBD because it exhibits excellent mechanical properties [23].

Trans 1,4 PBD was chosen over cis 1,4 PBD as the second crystalline PBD component because the difference between the melting points of trans 1,4 PBD and s-1,2 PBD is about 50°C compared to about 200°C for cis 1,4 PBD and s-1,2 PBD. The smaller melting point difference more readily allowed us to check for the presence of freezing point depression in the homopolymer blends.

Three (atactic 1,2 PBD)/(mixed cis+trans 1,4 PBD) amorphous diblocks were studied in blends with the semi-crystalline homopolymers. Two of the diblocks - one heterogeneous and one homogeneous - remained from previous research in this laboratory [18]. Both of these diblocks had a 1,2 PBD block molecular weight (MW) of approximately 30k g/mol. The 1,4 PBD block was 50k g/mol in the heterogeneous diblock and 200k g/mol in the homogeneous diblock. A third diblock having 1,2 PBD and 1,4 PBD blocks of 60k g/mol and 120k g/mol, respectively, was heterogeneous [24]. The availability of these diblock copolymers allowed us to investigate the effects of diblock phase-
Table I.1: Types of Copolymers

<table>
<thead>
<tr>
<th>Type</th>
<th>Monomer Units</th>
<th>Form</th>
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<tbody>
<tr>
<td>Homopolymer</td>
<td>A</td>
<td>...AAAAAAAAAAAAA...</td>
</tr>
<tr>
<td>Random Copolymer</td>
<td>A,B</td>
<td>...ABAABABBAAB...</td>
</tr>
<tr>
<td>Multiblock Copolymer</td>
<td>A,B</td>
<td>...AAAAABBBBBAAAAA...</td>
</tr>
<tr>
<td>Diblock Copolymer</td>
<td>A,B</td>
<td>...AAAAAAAAABBBBBBB...</td>
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<tr>
<td>Graft Copolymer</td>
<td>A,B</td>
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</table>

Figure I.1: Side-group Placement for Various Tacticities

1,4 PBD

$\mathbf{+C-C=C-C_{n}}$

1,2 PBD

$\mathbf{+C-C_{n}}$

Figure I.2: General Monomer Units for 1,4 PBD and 1,2 PBD
Figure 1.3: Side and end views of the chain conformations of the four stereoisomers of polybutadiene: (a) \textit{trans}-1,4; (b) \textit{cis}-1,4; (c) syndiotactic-1,2; (d) isotactic-1,2. [25]
behavior and MW on the morphology of the resulting ternary blends. We
distinguish the diblocks by the following notations: 30k/50k, 30k/200k, and
60k/120k.

Literature searches were performed to obtain information on the
following subjects: Characterization of PBD homopolymers; polybutadiene
blends; crystallizable blends where either one or two components crystalize,
including eutectic and isomorphic systems; and blends with diblocks, where
the blend components are either amorphous or semi-crystalline. Pertinent
information is referred to in discussions of related matters throughout this
document.

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Chapter II
THERMODYNAMIC CONSIDERATIONS

IIA. THERMODYNAMICS OF BINARY AMORPHOUS HOMOPOLYMER BLENDS

In order to obtain homogeneous mixtures, a necessary condition is

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} < 0 \quad (\text{II-1}) \]

where \( \Delta G_{\text{mix}} \) is the free energy of mixing, \( \Delta H_{\text{mix}} \) is the enthalpy of mixing, \( T \) is temperature, and \( \Delta S_{\text{mix}} \) is the entropy of mixing. When \( \Delta G_{\text{mix}} \) is greater than zero, a blend system exhibits phase separation. For polymer-polymer systems, \( \Delta H_{\text{mix}} \) is basically a measure of the difference between total polymer chain segment interaction energy in the mixture and that of the pure components. It can be considered to originate in the replacement of some of the contacts between like species with contacts between unlike species. For non-polar hydrocarbons, the contacts between different segments are generally repulsive, therefore \( \Delta H_{\text{mix}} \) is usually positive.

\( \Delta S_{\text{mix}} \) characterizes the increased number of configurational arrangements possible for polymer molecules of differing types in a mixture. Unlike small molecules free to distribute randomly, joined segments in a macromolecular chain limit the number of available sites for each repeat unit. As molecular weight increases, entropy decreases. \( \Delta S_{\text{mix}} \) for polymer systems is therefore positive but small compared to normal solutes [1]. Thus \( \Delta G_{\text{mix}} \) is usually positive, making polymer-polymer compatibility rare.

For a binary system of non-polar polymers in the absence of hydrogen bonding, Scatchard-Hildebrand theory [2] holds that

\[ \frac{\Delta H_{\text{mix}}}{V} = \phi_1\phi_2(\delta_1-\delta_2)^2 \quad (\text{II-2}) \]

where \( V \) is the total volume of the system, \( \phi_1 \) and \( \phi_2 \) are the volume fractions of the two components, and \( \delta_1 \) and \( \delta_2 \) are van Laar solubility parameters that provide a measure of attractive forces between identical molecules. The solubility parameter difference represents segmental interactions. Due to the squared term, a positive value of \( \Delta H_{\text{mix}} \) is always predicted. Components with similar solubility parameters yield a small value for \( \Delta H_{\text{mix}} \) and may lead to a negative value of \( \Delta G_{\text{mix}} \).

A Flory-Huggins type-expression for the extensive free energy of mixing per volume for a binary system of components 1 and 2 is as follows:

\[ \frac{\Delta G_{\text{mix}}}{V} = \frac{\Delta H_{\text{mix}}}{V} - T\Delta S_{\text{mix}}/V = B\phi_1\phi_2 + \]

\[ RT[(\phi_1/v_1)\ln\phi_1 + (\phi_2/v_2)\ln\phi_2] \quad (\text{II-3}) \]

27
where \( v_1 \) and \( v_2 \) are the molar volumes of polymers 1 and 2, \( T \) is temperature, \( R \) is the gas constant, and \( B \) is the polymer-polymer interaction parameter \([3]\). \( B \) is equal to \((\delta_1 - \delta_2)^2\) in Scatchard-Hildebrand notation, \( \chiRT/v_1 \) in Flory's notation \([4]\) and \( \chi x/v_1 \) in most other \( \chi \) notations \([3]\), with \( x \) equal to degree of polymerization.

Note that

\[
\phi_i = \frac{N_i v_i}{V}
\]

(II-4)

where \( i \) corresponds to component 1 or 2 and \( N \) is the number of moles of polymer chains. Also,

\[
V = N_1 v_1 + N_2 v_2,
\]

(II-5)

\[
\phi_1 + \phi_2 = 1.
\]

(II-6)

If a two component system has separated into two phases A and B, then we also know that

\[
\phi_{1A} + \phi_{2A} = 1 \quad \text{and} \quad \phi_{1B} + \phi_{2B} = 1.
\]

(II-7)

In terms of total volume, the extensive free energy of mixing can be written

\[
\Delta G_{\text{mix}} = G_{\text{mix}} - G_{\text{mix}}^0 = B \phi_1 N_2 v_2 + RT(N_1 \ln \phi_1 + N_2 \ln \phi_2) = B\phi_2 N_1 v_1 + RT(N_1 \ln \phi_1 + N_2 \ln \phi_2)
\]

(II-8)

The chemical potentials \( \mu_1 \) and \( \mu_2 \) are defined as \( \partial G_{\text{mix}} / \partial N_1 \) and \( \partial G_{\text{mix}} / \partial N_2 \), respectively, and are equal to \( \partial \Delta G_{\text{mix}} / \partial N_1 \) and \( \partial \Delta G_{\text{mix}} / \partial N_2 \) since \( G_{\text{mix}}^0 \) is a constant. Thus, in terms of \( \phi_2 \),

\[
\mu_1 = Bv_1 \phi_2^2 + RT[\phi_2(1-v_1/v_2) + \ln(1-\phi_2)],
\]

(II-9)

\[
\mu_2 = Bv_2(1-\phi_2)^2 + RT[(1-\phi_2)(1-v_2/v_1) + \ln(\phi_2)]
\]

(II-10)

To check for accuracy, the Gibbs-Duhem equation can be applied:

\[
N_2(\partial \mu_2 / \partial N_2) + N_1(\partial \mu_1 / \partial N_2) = 0
\]

(II-11)

Our expressions do satisfy this relationship.

The binodal curve for a two component system of given molecular weight at constant pressure depicts the compositions of the two equilibrium phases in a phase-separated system as a function of temperature, assuming nucleation is not suppressed so as to prevent phase separation. Flory-Huggins' expressions for free energy predict an upper critical solution temperature (UCST), as is expected in blends of non-polar, relatively non-interacting polymer components such as 1,2 and 1,4 PBD. Below the binodal curve in an UCST system, two equilibrium phases are present (A, B), i.e. the system is heterogeneous. Above the curve, no phase separation occurs, i.e. the system is homogeneous.
The binodal curve is defined by the points of double tangency on the extensive free energy curves. These points simultaneously satisfy the following two conditions: 1) the chemical potential in terms of component 1 is the same in both phases and 2) the chemical potential with respect to component 2 is the same in both phases:

$$\mu_1(\phi^A) = \mu_1(\phi^B) \quad \text{and} \quad \mu_2(\phi^A) = \mu_2(\phi^B)$$  \hspace{1cm} (II-12)

In terms of our expression for free energy, these conditions become

$$Bv_1[(\phi^B)^2 - (\phi^A)^2] + RT[(1-v_1/v_2)(\phi^B - \phi^A) + \ln((1-\phi^B)/(1-\phi^A))] = 0,$n

$$Bv_2[(1-\phi^B)^2 - (1-\phi^A)^2] + RT[(1-v_2/v_1)(\phi^A - \phi^B) + \ln(\phi^B/\phi^A)] = 0$$ \hspace{1cm} (II-13)

They completely define the composition of the two phases for a given temperature. For temperatures less than the UCST, the solution of these equations gives one composition for each of the two phases present. At the UCST, these conditions yield only one composition, and the resulting point is the critical point.

On the free energy curve at a temperature below the UCST, two points of inflection occur that satisfy the condition

$$\partial^2 \Delta G_{\text{mix}}/\partial N_1^2 = 0.$$  \hspace{1cm} (II-14)

Alternatively, the same points can be found by taking \(\partial^2 \Delta G_{\text{mix}}/\partial N_2^2 = 0\), \(\partial^2 \Delta G_{\text{mix}}/\partial \phi_2^2 = 0\), or \(\partial^2 \Delta G_{\text{mix}}/\partial \phi_1^2 = 0\). When this relationship is solved in terms of \(\phi_1\) or \(\phi_2\) and then plotted as a function of temperature, the result is the spinodal curve. The spinodal curve defines the limit of stability. When \(\partial^2 \Delta G_{\text{mix}}/\partial N_1^2\) is less than zero, as is the case below the spinodal curve in an UCST system, the blend is no longer stable and it spontaneously phase-separates. Between the binodal and spinodal curves, blends can achieve a metastable state, in which phase-separation normally associated with the binodal limit can be suppressed if nucleation is prevented. At the critical point, the spinodal and binodal conditions are both satisfied and the spinodal and binodal curves intersect. Mathematically, the critical point occurs when

$$\partial^3 \Delta G_{\text{mix}}/\partial N_2^3 = 0 \quad (= \partial^3 \Delta G_{\text{mix}}/\partial N_1^3 = \partial^3 \Delta G_{\text{mix}}/\partial \phi_1^3 = \partial^3 \Delta G_{\text{mix}}/\partial \phi_2^3).$$  \hspace{1cm} (II-15)

With our free energy expression,

$$\partial^2 \Delta G_{\text{mix}}/\partial N_2^2 = \partial \mu_2/\partial N_2 = (\partial \mu_2/\partial \phi_2)(\partial \phi_2/\partial N_2) =$$

$$\{ -2Bv_2(1-\phi_2) + RT[1/\phi_2 + v_2/v_1 - 1]\} (\phi_2(1-\phi_2)/N_2)$$ \hspace{1cm} (II-16)

Setting this expression to zero and eliminating the trivial solutions from the \(\partial \phi_2/\partial N_2\) factor, we obtain

$$B/RT = \{1/2 + 1/\{v_1(\phi_1) + 1/\{v_2(\phi_2)\}\}.$$  \hspace{1cm} (II-17)
and we can easily construct the spinodal curve by calculating $T$ as a function of $\phi_2$. At the critical point, $\partial^3 \Delta G_{\text{mix}} / \partial N_2^3 = 0$, which leads to
\[ 1/(v_1 \phi_1^2) - 1/(v_2 \phi_2^2) = 0 \]  
(II-18)
Substituting $(1 - \phi_2)$ for $\phi_1$, this equation is a quadratic in $\phi_2$ that yields
\[ \phi_{2\text{crit}} = v_1^{1/2} / (v_2^{1/2} + v_1^{1/2}) \]  
(II-19)
Note that the condition $x_x = Bv_1/RT = 2$ is valid when $\phi_1 = \phi_2 = 0.5$ and $v_1 = v_2$, but it is not a general criterion for determining the spinodal curve.

The Flory-Huggins' model assumes a "mean-field nature" [5, 6] which does not allow for dissimilarity between the free volumes of polymer and solvent molecules. As a result, this theory does not predict a second critical temperature and range of inhomogeneity observed in many binary systems as the solution temperature is raised. The second critical point is the lower critical solution temperature (LCST) and is predicted by other later theories [7, 8]. Mathematical models of these theories require additional parameters that are often difficult to determine or estimate.

However, the Flory-Huggins approach is satisfactory when the mixture consists of all non-polar long chain molecules in the absence of solvent because then the chains assume ideal Gaussian conformation unperturbed by the excluded volume effect [9]. In our experiments, this condition was applicable, therefore the Flory-Huggins model was expected to be adequate. We applied it to an amorphous system having the same molecular weights as the s-1,2 PBD and trans 1,4 PBD components in our experimental studies, as reported in Sections IIIA and IIIB.

The discussion above relates to thermodynamic behavior of blends, but note that non-equilibrium effects also play a role in the character and properties of polymer systems. Whether a blend is thermodynamically heterogeneous or homogeneous, diffusion limitations typically keep the polymers in a metastable state. As molecular weights of the chains increase, diffusion becomes more difficult. Thus, binary blends separate into island-type domains of one polymer in a matrix of the other rather than form a true homogeneous mixture when the system is thermodynamically homogeneous or form layers when the system is heterogeneous. With time, the size of the domains may change as the system attempts to equilibrate.
II.B. THERMODYNAMICS OF DIBLOCK COPOLYMERS

II.B.1. Diblock Copolymers

$\Delta H_{\text{mix}}$ for diblocks is the same as that described for homopolymer blends. $\Delta S_{\text{mix}}$ decreases because there is a reduction in possible conformations for molecular arrangement due to the constraint of the junction. Debate exists on exact expressions for $\Delta S_{\text{mix}}$, but all theories agree that at relatively high molecular weights, diblocks will display phase-separated behavior but at low molecular weights, diblocks may be homogeneous in nature. We showed above from spinodal conditions that $\chi x_{\text{crit}}=2$ for binary blends when $\phi_1=\phi_2=0.5$ and $\nu_1=\nu_2$. The critical molecular weight where phase separation first occurs ($M_{\text{crit}}$) for diblocks is on the order of five times the critical molecular weight of the corresponding blend.

Due to the junction between blocks in diblock copolymers, phase separation is restricted to the molecular dimensions of the radius of gyration of the copolymer. Copolymer radii of gyration are on the order of hundreds of angstroms or less [6] whereas domains of homopolymer blends are on the order of microns.

Heterogeneous diblocks form various equilibrium microdomain morphologies depending on the fraction of each polymer in the material. At low weight fractions of component A, spheres of A form in a matrix of B. As the weight fraction of block A increases, cylinders of A are seen in B. At approximately equal weight fractions, A and B blocks form alternating lamellae. Increasing B content further, cylinders of B in A and finally spheres of B in A are apparent. For PS/P1 star block copolymers, "ordered bicontinuous double diamond" structures form between the transition from cylinders to lamellae [10]. Helfand and Wasserman [11] developed a FORTRAN program that determines the domain size and shape with the lowest free energy for a specific weight fraction. The structure variations and heterogeneous-to-homogeneous microdomain transitions predicted by this program are in agreement with experiments on PBD/PS diblocks [1].

Torradas [12] lists a modification to Helfand's program to calculate the diblock molecular weight at the boundary between block homogeneity and heterogeneity. The calculation is accomplished by searching for the molecular weight where $\Delta G_{\text{mix}}=0$. Using the modified program at a weight fraction of 0.5 for each component, Cohen and Wilfong [13] found that $M_{\text{crit}}$ for the following diblocks is 5-6 times $M_{\text{crit}}$ of the corresponding blends:
polystyrene/mixed cis+trans 1.4 PBD; atactic 1.2 PBD/mixed cis+trans 1.4 PBD; 1.4 polyisoprene/mixed cis+trans 1.4 PBD; and 1.4 polyisoprene/atactic 1.2 PBD. \(M_{\text{crit}}\) for blends was obtained from the spinodal curve of the Flory-Huggins model.

Leibler [14] predicts microdomain configurations that are similar to Helfand's, and both predictions are shown in Figure II.1 [1]. Leibler's diagram is based on the mole fraction of \(A\) repeat units as opposed to weight fraction. He definitively predicts that \(M_{\text{crit}}\) of the diblock is equal to 5.25 times \(M_{\text{crit}}\) of the blend, which implies that \(x_{\text{crit}} = 10.5\) for diblocks. Minchau et al.'s [15] Monte Carlo simulations support Leibler's theory if the \(x\) parameter of of the diblock is taken to be that of the corresponding homopolymer blend.

IIB.2. Diblocks in Blends with Amorphous Homopolymer

As discussed in Section IA, diblocks can decrease the size of homopolymer domains in heterogeneous blends and reinforce the interface between the homopolymers. The \(A\) portion of an \(A-B\) diblock incorporates into the \(A\) phase of the homopolymer blend and the \(B\) block extends into the \(B\) phase. The extent of dispersion and reinforcement is dependent on the molecular weights of the blocks relative to the corresponding homopolymer molecular weights, and on the percent and nature of the diblock present in the blend.

At high diblock concentrations when the homopolymer MWs are not greater than the corresponding block MWs, the homopolymers may be solubilized in the microdomains of the like components of the copolymer. At low concentrations of diblock and if the block MWs are not greater than the corresponding homopolymer MWs, the diblocks locate preferentially at the homopolymer interfaces and lower interfacial tension. Micro-phase separation of the blocks promotes localization at the interface [16, 17]. As diblock content increases, the average size of the homopolymer domains decreases, yielding better dispersion. In Section IA, we referenced early experiments on polymer blends that depict these correlations. There are many more examples in the literature to date, including recent work by Tanaka et al. [18] and Elamans et al. [19]. When the conditions for solubilization of diblock into homopolymer or homopolymer into diblock are not met, the diblocks and homopolymers segregate from each other to form independent phases.
Figure II.1: Generalized phase diagram for a diblock copolymer based on the theories of Helfand (left ordinate) and Leibler (right ordinate). The solid curve indicates the border between microdomains and homogeneous phase. The broken lines represent the predicted transitions from one type of geometric array of domains to another.

[1]
Using the blend limit of stability from the Flory-Huggins derivation and Helfand's diblock transition from homogeneity to heterogeneity, Cohen and Wilfong [13] suggest the combined blend plus block phase diagram in Figure II.2. In this figure, log(M/M_{crit}) is shown as a function of weight fraction. For diblocks, M is the sum of both blocks. In most systems, the values of M_{crit} are so low that both heterogeneous diblocks and blends are expected at all molecular weights of practical significance [20]. Only when δ1 is close in value to δ2 are all regions of the diagram in a range of M that constitutes polymeric, as opposed to oligomeric, behavior.

Below the lower curve in Figure II.2, both the blend and the block are homogeneous. Above the upper curve, both are heterogeneous. This second region is where emulsification by diblock is often observed. The diblock is homogeneous and the blend is heterogeneous in the central region, and it is within this region that large quantities (>80 wt%) of mixed cis+trans 1,4 PBD/cis 1,4 polyisoprene diblocks homogenized the corresponding blends when the blocks were of equal length and the homopolymers were of equal molecular weight, as discussed in Section IIA [21, 22].

Cohen [20] proposed a three dimensional plot in Figure II.3 showing the effect of percent diblock as a function of composition, temperature, and molecular weight. This plot is useful for anticipating how much of a given diblock will be required to homogenize an incompatible non-polar, non-interacting polymer blend. For intermediate compositions of the diblock, Cohen used a first approximation linear combination of the Flory-Huggins phase separation prediction for blends and Helfand's prediction for blocks. Above the curve, the diblock is expected to be an emulsifier for the heterogeneous homopolymer blends, and below the curve, the diblock may function as an homogenizing agent. This general trend was confirmed by Bates [23], Torradas [12] and Hartney [5], though Hartney obtained a sigmoidal, not linear, locus of critical molecular weights for an amorphous 1,2 PBD/1,4 PBD system.

More rigorous thermodynamic treatments have since been developed by Xie et al. [24] and Meier [25] for solubilization of homopolymer into diblock domains, and by Noolandi et al. [26, 27] and Leibler [28, 29] for solubilization of blocks into homopolymer domains. Roe [30] modified Leibler's model to allow for asymmetric copolymers. Noolandi's and Leibler/Roe's work predict a critical diblock concentration above which diblocks form micelles rather than
Figure II.2: Combined Blend Plus Block Phase Diagram

Figure II.3: Schematic three-dimensional plot showing various planes of AB polymer/polymer composition. From left to right: homopolymer blends; blends containing 30 weight percent diblock copolymer; diblock copolymers.
mix with homopolymers. Up to this concentration, the theories predict the observed lowering of interfacial tension in blends with two immiscible homopolymers [27, 29].

With blends of PS/PBD diblock and PS homopolymer, Kinning et al. [31] recently showed that Roe's treatment successfully predicts qualitative trends in terms of copolymer concentration and component MWs, but predicts "critical micelle concentrations" (cmc) at least 1 order of magnitude high. Also, the model underestimates the amount of free copolymer dissolved in the homopolymer matrix at copolymer concentrations above the cmc. Kinning suggests that the error with respect to quantitative predictions is due to sensitivity of the interaction energy density parameter.

According to Shull and Kramer's application of mean-field theory [17], the effects of copolymer on interfacial properties are governed by extension of the blocks away from the interface. Compatibilization is thus determined primarily by the MW of the longer copolymer block. But in order for interfacial reinforcement to occur, Creton et al. [32] propose that the blocks must entangle with both homopolymers, thus the shorter block must not be shorter than the average chain length between entanglements of the homopolymers. This latter conclusion is based on experiments with blends of poly(styrene-co-2-vinylpyridene) diblocks and the corresponding homopolymers. If the MW is less the critical minimum, the copolymer will still act as a surfactant to decrease interfacial tension and modify morphology, but it will not prevent failure at the interface when high tensile stress is applied.

There are alternative diblock compatibilization approaches to the standard scheme of A-B diblock added to homopolymers A and B. For example, homopolymers can be compatibilized by an X-Y type diblock where X is compatible with homopolymer A, and Y is compatible with homopolymer B. Jo et al. [33] blended poly(1,4-dimethyl-2,6-phenylene oxide) [MPPO] and poly(styrene-co-acrylonitrile) [SAN] homopolymers with a diblock of PS/PMMA. Normally, blends of MPPO and PS are miscible, as are blends of SAN and PMMA at certain compositions. With only 1 wt.% copolymer, Jo's blends had a more regular and finer dispersion than without copolymer. Vilgis and Noolandi [34] modeled a system of A and B homopolymers with an X-Y diblock, but they added a new twist: X is incompatible with B but less incompatible with A, while Y is incompatible with A but less incompatible with B. The lowest free energy state is separation of copolymer from either homopolymer, but local
thermodynamic equilibrium is such that there is a driving force to orient the blocks at the homopolymer interface. With this model, they calculated interfacial tension for blends with 5% diblock, varying interaction parameters and block lengths. This approach predicts promotion of interfacial activity for various cases, and thereby advances the concept of universal compatibilizers that exploit preferential repulsive interactions between polymers.

II.C. POLYMER CRYSTALLIZATION

II.C.1. Homopolymer Crystallization

Polymer crystallization refers to the process in which polymer chains or chain segments align in an orderly fashion due to the chemical and geometric regularity of the molecules in the chains. Although alignment leads to unfavorable entropy for the system, the free energy is minimized because strong intermolecular forces result in favorable enthalpy. The intermolecular forces can be due to hydrogen bonding, dipole-dipole interactions, and/or van der Waals forces [35].

As crystallizable polymers are cooled below their melting points, diffusion and steric limitations do not allow all chains to arrange in the regular pattern needed for crystal formation [35]. Thus, regions of crystallinity form among regions of amorphous material that remain uncryrstallized.

Crystallizing chains fold on themselves in an accordion-like fashion and form lamellae about 100Å thick, as shown in Figure II.4. Polymer molecules are usually longer than the extended length of an unfolded lamella, thus individual polymer molecules probably contribute simultaneously to several crystalline and amorphous regions by weaving in and out of crystallizing sections, also illustrated in Figure II.4.

Crystallization typically initiates at a central nucleation site and then lamellae grow in a radial manner to form spherulitic structures. The nucleus may be a foreign particle (heterogeneous nucleation) or may arise spontaneously in the melt (homogeneous nucleation). The resultant spherulites can range from submicroscopic to millimeters in diameter. When two spherulites meet during crystallization, lamellae from both extend across the boundary into any uncryrstallized material available, and thereby form an interwoven system that holds the material together [8]. In a polarizing light
microscope, spherulites are seen as circular birefringent areas in a dark Maltese cross pattern.

Crystallization occurs at temperatures below the melting point \( (T_m) \) and above the glass transition temperature \( (T_g) \). A maximum growth rate exists between \( T_g \) and \( T_m \) because of competing effects of chain mobility and undercooling. The lower the temperature is below \( T_m \), the greater the driving force due to undercooling and the greater the rate of nucleation. Close to \( T_g \), however, the material becomes more viscous, chain transport is hindered, and alignment for crystallization is thus impeded. Rates of polymer crystallization can be estimated from the Avrami relationship

\[
X_C = \left[1 - \exp(-k t^n)\right]
\]

(II-20)
in conjunction with calorimetry measurements. \( X_C \) is the volume fraction that has crystallized within a given time \( t \), \( k \) is the bulk crystallization rate constant, and \( n \) is the Avrami exponent. The value of \( n \) is approximately 3 for heterogeneous nucleation and 4 for homogeneous nucleation [36].

IIC.2. Binary Blend Crystallization

Homogeneous mixing of one crystallizable polymer and one amorphous polymer leads to classical melting point depression of the crystalline component, as predicted by Scott's [37] and Flory's [4] expressions for thermodynamic mixing of polymers [38-40]. Burghardt [41] extended Flory's expressions to blends of two crystallizable polymers and calculated phase diagrams for various interaction parameters.

Heterogeneous blends of two crystallizable polymers give two distinct melting points for any composition, i.e. one melting point per homopolymer. Three temperature regions of importance can be delineated for such blends, as depicted in Figure II.5. Above the melting points of both homopolymers, the mixture is amorphous. Between the melting points, one homopolymer can crystallize while the second cannot. Below both melting points, both components crystallize. Burghardt's analysis predicts only negligible melting point depression for each component over the total composition range in such a system.

For an ideal homogeneous liquid solution of two substances A and B, the melting point forms a eutectic minimum, and generally, the melting point is dependent on composition as illustrated in Figure II.6. \( T_e \) is the eutectic temperature and \( \phi_e \) is the eutectic composition. A polymer eutectic can occur
Figure II.5: Temperature Regions for Heterogeneous Blends of Two Crystallizable Homopolymers

Figure II.6: Melting Point Depression in Eutectic and Isomorphic Systems
only if there is a true solution in the melt that coprecipitates to make a homogeneous crystallized polymer blend [42]. If eutectic-like melting point depression exists for any polymer blend, then only one melting point would be present at each composition, and the eutectic point would be observed in the bottom region in Figure II.5. No cases of true polymer-polymer eutectics have been documented [42, 43], but eutectic solidification has been observed for a few polymer/monomer blends [44-48].

With isomorphism, as with eutecticity, a single melting point is present at any composition. However, no minimum is observed in the melting point curve of isomorphic pairs. Rather it always lies between the two homopolymer Tm's. This type of behavior is also depicted in Figure II.6. Isomorphic cocrystallization of macromolecular pairs is rare but has been observed on a few occasions [7, 49-51]. Due to similarity between two different monomer units in isomorphic pairs, each monomer fits equally well in a crystal lattice, allowing the formation of mixed crystals. Isomorphism can occur within an individual copolymer consisting of isomorphic "mers" or in blends of isomorphic homopolymers. In blends, chain segments from the two types of polymers are able to adopt similar conformations and thereby replace each other as the crystals form [42].

A final possibility for two crystallizable homopolymers that are homogeneous in a melt is that they may crystallize independently while the fractions that ultimately remain uncrysrallized mix homogeneously. This phenomenon was observed in blends of polyethylene terephthalate with polybutylene terephthalate [52]. Homogeneous mixing of amorphous components may also occur in blends of one crystallizable polymer and one non-crystallizing polymer [53]. The amorphous material can reside between crystalline lamellae and/or be accepted in spherulitic or other crystalline structures [54].

As with amorphous polymer blends, thermodynamics of crystalline systems must be considered in conjunction with certain non-equilibrium effects. Polymer diffusion again plays a role in determining morphology. In addition, crystallization kinetics and the interplay between crystallization and phase behavior affect blend morphology [40]. By altering a crystallizable blend's thermal and processing history, we can obtain quite varied morphologies for a given blend composition [53, 55].

41
IIID. REFERENCES


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Chapter III
APPLICATION OF BINARY BLEND MODEL

IIIA. PRELIMINARY CALCULATIONS AND CONVERSIONS

As discussed in Section IIA, the Flory-Huggins' model predicts that $\chi x_{crit}=2$ for homopolymer blends when $\phi_1=\phi_2=0.5$ and $v_1=v_2$. From small-angle neutron scattering (SANS) experiments, Bates and Hartney [1] obtained the relationship

$$\chi = 0.561/T(K) + 6.79\times10^{-3}$$  \hspace{1cm} (III-1)

for protonated 1,2 PBD/deuterated 1,4 PBD systems with $\phi_1=\phi_2=0.5$. Applying this expression to 1,2/1,4 PBD blends, $M_{crit} = x_{crit} \times 54$ g/mol butadiene monomer is 12.5k g/mol at 298K. From solubility parameter data, Cohen and Wilfong [2] calculated a $M_{crit}$ of 13.8k g/mol for 1,2 PBD/1,4 PBD blends. At $T=\infty$, the $\chi$ expression above is minimized and gives a maximum $x_{crit}$ value of 295 for blends, which corresponds to an $M_{crit}$ of 15.9k g/mol for PBD systems. This preliminary analysis implies that no UCST exists for PBD homopolymer blends with $\phi_1=\phi_2=0.5$ for which the average molecular weight is greater than 15.9k g/mol. Therefore, such blends are expected to be heterogeneous at all temperatures. In our work, the homopolymer molecular weights are greater than 15.9k g/mol. If we assume that this expression for $\chi$ is suitable for s-1,2 PBD/trans 1,4 PBD blends then we can expect that 50/50 mixtures of our materials will not be homogeneous at any temperature.

With Leibler's 5.25 factor for diblocks, 1,2 PBD/1,4 PBD diblock $M_{crit}$ is thus 83.5k g/mol at $T=\infty$ and 72.5k g/mol at 298K. Yet these numbers are valid only at equal volume fractions of the two components. Homogeneity can occur for diblocks with higher molecular weights when the fractions are unequal, as is the case with Cohen and Wilfong's 30k/200k diblock.

The thermodynamic model described in Section IIA for amorphous binary systems allows predictions of phase behavior across the complete range of composition, as long as a reliable $\chi$ or $B$ expression is available. We applied this model for mixtures of 1,2 PBD and 1,4 PBD materials in order to predict the phase behavior of s-1,2 PBD/trans 1,4 PBD blends in the melt state. Spinodal and binodal curves were developed for blends of 1,2 PBD with molecular weight 32.5k g/mol and 1,4 PBD molecular weight of 425k g/mol. These molecular weights correspond to the average $M_v$ values for our
homopolymers. Degree of polymerizations are thus 601 and 7857, respectively. Determination of these $M_w$ and $x$ values is detailed in Section VA.

To perform the desired calculations, values for $V_1$, $V_2$, and $x$ or $B$ were needed. The parameter $v_i$ can be determined in a number of equivalent ways:

$$v_i = v_i(r.u.)*x_i = v_i(r.u.)*[M_W/r_M(r.u.)] = M_W/P_i(r.u.) = M_W/P_i \quad (III-2)$$

The notation r.u. denotes polymer repeat unit. We used group contribution methods to obtain $v_i(r.u.)$ [3] and then employed the expression $v_i = v_i(r.u.)*[M_W/r_M(r.u.)]$. Also, $v_i = (M_v)/P_i$ was determined using published polymer density values for amorphous 1,2 PBD and 1,4 PBD. For each homopolymer, the $v_i$ values ultimately used in the model were the average of the $v_i$ values from these two relationships.

From group contribution summations for $v_i(r.u.)$, we obtained $v_1(r.u.) = 57.1$ cc/mol and $v_2(r.u.) = 59.2$ cc/mol, where 1,2 PBD is component 1 and 1,4 PBD is component 2. Table III.1 shows the origin of these numbers. Multiplying by the $x$ values given earlier, $v_1$ and $v_2$ are $3.47 \times 10^4$ and $4.65 \times 10^5$. Natta and Corradini [4] reported a density $\rho_1$ of 0.92 g/mol for the amorphous portion of s-1,2 PBD and Iwayanagi et al. [5] obtained a density $\rho_2$ of 0.89 g/mol for amorphous 1,4 PBD. With these density values, $v_1$ is $3.53 \times 10^4$ cc/mol and $v_2$ is $4.77 \times 10^5$ cc/mol by the second calculation method. Dividing by the appropriate $x$ value, $v_1(r.u.)$ and $v_2(r.u.)$ are 58.8 and 60.7 cc/mol. The average $v_1$ and $v_2$ are thus $3.50 \times 10^4$ cc/mol and $4.71 \times 10^5$ cc/mol, respectively and the average $v_1(r.u.)$ and $v_2(r.u.)$ values are 58 and 60 cc/mol.

Five expressions for $B$ were tested in the model. Three of these were calculated from the relationship

$$B = (\delta_i - \delta_2)^2 \quad (III-3)$$

where $\delta_i$ is the van Laar solubility parameter. The $\delta_i$ parameter is equal to the square root of the cohesive energy density, $[E_i/v_i(r.u.)]^{1/2}$, where $E_i$ is cohesive density, typically expressed in cal/mol. $E_i$, like $v_i(r.u.)$, can be obtained by a group contribution technique, and calculations for $E_1$ and $E_2$ are given in Table III.1 [3]. With $v_i(r.u.)$ values calculated above by group contribution, $B = (0.21)^2$ cal/cc = 0.0441 cal/cc. Alternatively, $\delta_i$ can be expressed as $[F_i/v_i(r.u.)]$ where $F_i$ is the molar attraction coefficient. This parameter is also estimated by group contribution and listed in Table III.1. With molar attraction coefficients and $v_i$ values from density calculations, $B = (0.42)^2 = 0.1764$ cal/cc. These two $B$ values, 0.0441 cal/cc and 0.1764 cal/cc, are referred to as $B_{low}$ and $B_{high}$ in the remainder of this chapter. A value for $B$ of
Table III.1: Group Contribution Values for the Determination of 1,2,1,4 PBD Interaction Parameters

The group values presented here are tabulated in Van Krevelen (1976). [3]

For syndio, each monomer contains the following groups: \( -\text{CH}_2-\), \( -\text{CH}-\), \( -\text{CH}^=\), \( \text{CH}^=\)

For trans, each monomer contains the following groups: \( 2\times \) (\( -\text{CH}_2-\), \( -\text{CH}^=\) )

<table>
<thead>
<tr>
<th>Group</th>
<th>( E) (Fedors) (cal/mol)</th>
<th>( v) (Fedors) (cm³/mol)</th>
<th>( F) (Hoy) ((\text{cal} \cdot \text{cm}^3)^{1/2}/\text{mol})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{CH}^-)</td>
<td>823.2</td>
<td>-1.0</td>
<td>86.0</td>
</tr>
<tr>
<td>(-\text{CH}_2^-)</td>
<td>1185.6</td>
<td>16.1</td>
<td>131.5</td>
</tr>
<tr>
<td>(-\text{CH}^=)</td>
<td>1034.4</td>
<td>13.5</td>
<td>121.5</td>
</tr>
<tr>
<td>\text{CH}^=)</td>
<td>1034.4</td>
<td>28.5</td>
<td>126.5</td>
</tr>
</tbody>
</table>

| Sum, syndio | 4077.6                     | 57.1                      | 465.6                             |
| Sum, trans  | 4440.0                     | 59.2                      | 506.1                             |
0.107 cal/cc, which is near the average of \( B_{\text{low}} \) and \( B_{\text{high}} \), was also tested and is referred to as \( B_{\text{avg}} \).

Note that experimental interaction parameters may be temperature and composition dependent [6, 7], especially if they are determined via experiments that rely on Flory-Huggins theory [8]. The group contribution values we derived are for 25°C and are not composition specific. Experimental attempts to obtain an interaction parameter are reported in Section IIIC.

The final two expressions for \( B \) that were tested in our model were converted from \( \chi \) expressions in the literature for 1,2/1,4 PBD blends at specific compositions. One of the \( \chi \) relationships is the Bates and Hartney expression mentioned earlier for the case of \( \phi_1 = \phi_2 = 0.5 \). The second \( \chi \) relationship was reported by Sakurai et al. [9] as

\[
\chi = [1.87/T + 2.69 \text{ E-3}]
\]

at \( \phi_2 = 0.3 \). The conversion

\[
B = \chi \times RT / v_1 = \chi \times RT / v_1(\text{r.u.})
\]

was applied with a value of 59 cal/cc for \( v_1(\text{r.u.}) \) for both \( \chi \) expressions. We thus obtain \( B = [1.9 \times 2 + (2.3 \times 4) \times T] \) cal/cc for the Bates and Hartney parameter and \( B = [6.3 \times 2 + (9.1 \times 5) \times T] \) cal/cc for the Sakurai parameter. For reference sake, the Bates and Hartney expression gives a \( B \) value of 0.087 at 25°C while the Sakurai expression gives 0.090. Both of these values are closer to \( B_{\text{avg}} \) than to \( B_{\text{low}} \) or \( B_{\text{high}} \).

A sixth expression for \( B \) was collected later in the course of our research. Trask and Roland [10] report a value of \( \chi = 0.0043 \) for 1,2 PBD/1,4 PBD blends, which converts to \( B = [T \times 1.45 \times 4] \), or 0.043 cal/cc at 25°C.

IIIB. RESULTS OF THE MODEL

With \( v_1 \) and \( v_2 \) values of \( 3.50 \times 10^4 \) and \( 4.71 \times 10^5 \) cc/mol from above, the critical composition is \( \phi_2 = 0.214 \). When \( \Delta G_{\text{mix}} \) is evaluated as a function of \( \phi_2 \), we find that with the Bates and Hartney \( B \) expression, there is no temperature for which \( \Delta G_{\text{mix}} < 0 \) is satisfied when \( 1.0 \times 10^{-6} < \phi_2 < 0.96 \). Similarly, with the Sakurai \( B \) expression, there is no temperature for which \( \Delta G_{\text{mix}} < 0 \) is satisfied at any composition \( 1.0 \times 10^{-5} < \phi_2 < 0.58 \). The other three \( B \) values always gives \( \Delta G_{\text{mix}} < 0 \) at some temperature, indicating that if a high enough temperature could be achieved without damaging the polymers, homogeneity would occur for all compositions.
Spinodal conditions were calculated for all five B values and the resulting spinodal curves are shown in Figure III.1. In Figure III.1a, the temperature ranges from 0K to 5000K, and in Figure III.1b, the temperature ranges from 0K to 1000K. For $B_{\text{low}}$, $B_{\text{high}}$, and $B_{\text{avg}}$, the spinodal curves show a maximum at the expected critical composition and the critical temperatures are 959.3K, 2327.6K, and 3837.2K, respectively. The B expressions that were converted from literature $X$ expressions yield spinodals that diverge rapidly to infinite temperature. This prediction occurs for these B expressions because, as mentioned above, $\Delta G_{\text{mix}}$ is never less than zero within certain compositional ranges no matter how high the temperature becomes. However, the plots in Figure III.1b show that at temperatures less than 500K (which is approximately where crosslinking and degradation occur in samples heated at 20°C/min), the spinodal with the Bates and Hartney B expression can be approximated by $B_{\text{low}}$ at $\phi_2 > 0.92$. Similarly, the spinodal with the Sakurai B expression can be approximated by $B_{\text{avg}}$ at temperatures below 510K.

Binodal curves were developed for $B_{\text{low}}$ and $B_{\text{avg}}$ only. For both of these B values, equilibrium $\phi_2$ values were determined for six arbitrary temperatures below the respective critical points. The $\phi_2$ values were obtained by calculating and plotting $\mu_1$ and $\mu_2$ as a function of $\phi_2$ for each temperature and then checking for the two $\phi_2$ values that simultaneously satisfied the two binodal conditions: $\mu_1(\phi_2^A) = \mu_1(\phi_2^B)$ and $\mu_2(\phi_2^A) = \mu_2(\phi_2^B)$. The error in $\phi_2$ is ±0.0005. The resulting binodal points are plotted in Figure III.2 along with the corresponding spinodal curves. The results are portrayed up to 2500K in Figure III.2a and up to 1000K in Figure III.2b.

We conclude from these plots that 1,2 PBD/1,4 PBD binary blends with MWs of 32.5k g/mol and 425k g/mol, respectively, are heterogeneous at temperatures less than the PBD degradation temperature over most of the composition spectrum, except, perhaps, at compositions of 85% or more 1,4 PBD. The region that corresponds to a melt of our s-1,2 PBD and trans 1,4 PBD blends falls above the s-1,2 PBD melting point around 460K (187°C). The model therefore predicts that our s-1,2 PBD/ trans 1,4 PBD system is heterogeneous in the melt at any temperature and composition of practical interest.

**III.C. EXPERIMENTAL VERIFICATION OF THE INTERACTION PARAMETER**

Heterogeneous-to-homogeneous phase transitions are sometimes observable via dynamic mechanical tests. As a heterogeneous sample is
III.1a: 0K to 5000K

III.1b: 0K to 1000K

Figure III.1 Spinodal Curves
Figure III.2: Binodal and Spinodal Curves for $B_{\text{low}}$ and $B_{\text{avg}}$
heated, the storage modulus (G') drops during phase transition, yielding a step-like curve in plots of G' as a function of temperature [11-13]. Alternatively, heterogeneous-to-homogeneous phase transitions may be apparent in calorimetry data. Once the binodal temperature is obtained for a given composition, a corresponding B value can be determined from the equations for binodal phase-separation listed above. Yet, caution must be taken in assessing the validity of polymer-polymer interaction parameters obtained over limited temperature, composition, and molecular weight ranges since this parameter may be a function of all these variables.

In order to determine which B value is most appropriate for 1,2 PBD/1,4 PBD binary systems, we looked for heterogeneous-to-homogeneous transitions in binary blends of an amorphous atactic 1,2 PBD with an amorphous mixed cis+trans 1,4 PBD of molecular weights 15k g/mol and 182k g/mol, respectively. These molecular weights were chosen because the materials were available to us. Binodal and spinodal curves were calculated for this blend with the model and interaction parameters employed above in order to give us predictions of the compositions and temperatures at which we would expect to see a phase transition assuming the various B values discussed earlier.

Applying the model with $B_{\text{low}}$ and $B_{\text{avg}}$ values from above, we predict heterogeneous-to-homogeneous transitions around the following temperatures for blends of 1,2 PBD and 1,4 PBD homopolymers with MWs 15k g/mol and 182k g/mol respectively:

<table>
<thead>
<tr>
<th>composition</th>
<th>$B_{\text{low}}$</th>
<th>$B_{\text{avg}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,2/1,4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80/20</td>
<td>430 K*</td>
<td>1050 K</td>
</tr>
<tr>
<td>60/40</td>
<td>410 K*</td>
<td>1000 K</td>
</tr>
<tr>
<td>40/60</td>
<td>355 K*</td>
<td>880 K</td>
</tr>
<tr>
<td>30/70</td>
<td>310 K*</td>
<td>770 K</td>
</tr>
<tr>
<td>20/80</td>
<td>260 K</td>
<td>640 K</td>
</tr>
<tr>
<td>10/90</td>
<td>200 K</td>
<td>480 K*</td>
</tr>
<tr>
<td>4/96</td>
<td>120 K</td>
<td>360 K*</td>
</tr>
<tr>
<td>0/100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The binodal and spinodal plots are given in Figure III.3.

In order to observe such a transition experimentally, it must fall between a lower limit of 258K, which is the $T_g$ of atactic 1,2 PBD [14], and an upper limit of 500K, where degradation and crosslinking of PBDs become significant. The starred temperatures above indicate points that fall between these boundaries.

We prepared blends with approximately these compositions. Atactic 1,2 PBD with $M_w=15k$ g/mol was synthesized by K. Douzinias of our laboratory, and amorphous mixed cis+trans 1,4 PBD with $M_w=182k$ g/mol was obtained from Polysciences, Inc. (Warrington, PA). The microstructure of the 1,4 PBD is approximately 40% cis, 50% trans, 10% vinyl. The microstructure of the 1,2 PBD is approximately 99% atactic 1,2 PBD and its polydispersity is 1.07 [15]. Films 0.3 mm to 0.7 mm thick were static-cast from tetrafluoro solution containing 5% polymer with total polymer content of 0.5-1.0g. Irganox 1076 antioxidant was added at an amount equal to 1% antioxidant per gram polymer. The solution was poured into teflon-coated foil boats mounted on inverted glass petri dishes and left at room temperature in the hood until the solvent evaporated and the resulting films reached constant weight. Drying time was on the order of 3-4 weeks. A faint solvent smell remained in many of the samples but subsequent drying did not remove any measurable amount of solvent. Higher temperatures were not used to expedite drying because PBD is sensitive to degradation and crosslinking when exposed to elevated temperatures for extended periods of time.

All of the blends except the 30/70 blend were heated in a Differential Scanning Calorimeter, as described in Section IVD.4. We detected no discernable transitions between 0°C and 220°C for any of the blends when heated at a rate of 10°C/min. This result may have been due to lack of sensitivity of the DSC testing method. Alternatively, the samples were then irradiated with two consecutive doses of 10 MRad in order to crosslink them lightly so that they could be tested on a Rheovibron Dynamic Viscoelastometer. The irradiation was performed by Prof. Kenneth Wright of M.I.T.'s High Voltage Research Laboratory by means of a Van de Graaff electron accelerator operated with a 3 MeV beam. However, even after irradiation, the moduli of the films were still too low to allow Rheovibron testing at temperatures much above 25°C, no matter the size of the sample. Cohen and Wilfong [2] applied Rheovibron testing to 30 MRad crosslinked amorphous PBD blends, but that
Figure III.3:
Binodals and Spinodals for 1,2/1,4 PBD Interaction Parameter Verification
work focused on obtaining $T_g$ values at temperatures below 25°C, whereas our experiments necessitated working at much higher temperatures.

For low modulus materials, a mechanical spectrometer is the appropriate tool for measuring dynamic mechanical properties. We conducted mechanical spectrometry tests on four (non-irradiated) blends with compositions 0/100, 10/90, 30/70, and 60/40. The samples were prepared as described above. A 100/0 sample was also prepared but did not dry to an adequate extent, thus it was not tested. Frequency sweeps from 0.1 to 100 rad/s were taken sequentially at temperatures of 25°, 65°, 110°, 155°, and 200° C in a nitrogen atmosphere. Total exposure to temperatures above 25°C for a given sample did not exceed 30 minutes. Thermal expansion of the plates caused a reduction in the gap distance equal to 1.3μ/°C. At elevated temperatures the polymer flowed from between the plates, thus when a testing temperature was reached, the gap distance was adjusted so that the film completely filled the plate gap. We accounted for both of these temperature effects in the calculated material functions by entering corrected gap distances into the software for every frequency sweep at temperatures above 25°C. The thermal expansion value of 1.3μ/°C was determined experimentally and is accurate up to 235°C. Additional details of operation are found in Section IVD.4.

The results of the mechanical spectrometry tests are given in Figure III.4 as plots of log $G'$ vs. temperature. $G'$ decreases as the frequency is lowered, as expected. Also, the viscosities are relatively linear with frequency and decrease appropriately with increasing temperature. But the $G'$ data for the 0/100 sample (1,4 PBD homopolymer) goes through a minimum somewhere around $T=110°$C, especially at low frequencies. This minimum is probably due to the onset of crosslinking at higher temperatures. The other $b'$'s exhibit the same trends as the 0/100 sample and a give a minimum at the same point. The minimum becomes more pronounced as the 1,2 content increases.

Most importantly, the blends do not go through any transition in this temperature range that the homopolymer does not also go through. Thus we probably are not in a temperature range where these blends achieve a heterogeneous-to-homogeneous transition. We conclude that an appropriate $B$ value or expression is one that predicts heterogeneity at temperatures up to 200°C (473K) for the blends tested here. $B_{avg}$ and $B_{high}$ fall into this category. Expressions that yield $B$ values less than $B_{avg}$ are therefore inaccurate over the full range of composition.
Figure III.4
Storage Modulus (G') of Amorphous PBD Blends as a Function of Temperature
III.4c: 40/60 Blend

III.4d: 70/30 Blend
This conclusion reinforces the prediction in section IIIB that 1.2 PBD/1.4 PBD blends with MWs of 32.5K and 425K g/mol are heterogeneous over all but the extreme ends of the composition spectrum and that our s-1,2 PBD/trans 1,4 PBD system is heterogeneous in the melt at any condition with practical significance.

Finally, results of frequency sweeps from 0.1 to 100 rad/s performed at 25°C were compared for two films with composition 0/100. One of these films was irradiated as described earlier and the other film was not irradiated. When plotted on a log-log scale, sections from both samples displayed a two-decade drop in viscosity. However, sections of the non-irradiated sample showed an increase in G' of 0.5 to 1.2 decades while the G' of the irradiated film increased less than 0.2 decades. These data indicate that irradiation can seriously change or mask some polymer properties. Dynamic mechanical behavior of polymers that are irradiated or otherwise crosslinked must be evaluated with caution if the resulting information is to be applied to similar materials processed in a different manner.

IIID. REFERENCES


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Chapter IV
MATERIALS AND EXPERIMENTAL TECHNIQUES

IVA. MATERIALS

Both homopolymers and all diblock copolymers in this work were provided by Dr. Adel Halasa (Goodyear Tire and Rubber Company, Akron, OH).

The homopolymers were synthesized via Zeigler-Natta catalysis. The s-1,2 PBD was produced in 1985 prior to November of that year. Its Tm, Tg, and Mv are approximately 185°C, 25°C, and 32.5k g/mol, respectively but its polydispersity is unknown. The trans 1,4 PBD was synthesized in March, 1987, and its Tm, Tg, and Mv are approximately 135°C, -85°C, and 425k g/mol, respectively, with Mw/Mn=2.3 [1]. The s-1,2 PBD material has approximately 95±3% 1,2 content and the trans 1,4 PBD has 91±6% 1,4 content, as determined by ¹H NMR and discussed further in Section VB.2. The s-1,2 PBD has a pale yellow color while the trans 1,4 PBD is primarily white with a slight tan discoloration. When not in use, the polymers were stored in the dark at -15°C. Characterization is extensively detailed in Chapter V. Also, both s-1,2 and trans 1,4 PBD have monomer repeat unit molecular weights (MWr,u.) of 54.09 grams.

Three (atactic 1,2 PBD)/(mixed cis+trans 1,4 PBD) diblock copolymers were blended with the homopolymers described above. Two of the three diblocks were obtained by D.E. Wilfong for his Master's Thesis [2] in this laboratory and were synthesized in 1979 at Firestone Tire and Rubber Company (Akron, OH). Wilfong verified the diblock molecular weights by GPC. The block MWs of one of the diblocks are 30k/50k g/mol (1,2/1,4 PBD), and the MWs of the other diblock are 30k/200k g/mol. As mentioned in Section IC, the 30k/50k diblock is heterogeneous and the 30k/200k diblock is homogeneous [3]. The third diblock in our work is a heterogeneous 60k/120k sample synthesized around April 1990 at Goodyear. (Note that Goodyear nominally labeled this third diblock as 100k/100k g/mol, but NMR data obtained by K. Douzinias in this laboratory indicated that the block MWs are approximately 60k/120k g/mol.) For the 30k/50k and 30k/200k diblocks, the 1,4 PBD blocks are approximately 90% 1,4 PBD and the 1,2 PBD blocks are approximately 95% or more 1,2 PBD, as determined from ¹H NMR data in Section VIIA.3. For the 60k/120k diblock, the 1,4 PBD block is 90% 1,4 PBD and the 1,2 PBD block is 99% 1,2 PBD [4].
The polymers must be in solution for certain characterization tests and for blend preparation. Ashitaka et al. [5, 6] reported that s-1,2 PBD is insoluble in boiling toluene (110°C) and boiling benzene (80°C) and is mostly but not completely soluble in boiling xylene (140°C). The same researchers used o-dichlorobenzene, which has a boiling point of 177°C, and tetralin (1,2,3,4 tetrahydrodronaphthalene), which has a boiling point of 207°C, as solvents for s-1,2 PBD at 140°C. We checked the solubility of our homopolymers in all of these solvents except benzene. Trans 1,4 PBD goes into o-dichlorobenzene at about 130°C but then separates from the solvent into a congealed mass when the temperature dropped. Both homopolymers went into solution easily in tetralin - trans 1,4 PBD at 105°C and s-1,2 PBD at 125°C - thus tetralin was selected as the solvent for further experiments. PBD concentration was kept at or below 2% polymer, otherwise the solutions were too viscous to handle successfully. These solutions formed a continuous gel when the temperature of the tetralin dropped, perhaps similar to the reported thermoreversible gels of other polymers in decalin solvent [7].

IVB. SAMPLE PREPARATION

IVB.1. Solution Casting

Blending and film preparation on a small scale is typically accomplished in one of three ways: 1) mechanical blending of the melt followed by compression-molding, 2) solution precipitation followed by compression-molding or 3) solution casting directly into films.

The latter procedure can be accomplished by solvent evaporation from a flat glass plate, as described for the preparation of amorphous PBD blends in Section IIIC, or by a spincasting procedure that other researchers in our laboratory applied extensively in the past [8].

With spincasting, polymer solution is spun at high speed in a cylindrical aluminum cup, the solvent is driven off by a stream of nitrogen, and a film subsequently forms on the cup wall. The wall is lined with mylar so that the film can be removed from the cup and peeled from the mylar. Infrared lamps are capable of heating the whole apparatus to temperatures above 200°C, thus this technique is frequently appropriate for polymers that go into solution only at elevated temperatures. If elevated temperatures are employed, the resulting film is allowed to cool, removed from the cup, and annealed in a vacuum oven. Only a few grams of polymer are required for
each film. The casting cup holds up to 200 ml, and a typical initial solution concentration is 2.5 wt% polymer in 100 ml of solution. Film thickness is about 0.1 mm per gram of polymer charged to the spin caster.

We produced a number of spincast films from s-1,2 PBD and trans 1,4 PBD and later studied their thermal properties. We used initial solution concentrations of 1.0-1.5% PBD in the spincaster. The solutions were premixed in hot tetralin (160°C), poured into a preheated spincasting cup (120°C-150°C), and then spun at 160°C or 120°C for 16 hours. Degradation was minimized by blowing 10 SCFH of nitrogen through the casting chamber. After 16 hours, the temperature controller was turned to room temperature and the cup was kept spinning as it cooled. When the cup temperature decreased to about 40°C, generally after a period of about three hours, the film was removed from the cup and placed in a room temperature vacuum oven for at least 24 hours to remove residual solvent. Antioxidant Ethanol 330 (1,3,5 trimethyl-2,4,6-tris[3,5-di-tert-butyl-4-hydroxybenzyl]benzene) was added to all solutions in concentrations of 0.05g/g polymer prior to spincasting them.

These conditions gave tan-colored trans 1,4 PBD films and pale yellow s-1,2 PBD films, yet there was a distinct color difference between the starting materials and the ending films. Films spun for longer times or at lower nitrogen flow rates oxidized and degraded to an extensive degree. When processed at 160°C, trans 1,4 PBD solutions produced films that adhered to the mylar and could not be peeled away without ruining the film. S-1,2 PBD films peeled from the mylar easily. When processed at 120°C, which is below the trans 1,4 PBD melting point, trans 1,4 PBD films still adhered to the mylar but were removable when peeled off slowly and carefully. Fifty/fifty blends of the two homopolymers cast at both 160°C and 120°C produced films that stuck to the mylar yet came off with the aid of a razor blade. The texture and color of these blends were intermediate between those of the homopolymer films. In addition to these problems, complete solvent removal was difficult due to tetralin's low vapor pressure. Also, film thickness was limited because of the 2% polymer limit for PBD solutions in tetralin.

IVB.2. Precipitation

Alternatively, we changed our sample preparation method: Rather than spincast solutions, we precipitated them in methanol (MeOH). The precipitated polymer was filtered, dried, and pressed into films. This process was easier,
faster, and safer than spin-casting and allowed us to produce films with less degradation and of any desired shape and thickness. Solvent removal was facilitated because tetralin is soluble in MeOH thus most of the tetralin separated from the polymer in the filtration step.

We prepared precipitated polymer in batches of 1.00±0.02g. The polymer or polymer blend and 0.01g of Irganox 1076 antioxidant were stirred in hot tetralin. The total volume of solution was always 50 ml. For samples prepared prior to March 1990, the polymers were added to room temperature tetralin and then stirred at 140°C-180°C for at least 30 minutes. From March 1990 onward, the homopolymers were added to preheated tetralin at 135°C and then stirred at 135°C±3°C for exactly 60 minutes to ensure a Mv for the trans 1,4 PBD component close to 425k g/mol. (When comparing data in this thesis from the two procedures, the procedure prior to March 1990 is referred to as the "original precipitation procedure" while the procedure following March 1990 is referred to as the "improved precipitation procedure.") For blends with diblock copolymer, the diblock was added from a 0.05g/ml stock solution immediately after the homopolymers were placed in the hot tetralin. The diblock stock solution was typically prepared the night before in room temperature tetralin.

In all cases, the hot blend solution was then dripped into 300-350 ml of stirred MeOH in a beaker surrounded by dry ice. The MeOH was cooled to hasten the formation of precipitated material. Next, the precipitated polymer was vacuum filtered through filter paper (#595, Schleicher and Schuell, Inc., Keene, NH) in a buchner funnel. The damp, filtered polymer was dried at room temperature in a vacuum oven or in the hood until the sample achieved a constant weight less than 1.0 gram. The drying step took at least 2-3 weeks. As with the solvent cast films discussed in Section IIIIC, a faint solvent smell frequently remained in the sample but subsequent drying did not remove any measurable amount of solvent. Higher temperatures were not used to expedite drying because PBD is sensitive to degradation and crosslinking when exposed to elevated temperatures for extended periods of time. When not in use, the dried precipitates were stored in sealed vials in a freezer at -15°C.

Additional details of this procedure are as follows: When the tetralin/polymer solution was not dripped slowly enough into the MeOH, the precipitated particles were not small and flaky and subsequently did not dry or mold well. When the level of stirring of the hot tetralin/polymer solution was
not high enough prior to precipitation, the trans 1,4 PBD agglomerated in the tetralin and did not go into solution completely by 60 minutes. Finally, when the initial trans 1,4 PBD powder was exposed to excess moisture prior to being solvated by tetralin, as occurred when the freezer containing unprecipitated homopolymer powders accidentally defrosted, then the trans 1,4 PBD agglomerated into a balled fibrous mass upon precipitation in MeOH. Before the freezer defrosted, precipitations of trans 1,4 PBD gave small distinct flakes of polymer. No change was seen in s-1,2 PBD precipitations, probably because the initial s-1,2 PBD material is a dense, relatively non-absorbant granular powder. In contrast, the initial trans 1,4 PBD polymer prior to precipitation is a soft, void-filled, flaky powder that may readily absorb moisture. Following the defrosting incident, a precipitation was conducted with trans 1,4 PBD that was vacuum dried overnight at room temperature before it was added to tetralin. Agglomeration during precipitation still occurred but to a lesser degree than with samples that had not been vacuum dried prior to precipitation.

IVB.3. Compression-Molding

To make polymer films, the precipitated powders were compression-molded in the melt. About 0.55 g of polymer was placed in a copper mold with a molding chamber 0.5 inches x 2.5 inches x 0.02 inches. The mold was then pressed in a preheated laboratory press (Carver, 11 metric ton capacity) at 200°-205°C and 3 tons of pressure for 2 minutes. At the two minute mark, the pressure was immediately released and the mold was taken off the press. For samples prepared by the original precipitation procedure, the mold was allowed to cool on its own to room temperature. For samples prepared by the improved precipitation procedure, the mold was cooled quickly by placing it between two slabs of dry ice. In either case, after the mold cooled, the top and bottom plates were separated and the film was carefully removed. All films were stored at room temperature away from light until further use. Also, before a new sample was placed in the mold, the mold surfaces were cleaned and sprayed with Fluoroglide (Norton Company, Wayne, NJ) to ensure easy film removal.

Copper was chosen for its thermal conductivity properties. The size of the chamber was designed so that the films could be used for Rheovibron and Instron tensile tests. Assuming a polymer density of 1.0 g/cc, 0.45 g of
polymer is theoretically needed to fill the molding chamber. We pressed 0.55g
to guarantee complete packing of the chamber. The molding temperature of
200-205°C is above the melting point of s-1,2 PBD yet below the onset of
degradation as determined in the study discussed in Section IVC. We wanted to
minimize molding time, yet at times less than 2 minutes, the s-1,2 PBD
component often did not melt completely.

IVB.4. Compositions of Prepared Films and Effects of Processing Procedures

The overall procedure for making films via polymer precipitation is
reviewed in pictorial form in Figure IV.1. Altogether, films with forty-nine
different compositions were prepared by this method, comprising binary
homopolymer blends and blends of homopolymers plus one of the three
different diblock copolymers. All of the compositions are pictured in Chapter
VII in Figure VII.1 and are labeled in ternary diagrams in Appendix A.1.

A number of blends degraded significantly during compression-
molding. Residual tetralin in the precipitated polymer was probably
responsible for this degradation, which tended to be more of a problem in
samples with s-1,2 PBD than in samples with trans 1,4 PBD. We assigned a "D-
value" of 0 to 4 for each sample after it was molded, where 0 indicates no
visible degradation and 4 indicates nearly total degradation throughout the
sample. Only samples with D-values of 2 or less were kept for further study.
Samples with D-values over 2 were prepared over again with new material.
Appendix A.1 presents D-values and final weights of all samples ultimately
subjected to further testing.

Other possible effects of precipitation and molding on molecular
structure were monitored via 13C and 1H NMR on solutions of precipitated and
molded homopolymers resuspended in tetralin at 150°C and by WAXS 2θ scans
of compression-molded films. NMR spectra revealed no noticeable differences
in microstructure between samples subjected to these processing procedures
and samples that were not precipitated or compression-molded. Similarly, The
calculated d-spacings for samples that were precipitated or noticeably
degraded were not significantly different from d-spacings in samples that had
not been precipitated and were not degraded.
IVC. EVALUATION OF ANTIOXIDANTS

Spin-cast materials with and without Ethanol 330 antioxidant exhibited no apparent difference in susceptibility to oxidative degradation, thus we evaluated two alternate antioxidants and compared them to Ethanol 330. We tested Irganox 1076 (Ciba-Geigy Corporation, Hawthorne, NY) and Wytox HPM (Olin Chemicals, Stamford, CT). These products were selected based upon the manufacturers’ recommendation for high temperature stabilization of polybutadiene and based on their melting and decomposition temperatures. Additional information on all three antioxidants is given below.

<table>
<thead>
<tr>
<th>Antioxidant</th>
<th>Chemical Structure</th>
<th>Tm/Tdeg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol 330</td>
<td>1,3,5-trimethyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxy-benzyl) benzene.</td>
<td>Tm = 244°C</td>
</tr>
</tbody>
</table>
| Irganox 1076      | octadecyl-3,5-di-tert-butyl-4-hydroxy-hydrocinnamate                               | Tm = 50°C  
|                   |                                                                                    | Tdeg >220°C |
| Wytox HPM         | bis-2,2-methylene bis(6-t-butyl-4-methylphenyl)terephthalate                      | Tm = 250°C |

The antioxidants were added to both 1% s-1,2 PBD and 1% trans 1,4 PBD solutions in tetralin at a concentration of 1% antioxidant per gram of polymer. The solutions were precipitated in cold MeOH and dried to constant weight as discussed above. All precipitated samples, including controls without antioxidant, were heated in the DSC at 20°C/min to determine the onset and extent of degradation. In a second set of tests with s-1,2 PBD, this procedure was repeated for the two most effective antioxidants. For some of the samples in this second round of experiments, the more effective antioxidants were added not only to the polymer solution but also to the MeOH in a concentration of 1% antioxidant per gram MeOH. This amount of antioxidant resulted in a saturated MeOH solution with excess antioxidant that precipitated out of the cold MeOH.

Results of the DSC testing are tabulated in Table IV.1. For a given test, the melting points are reproducible. The onset of degradation was taken as the temperature where the slope of the DSC curve became negative, assuming a
Table IV.1: Results of Antioxidant Study
(All temperatures in °C)

<table>
<thead>
<tr>
<th>PRD sample</th>
<th>Melting Point</th>
<th>Degradation Onset</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-1.4</td>
<td>131°</td>
<td>230°</td>
</tr>
<tr>
<td>t-1.4 + 1% Ethanol 330</td>
<td>132°</td>
<td>240°</td>
</tr>
<tr>
<td>t-1.4 + 1% Irganox 1076</td>
<td>130°</td>
<td>255°</td>
</tr>
<tr>
<td>t-1.4 + 1% Wytox HPM</td>
<td>130°</td>
<td>229°</td>
</tr>
<tr>
<td>s-1.2</td>
<td>186°</td>
<td>210°</td>
</tr>
<tr>
<td>s-1.2 + 1% Ethanol 330</td>
<td>186°</td>
<td>222°</td>
</tr>
<tr>
<td>s-1.2 + 1% Irganox 1076</td>
<td>186°</td>
<td>211°</td>
</tr>
<tr>
<td>s-1.2 + 1% Wytox HPM</td>
<td>186°</td>
<td>207°</td>
</tr>
<tr>
<td>s-1.2</td>
<td>185°</td>
<td>212°</td>
</tr>
<tr>
<td>s-1.2 + 1% Ethanol 330</td>
<td>184°</td>
<td>204°</td>
</tr>
<tr>
<td>s-1.2 + Ethanol 330 - 2X</td>
<td>186°</td>
<td>216°</td>
</tr>
<tr>
<td>s-1.2 + 1% Irganox 1076</td>
<td>189°</td>
<td>216°</td>
</tr>
<tr>
<td>s-1.2 + 1% Irganox - 2X</td>
<td>170°</td>
<td>237°</td>
</tr>
</tbody>
</table>

Notes:
1% antioxidant with respect to mass of polymer in tetralin.
2X indicates 1% antioxidant (as above) in addition to antioxidant in the MeOH.

Figure IV.1. Sample Preparation via Precipitation
straight baseline. The results show that without any antioxidant, trans 1,4 PBD degrades at about 230°C and s-1,2 PBD degrades at about 210°C. In the first set of tests, Irganox 1076 delayed degradation most effectively for the trans 1,4 PBD (by about 25°C) but had no effect on the s-1,2 PBD. Ethanol 330 delayed degradation by about 10°C for both polymers. Wytox HPM did not help either homopolymer. In the second set of tests, Irganox 1076 and Ethanol 330 were reevaluated. This time, Ethanol 330 did not have a significant effect while Irganox 1076 was more effective than previously observed. However, with 1% antioxidant per gram of MeOH, the amount of Irganox 1076 in the final dry polymer sample was greater than 50% of the total weight and it lowered the s-1,2 PBD melting point by 20°C!

In summary, Wytox HPM had no apparent effect and Irganox 1076 was more advantageous than Ethanol 330 in most of the cases examined. At concentrations of 1% antioxidant per gram of polymer, the Irganox product delayed the onset of degradation by about 10-20°C when samples were heated at a rate of 20°C/minute in the DSC. Thus Irganox 1076 was selected as the preferred antioxidant for subsequent preparations. The results also suggest that antioxidant in the MeOH is desirable, but only in concentrations low enough so as not to cause melting point depression. However, we did not add antioxidant to the MeOH in subsequent precipitations.

IVD. STRUCTURE AND PROPERTY CHARACTERIZATION TECHNIQUES

The primary techniques we employed to characterize the structure and properties of our polymer materials are listed below. Sample preparation for each of these techniques is described briefly. In some cases, additional details are found in other chapters as various experiments are related.

IVD.1. Molecular Weight:  Viscometry, Gel Permeation Chromatography (GPC)

To determine the homopolymer molecular weights, high temperature GPC was attempted with a Waters 150C GPC but was not successful due to PBD degradation within the apparatus, as will be discussed in Section VA. Instead, viscometry was ultimately employed. A Cannon-Fenske routine viscometer, size 150, was used for all viscometry tests. Sample temperature was controlled by placing the viscometer in a stirred oil bath (550 Fluid, Dow Corning Corporation, Midland, MI) maintained at 135°±2°C by an electric heating tape. The cylindrical glass bath chamber was also heated by the stir plate beneath it.
All samples were prepared and tested in 10 ml of tetralin with Irganox 1076 antioxidant (Ciba-Geigy Corporation, Hawthorne, NY). The samples were mixed at 135°C for at least thirty minutes. Between runs, the viscometer was rinsed with pure tetralin until to, the time for 10 ml of pure solvent to pass between two marks on the viscometer, was reproducible.

Room temperature GPC was conducted on the 30k/50k and 30k/200k diblocks and on a s-1,2 PBD material (Polysciences, Inc., Warrington, PA) with a low melting point of 90°C. This s-1,2 PBD material was a control in the viscometry experiments mentioned above. Solution concentration was approximately 0.2% polymer in toluene. The instrument employed was a Waters GPC II Liquid Chromatograph (Waters Associates, Milford, MA).

IVD.2. Microstructure: IR, NMR Spectroscopies

IR, ¹H NMR, and ¹³C NMR spectroscopy characterization verified the microstructure of our starting materials. With ¹H NMR, we quantified 1,2 PBD and 1,4 PBD content of the homopolymers and the 30k/50k and 30k/200k diblock copolymers. IR and ¹³C NMR were employed to verify homopolymer tacticities. All homopolymer spectra were compared to data reported in the literature for s-1,2 PBD and trans 1,4 PBD. Solution NMR spectra were obtained by personnel in the Chemistry Department's analytical facilities. Cross-polarized, Magic Angle Spinning (MAS) solid state NMR was conducted with equipment in MIT's Center for Material Science and Engineering (Central Polymer Facility). Operating frequencies were 250-300 MHz, 75 MHz, and 50 MHz for ¹H, solution ¹³C, and solid state ¹³C NMRs, respectively.

IR homopolymer films were prepared as follows: Unprecipitated (as-received) powders were placed between two glass slides and heated on a hot plate until the polymer melted. The slides were then removed from the hot plate and allowed to cool to room temperature, after which they were carefully pried apart. The pressed polymers were scraped from the slides with a razor blade and taped onto sample holders for the spectrometer (Perkin-Elmer, model 727B). The polymer films were at least 1/2 inch in diameter. To check for reproducibility, spectra were obtained for various positions of the samples. For each position, the sample was run twice on the same sheet of paper.

Solution NMR on our homopolymers required high temperature operation since the polymers are not soluble at room temperature. ¹H NMR and ¹³C NMR were performed on 2% s-1,2 PBD solutions and 2% trans 1,4 PBD
solutions in deuterated tetralin (Aldrich Chemicals, Milwaukee, WI) at approximately 150°C. I was advised not to use an internal standard for high temperature NMR work because it can cause the NMR tube cap to pop off [9]. Instead, spectra of polymers in tetralin at 150°C were referenced to spectra of deuterated tetralin without polymer at 150°C. The samples of solvent without polymer contained a trace of reference TMS. The $^1$H NMR spectrum for 150°C tetralin, depicted in Figure IV.2a, gives major peaks at 1.56, 2.54, and 6.86 ppm and minor peaks at 6.88 and 6.92 ppm. The $^{13}$C NMR spectrum for 150°C tetralin is in Figure IV.2b. This spectrum shows five groups of peaks: the first group has seven peaks from 21.93-23.10 ppm, the second group has seven peaks from 28.10-29.25 ppm, the third group has three peaks from 124.88-125.50 ppm, the fourth group has three peaks from 128.37-128.97, and the fifth "group" is a single peak at 137.01. These data are close to but slightly shifted from literature data for room temperature tetralin, shown in Figure IV.2c for $^1$H NMR [10] and in Figure IV.2d for $^{13}$C NMR [11].

Room temperature solution NMR for the 30k/50k and 30k/200k diblocks was conducted on 2-5% solutions of diblock in both deuterated toluene and carbon tetrachloride.


Via Bragg's Law, X-ray diffraction patterns and scattering measurements allow the calculation of characteristic, repeated "d-spacings" in various materials. These d-spacings elucidate crystalline structure. The SAXS setup available to us can identify the presence of repeated structures less than 600Å. With WAXS, spacings between about 2Å and 20Å can be identified. We used a Rigaku X-ray Diffraction System with a rotating anode x-ray generator and point focus. The CuK$_\alpha$ x-ray source emits radiation with a wavelength of 1.54Å.

To obtain WAXS 20 measurements, films were scanned continuously at a rate of 5°/min from approximately 5° to 45°. The data were then displayed and manipulated via a Micro VAX II computer. For SAXS, scattering data were collected for 2-20 minutes and the diffraction patterns were detected on a 2-dimensional (512x512 pixel) Nicolet area detector. For the wide angle scattering of melt blend samples discussed in Section VIB.3, we utilized the SAXS equipment and set the detector as close to the sample as possible. The
IV.2a: $^1H$ NMR at 150°C

IV.2b: $^{13}C$ NMR at 150°C

Figure IV.2: NMR Spectra for Tetralin Solvent
IV.2c: $^1$H NMR at 25°C

IV.2d: $^{13}$C NMR at 25°C
specimens were heated to approximately 190°-200°C in a heating chamber designed by L. Cazzaniga, previously of this laboratory. Since we showed in Section IVB.4 that degradation does not alter the scattering behavior in our PBDs, the melt experiments were conducted without the use of an inert atmosphere. A trans 1,4 PBD sample at 25°C served as a standard since it has a prominent peak at 2θ = 22.4°C. The sample-to-detector distance was then calculated to be 7.7 cm from the following relationship:

\[(\text{scattering peak radius [in pixels]} \times 200 \mu \text{/pixel})/\text{(detector distance)} = \tan 2\theta\]

**IVD.4. Thermal Properties: DSC, Dynamic Mechanical Testing**

Differential scanning calorimetry was performed to obtain thermal transitions and percent-crystallinity via enthalpy measurements. The DSC data in this thesis were obtained primarily on a Perkin-Elmer DSC-4 and occasionally on a DSC-7. Five to 15 mg of polymer were heated and cooled in aluminum pans at a rate of 20°C/min, unless otherwise specified. At the end of a heating trial, samples were quenched from the melt to room temperature at a rate of 320°C/min. Testing was typically conducted in a nitrogen atmosphere. Unless otherwise noted, indium standards were run every day that testing occurred. All transition temperatures were adjusted based on an indium value of 160.5°C for a heating rate of 20°C/min, i.e. when the indium melting point varied from this value, all subsequent temperature measurements taken at a heating rate of 20°C/minute were corrected by an amount equal to the difference between the observed indium melting point and 160.5°C. Additional details of DSC imposed histories are given as DSC studies are discussed in the chapters to follow. The error associated with DSC operation is approximately ±2°C for temperature data and ±1 cal/g for enthalpy data, as determined from duplicate trials.

DSC isothermal crystallization studies are discussed in Sections VC.2 and VIB.1. For these tests, precipitates were heated to melt conditions at 205°C and held there for one minute, quenched at 200°C/min to one of six temperatures, held at that temperature for two minutes, and then quenched back to room temperature at a rate of 200°C/min. After an additional five minutes at room temperature, the samples were scanned at a rate of 20°C/min to determine transition temperatures and associated enthalpies. The samples in the isothermal crystallization studies were prepared by the original precipitation procedure and were not compression-molded.
Dynamic mechanical properties as a function of temperature were obtained via a Rheovibron Direct Reading Dynamic Viscoelastometer, Model DDV-II-C (Toyo Baldwin Co., Ltd., Tokyo, Japan; marketed by IMASS Inc., So. Hingham, MA). Compression-molded films 0.3 mm to 0.7 mm thick were cut to a length and width of about 40 mm x 3 mm. Samples were heated in a nitrogen atmosphere at a rate of 2°-4°C/min from -120°C to a temperature just below complete melting. Measurements were taken at a frequency of 11 Hz. To analyze the data, onsets and peaks of thermal transitions were recorded for any increase in the slope of the tan δ curve. The onset was taken to be the extrapolation of the steepest part of the slope to the baseline. With this assignment, PET controls gave reproducible Tg onset values of 90°C. All temperature values reported from Rheovibron data have an associated error of about ±5°C. Also, from tan δ data we calculated the storage and loss moduli, G' and G'', from the following expressions [12, 13]:

\[ G' = |G|^\cos \delta \]  \hspace{1cm} (IV-1)
\[ G'' = |G|^\sin \delta \]  \hspace{1cm} (IV-2)
\[ G^* = (2L/ADS) \times 10^9 \]  \hspace{1cm} (IV-3)

where G* is the complex modulus in dynes/cm², L is the length of the sample in cm at the test point, A is the amplitude scale factor (typically equal to 1.0, but may be 3.16 or 10.0 depending on the appropriate amplitude setting for the material), D is the dynamic force potentiometer reading corrected for slippage, and S is the specimen cross-sectional area in cm².

Mechanical spectrometry allows determination of dynamic mechanical behavior as a function of temperature for materials with moduli too low to be measured by the Rheovibron. A Rheometrics [RMS-800] Mechanical Spectrometer in dynamic mode was used for the experiments discussed in Sections IIIC and VC.4c. Unless otherwise specified, films of uniform thickness were placed between 12.5 mm radius parallel plate fixtures. The strain rate was held at 5%. In the experiments in Section IIIC, film thickness ranged between 0.3 mm and 0.7 mm. In the experiments in Section VC.4c., film thickness was 1.3 mm. All temperature changes went from lower to higher temperatures to minimize loss of material between the plates due to flow at elevated temperatures. Also, all tests above room temperature were conducted in a nitrogen atmosphere. Operating with a gaseous nitrogen supply via 220 liter gas packs is easier and more reliable than operating with gaseous
nitrogen in smaller cylinders or with a liquid nitrogen supply that is subsequently boiled off within the spectrometer.


To visually monitor melting and crystallization of our homopolymers and binary blends, we employed a Nikon AFX-II Optiphot-pol Polarizing Microscope fitted with a Polaroid 4x5 Land film attachment and Mettler FP82 Hot Stage. Prior to observation, compression-molded samples were microtomed to a thickness of 2-10µ, then placed on a slide and covered with a glass cover slip. Most photographs were taken with the polarizing filters aligned at an angle of 80°C-90°C to give maximum contrast between crystalline and noncrystalline components.

With a Cambridge (England) S240 SEM, we inspected freeze-fractured and tensile-fractured surfaces of various blends, as discussed in Section VIC. Images were obtained via secondary emissions at voltages of 15 kV for freeze-fractured samples and 1.0 kV for tensile-fractured samples. All samples were mounted and lightly gold coated. Micrographs were taken at magnifications around 40X, 125X, and 4000X. The highest magnifications show details on the order of 1µ to 10µ.

TEM was utilized to measure sizes of s-1,2 PBD and trans 1,4 PBD domains in blends. We used a Phillips 300 TEM operated at 100 keV with magnification capabilities to 2.11x10^5X and resolution on the order of 20Å [14]. Stained, compression-molded films were sectioned on a LKB Ultratome III (LKB Instruments, Inc., Rockville, MD; also, Sweden) with freshly cut glass knives and then collected on 200 mesh copper grids. The microtomed slices ranged in color (and thickness) from silver (700-900Å) to gold (900-1300Å) [15]. Micrographs were calibrated against a diffraction grating carbon replica with 21,600 lines/cm.

The Smith-Andries [16] ebonite staining method was applied for all TEM samples. With this method, double-diene systems are stained by a 90:5:5 mixture of sulfur, zinc stearate, and (N-tert-butyl-2-benxothiazolyl)sulfenamide rubber accelerator (R.T. Vanderbilt Company, Inc., Norwalk, CT) at 120°C. The 1,4 component is preferentially vulcanized by means of the reaction depicted in Figure IV.3 for natural rubber [17]. Although the Smith-Andries paper suggests a staining time of 8 hours,
Wilfong [2] successfully stained radiation-crosslinked amorphous 1,2 PBD and 1,4 PBD blends for 24 hours. To determine optimum staining times for our double-diene crystalline system, we stained blends as follows: 8 mm x 3 mm x 0.5 mm sections of a 50/50 blend prepared by the original precipitation procedure were stained for 10 minutes, 30 minutes, 1 hour, 2 hours, 4 hours, 8 hours, and 20 hours. Staining was accomplished by completely immersing the sections in the molten sulfur mixture at 120°C. At times under 4 hours, the stain did not completely penetrate the samples. Then four samples prepared by the improved precipitation procedure with compositions of 100/0, 0/100, 67/33, and 33/67 were stained for 4 hours, 8 hours, and 24 hours in sections 4 mm x 2 mm x 0.5 mm. We observed lamellar-type morphology in a number of sections for each of these staining times. In general, contrast in the homopolymers was most pronounced for samples stained approximately 24 hours. In the blends, the component comprising the majority of the blend was stained more effectively at longer staining times (8-24 hours) but the minor component was observable only in samples stained for shorter times (4-8 hours). Since one staining time was not consistently more effective than another, we stained subsequent blend preparations for 8 hours.

IV/D.6. Mechanical Tensile Properties: Instron

Room temperature tensile properties were obtained on a Model 4201 Instron device (Instron Corporation, Canton, MA) for all precipitated, compression-molded blends and homopolymers, and for unprecipitated, compression-molded homopolymers. "Micro-dogbone" samples with test dimensions of approximately 5.2 mm x 2 mm were cut from films between 0.3 mm and 0.7 mm thick, as illustrated in Figure IV.4. Because of the rubbery nature of most of the samples, they were not polished. Typically, three tensile specimens were cut and tested in tension from each compression-molded sample. For the most rubbery materials, only two specimens were tensile tested if the second specimen gave results that were nearly identical to the first specimen. Crosshead speed was 0.2 mm/min unless otherwise stated, and the grips were rated at 10 psi. A 5 kN tension/compression load cell was used for all tests except those with pure diblock samples. For the pure diblock samples, a 1 kN tension/compression load cell was employed. Stress-strain data were automatically reported and recorded via Instron Series IX software.
Figure IV.3: Vulcanization of Rubber [17]

Figure IV.4: "Micro-dogbone" Tensile Specimen Dimensions
From the resulting stress-strain curves, we determined the modulus, yield stress, stress at break and percent elongation at break for each sample. The modulus and yield stress values are based on an average for all specimens of a given composition. None of the samples exhibited an obvious maximum at the yield point, thus we designate the yield stress as the intersection of the tangents to the stress-strain curve before and after the sample yielded. The reported values for stress and percent elongation at break are based on the maximum value observed for any of the specimens of a given composition.

Permanent set was calculated as the composite percent elongation of the two broken but relaxed pieces from each tensile specimen after tensile testing. The value is based on the average relaxed percent elongation for all specimens of a given composition. The term "relaxed" refers to the fact that these measurements were taken days or weeks after the samples were tested.

Finally, compression data were taken for the unprecipitated (as-received) homopolymers. Powders were compression-molded at 200°C for 4 minutes into cylinders 3 mm in diameter and 4 mm in height, then the samples were annealed for 18 hours at 63°C. Compression testing was performed at rates of 0.05 mm/min and 0.1 mm/min until either 2.88 mm or 0.56 mm of compression were achieved. The choice of endpoint was arbitrary.

**References**


Chapter V
HOMOPOLYMER CHARACTERIZATION

VA. MOLECULAR WEIGHT DETERMINATION

High temperature GPC was attempted with a Waters 150C GPC to determine the homopolymer molecular weights. The GPC was flushed with 0.5µ-filtered tetralin and equilibrated at the testing temperature before each trial. Polybutadiene standards of 5, 23, and 150k g/mol at 25°C and 100°C as well as polystyrene standards of 2.4k, 15k, 110k, and 170k g/mol at 140°C gave reliable standard curves. The concentration of the standards ranged from 0.1-0.3% in tetralin. Homopolymer powders were solubilized in concentrations of 0.1%, 0.4%, and 0.8% but none of these concentrations gave appropriate peaks at 140°C. The only consistently reproducible peaks occurred at retention times around 33.2 and 34.9 minutes, but these times are longer than that of the 2.4k g/mol polystyrene standard. Thus, significant amounts of degradation occurred within the GPC system and/or during preliminary sample temperature equilibration at 140°C. The fact that the peaks increased in size with subsequent trials indicates that degraded material accumulated with successive runs. The presence of brown liquid in the oven chamber that had leaked from the end of the first column substantiated this conclusion. In summary, high temperature GPC was not successful due to PBD degradation within the GPC apparatus.

Alternatively, molecular weights were obtained by viscometry. Viscometry allows the determination of intrinsic viscosity, which is related to the molecular weight of linear-chain polymers by the relationship

\[ [\eta] = K \times (MW)^a \]  \hspace{1cm} (V-1)

where \([\eta]\) is intrinsic viscosity, \(K\) and \(a\) are Mark-Houwink parameters for a given polymer in a specified solvent at a specified temperature, and \(MW\) is the molecular weight. Thus if \([\eta]\), \(K\), and \(a\) are known, \(MW\) can be calculated. Or if \([\eta]\) is measured for a series of \(MW\) standards, then \(a\) and \(\log K\) can be obtained from the slope and intercept of a plot of \(\log [\eta]\) vs. \(\log MW\).

For a given polymer, solvent, and temperature, \(\eta\) is the y-intercept on a plot of \(\eta_s/\gamma c\) or \(\ln(\eta_r)/c\) as a function of \(c\) (concentration), where

\[ \eta_r = \eta/\eta_0 = \text{relative viscosity}, \]  \hspace{1cm} (V-2)

\[ \eta_s = (\eta-\eta_0)/\eta_0 = \eta_r-1 = \text{specific viscosity}, \]  \hspace{1cm} (V-3)

\(\eta\) is true sample viscosity, and

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\( \eta_0 \) is the viscosity of the solvent.

In viscometry experiments, \( \eta/\eta_0 = \eta_r \) is approximated by \( t/t_0 \), the ratio of the time for the polymer solution to pass between two marks on the viscometer to the time for pure solvent to pass between the marks. MW determined by this method is the viscometry molecular weight, \( M_v \). All of the relationships listed above are discussed in Collins et al. [1].

Ashtaka et al. [2] report osmometry-determined \( K \) and \( a \) values of 9.41E-3 ml/g and 0.854, respectively, for s-1,2 PBD in tetralin at 135°C. Since we did not find viscometry-determined s-1,2 PBD \( K \) and \( a \) values in the literature, the osmometry \( K \) and \( a \) values were applied in our analysis. For trans 1,4 PBD in tetralin at 135°C, no literature data were found at all. Instead, we determined \( K \) and \( a \) values for amorphous mixed cis+trans 1,4 PBD from equation V-1 above by measuring \([\eta]\) for a series of mixed cis+trans 1,4 PBD standards in tetralin at 135°C. The standards had known molecular weights of 5k, 23k, 150k, and 240k g/mol and polydispersities of 1.1-1.3. (American Polymer Standards Corporation, Mentor, OH). Microstructure was reported to be approximately 40% cis 1,4, 50% trans 1,4, and 10% 1,2 PBD.

\( M_v, a \) were then evaluated for the following three materials: Our s-1,2 PBD and trans 1,4 PBD homopolymers, and a different s-1,2 PBD material from Polysciences, Inc. (Warrington, PA) with nominal \( M_w \) of 100k g/mol. This last polymer was utilized only as a control. Its melting point is 90°C and the reported microstructure is 90% 1,2 PBD. Four concentrations were tested for each s-1,2 PBD and trans 1,4 PBD sample, and five concentrations were tested for each 1,4 PBD standard. The concentrations, listed in Table V.1, were selected to give approximately \( 1.2 < t/t_o < 2.0 \). For all tests, sample temperature was maintained at 135°C±2°C. Immediately prior to the test, tetralin solutions were mixed at 135°C for at least thirty minutes. Additional details of sample preparation are given in Section IVD.1. The value of \( t_0 \) was 19.7±0.2 seconds for 10 ml of tetralin.

Most of the 1,4 PBD samples, particularly the trans 1,4 PBD samples and higher MW 1,4 PBD standards, degraded significantly with time in the hot solution. This degradation was evident because \( t \) values became successively shorter with longer exposures to 135°C tetralin. As a result, viscometry determinations were executed for these samples as a function of time, as well as a function of concentration. In order to obtain reliable \( K \) and \( a \) values, \( t \) measurements of the standards were extrapolated back to time zero for each.
concentration tested. These $K$ and $a$ values were then used to figure $M_v$ of the trans 1,4 PBD samples at 60 minutes, 30 minutes and zero minutes in 135°C tetralin, with the zero minute trans 1,4 PBD determination found by extrapolation of $t$ measurements of the trans 1,4 PBD samples. S-1,2 PBD samples showed negligible or no degradation in tetralin with time.

Figures V.1a, V.1b, V.1d, and V.1e are plots for specific viscosity and relative viscosity correlations for the 1,4 PBD standards and all of the homopolymers. Figure V.1c is the regression plot of log $[\eta]$ as a function of log $M_v$ that allowed us to determine Mark-Houwink parameters from the 1,4 PBD standards. Results and conclusions from the viscometry tests are as follows:

1) $K$ and $a$ values for the 1,4 PBD standards (extrapolated to time zero for those that showed degradation with time) are $0.0145 \pm 0.0022$ ml/g and 0.75, respectively, when analysis is based on $\ln(\eta_r)$; $K$ and $a$ are $0.0161 \pm 0.0025$ ml/g and 0.74 when based on $\eta_{sp}$ analysis. In both cases, correlation coefficients ($R^2$) were greater than 0.992. These values are presented along with literature $K$ and $a$ values for PBD at other conditions in Table V.2. Correlation coefficients for determination of $[\eta]$ values for the standards are not as good, but analysis based on $\eta_{sp}$ gives better correlation coefficients than analysis based on $\ln(\eta_r)$.

2) For trans 1,4 PBD using $\ln(\eta_r)$ based calculations, $M_v$ is 410k g/mol at 60 minutes, 590k g/mol at 30 minutes, and 770k g/mol at zero minutes. With $\eta_{sp}$-based calculations, $M_v$ is 440k g/mol at 60 minutes, 670k g/mol at 30 minutes, and 910 k/mol at zero minutes. Correlation coefficients are better with $\ln(\eta_r)$ analysis.

3) $M_v$ for the Goodyear s-1,2 PBD sample is 29.4±11.0k g/mol based on $\eta_{sp}$, and 35.7±8.0k g/mol based on $\ln(\eta_r)$. For the Polysciences sample, $M_v$ is 36.1±1.0k g/mol and 37.0±0.7k g/mol for $\eta_{sp}$ and $\ln(\eta_r)$ analyses, respectively. In both cases, $[\eta]$ regression based on $\eta_{sp}$ gives better correlation than regression based on $\ln(\eta_r)$.

4) Degree of polymerization ($x$), based on the average $M_v$ reported above at one hour of mixing, is found by dividing the polymer molecular weight by the monomer molecular weight, which is 54.09 for butadiene. Thus $x$ for s-1,2 PBD is approximately 601±59. For trans 1,4 PBD, $x$ is approximately 7857±277.
Table V.1: Samples and Concentrations from Viscometry Experiments

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentrations (% polymer in tetralin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-1,2 PBD (Goodyear)</td>
<td>0.10%, 0.30%, 0.40%, 0.50%</td>
</tr>
<tr>
<td>trans 1,4 PBD (Goodyear)</td>
<td>0.10%, 0.15%, 0.20%, 0.25%</td>
</tr>
<tr>
<td>s-1,2 PBD control (nominally 100k g/mol)</td>
<td>0.18%, 0.36%, 0.55%, 0.80%</td>
</tr>
<tr>
<td>5k 1,4 PBD standard</td>
<td>0.21%, 0.52%, 0.73%, 0.82%, 1.27%, 2.03%</td>
</tr>
<tr>
<td>23k 1,4 PBD standard</td>
<td>0.10%, 0.22%, 0.43%, 0.82%, 1.24%</td>
</tr>
<tr>
<td>150k 1,4 PBD standard</td>
<td>0.10%, 0.25%, 0.39%, 0.52%, 0.60%</td>
</tr>
<tr>
<td>240k 1,4 PBD standard</td>
<td>0.10%, 0.20%, 0.30%, 0.41%</td>
</tr>
</tbody>
</table>

Table V.2: K and a Values for 1,4 Polybutadiene

All K and a values, other than the two for tetralin at 135°C, were taken from Brandrup and Immergut, 1975 (Polymer Handbook). [3]

<table>
<thead>
<tr>
<th>Composition, conditions</th>
<th>K (ml/g)</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>97% trans / 3% 1,2</td>
<td>0.0294</td>
<td>0.753</td>
</tr>
<tr>
<td>toluene, 30°C, light scattering, narrow MWD, 50K-160K g/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55% trans / 35% cis / 10% 1,2</td>
<td>0.0142</td>
<td>0.80</td>
</tr>
<tr>
<td>toluene, 25°C, osmometry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51% trans / 43% cis / 6% 1,2</td>
<td>0.039</td>
<td>0.713</td>
</tr>
<tr>
<td>toluene, 30°C, osmometry, narrow MWD, 100K-250K g/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25% trans / 10% cis / 65% 1,2</td>
<td>0.110</td>
<td>0.62</td>
</tr>
<tr>
<td>toluene, 25°C, MWD = 1.5-1.75, 70K-700K g/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.3% trans / 94.3% 1,2</td>
<td>0.0901</td>
<td>0.81</td>
</tr>
<tr>
<td>toluene, 25°C, osmometry</td>
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</tr>
<tr>
<td>50% trans, 42% cis, 8% 1,2 (average, see below)</td>
<td>0.0145</td>
<td>0.75</td>
</tr>
<tr>
<td>tetralin, 135°C, viscometry, narrow MWD, 5K-240K g/mol</td>
<td>0.0161</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Note: Microstructures of the standards used in the tetralin experiment are as follows:

6K: 55% trans, 36% cis, 9% 1,2
23K: 52% trans, 40% cis, 8% 1,2
150K: 44.5% trans, 47.1% cis, 8.4% 1,2
240K: 43.5% trans, 49.5% cis, 7% 1,2
average: 80% trans, 42% cis, 8% 1,2

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V.1a: Specific Viscosity of 1,4 PBD Standards

V.1b: Relative Viscosity of 1,4 PBD Standards
V.1c: Regression Plots for Determination of Mark-Houwink Parameters for 1,4 PBD

- \( y = -1.80 + 0.74x \) relative viscosity correlation
- \( y = -1.84 + 0.75x \) specific viscosity correlation
V.1d: Specific Viscosity of Homopolymers

V.1e: Relative Viscosity of Homopolymers
GPC of the Polysciences s-1,2 PBD material in toluene at 25°C gave $M_w = 40.3\, \text{k g/mol}$ and $M_n = 22\, \text{k g/mol}$ in one trial and $M_w = 32.2\, \text{k g/mol}$ and $M_n = 20\, \text{k g/mol}$ in a second trial. The GPC chromatographs are shown in Figure V.2. The MW values were determined via universal calibration with a standard curve based on six polystyrene (PS) standards with $M_w$s from 14k g/mol to 400k g/mol. We took $K(\text{PS, toluene, 25°C}) = 0.0105\, \text{ml/g}, a = 0.73$ for polystyrene and $K(\text{PBD, toluene, 25°C}) = 0.0901\, \text{ml/g}, a = 0.81$ for 94.3% 1,2 PBD [3]. With Ashitaka's $K$ and $a$ values for s-1,2 PBD in tetralin at 135°C, the $M_v$ cited earlier for the Polysciences s-1,2 PBD falls between the GPC $M_w$ and $M_n$ results, thus Ashitaka's parameters are reliable. Note, however, that the GPC retention time for this material is comparable to that of 100k g/mol polystyrene. This result may explain why Polysciences, Inc. reported a $M_w$ of 100k g/mol for this material.

For modeling purposes, we took the average of the $M_v$s reported above for each of the homopolymers to get a $M_v$ for s-1,2 PBD of 32.5k g/mol and a $M_v$ for trans 1,4 PBD of 425k g/mol.

**VB. STRUCTURE VERIFICATION**

As mentioned in Section IVD.2, IR, $^1\text{H NMR}$, and $^{13}\text{C NMR}$ spectroscopies were utilized to verify 1,2 PBD and 1,4 PBD content of the homopolymers. IR and $^{13}\text{C NMR}$ were additionally employed to verify tacticity. All homopolymer spectra were compared to data reported in the literature for s-1,2 PBD and trans 1,4 PBD. Solution and solid state $^{13}\text{C NMR}$ techniques were applied. The results and their implications are discussed below.

**VB.1. IR Spectroscopy**

IR spectra are in Figure V.3 for the Goodyear s-1,2 PBD and trans 1,4 PBD homopolymers. Peak locations from these spectra are also listed in the first column of Tables V.3a and V.3b. The most detailed spectra to appear in the literature for these polymers were obtained by Morero et al. [4, 5] and are shown in Figure V.4. The corresponding bond assignments are found in these references. For comparison with our data, the Morero peak locations are listed in the second column of Tables V.3a and V.3b. Other published PBD IR data list only certain bands, and they are given in the third columns of Tables V.3a and V.3b. Our data encompass almost all of the published data and agree very well with Morero's results. In addition, bands between 2130 and 2330 cm$^{-1}$ are
Figure V.2: GPC Chromatographs of s-1,2 PBD Control Sample
Figure V.3: IR Spectra for Homopolymers
Table V.3: IR Data for Homopolymers

V.3a: S-1,2 PBD  
(values in cm⁻¹)

<table>
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<th>this work</th>
<th>Moreno et al. [4]</th>
<th>other sources**</th>
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** other sources:  
B = Binder [33];  
M = Moreno et al. [34]  
S = Silas et al. [35];  
T = Tusaka et al. [36]  
Z = Zerbi and Guisani [37]  

s = syndiotactic, i = isotactic, a = atactic.
V.3b: Trans 1,4 PBD
(values in cm⁻¹)

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</tr>
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</table>

* this band reflects presence of 1,2 units

** other sources:
B = Binder [33];
H = Hampton [38];
He = Hendrix et al. [39];
N = Nasa [40];
No = Noguchi et al. [41];
S = Silas et al. [35];
W = White et al. [42];
V.4a: S-1,2 PBD

V.4b: Trans 1,4 PBD

Figure V.4: Morero's Homopolymer IR Spectra
present in our s-1,2 PBD spectra and a broad band at 2340 cm\(^{-1}\) appears in our trans 1,4 PBD spectra, but none of these bands are documented in the literature.

**VB.2. \(^1\)H NMR Spectroscopy**

With \(^1\)H NMR, we quantified 1,2 PBD and 1,4 PBD content of the homopolymers and the 30k/50k and 30k/200k diblock copolymers. Spectra for the homopolymers in tetralin are presented in Figure V.5. Other than peaks due to solvent, peaks occurred at 1.30, 2.29, 4.96, and 5.53 ppm for s-1,2 PBD and at 2.07 and 5.44 ppm for trans 1,4 PBD. Table V.4 lists our \(^1\)H NMR data along with literature values and bond assignments for both 1,2 PBD and 1,4 PBD, and our data agree well with those in the literature for s-1,2 PBD and trans 1,4 PBD.

Additionally, small 1,2 PBD peaks were present in the trans 1,4 PBD homopolymer spectra. Similarly, small 1,4 PBD peaks were present in the s-1,2 PBD spectra. We calculated a 1,2 PBD content of 95±3% for the s-1,2 PBD material and a 1,4 PBD content of 91±6% for the trans 1,4 PBD material.

**VB.3. \(^13\)C NMR Spectroscopy**

Solution \(^13\)C NMR spectra are in Figure V.6 for s-1,2 PBD and trans 1,4 PBD in tetralin. Table V.5 lists the literature values and bond assignments along with our results. We obtained non-solvent peaks at 39.6, 42.4, 114.4, and 143.8 ppm for the s-1,2 PBD and at 33.1 and 130.4 ppm for the trans 1,4 PBD. Again, our data agree with data in the literature for these homopolymers. Mochel [6] reports peaks for cis 1,4 PBD at 27.9 and 129.8 ppm, but no cis 1,4 PBD peaks were discernible in the \(^13\)C NMR spectra for our trans 1,4 PBD material. Mochel also distinguishes relative amounts of isotactic, atactic, and syndiotactic 1,2 PBD from peaks at approximately 113.4, 113.8, and 114.5 ppm, respectively. Since our s-1,2 PBD spectra show only a single peak at 114.4, this homopolymer contains negligible amounts of isotactic and atactic chain segments.

Solid state MAS \(^13\)C NMR was also performed on both homopolymers. Cross polarized, proton decoupled spectra are given in Figure V.7. For trans 1,4 PBD, a doublet occurred at 33.35 ppm and at 130.131 ppm. The smaller peaks in this spectrum are side-bands of the latter doublet and appear due to limits in the sample spinning speed. In Table V.6, our trans 1,4 PBD solid state results are listed with room temperature solid state data of Schilling et al. [7, 8] and
Figure V.5: $^1$H NMR Homopolymer Spectra
### Table V.4: $^1$H NMR Homopolymer Data

(values are in ppm)

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<th>Researchers</th>
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<th>1,4 PBD assignments</th>
<th>Conditions</th>
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<td>$\text{CH}$</td>
<td>$=\text{CH}_2$</td>
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</tr>
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<td>Seen [44]</td>
<td>[1,2]</td>
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<td>Tanaka et al. [36]</td>
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V.6a: S-1,2 PBD

V.6b: Trans 1,4 PBD

Figure V.6: $^{13}$C (solution) NMR Homopolymer Spectra
Figure V.7 $^{13}$C (solid state) NMR Homopolymer Spectra
Moller [9]. Assignments are the same as for the solution $^{13}$C NMR above, except that the doublets here demonstrate resonances of the amorphous and crystalline carbons, with the crystalline signal slightly downfield from the amorphous signal [7]. We found no literature on solid state NMR for s-1,2 PBD, but by analogy to solution $^{13}$C NMR, we expect four peaks around 39, 41-42, 114, and 143 ppm. Our solid state s-1,2 PBD data showed peaks at 40, 118, and 143 ppm, thus the band at 40 ppm may actually be a series of overlapping bands.

Schilling et al. [8] and Moller also report solid state data for trans 1,4 PBD at various temperatures above room temperature, and these data are included in Table V.6. Trans 1,4 PBD is a polymorphic material: It has one crystal form below about 75°C, referred to as modification (mod) I, and a second crystal form between 75°C and the melting point, referred to as modification (mod) II. The transition from mod I to mod II is reversible and is characterized by a 9% increase in volume [10]. Moller's spectra at 27°, 52°, 67°, 122°, and 134°C respectively correspond to the following states of trans 1,4 PBD: mod I, mod I, transition between mod I and mod II, mod II, and melt. Schilling obtained data at 23°, 59°, 62°, and 65°C, which he claims represent mod I, transition between mod I and mod II, transition between mod I and mod II, and mod II. Moller would probably argue that Schilling's 65°C data represents the transition between mod I and II while the other temperatures are various representations of mod I. Our spectra are most similar to Schilling et al.'s [7] room temperature spectra and to Moller's 52°C spectra.

VB.4. Wide Angle X-ray Scattering (WAXS)

S-1,2 PBD crystal structures are orthorhombic and have unit cell dimensions a=10.98Å, b=6.60Å, and c=5.14Å [11]. There is disagreement in the literature over the type and dimensions of trans 1,4 PBD crystal structures: According to Natta and Corradini [10], mod I structures are pseudohexagonal with unit cell dimensions a=4.54Å and c=4.92Å and mod II structures are pseudohexagonal with dimensions a=4.88Å, c=4.68Å. Suehiro and Takayanagi [12] also claim that mod I and mod II are pseudohexagonal but report a=4.60Å and c=4.83Å for mod I and a=4.95Å, c=4.66Å for mod II. According to Iwayanagi et al. [13], mod I crystals are monoclinic with dimensions a=8.63Å, b=9.11Å, and c=4.83Å. A summary of these unit cell dimensions are presented in Table V.7a.

We conducted WAXS 2θ scans on precipitated, compression-molded homopolymers prepared via the original precipitation procedure, as described
Table V.5: $^{13}$C (solution) NMR Homopolymer Data

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<th>Researchers</th>
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* according to Shonnong and Yangro [49]
**according to Hochel [6]
* these values are specific for $\delta 1,2$

Table V.6: $^{13}$C (solid state) NMR Homopolymer Data

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in Section IVB.2. For comparison, scans were also obtained for an amorphous mixed cis+trans 1,4 PBD sample (36% cis, 55% trans, 9% vinyl; M_w=200k g/mol, M_w/M_n=2.1; Polysciences, Inc.) and two cis 1,4 PBD samples (99% cis, M_w=250k g/mol, M_w/M_n=1.9-2.2; from Goodyear Tire and Rubber Company. Also, 98% cis; M_w=400k g/mol, M_w/M_n=4.0-4.5; from Polysciences, Inc.). Cis 1,4 PBD has a melting point of approximately 2°C [3], thus it is amorphous at 25°C.

Figure V.8 shows the s-1,2 PBD and trans 1,4 PBD homopolymer scans. Averaging results from all scanned samples that contained s-1,2 PBD, peaks occurred at 2θ values of 13.4°, 16.1°, 21.1°, 23.4°, 28.0°, 31.6°, and 35.9°. These peaks correspond to d-spacings of 6.6Å, 5.5Å, 4.2Å, 3.8Å, 3.2Å, 2.8Å, and 2.5Å, respectively, where the d-spacings are calculated from Bragg's Law,

\[ d = \frac{\lambda}{2 \sin \theta} \]  \hspace{1cm} (V-4)

with \( \lambda = 1.54\)Å. The peak corresponding to the 2.8Å spacing was small and did not appear in all spectra. Trans 1,4 PBD peaks for precipitated/molded samples occurred at 2θ values of 22.4° and 39.1°, which correspond to d-spacings of 4.0Å and 2.3Å.

Miller index plane assignments were determined based on Natta and Corradini's crystal dimensions and equations listed by Cullity [14] for orthorhombic and hexagonal cells:

orthorhombic cells: \[ 1/d^2 = \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) \]  \hspace{1cm} (V-5)

hexagonal cells: \[ 1/d^2 = \left( \frac{4}{3} \right) \left( \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right). \]  \hspace{1cm} (V-6)

Suchiro and Takayanagi's trans 1,4 PBD unit cell dimensions gave the same assignments as Natta and Corradini's unit cell. Representative peak positions, d-spacings, and plane assignments are summarized in Table V.7b.

Natta and Corradoini [11] list four primary peaks for s-1,2 PBD that correspond to d-spacings of 6.6Å, 5.5Å, 4.2Å, and 3.8Å, thus our data agree with the reported data. Bermudez and Fatou [15] observed a trans 1,4 PBD peak at 22.5° for the (100) reflection while Iwayanagi et al. [13] and Natta et al. [16] observed it at 22.6°. These values are effectively the same as the 2θ value of 22.4° that we obtained.

WAXS scans of the two amorphous cis 1,4 PBD samples and the mixed cis+trans 1,4 PBD sample are presented in Figure V.9. In all of the amorphous PBDs, there is a single broad peak centered around a 2θ value of approximately 19.6°, corresponding to an average d-spacing of 4.5Å. In Section VIB.3, we discuss scattering data for melt samples of trans 1,4 PBD and s-1,2 PBD. There, melted trans 1,4 PBD and s-1,2 PBD homopolymers gave amorphous d-spacings
Figure V.8: WAXS Scans of Homopolymers
Figure V.9: WAXS Scans of Amorphous 1,4 PBD Samples
of 4.7Å and 6.4Å, respectively. The larger interchain spacing for melted s-1,2 PBD, compared to those for amorphous 1,4 PBDs, is probably due to the presence of pendant vinyl groups.

**VC. THERMAL PROPERTIES**

**VC.1. Glass Transitions**

Glass transitions are often observed by DSC, but DSC is not sensitive enough to indicate glass transitions in our PBD samples. Alternatively, precipitated, compression-molded homopolymers were subjected to Rheovibron tests to determine glass transitions. Also, unprecipitated homopolymer powders were compression-molded and tested for comparison with precipitated powders. All temperature values reported from Rheovibron data have an associated error of about ±5°C.

Tan δ is plotted as a function of temperature in Figure V.10 for precipitated homopolymers prepared by the original precipitation procedure and in Figure V.11 for precipitated homopolymers prepared by the improved precipitation procedure. (The differences between these procedures was discussed in Section IVB.2.) Plots for unprecipitated homopolymer are given in Figure V.12. Unprecipitated s-1,2 PBD samples gave Tg onsets of 20º-25ºC with peaks at 44º-53ºC. Tg onsets of the two precipitated s-1,2 PBD samples mentioned above were 35º and 5ºC, respectively, and the peaks were at 54º and 53ºC. Trans 1,4 PBD samples gave Tg onsets of approximately -85ºC to -80ºC for both unprecipitated and precipitated samples. The peak of the unprecipitated trans 1,4 PBD sample is at -45ºC. The peak of the precipitated trans 1,4 PBD prepared by the original precipitation procedure is located at approximately -51ºC, though this result is ambiguous due to the shape of the tan δ plot from which it was taken. The peak of the precipitated trans 1,4 PBD prepared by the improved precipitation procedure is located, unambiguously, at -43ºC. These results are summarized in Table V.8. Basically, there is no significant difference in glass transition data between precipitated and unprecipitated samples. All trans 1,4 PBD samples also displayed an additional transition beginning at 70º-90ºC, which corresponds to the crystal-crystal modification discussed earlier. Plots for unprecipitated s-1,2 PBD samples also indicate the melting onset at 185º-190ºC.

Ashitaka [17] reported a Tg peak for s-1,2 PBD at 40ºC, thus our s-1,2 PBD data are somewhat higher in value. For 94% trans 1,4 PBD, Dainton [18] gave a
### Table V.7a: Unit Cell Dimensions

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<tr>
<th>PBD</th>
<th>Cell Type</th>
<th>Dimensions</th>
<th>Source</th>
</tr>
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| s-1,2  | orthorhombic| a=10.98Å  
b=6.60Å  
c=5.14Å | Natta & Corradini [11]       |
| t-1,4 (mod I) | monoclinic | a=8.63Å  
b=9.11Å  
c=4.83Å | Iwayanagi et al. [13]        |
|         | hexagonal   | a=4.54Å   
b=4.92Å   | Natta & Corradini [10]       |
|         |             |           | Suehiro & Takayanagi [12]    |
| t-1,4 (mod II) | hexagonal | a=4.88Å   
b=4.68Å   | Natta & Corradini [10]       |
|         |             |           | Suehiro & Takayanagi [12]    |

### Table V.7b: WAXS Homopolymer Data

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### Table V.8: Summary of Homopolymer Rheovibron Tg Results

(Appall temperatures in °C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>History</th>
<th>Tg onset</th>
<th>Tg peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-1,2</td>
<td>Unprecipitated</td>
<td>20° to 25°</td>
<td>44° to 53°</td>
</tr>
<tr>
<td></td>
<td>Precipitated</td>
<td>5° to 35°</td>
<td>53° to 54°</td>
</tr>
<tr>
<td>t-1,4</td>
<td>Unprecipitated</td>
<td>-85°</td>
<td>-45°</td>
</tr>
<tr>
<td></td>
<td>Precipitated</td>
<td>-80° to -83°</td>
<td>-51°(?) to -43°</td>
</tr>
</tbody>
</table>

**Notes**

All samples were compression-molded.

"?" indicates that the Tg peak in one precipitated trans 1,4 PBD sample was not clear but was probably at -51°C.
Figure V.10: Tan δ for Precipitated Homopolymers

V.10a: S-1,2 PBD

V.10b: Trans 1,4 PBD

Figure V.11
Tan δ for Precipitated Homopolymers with Improved Precipitation Procedure

V.11a: S-1,2 PBD

V.11b: Trans 1,4 PBD

Figure V.12: Tan δ for Unprecipitated Homopolymers

V.12a: S-1,2 PBD

V.12b: Trans 1,4 PBD
T_g of -83°C determined by heat capacity measurements. This value corresponds well with our trans 1,4 PBD onset data.

**VC.2. Melting Points and Percent-Crystallinity (%C) Data**

Melting points and associated enthalpies of melting are dependent on a sample's thermal history. In Table V.9, we list DSC-determined melting points and percent-crystallinity (%C) data for samples from our studies with representative thermal histories. To obtain the DSC data, the samples were heated at 20°C/min following the imposition of the histories listed in the table. T_t, T_s, %C_t, and %C_s refer respectively to the trans 1,4 PBD melting point, the s-1,2 PBD melting point, percent-crystallinity of the trans 1,4 PBD component, and percent-crystallinity of the s-1,2 PBD component. The error associated with DSC operation is approximately ±2°C for temperature data and ±1 cal/g for enthalpy data, as determined from duplicated trials.

Percent-crystallinity values are the DSC-determined enthalpies of melting ΔH_m (per gram of sample) relative to the heat of fusion (ΔH_f *) of the corresponding pure and completely crystalline homopolymer:

\[
%C = (ΔH_m/ΔH_f^*) \times 100% \quad (V-7)
\]

Ashitaka et al. [19] calculated a ΔH_f^* of 24.6 cal/g for s-1,2 PBD. For trans 1,4 PBD, there is disagreement in the literature as to the temperatures and enthalpies associated with the various trans 1,4 PBD transitions. The reported values are listed in Table V.10. We accepted Danusso's ΔH_f^* of 20.3 cal/g for the trans 1,4 PBD melting transition [20]. The error associated with calculation of %C data is approximately ±4%.

Bermudez and Fatou [15] observed that the crystallinity of trans 1,4 PBD decreases during the transition from mod I to mod II, thus conversion from mod I to mod II is typically incomplete. As a result, we should have calculated %C_t based on the crystal-crystal transition enthalpy rather than the enthalpy of melting. Nevertheless, our %C_t values were consistently calculated from trans 1,4 PBD melting data.

In Table V.9, T_s ranges from 186°C to 194°C and %C_s runs from 35% to 78%. T_t ranges from 132° to 150°C while %C_t runs from 38% to 58%. In general, the highest melting point and %C values correspond to as-received polymer and the low values correspond to samples that were precipitated then compression-molded in the melt and then remelted again in an inert atmosphere. The inert atmosphere was gaseous N2, if remelting was
Table V.9: Thermal Histories and Properties of Homopolymer Samples  
(All temperatures in °C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>History</th>
<th>T₁</th>
<th>T₂</th>
<th>%C₁</th>
<th>%C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-1,2</td>
<td>as-received**</td>
<td>193°</td>
<td></td>
<td>78%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip**</td>
<td>189°</td>
<td></td>
<td>74%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip</td>
<td>189°</td>
<td></td>
<td>70%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>melt, quench†**</td>
<td>194°</td>
<td></td>
<td>44%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip, melt, quench**</td>
<td>188°</td>
<td></td>
<td>46%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip, melt, hold* T, quench</td>
<td></td>
<td>188°</td>
<td>39%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td></td>
<td>187°</td>
<td>38%</td>
<td></td>
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<tr>
<td></td>
<td>T= 155°</td>
<td></td>
<td>187°</td>
<td>38%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td></td>
<td>186°</td>
<td>38%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 125°</td>
<td></td>
<td>187°</td>
<td>38%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 110°</td>
<td></td>
<td>186°</td>
<td>39%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 25°</td>
<td></td>
<td>187°</td>
<td>39%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip, mold</td>
<td></td>
<td>186°</td>
<td>36%</td>
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</tr>
<tr>
<td></td>
<td>precip, mold, melt, cool at 25°</td>
<td></td>
<td>187°</td>
<td>35%</td>
<td></td>
</tr>
<tr>
<td>l- 1,4</td>
<td>as-received**</td>
<td>150°</td>
<td></td>
<td>58%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip**</td>
<td>134°</td>
<td></td>
<td>54%</td>
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<td></td>
<td>precip</td>
<td>134°</td>
<td></td>
<td>52%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>melt, quench**</td>
<td>141°</td>
<td></td>
<td>41%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip, melt, quench**</td>
<td>133°</td>
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<td>42%</td>
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</tr>
<tr>
<td></td>
<td>precip, melt, hold* T, quench</td>
<td></td>
<td>133°</td>
<td>44%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td></td>
<td>132°</td>
<td>42%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 155°</td>
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<td>133°</td>
<td>42%</td>
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</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td></td>
<td>133°</td>
<td>41%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 125°</td>
<td></td>
<td>133°</td>
<td>42%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 110°</td>
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<td>132°</td>
<td>44%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 25°</td>
<td></td>
<td>132°</td>
<td>44%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip, mold</td>
<td></td>
<td>137°</td>
<td>52%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>precip, mold, melt, cool at 25°</td>
<td></td>
<td>132°</td>
<td>38%</td>
<td></td>
</tr>
</tbody>
</table>

Notes:
Error is approximately ±2°C for temperature values and ±4% for %C values.
Where tests were duplicated, average data are presented here.
† All "melted" samples were typically held in the melt in an inert atmosphere for 1-3 minutes.
All quenched samples were cooled from the melt at a rate of -320°C/min.
** No indium standard data were obtained for these samples.
* Isothermally held samples were kept at the hold temperature for 1 minute.
accomplished in the DSC, or gaseous argon. Note that compression-molding also occurs in the melt state.

Melting of the as-received powders substantially lowered their crystallinity but had less of an effect on their resulting melting points than did other treatments. Possibly, even brief periods of melting cause some crosslinking such that the overall amount of material that can recrystallize is lowered, yet the crystallites that do form again upon cooling are almost as large and well-formed as the original crystallites. Precipitation, on the other hand, substantially lowered the melting points but had only a minor negative effect on the percent-crystallinity of the samples. Thus, the crystallites that do form upon precipitation are at least as numerous as in the original powder but are probably smaller and less well-formed. This relationship between melting point and crystallite size is documented in the literature [21].

Precipitated (but not compression-molded) samples were also isothermally crystallized at 165°C, 155°C, 140°C, 125°C, 110°C, and 25°C. The data from these samples are included in Table V.9. The melting points and %C values for all of these samples, which are included in Table V.9, are essentially the same, thus independent of the crystallization temperature. This result is probably due to the relatively fast crystallization kinetics of both homopolymers, as discussed in Section VC.3, which may have prevented true isothermal crystallization. Rather, the components crystallized during the quench to the isothermal setpoint or to the final temperature of 25°C. The DSC was limited to cooling rates of -200°C/min in the program mode, so we were not able to quench at faster rates.

Finally, DSC scans of s-1,2 PBD samples crystallized at temperatures ≥125°C include a small peak about 5°-10°C above the isothermal crystallization temperature, as depicted in Figure V.13. This peak indicates the presence of secondary crystallization. It was also observed by Obata et al. [22] for s-1,2 PBD and by Yagpharov [23] for polydimethylvinylsiloxane (PDMS), polyethylene terephthalate (PET), and polyurethane. The lower the concentration of s-1,2 PBD or the lower the crystallization temperature, the smaller the size of the secondary peak, thus we did not observe a secondary peak when crystallization temperatures were less than 125°C (or in blends where the s-1,2 PBD content was less than 25%). Secondary crystallization was not discernable in trans 1,4 PBD scans.
Figure V.13: DSC Scan of Secondary Crystallization of S-1,2 PBD
Table V.11 summarizes %C values as a function of thermal history. The various thermal histories in Table V.11 are as follows: a) As-received powders (i.e., unprecipitated), b) precipitated powders, c) as-received powders melted then recrystallized, d) precipitated powders melted then recrystallized, and e) precipitated, compression-molded films remelted, then recrystallized. Note that compression-molding takes place in the melt state in the presence of atmospheric O2. Table V.11 indicates that the greater the exposure to elevated temperatures, the lower the percent-crystallinity. For samples that were precipitated then melted only once, as in compression-molded samples, the percent-crystallinity is in the neighborhood of 40-50% for both s-1,2 PBD and trans 1,4 PBD, though trans 1,4 PBD may be as much as 10-15% more crystalline than s-1,2 PBD under such conditions.

Percent-crystallinity was also obtained via WAXS data for a few homopolymer films. The ratio of crystalline peak area to the total peak area for a given sample, where crystalline peak area is defined as the total peak area minus the amorphous peak area, gives %C. By this method, precipitated, compression-molded s-1,2 PBD was 51±3% crystalline, while unprecipitated, compression-molded s-1,2 PBD was 52±1% crystalline. Precipitated, compression-molded trans 1,4 PBD was 66±1% crystalline while unprecipitated, compression-molded trans 1,4 PBD was 61±2% crystalline. DSC-determined %C values for the same materials gave lower figures, as reported above, but the difference between s-1,2 PBD and trans 1,4 PBD %C values obtained by each of these two methods is consistent. For the remainder of this report, %C data always refer to DSC-determined values.

**VC.3. Crystallization Kinetics**

As mentioned in Section IIC.1, Avrami [24] relates the extent of isothermal crystallization with time by the following expression:

\[ X_c = 1 - \exp(-k^n) \]  \hspace{1cm} (V-8)

where \( X_c \) is the degree of crystallinity at time \( t \) relative to the crystallinity of the sample at infinite time, \( k \) is the bulk crystallization rate constant, and \( n \) is the Avrami exponent. A log-log plot of -\( \ln(1-X_c) \) versus \( t \) yields a y-axis intercept of \( \log k \) that corresponds to \( t=1 \) minute. The slope of the plot is \( n \). For spherulitic growth with thermal, heterogeneous nucleation, \( n \) is equal to 4; for spherulitic growth with athermal nucleation, \( n \) is 3.

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### Table V.10: Polymorphism of Trans 1,4 PBD

(All temperatures in °C, all ΔH values in cal/g)

<table>
<thead>
<tr>
<th>Authors</th>
<th>T&lt;sub&gt;t&lt;/sub&gt;</th>
<th>ΔH&lt;sup&gt;*&lt;/sup&gt;</th>
<th>T&lt;sub&gt;(mod 1→11)&lt;/sub&gt;</th>
<th>ΔH&lt;sub&gt;(mod 1→11)&lt;/sub&gt;</th>
<th>ΔH&lt;sub&gt;1→11/ΔH&lt;sup&gt;*&lt;/sup&gt;&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moraglio et al. [59]</td>
<td>145°</td>
<td>20.3</td>
<td>76°</td>
<td>40.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Danusso [20]</td>
<td>145°</td>
<td>20.3</td>
<td>76°</td>
<td>40.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Natta et al. [16]</td>
<td>145°</td>
<td>-</td>
<td>75°</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bautz et al. [60]</td>
<td>135°</td>
<td>-</td>
<td>70°</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Finter and Wegner [61]</td>
<td>164°</td>
<td>16.6</td>
<td>83°</td>
<td>34.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Bermudez and Fatou [15]</td>
<td>142°</td>
<td>16.0</td>
<td>50-55°</td>
<td>28.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Dainton et al. [18]</td>
<td>-</td>
<td>-</td>
<td>44°</td>
<td>15.1</td>
<td>-</td>
</tr>
<tr>
<td>Kijima et al. [62]</td>
<td>135-136°</td>
<td>17.1</td>
<td>75-78°</td>
<td>31.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Stellman et al. [63]</td>
<td>139°</td>
<td>-</td>
<td>73°</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Berger and Buckley [64]</td>
<td>-</td>
<td>60-65</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Marchetti and Martuscelli [65]</td>
<td>139°</td>
<td>20.4</td>
<td>75°</td>
<td>40.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Mandelkern et al. [66]</td>
<td>-</td>
<td>18.5</td>
<td>74°</td>
<td>26.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Moller [9]</td>
<td>134°</td>
<td>-</td>
<td>67°</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iwayanagi et al. [13]</td>
<td>148°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table V.11

**Percent-Crystallinity of Homopolymers as a Function of Thermal History**

<table>
<thead>
<tr>
<th>History</th>
<th>%C&lt;sub&gt;1&lt;/sub&gt;</th>
<th>%C&lt;sub&gt;5&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>58%</td>
<td>78%</td>
</tr>
<tr>
<td>Precipitated</td>
<td>52-54%</td>
<td>70-74%</td>
</tr>
<tr>
<td>As-received + melted in inert gas</td>
<td>38-43%</td>
<td>44%</td>
</tr>
<tr>
<td>Precipitated + melted in inert gas</td>
<td>39-45%</td>
<td>38-46%</td>
</tr>
<tr>
<td>Precipitated + molded</td>
<td>52%</td>
<td>36%</td>
</tr>
<tr>
<td>Precipitated + molded + melted in inert gas</td>
<td>33-35%</td>
<td>37-38%</td>
</tr>
</tbody>
</table>
Precipitated (not compression-molded) homopolymer powders were subjected to Avrami analysis. To obtain preliminary crystallization data, samples were heated at 20°C/min to a temperature above their melting point, then cooled at 2°C/min until crystallization was complete. For trans 1,4 PBD, the melting point was 132.6°C and crystallization occurred between 120.0°C and 115.0°C, corresponding to an undercooling of 12.6°C for the onset of crystallization. For s-1,2 PBD, the melting point was 184.4°C and crystallization occurred between 162.0°C and 151.4°C, corresponding to an undercooling of 24.4°C. For Avrami calculations, untested portions of the same samples were isothermally crystallized: The s-1,2 PBD sample was heated at 200°C/min to 205°C, held in the melt at 205°C for 1 minute, cooled at 200°C/min to the isothermal crystallization temperature, held isothermally for the duration of crystallization (typically 5-10 minutes, or until the DSC scan line returned to the original baseline), then cooled at 200°C/min back to 25°C. Tests were run for crystallization temperatures of 156.5°C and 160.0°C. Similarly, two trans 1,4 PBD samples were heated at 200°C/min to 150.0°C, held in the melt at 150.0°C for 1 minute, cooled at 200°C/min to isothermal crystallization temperatures of 117.8°C and 120.0°C, and held isothermally until crystallization was complete.

A second set of s-1,2 PBD and trans 1,4 PBD samples was tested to obtain additional data points and to verify the previous results. In this set, the s-1,2 PBD had a melting point of 188.3°C and crystallized from 164.0° to 150.0°C, giving again an undercooling of 24.3°C. The trans 1,4 PBD had a melting point of 132.5°C and crystallized from 119.5° to 111.5°C, which corresponds to an undercooling of 13°C and is therefore consistent with the previous trans 1,4 PBD sample. For this experiment, s-1,2 PBD was held isothermally at 158.0°C, 163.0°C, and 164.5°C and trans 1,4 PBD was held isothermally at 116.0°C, 119.0°C, and 120.5°C.

By taking ten equal time increments along each isothermal DSC crystallization curve, Xc as a function of time was calculated as the ratio of the area under the curve at a given time relative to the total area for the crystallization process. Instrument-based transients in the DSC scans were removed by extrapolating the crystallization curve back to the position at which the temperature reached the isothermal setpoint. The resulting Xc versus time curves are shown in Figure V.14 for the two homopolymers crystallized at various temperatures. The log-log plots are shown in Figure V.15, and k and n values are listed in Table V.12. The plots are not linear,
Figure V.14

Xc versus Time Curves for Isothermally Crystallized Homopolymers

See note for Table V.12

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Figures V.15: Homopolymer Avrami Plots

See note for Table V.12
rather they exhibit a decrease in slope with time. Consequently, Table V.12 includes $k_{avg}$ and $n_{avg}$ which are the averages of the two $k$ and $n$ values obtained from: a) the line composed of the data points from the three shortest time measurements and b) the line composed of the data points of the five longest time measurements from the curves in Figure V.15.

As shown in Figure V.16, $k_{avg}$ values increase exponentially with degree of undercooling due to the increased driving force for crystallization at lower temperatures. If the crystallization temperatures were to approach much closer to $T_g$, we would expect $k$ values to level off and finally decrease due to transport limitations as the polymer becomes glassy. The smaller degree of undercooling needed for trans 1,4 PBD crystallization indicates that trans 1,4 PBD requires a smaller crystallization activation energy than s-1,2 PBD. Trans 1,4 PBD may be ordered to a higher degree in the melt than s-1,2 PBD and thus crystallize with a lower activation energy.

The change in slope in Figure V.15 reflects a decrease in nucleation rate and is indicative of secondary crystallization of amorphous material. Wunderlich [25] suggests that secondary crystallization occurs after initial nuclei are exhausted during thermal heterogeneous nucleation and that crystal perfection, after impingement of the initial crystal formations, also contributes to the decrease in slope with time. Yagharov [23] claims that secondary crystallization yields "fringed micelle" crystal formations that are independent of primary crystallization. From DSC studies discussed earlier, we verified that secondary crystallization occurs for isothermally crystallized s-1,2 PBD.

From our plots, $n$ for s-1,2 PBD at short times are 4.7-5.9 and at longer times are 1.4-3.3. These numbers encompass data obtained by Obata et al. [22]. Obata reported $n$ values of 3.1-3.3 for 25% crystalline s-1,2 PBD and 2.6-3.5 for 46% crystalline s-1,2 PBD. For trans 1,4 PBD, we obtained $n$ values of 3.7-6.7 at short times and 1.5-2.9 at longer times. Bermudez et al. [26] found $n$ to be $2.2\pm0.4$ for trans 1,4 PBD, which agrees with our $n$ value for longer times.

There are a number of limitations to Avrami analysis, thus it is difficult to interpret such varied $n$ values. However, the $X_c$ versus time data is also useful for determining crystallization half times, $\tau_{1/2}$. Plots of $\tau_{1/2}$ as a function of degree of undercooling are given in Figure V.17 for our homopolymers, up to 16.5°C undercooling for trans 1,4 PBD and 30.3°C undercooling for s-1,2 PBD. At these points, $\tau_{1/2}$ is less than 50 seconds for
Figure V.16: $k_{avg}$ versus Undercooling

Figure V.17: Crystallization Half-Times as a Function of Undercooling
either homopolymers. For greater degrees of undercooling, most of the crystallization process already took place by the time the DSC curves no longer reflected instrument-based transients upon reaching the crystallization temperature, thus the resulting crystallization curves are not reliable even with extrapolation.

What are the implications of these kinetics? Another study was performed to determine if quenching melt s-1,2 PBD samples in liquid nitrogen could "lock in" the melt morphology. Compression-molded s-1,2 PBD samples 0.5 mm thick were cut into 3 mm x 3 mm squares and sealed in two rubber-stoppered glass test tubes. The test tubes were then evacuated and filled with 99.999% argon gas (Matheson Gas Products, Secaucus, NJ) six times and finally set in a 200°C oil bath for about two minutes so that the samples melted. As evidence that melting conditions were achieved, the samples became translucent. Then one tube was immediately dunked into liquid nitrogen. When the liquid nitrogen stopped boiling, the tube was removed and allowed to come to 25°C. At 25°C, s-1,2 PBD is close to its Tg, thus if the crystallization kinetics were slow enough to prevent crystallization during the quench, the sample would have retained its noncrystallized melt morphology. However, the opaqueness of this sample indicated that crystallization had occurred and that it was not possible to prevent crystallization in this manner. The second tube was simply taken out of the oil bath and allow to cool directly to 25°C as a control. DSC on both samples showed that the liquid nitrogen quenched sample had crystallized to an amount equal to 93% of the control. However, crystallization may have occurred in the quenched sample as it was heated in the DSC, thus the 93% figure may be erroneously high.

In another trial, a trans 1,4 PBD sample with the same dimensions was held by tweezers and dipped directly in 165°C oil until it was translucent, then transferred directly into a dewar of liquid nitrogen. It also appeared opaque while it was in the liquid nitrogen, thus it was not possible to "lock in" the melt morphology of trans 1,4 PBD, either. In conclusion, the kinetics of crystallization of both homopolymers are too fast to allow the noncrystallized melt morphologies to be maintained during a quenching process.

**VC.4. High Temperature Behavior: Degradation and Crosslinking**

Because of their fast kinetics, we were not able to quench the homopolymers in order to study their melt morphologies at room temperature,
and unfortunately, undesired events occurred at melt temperatures. For example, during the viscometry tests described in Section VA, trans 1,4 PBD degraded in tetralin at 135°C. During compression-molding at 200°C, a number of samples degraded, as discussed in Section IVB.4. In the latter case, samples with s-1,2 PBD were more likely to degrade than samples with trans 1,4 PBD. In this section we report on additional instances and effects of high temperature on PBD samples, specifically the occurrence of degradation and crosslinking. These effects hindered our ability to study s-1,2 PBD and trans 1,4 PBD in the melt state.

**VC.4a. Effect of Oxygen on PBD**

In spin-casting experiments, a nitrogen atmosphere did not prevent film discoloration, but the discoloration was much greater when nitrogen was not purged through the casting chamber. In air, the films turned dark brown by the time casting was complete. To differentiate between oxygen-induced degradation and degradation independent of oxygen, two sets of four PBD samples were heated in the DSC at 20°C/min - one set was heated in the presence of a nitrogen environment and the second set was heated in presence of air, thus oxygen. The four PBD samples were trans 1,4 PBD homopolymer, s-1,2 PBD homopolymer, 1,2/1,4 PBD (amorphous) diblock, and amorphous (mixed cis+trans) 1,4 PBD.

In the nitrogen atmosphere, an exothermic transition began at 200°C for s-1,2 PBD and at 240°C-250°C for the other PBDs. In the presence of oxygen, all samples displayed an exothermic peak that began around 185°C and went through a minimum around 210°C. This latter phenomenon is illustrated in Figure V.18a for trans 1,4 PBD in an air atmosphere. A scan of the same material in a nitrogen atmosphere is illustrated in Figure V.18b. Thus degradation due to oxidation is distinct from degradation that occurs in the absence of oxygen, and the former can be minimized during high temperature experiments by the application of an inert atmosphere.

**VC.4b. Effect of Time at 200°C on Crystallinity**

In Table V.11, we showed that the longer a sample is exposed to elevated temperatures, the lower the crystallinity content. An additional set of tests was performed to determine more precisely the effect of time on samples held in the melt in an inert atmosphere. Specifically, we monitored the
Figure V.18: DSC Scans of Trans 1,4 PBD

V.18a: Heated in the Presence of Oxygen

V.18b: Heated in the Absence of Oxygen
crystallinity and melting points of a 50/50 precipitated/compression-molded blend of s-1,2 PBD and trans 1,4 PBD homopolymers held at 200°C for different lengths of time. In blend form, the enthalpies of the two PBD components are nearly the same as the enthalpies of the two homopolymers when they are not blended, as is discussed in Section VI.B.2, thus the results of this study are applicable to 100% homopolymer systems as well.

Sections of the 50/50 blend sample were placed in test tubes and then repeatedly evacuated and filled with high purity argon, as in the quenching study in Section VC.3. Then all of the tubes were placed in an oil bath at 195°C. One test tube was removed from the bath and allowed to cool to room temperature after 15 minutes, another after 2 hours, and a third after 16 hours. In addition, one s-1,2 PBD homopolymer sample and one trans 1,4 PBD homopolymer sample were removed from the bath after only two minutes. A similar test was performed on 50/50 blends in the DSC with a nitrogen gas atmosphere during which samples were held at 195°C for 15 minutes, 2 hours, and 16 hours.

Table V.13 shows the effect of time on the resulting melting points and enthalpies, as determined by DSC following the exposure described above. With increased time, the melting points and enthalpy values of both the s-1,2 PBD and the trans 1,4 PBD components clearly decreased. S-1,2 PBD was affected to a greater degree than trans 1,4 PBD. Within 2 hours, 40-49% of the initial trans 1,4 PBD crystallinity was lost and 51-60% of the initial s-1,2 PBD crystallinity was lost. The 50/50 samples had a light brown color when they were removed from the oil bath, thus degradation occurred. Also, the samples were translucent in the melt yet retained their form and didn't flow. This phenomenon is also true for the quenching tests described at the end of Section VC.3. Loss of crystallinity, decreased melting point behavior, and a tendency to retain form in the melt are all characteristics of crosslinked materials.

VC.4c. Tests for Crosslinking: Mechanical Spectrometry and Solvent Swelling

The storage modulus, G', is a measure of a material's elastic, or solid-like, rheological properties. When crosslinking occurs, a polymer loses its ability to flow, thus G' typically increases with increasing extent of crosslinking. A material that melts without crosslinking is expected to have a constant G' with time at a given temperature and to show a decrease in G' as temperature
Table V.12: Summary of k and n Values from Avrami Analysis

<table>
<thead>
<tr>
<th>sample</th>
<th>melt T</th>
<th>cryst T</th>
<th>undercool</th>
<th>n short</th>
<th>log k short</th>
<th>n long</th>
<th>log k long</th>
<th>n avg</th>
<th>log k avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/18 trans</td>
<td>132.6</td>
<td>117.8</td>
<td>14.8</td>
<td>6.77</td>
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<td>2.13</td>
<td>-0.02</td>
<td>4.45</td>
<td>-0.31</td>
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<tr>
<td>7/18 trans</td>
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<td>120.0</td>
<td>12.6</td>
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<td>1.48</td>
<td>-0.52</td>
<td>3.21</td>
<td>-1.24</td>
</tr>
<tr>
<td>7/19 trans</td>
<td>132.5</td>
<td>116.0</td>
<td>16.5</td>
<td>4.14</td>
<td>0.23</td>
<td>1.74</td>
<td>0.21</td>
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<td>0.22</td>
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<td>2.85</td>
<td>-1.27</td>
<td>3.29</td>
<td>-1.40</td>
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<tr>
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</tr>
<tr>
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<td>160.0</td>
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<td>1.89</td>
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<td>3.38</td>
<td>-0.73</td>
</tr>
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<td>7/19 syndio</td>
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<td>158.0</td>
<td>30.3</td>
<td>5.59</td>
<td>0.99</td>
<td>1.85</td>
<td>0.53</td>
<td>3.72</td>
<td>0.76</td>
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<td>3.35</td>
<td>-0.46</td>
<td>4.56</td>
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<tr>
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<td>3.30</td>
<td>-1.03</td>
<td>4.00</td>
<td>-1.18</td>
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</tbody>
</table>

"7/18" and "7/19" refer to test dates in 1988. Samples tested on 7/18 were also prepared on a different day than samples tested on 7/19.

Table V.13: Effect of Time on Samples in the Melt

These samples were held at 195°C in an inert atmosphere for the time indicated, then cooled to 25°C. Prior to the experiment, the samples were precipitated and compression-molded.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time, gas</th>
<th>Tm, trans (°C)</th>
<th>Tm, syndio (°C)</th>
<th>Hm, trans (cal/g)</th>
<th>Hm, syndio (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% trans</td>
<td>2 min, Ar</td>
<td>132.0*</td>
<td>-</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>100% syndio</td>
<td>2 min, Ar</td>
<td>132.0*</td>
<td>-</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>50/50 blend</td>
<td>15 min, Ar</td>
<td>127.7*</td>
<td>175.4*</td>
<td>6.0</td>
<td>7.4</td>
</tr>
<tr>
<td>50/50 blend</td>
<td>2 hr, N2</td>
<td>116.7*</td>
<td>160.5*</td>
<td>4.0</td>
<td>3.4</td>
</tr>
<tr>
<td>50/50 blend</td>
<td>16 hr, N2</td>
<td>85.5*</td>
<td>np</td>
<td>2.2</td>
<td>np</td>
</tr>
<tr>
<td>50/50 blend</td>
<td>15 min, N2</td>
<td>128.3*</td>
<td>177.5*</td>
<td>7.4</td>
<td>8.2</td>
</tr>
<tr>
<td>50/50 blend</td>
<td>2 hr, N2</td>
<td>113.4*</td>
<td>153.1*</td>
<td>4.8</td>
<td>4.4</td>
</tr>
<tr>
<td>50/50 blend</td>
<td>16 hr, N2</td>
<td>75.5*</td>
<td>np</td>
<td>2.2</td>
<td>np</td>
</tr>
</tbody>
</table>

"np" indicates that no peak was discernable on the DSC scan

Tm = melting point, Hm = enthalpy of melting

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increases. Polymers that degrade without crosslinking are expected to show a decrease in $G'$ with time or temperature if the decrease in overall molecular weight is sufficient enough to lead to enhanced chain mobility and, consequently, increased fluidity.

By means of mechanical spectrometry, we obtained $G'$ measurements for our s-1,2 PBD and trans 1,4 PBD homopolymers in the melt as a function of time. Precipitated, compression-molded homopolymer samples were monitored at 200°C for 70 minutes in a nitrogen atmosphere. From minute 10 to minute 70, a s-1,2 PBD specimen showed an increase in $G'$ from 139 kPa to 512 kPa. A second s-1,2 PBD sample tested at 2% strain rate had an initial $G'$ of 105 kPa and increased to 284 kPa within the same time period. With a trans 1,4 PBD sample tested at 2% strain rate, $G'$ was initially 7.6 kPa and increased to 168 kPa. The results of these runs are shown in Figure V.19. Note that time zero on these graphs marks the beginning of the $G'$ measurement, but the sample was in the testing chamber at 200°C for ten minutes before measurements were taken. By the criteria proposed in the preceding paragraph, these data are characteristic of crosslinked materials.

With solvent swelling experiments, we independently verified that crystalline PBD homopolymers crosslink when exposed to melt conditions. Heavily crosslinked polymers do not go into solution in an otherwise good solvent because elastic free energy constraints imposed by the crosslinks counter the free energy of solution (or dissolution). Lightly crosslinked materials may exhibit partial dissolution at equilibrium. Two sets of s-1,2 PBD and trans 1,4 PBD samples of approximately 0.4g each were cut into small shavings, placed in stirred beakers containing 10 ml tetralin solvent at or near 150°C, and monitored to determine relative extents of swelling. Both sets of samples had been compression-molded at 200°C for 3 minutes, but one set was prepared from unprecipitated homopolymer while the second set was prepared from precipitated homopolymers. The specimens from the mechanical spectrometry experiments above comprised the second set, thus they had been held at 200°C for more than one hour. A third set of homopolymers that had been precipitated, but were not otherwise exposed to elevated temperatures, was also studied as a control.

The results are as follows:

1) Trans 1,4 PBD and s-1,2 PBD precipitated controls (that were not otherwise exposed to elevated temperatures before this test) showed
signs of swelling after 1.5 hours in tetralin. They went into solution completely within 8 hours, though the solutions were slightly turbid and more viscous than typical homopolymer solutions prior to precipitation.

2) With compression-molded samples prepared from unprecipitated powder, s-1,2 PBD partially dissolved after 1 hour: The film shavings swelled extensively but had not completely dissolved, yet the tetralin was more viscous than at the beginning of the experiment. After two hours, trans 1,4 PBD pieces had swelled to at least 3 times their original volume but had not dissolved to a significant extent. After a total of 8 hours, the solvent in the trans 1,4 PBD sample was even more viscous but total dissolution still did not occur. With both the s-1,2 PBD and the trans 1,4 PBD, the solutions gelled when they were finally allowed to cool to room temperature, thus some polymer definitely dissolved in the solvent in both cases.

3) With samples that had been precipitated, compression-molded, and held at 200°C for at least 70 minutes, s-1,2 PBD barely swelled even after 7 hours in hot tetralin. Trans 1,4 PBD swelled but to a lesser degree than the trans 1,4 PBD discussed in the preceding paragraph, and the solvent showed no evidence of increased viscosity. Upon cooling to room temperature, the solvent did not gel for either sample, thus there was relatively no dissolution of polymer.

In summary, the relative degrees of crosslinking as a function of thermal history are as follows:

precipitated polymer, not molded (near total dissolution in 8 hr) < unprecipitated polymer, molded (partial dissolution in 8 hr) < precipitated polymer, molded + 200°C for ≥1 hour (no dissolution at 7 hr).

**VC.4d. **Reported Thermal Crosslinking of PBD

The effect of temperature on PBD is described in the literature by McCready and Keskkula [27]. They observed anaerobic crosslinking and cyclization of PBD at 200°-300°C. Around 350°C, main chain scission occurs, followed by additional crosslinking, cyclization, and depolymerization. According to Vanderhoff [28] and Loan [29], polybutadienyl radicals attack double bonds and then propagate through the polymer, with one radical producing up to 40-50 crosslinks. McCready and Keskkula propose that the
initiation of this chain reaction may be due to the abstraction of an allylic hydrogen or due to a bimolecular hydrogen transfer reaction. Their scheme of thermal decomposition of PBD is summarized in Figure V.20. Additionally, they suggest that 1,2 PBD material crosslinks more readily than 1,4 PBD. Our G' data in Section VC.4b support this claim.

**VD. MORPHOLOGY**

Homopolymer morphology was observed by TEM and by polarized light microscopy in conjunction with a hot stage. With light microscopy, we discerned spherulitic structures about 12μ in diameter in a s-1,2 PBD sample. This sample was crystallized isothermally for 8 minutes 18.5°C below its Tm of 185°C. A trans 1,4 PBD sample with a Tm of 135°C gave rod-like crystal structures 5μ to 10μ in length after 8 minutes at 11.5°C undercooling. Micrographs of both structures are shown in Figure V.21. The samples had been microtomed to a thickness of 5μ to 10μ from precipitated, compression-molded films.

TEM samples were cut from precipitated, compression-molded films. Though the sulfur-stain we employed typically shows contrast between 1,2 PBD and 1,4 PBD components, we suspected that it would also distinguish amorphous from crystalline regions in homopolymer samples. In Figures V.22a and V.22b for s-1,2 PBD and trans 1,4 PBD homopolymers, respectively, ordered regions of stained material are apparent. The stained regions represent amorphous material alternating with relatively unstained crystalline material. In s-1,2 PBD, stained parallel segments are regularly spaced about 200Å (0.02 microns) apart. In trans 1,4 PBD, stained segments approximately 1000Å (0.1 microns) apart are evident. The trans 1,4 PBD segments are not as evenly spaced as the s-1,2 PBD segments, rather they are reminiscent of a sheaf-like, imperfect fibrillar spherulitic structure of polyethylene documented by Raff and Doak [30].

SAXS scans of precipitated, compression-molded homopolymer films were obtained to verify the presence and dimensions of the ordered material. Since we cannot measure ordered spacings much above 600Å with our current SAXS set-up, this tool was more appropriate for s-1,2 PBD. Nevertheless, both homopolymers were scanned for 20 minutes with the detector set at 2.5m. Unfortunately, we did not discern reproducible SAXS patterns for any of the samples, even when they were annealed for 5 hours or stained.
Figure V.19
Storage Modulus of Homopolymers at 200°C as a Function of Time

Figure V.20: Thermal Decomposition of PBD [27]
Figure V.21: Light Micrographs of Homopolymer Crystal Structures
(sample thickness: 5-10μ)
V. MECHANICAL PROPERTIES

In the Rheovibron studies described in Section VC.1 for determination of Tg, we also calculated homopolymer G' and G" parameters as a function of temperature. Figure V.23 gives G' and G" plots for precipitated, compression-molded samples. Results for compression-molded samples that had not been precipitated are nearly identical. For both s-1,2 PBD and trans 1,4 PBD, G' is between $1 \times 10^{11}$ and $1 \times 10^{10}$ dynes/cm² (10⁴ and 10³ MPa) when the polymer is in the glassy regime, then G' falls to less than $1 \times 10^{9}$ dynes/cm² (100 MPa) by 100°C. For the sake of comparison, 120k g/mol amorphous mixed cis+trans PBD crosslinked with a 30 Mrad dose of electrons also gave G' between 10⁴ and 10³ MPa in the glassy regime, but then G' dropped immediately to under 10 MPa once the glass transition was achieved [31]. G" of s-1,2 PBD and trans 1,4 PBD was approximately 100 MPa at temperatures below the respective Tg's; by 100°C G" dropped to less than 10 MPa.

Instron testing was conducted at 25°C. We tested both unprecipitated and precipitated homopolymers in tension as well as unprecipitated homopolymers in compression. As detailed in Section IVD.6, "micro-dogbone" samples with test dimensions of 5.2 mm x 2 mm were utilized for tensile testing, and cylinders 3 mm in diameter and 4 mm in height were utilized for the compression testing.

Tensile stress-strain results are given in Figure V.24 for unprecipitated homopolymers. The moduli, yield stress, percent elongation at break, and stress at break data are listed in Table V.14. S-1,2 PBD has a modulus more than twice that of trans 1,4 PBD, but s-1,2 PBD breaks at a strain of only 10%. Trans 1,4 PBD displays rubbery behavior and doesn't break until elongations greater than 150%. These results are sensible considering that s-1,2 PBD is at or slightly below its glass transition at the test temperature, while trans 1,4 PBD is at least 100°C above its Tg.

Stress-strain data of unprecipitated homopolymers in compression are shown in Figure V.25. The compression moduli are 750 MPa and 300 MPa for the s-1,2 PBD and trans 1,4 PBD, respectively. These values are about twice as high as the moduli of the same materials in tension. Yield stresses from compression are approximately 40±4 MPa and 18±4 MPa, respectively, and are thus close to results for both precipitated and unprecipitated homopolymers in tension. Despite that both materials are at least 40% crystalline, neither homopolymer exhibited brittleness or failure up to 75% compression when the
Figure V.23: Homopolymer Storage and Loss Moduli ($G'$ and $G''$)
Figure V.24: Tensile Stress-Strain Data for Unprecipitated Homopolymers

Figure V.25
Stress-Strain Data from Compression Testing of Unprecipitated Homopolymers
experiments were arbitrarily concluded. For both homopolymers, the general shape of the stress-strain curves from the compression tests are similar to those from tensile tests.

Figure V.26 shows tensile stress-strain curves of precipitated homopolymers. The results are also included in Table V.14 together with results from the unprecipitated homopolymer samples. Comparing precipitated to unprecipitated tensile samples, unprecipitated s-1,2 PBD broke at an elongation of 10% whereas precipitated s-1,2 PBD gave elongations up to 52%. Similarly, unprecipitated trans 1,4 PBD broke at an elongation of 151% while precipitated trans 1,4 PBD broke at an elongation of 354%. As shown in Section VC.2, melted (or molded) s-1,2 PBD and trans 1,4 PBD are 40-50% crystalline whether or not they were precipitated, yet precipitated samples have lower melting points than unprecipitated samples. We suggested in the related discussion that crystallites formed upon precipitation from solution are smaller and less perfect than the original unprecipitated crystallites. The tensile data here further suggest that the larger, more well-formed crystallites in the unprecipitated, molded material yield samples that are more brittle than their precipitated analogues. Modulus and yield stress, however, are independent of whether the sample was precipitated or not.

Wilfong [32] obtained tensile data for atactic 1,2 PBD and mixed cis+trans 1,4 PBD homopolymers with MWs of 90k g/mol and 100k g/mol, respectively. These materials are amorphous, so they were crosslinked with a 30 MRad electron dose prior to tensile testing. His data are included in Table V.14 for comparison with our crystalline homopolymers.

VI. SUMMARY OF HOMOPOLYMER CHARACTERIZATION

Homopolymer molecular weights were determined by viscometry. After samples are mixed for one hour in tetralin at 135°C, s-1,2 PBD Mv is approximately 32.5k g/mol and trans 1,4 PBD Mv is approximately 425k g/mol. Degree of polymerization, x, is thus 601 ± 59 for s-1,2 PBD and is 7857 ± 277 for trans 1,4 PBD.

Mark-Houwink parameters were obtained for 1,4 PBD based on four standards. K and a values are 0.0145 ± 0.0022 ml/g and 0.75, respectively, by ln(ηr) analysis. By ηsp analysis, K and a are 0.0161 ± 0.0025 ml/g and 0.74.

IR data for our homopolymers match literature spectra reported by Moreto et al. [4, 5] for s-1,2 PBD and trans 1,4 PBD. From 1H NMR, we calculated
Figure V.26: Tensile Stress-Strain Data for Precipitated Homopolymers
that our s-1,2 PBD has approximately 95±3% 1,2 PBD content and that our trans 1,4 PBD has approximately 91±6% 1,4 PBD content. No cis 1,4 PBD peaks were discernable in either $^1$H or $^{13}$C NMR spectra for the trans 1,4 PBD homopolymer. A single $^{13}$C NMR peak at 114.4 ppm, as opposed to a triplet, indicates that the s-1,2 PBD homopolymer contains negligible amounts of isotactic and atactic segments.

WAXS 2θ scans of our s-1,2 PBD gave four major peaks that correspond to d-spacings of 6.6Å, 5.5Å, 4.2Å, and 3.8Å. These peaks were also observed by Natta and Corradini [11]. With our trans 1,4 PBD, we observed a single peak at a 2θ value of 22.4°. Again, our data agree with data in the literature by a number of researchers.

Rheovibron data gave $T_g$ onsets and peaks for trans 1,4 PBD at -80°C to -85°C and -51°C to -43°C, respectively, and $T_g$ onsets and peaks for s-1,2 PBD at 5°C to 35°C and 44°C to 54°C. There was no significant difference between unprecipitated and precipitated materials. Melting points ranged from 186°C to 194°C for s-1,2 PBD and 132° to 150°C for trans 1,4 PBD, depending on thermal history. Samples with the highest melting points and %C values were generally the as-received unprecipitated polymers. These samples had crystallinities of 78% and 58% for s-1,2 PBD and trans 1,4 PBD, respectively. Also, s-1,2 PBD displayed secondary crystallization in samples crystallized at or above 125°C.

Melting of as-received powders substantially lowered their crystallinity but had less of an effect on the resulting melting points than did other treatments. Conversely, upon precipitating homopolymers from solution, the total amount of crystallinity is nearly retained yet the melting points are significantly lowered. Thus the crystallites that form during precipitation are probably smaller and less perfect than the original unprecipitated crystallites.

For precipitated, compression-molded homopolymers that were otherwise not subjected to elevated temperatures, $T_s$ is 186°C, $T_t$ is 137°C, %Cs is 36%, and %Ct is 52%. WAXS data for the same samples gave crystallinities of 51% and 63% for s-1,2 PBD and trans 1,4 PBD, respectively. Table V.15 summarizes characteristics of precipitated, compression-molded homopolymers.
Table V.14: Instron Tensile Properties of PBD Homopolymers

<table>
<thead>
<tr>
<th>composition</th>
<th>modulus</th>
<th>yd stress</th>
<th>% elong(break)</th>
<th>stress(break)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
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<td></td>
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<tr>
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<td>79 MPa</td>
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<td></td>
</tr>
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<td>354%</td>
<td>163 MPa</td>
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<tr>
<td>(trans 1,4)</td>
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<td>amorphous PBD [32]</td>
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<tr>
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<td>229 MPa</td>
<td>-</td>
<td>12%</td>
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</tr>
<tr>
<td>1,4 PBD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table V.15: Summary of Homopolymer Characterization Data

<table>
<thead>
<tr>
<th>Trans 1,4</th>
<th>Syndio 1,2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{fC}-\text{C}=\text{C}-\text{C}^+_{n})</td>
<td>(\text{fC}-\text{C}^+_{n})</td>
</tr>
<tr>
<td>MW</td>
<td>425,000 g/mol</td>
</tr>
<tr>
<td>m-struct.</td>
<td>91 +/- 6% 1,4</td>
</tr>
<tr>
<td>Tg (os, pk)</td>
<td>-83, -43°C</td>
</tr>
<tr>
<td>Tm</td>
<td>137°C</td>
</tr>
<tr>
<td>Tdeg</td>
<td>245°C</td>
</tr>
<tr>
<td>% crys.</td>
<td>~40%</td>
</tr>
<tr>
<td>crystal</td>
<td>rod-like</td>
</tr>
<tr>
<td>spacing</td>
<td>~1000Å</td>
</tr>
</tbody>
</table>
Crystallization half-times are plotted as a function of undercooling in Figure V.17. At undercoolings of 16.5°C for trans 1,4 PBD and 30.3°C for s-1,2 PBD, crystallization half-times are less than 50 seconds. With these relatively fast crystallization properties, it is not possible to "lock-in" melt morphology of either homopolymer by transferring melt samples directly into liquid nitrogen. Also, the fast crystallization kinetics may have masked any difference in melting points and crystallinity contents for samples isothermally crystallized at various temperatures below the melting point.

At temperatures near the melting point of s-1,2 PBD, all PBD materials are sensitive to degradation and crosslinking in either the presence or relative absence of oxygen. DSC tests indicate that a reaction with oxygen takes place at about 185°C when PBD samples are heated at a rate of 20°C/min. At approximately 240°C, an anaerobic reaction takes place. McCreedy and Keskkula [27] report that anaerobic crosslinking occurs between 200°-300°C, and they suggest a mechanism for the reaction. We observed crosslinking in trans 1,4 PBD and s-1,2 PBD held at 200°C for various lengths of time up to 16 hours. With increased time, melting points and enthalpies of both the s-1,2 PBD and the trans 1,4 PBD significantly decreased. Compression-molded samples exposed to a 200°C nitrogen atmosphere for one hour and then placed in 150°C tetralin barely swelled even after 7 hours in the solvent.

Polarized light microscopy showed s-1,2 PBD spherulites approximately 12µ in diameter when crystallized at 18.5°C undercooling for 8 minutes. Trans 1,4 PBD crystallized into rod-like structures 5µ to 10µ in length when held at an undercooling of 11.5°C for 8 minutes. In sulfur-stained TEM specimens, we observed regularly spaced segments approximately 200Å (0.02 microns) apart in s-1,2 PBD samples. In stained trans 1,4 PBD, segments about 1000Å were apparent but were spaced less evenly than in the s-1,2 PBD specimens.

Results of Instron tensile tests for unprecipitated and precipitated homopolymers are given in Table V.14. S-1,2 PBD has a modulus that is more than twice that of trans 1,4 PBD, but it breaks at much lower elongations. At higher strains, trans 1,4 PBD displays rubbery behavior. These results are sensible considering that at the test temperature of 25°C, s-1,2 PBD is at or slightly below its glass transition while trans 1,4 PBD is at least 100°C above its Tg.

Comparing precipitated tensile samples to unprecipitated tensile samples, unprecipitated s-1,2 PBD broke at an elongation of 10% whereas
precipitated s-1,2 PBD exhibited elongations up to 52%. Similarly, unprecipitated trans 1,4 PBD broke at an elongation of 151% while precipitated trans 1,4 broke at an elongation of 354%. These data suggest that the larger, more well-formed crystallites in the unprecipitated, molded material yield samples that are more brittle than their precipitated analogues. However, each material's modulus and yield stress was independent of whether it was precipitated or not.

VG. REFERENCES


Chapter VI
CHARACTERIZATION OF HOMOPOLYMER BINARY BLENDS

VI.A. WAXS CRYSTAL STRUCTURE

WAXS 2θ scans for precipitated, compression-molded binary blends of s-1,2 PBD and trans 1,4 PBD prepared by the original precipitation procedure, as discussed in Section IVB.2, are presented in Figures VI.1a through VI.1e. The peaks in these figures are located at 2θ values that correspond to peaks for both of the individual homopolymers, as listed in Section VB.4. Homopolymer scans were given in Figure V.8. Peak areas for each of the two components reflect the proportion of that component in the sample.

These results indicate that no new, distinct crystal formation is achieved by blending s-1,2 PBD and trans 1,4 PBD in these proportions. Therefore, neither isomorphic nor eutectic behavior exists for this system. This conclusion is independently confirmed by binary blend melting point data in Section IVB.2 that show two melting points for every composition tested. In Section IIC.2, we discussed that isomorphism and eutecticity are characterized by the presence of only one melting point at each composition.

VI.B. THERMAL PROPERTIES AND PHASE BEHAVIOR

VI.B.1. Glass Transitions

Rheovibron Tg peak and onset data for precipitated, compression-molded binary blends are reported in Table VI.1 together with homopolymer data from Table V.8 in Section VC.1. We see two recurring transitions for every blend sample. One begins between -88° and -50°C and peaks at -57° to -43°C. The other begins between 5° and 35°C and peaks at 47° to 62°C. These transitions corresponds, respectively, to the Tg of trans 1,4 PBD and s-1,2 PBD. An example of a tan δ plot as a function of temperature is shown in Figure VI.2a for a 67/33 blend. The presence of these two Tg's proves that the amorphous components of these blends are not thermodynamically mixing to give a single homogeneous amorphous phase. Rather, the blends are heterogeneous for temperatures at and below the Tg of s-1,2 PBD. This finding correlates with the model predictions in Section IIIB for binary blends of amorphous 1,2 and 1,4 PBDs with MWs equivalent to those in our crystalline system.

In addition to the two major Tgs, a transition between -100°C and -81°C occurs in blends with trans 1,4 PBD content greater than 66%. This transition

143
Figure VI.1: WAXS 20 Scans of Precipitated, Compression-Molded Blends
**Table VI.1: Rheovibron Tg data for Homopolymer Binary Blends**
(All temperatures in °C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
<th>Tg(1.4) onset</th>
<th>Tg(1.4) peak</th>
<th>Tg(1.2) onset</th>
<th>Tg(1.2) peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>before March '90</td>
<td>np</td>
<td>np</td>
<td>35°</td>
<td>54°</td>
</tr>
<tr>
<td>95/5</td>
<td>&quot;</td>
<td>-50°</td>
<td>-49°</td>
<td>25°</td>
<td>57°</td>
</tr>
<tr>
<td>75/25</td>
<td>&quot;</td>
<td>-60°</td>
<td>-44°</td>
<td>20°</td>
<td>57°</td>
</tr>
<tr>
<td>50/50</td>
<td>&quot;</td>
<td>-70°</td>
<td>?</td>
<td>30°</td>
<td>61°</td>
</tr>
<tr>
<td>25/75</td>
<td>&quot;</td>
<td>-85°</td>
<td>?</td>
<td>?</td>
<td>62°</td>
</tr>
<tr>
<td>5/95</td>
<td>&quot;</td>
<td>-80°</td>
<td>-51°</td>
<td>5°</td>
<td>53°</td>
</tr>
<tr>
<td>0/100</td>
<td>&quot;</td>
<td>-85°</td>
<td>-57°</td>
<td>5°</td>
<td>58°</td>
</tr>
<tr>
<td>100/0</td>
<td>after March '90</td>
<td>-87°</td>
<td>-45°</td>
<td>25°</td>
<td>56°</td>
</tr>
<tr>
<td>33/67</td>
<td>&quot;</td>
<td>-88°</td>
<td>-44°</td>
<td>10°</td>
<td>55°</td>
</tr>
<tr>
<td>10/90</td>
<td>&quot;</td>
<td>(-100°)</td>
<td>(-89°)</td>
<td>-49°</td>
<td>18°</td>
</tr>
<tr>
<td>0/100</td>
<td>&quot;</td>
<td>(-92°)</td>
<td>(-83°)</td>
<td>-43°</td>
<td>7°</td>
</tr>
</tbody>
</table>

**Notes**

"np" indicates no peak was discernable.
"?" indicates that the Tg peak was not clear.
agrees with literature $T_g$ values for cis 1,4 PBD and mixed cis+trans 1,4 PBD [1], which may be present in very small amounts in both the trans 1,4 PBD and s-1,2 PBD homopolymers.

$T_g$ data is plotted as a function of composition in Figure VI.2b for samples prepared by the original precipitation procedure and in Figure VI.2c for samples prepared by the improved precipitation procedure. (The differences between these two procedures are discussed in Section IVB.2. In both figures, the $T_g$ of the s-1,2 PBD component is independent of composition. With respect to the trans 1,4 PBD $T_g$, composition has a significant effect in the first set of samples, such that the $T_g$ onset increases from -80°C to -50°C over the range of composition. The increase in trans 1,4 PBD $T_g$ might reflect loss of mobility of that component due to the presence of glassy s-1,2 PBD. As the content of glassy s-1,2 PBD increases, so does the the $T_g$ of the trans 1,4 PBD. In contrast, the $T_g$ of the s-1,2 PBD component remains relatively constant because s-1,2 PBD becomes glassy at a temperature where trans 1,4 PBD is still rubbery. However, the increase in trans 1,4 PBD $T_g$ onset may occur for other reasons since the same trend is not observed in the corresponding trans 1,4 PBD peaks, nor in the trans 1,4 PBD onsets and peaks of the second set of samples. In the second set, trans 1,4 PBD $T_g$ onsets and peaks remained close to the homopolymer values of -83°C and -43°C, respectively. We monitored the tetralin/polymer solutions (prior to precipitation) more carefully for samples prepared by the improved precipitation procedure, thus data from the second set of samples are more reliable than that of the first set.
VI.2a: Tan δ Plot for 67/33 Blend

VI.2b: Tg Onsets of Samples Prepared by Original Precipitation Procedure

Figure VI.2: Tg Data for Binary Blends
VI.2c: Samples Prepared by Improved Precipitation Procedure
VIB.2. Melting Points and Percent-Crystallinity Data

Just as there is one $T_g$ per blend component, there is also one melting point per component in all of the binary blends we prepared. As mentioned earlier, we therefore know that our blends are not eutectic or isomorphic ones.

In any heterogeneous blend of two crystallizable polymers, one component's polymer chains must crystallize in the presence the other component's dissimilar polymer chains. Dissimilar, phase-separated components can act as diluents for each other [2, 3] and thereby impede the ability of a crystallizing species to find matching chains with which to crystallize. The crystallites that do form then consist of fewer and shorter interlocking chain segments. Consequently, melting points and enthalpies may be lower in blends than in homopolymer samples where all chains are nearly identical. The greater the concentration of diluent species, the more the melting point and enthalpy may be depressed. This scenario is supported by Burghardt's [4] model mentioned in Section IIC.2 for immiscible crystalline binary polymer systems. On the other hand, already crystallized material of one component may act as a nucleating agent for the second component and thereby promote crystallization of the second component [2, 3].

DSC-determined melting points and calculated component %C values are given in Table VI.2 for various compositions of precipitated s-1,2 PBD/trans 1,4 PBD binary blend samples. The %C data are relative to the mass of the given component in the blend.

To test if the extent of s-1,2 PBD crystallization affects subsequent crystallization of the trans 1,4 PBD component, we isothermally crystallized binary blends at temperatures above and below the trans 1,4 PBD melting point. This investigation was conducted in the same manner as the isothermal crystallization study described in Section VC.2 for homopolymer samples. Precipitated samples (not compression-molded) prepared by the original precipitation procedure were melted and then quenched to one of the following crystallization temperatures: 165°C, 155°C, 140°C, 125°C, 110°C, and 25°C. These temperatures represent three temperatures between the melting points of trans 1,4 PBD and s-1,2 PBD and three temperatures below both melting points. After two minutes at the isothermal crystallization temperature, the samples were quenched to 25°C. Five compositions were tested: 5/95, 25/75,50/50, 75/25, and 95/5. We figured that by crystallizing
blends above the trans 1,4 PBD melting point, e.g. at the first three temperatures listed above, we might be able to increase the size and perfection of s-1,2 PBD crystallites prior to crystallization of the trans 1,4 PBD component.

The resulting melting points and component %C data from the isothermal crystallization study are included in Table VI.2. We concluded in Section VC.2 that crystallization temperature did not affect the melting point of pure homopolymer samples, perhaps because the fast crystallization kinetics of both homopolymers prevented true isothermal crystallization. Similarly, crystallization temperature did not affect the subsequent melting points of any given blend, as illustrated in a plot of melting point versus composition in Figure VI.3a. This figure includes homopolymer data from Section VC.2. Again due to fast crystallization kinetics, the s-1,2 PBD probably crystallized during
Table VI.2: Thermal Properties of Homopolymer Binary Blends
(All temperatures in °C; see notes from Table V.9)

<table>
<thead>
<tr>
<th>Sample</th>
<th>History</th>
<th>T_s</th>
<th>T_M</th>
<th>%C_1</th>
<th>%C_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>precip, melt, hold* at iso T, quench</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td>188°</td>
<td></td>
<td>38%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 155°</td>
<td>187°</td>
<td></td>
<td>37%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td>186°</td>
<td></td>
<td>38%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 125°</td>
<td>187°</td>
<td></td>
<td>37%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 110°</td>
<td>186°</td>
<td></td>
<td>38%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 25°</td>
<td>187°</td>
<td></td>
<td>38%</td>
<td></td>
</tr>
<tr>
<td>95/5</td>
<td>precip, melt, hold* at iso T, quench</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td>124°</td>
<td>189°</td>
<td>10%</td>
<td>39%</td>
</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td>125°</td>
<td>188°</td>
<td>20%</td>
<td>39%</td>
</tr>
<tr>
<td>75/25</td>
<td>precip, melt, hold* at iso T, quench</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td>125°</td>
<td>187°</td>
<td>35%</td>
<td>38%</td>
</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td>126°</td>
<td>186°</td>
<td>35%</td>
<td>38%</td>
</tr>
<tr>
<td>50/50</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td>132°</td>
<td>188°</td>
<td>40%</td>
<td>41%</td>
</tr>
<tr>
<td></td>
<td>T= 155°</td>
<td>133°</td>
<td>188°</td>
<td>42%</td>
<td>41%</td>
</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td>134°</td>
<td>188°</td>
<td>40%</td>
<td>41%</td>
</tr>
<tr>
<td></td>
<td>T= 125°</td>
<td>133°</td>
<td>187°</td>
<td>44%</td>
<td>41%</td>
</tr>
<tr>
<td></td>
<td>T= 110°</td>
<td>133°</td>
<td>187°</td>
<td>45%</td>
<td>39%</td>
</tr>
<tr>
<td></td>
<td>T= 25°</td>
<td>133°</td>
<td>188°</td>
<td>43%</td>
<td>39%</td>
</tr>
<tr>
<td>25/75</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td>130°</td>
<td>187°</td>
<td>43%</td>
<td>42%</td>
</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td>129°</td>
<td>186°</td>
<td>47%</td>
<td>47%</td>
</tr>
<tr>
<td>5/95</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td>133°</td>
<td>186°</td>
<td>45%</td>
<td>57%</td>
</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td>135°</td>
<td>186°</td>
<td>45%</td>
<td>61%</td>
</tr>
<tr>
<td>0/100</td>
<td>precip, melt, hold* at iso T, quench</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 165°</td>
<td>133°</td>
<td></td>
<td>43%</td>
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<tr>
<td></td>
<td>T= 155°</td>
<td>132°</td>
<td></td>
<td>41%</td>
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</tr>
<tr>
<td></td>
<td>T= 140°</td>
<td>133°</td>
<td></td>
<td>41%</td>
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<td></td>
<td>T= 125°</td>
<td>133°</td>
<td></td>
<td>41%</td>
<td></td>
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<td></td>
<td>T= 110°</td>
<td>133°</td>
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<td>41%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T= 25°</td>
<td>132°</td>
<td></td>
<td>43%</td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>precip, mold</td>
<td></td>
<td>186°</td>
<td></td>
<td>36%</td>
</tr>
<tr>
<td>90/10</td>
<td>precip, mold</td>
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<td>125°</td>
<td>184°</td>
<td>17%</td>
</tr>
<tr>
<td>67/33</td>
<td>precip, mold</td>
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<td>128°</td>
<td>186°</td>
<td>28%</td>
</tr>
<tr>
<td>50/50</td>
<td>precip, mold</td>
<td></td>
<td>132°</td>
<td>188°</td>
<td>38%</td>
</tr>
<tr>
<td>33/67</td>
<td>precip, mold</td>
<td></td>
<td>133°</td>
<td>187°</td>
<td>42%</td>
</tr>
<tr>
<td>10/90</td>
<td>precip, mold</td>
<td></td>
<td>133°</td>
<td>184°</td>
<td>41%</td>
</tr>
<tr>
<td>0/100</td>
<td>precip, mold</td>
<td></td>
<td>137°</td>
<td></td>
<td>52%</td>
</tr>
</tbody>
</table>
the quench to the isothermal setpoint, making the "layover" at the isothermal temperature inconsequential to the final properties of the two components.

Yet, when observed over the full range of composition, the data in Figure VI.3a do reveal slight melting point depression of both components, as predicted earlier in this section. Also, the melting point of the trans 1,4 PBD component is depressed to a greater extent than the melting point of the s-1,2 PBD component. \( T_1 \) at 5% trans 1,4 PBD is 8°C less than that of the trans 1,4 PBD homopolymer, while \( T_5 \) at 5% s-1,2 PBD is 3°C less than that of the s-1,2 PBD homopolymer.

The trends in Figure VI.3a are reproduced in Figure VI.3b with melting point data from compression-molded binary blends prepared by the improved precipitation procedure. For this second set of samples, \( T_1 \) at 10% trans 1,4 PBD is 11°C less than that of the trans 1,4 PBD homopolymer, and \( T_5 \) at 10% s-1,2 PBD is 2°C less than that of the s-1,2 PBD homopolymer. Data from Figures VI.3a and VI.3b are plotted together in Figure VI.3c.

These results suggest that, in blends, trans 1,4 PBD crystallization is affected more adversely by the presence of s-1,2 PBD than s-1,2 PBD crystallization is affected by the presence of trans 1,4 PBD. Since s-1,2 PBD has the higher crystallization temperature, it begins to crystallize while the trans 1,4 PBD component is still in an amorphous melt state. Then trans 1,4 PBD must crystallize in the presence of already-crystalline s-1,2 PBD chains, which may act as rigid barriers to crystallizing trans 1,4 PBD chains and thereby impede trans 1,4 PBD crystallization. Such behavior was also observed in PE/PP blends [5] and may be true for any heterogeneous binary system where the component with the higher \( T_m \) crystallizes at a fast rate.

Plots of \( \%C_1 \) and \( \%C_5 \) as a function of composition corroborate the notion that s-1,2 PBD impedes trans 1,4 PBD crystallization while s-1,2 PBD crystallization is minimally hindered by the presence of trans 1,4 PBD. Figure VI.4a and VI.4b depict \%C data for the isothermally crystallized blends and for the compression-molded blends prepared by the improved precipitation procedure. For each composition in Figure VI.4a, component \%C values from Table VI.2 were averaged since there is no correlation between crystallization temperature and the resulting thermal data. In both figures, \%C_1 \) falls significantly as s-1,2 is added to trans 1,4 PBD, but \%C_5 \) does not drop as trans 1,4 PBD is added s-1,2 PBD.
VI.3a. Isothermally Crystallized Samples

VI.3b. Samples Prepared by Improved Precipitation Procedure

Figure VI.3: Melting Points of Binary Blends as a Function of Composition
VI.3c. All Samples
VI.4a: Samples Prepared by Original Precipitation Procedure

VI.4b: Samples Prepared by Improved Precipitation Procedure

Figure VI.4: Percent-Crystallinity as a Function of Composition
In fact, %C₅ tends to increase as trans is added to s-1,2 PBD! In Figure VI.4b, the increase is gradual. It may indicate enhanced nucleation of s-1,2 PBD when s-1,2 PBD is the minor component, or it may reflect what is actually a constant value for the range of composition. In Figure VI.4a, %C₅ peaks at the 5/95 blend. This point may be artificially high due to ambiguity in estimating limits of the small s-1,2 PBD DSC peak at this composition. However, since we also observed unusual property enhancement for binary PBD blends with low 1,2 PBD content, this result becomes significant and we will refer to it again in our discussion of mechanical properties in Section VID.

VIB.3. Phase Behavior in the Melt: High Temperature X-ray Scattering

In Section VIB.1, we concluded from Tg data that binary blends of our homopolymers are heterogeneous at and below temperatures of 25°C. From model predictions, we also expect that these blends are heterogeneous in the melt. This prediction was tested by WAXS experiments similar to those of Halasa et al. [6]. Halasa et al. suggests that the average molecular interchain spacing (∝<R>) is greater than the weighted average of <R> of the component homopolymers in compatible amorphous PBD blends, but is equal to the weighted average in incompatible PBD blends. The parameter <R> is equal to 1.25 times the average d-spacing [7], and for the case of amorphous polymers, the d-spacing corresponds to that of the peak of the WAXS amorphous halo.

We applied this technique to melted films of our binary PBD blends. Data were obtained via a SAXS apparatus with the detector positioned 7.7 cm from the sample. For unblended s-1,2 PBD, we observed a single amorphous halo with a peak at 2θ=13.9°, which corresponds to a d-spacing of 6.4Å. For unblended trans 1,4 PBD, a single amorphous halo occurred at 2θ=18.7°, which corresponds to a d-spacing of 4.7Å. But in the 67/33 and 50/50 blends, the amorphous halo was clearly a composite of the peaks from each of the homopolymers. Figures VI.5a through VI.5g reveal diffraction patterns and intensity plots for the samples studied. Patterns for the crystallized homopolymers at 25°C are shown in Figures VI.5h and VI.5i for comparison. The 10/90, 33/67, and 90/10 blends give distinct peaks at the position corresponding to that of the major component, but the asymmetric shape of their curves suggests that a peak from the minor component is present as well. The d-spacings from all of the melt blends are plotted as a function of composition in Figure VI.6. Despite the fact that we did not obtain Halasa's
Figure VI.5: X-ray Scattering Patterns for Binary Blend Melts and for Crystallized Homopolymers
VI.5d:  50/50 Melt

VI.5c:  33/67 Melt

VI.5f:  10/90 Melt

VI.5g:  0/100 (Trans 1,4 PBD) Melt
Figure VI.6: WAXS Peak d-Spacings for Binary Blend Melts
single peak correlation, the presence of two amorphous peaks verifies that these PBD blends are heterogeneous in the melt, as predicted by our thermodynamic model.

**VIC. MORPHOLOGY**

By means of polarized light microscopy fitted with a hot stage, we monitored the melting process in binary homopolymer blends. In a preliminary study, two 50/50 blend samples were heated from room temperature to about 300°C at a rate of 6°C/min in a nitrogen atmosphere. The specimens were 0.1 mm thick. One sample had been precipitated but had no additional thermal history; the second sample had been precipitated and then compression-molded at 200°C for 2.75 minutes. Micrographs were taken at intervals of about 15-30°C with the cross polarizers set at an angle of 80°-90° from each other. S-1,2 PBD and trans 1,4 PBD homopolymers were observed in the same manner for comparison.

With the homopolymers, transmission of polarized light through crystallized regions was relatively uniform until the homopolymer melting point was approached. At which point, the crystallinity started to fade from the sample edges. After complete melting was achieved, the field was completely dark.

For both molded and unmolded blends, we saw two distinct melting events as expected: The first occurred from 120°-140°C as the trans 1,4 PBD component melted, and the second occurred from 175°-190°C as the s-1,2 PBD melted. The transitions were characterized by abrupt changes in the transmission of light through the sample. All traces of crystallinity disappeared around 195°C. Once the s-1,2 PBD component melted, there was no obvious contrast between s-1,2 PBD and trans 1,4 PBD melt regions. Furthermore, we saw no changes in optical properties as the melted samples continued to be heated, except that the light intensity steadily decreased due to the development of degradation and cross-linking. Thus we were not able to observe phase behavior in the melt.

In a subsequent study, precipitated, compression-molded binary blends micromted to thicknesses of 5μ to 10μ were monitored as they melted. The blends had the following compositions: 95/5, 75/25, 50/50, 25/75, and 5/95. Between 140°C and 180°C, where trans 1,4 PBD had melted but s-1,2 PBD had not yet melted, spherulites of s-1,2 PBD were readily visible in all of the blends.
between. These spherulites had diameters on the order of 1µ to 5µ, and the melted trans 1,4 PBD domains between the spherulites were also on the order of 1µ to 5µ. In Figure VI.17a, a micrograph of a 75/25 blend section is shown at 75°C before the trans 1,4 PBD melted, and in Figure VI.17b, the same section is shown at 140°C after the trans 1,4 PBD melted and left only s-1,2 PBD crystallites. It is not possible to discern rod-like trans 1,4 PBD crystals in Figure VI.17a, as we observed for the 100% trans 1,4 PBD homopolymer in Figure V.23b. Thus it is not clear if trans 1,4 PBD in blends assumes this rod-like morphology.

Wilfong [8] studied two binary blends of completely amorphous 1,2 PBD and 1,4 PBD with molecular weights of 90k g/mol and 100k g/mol, respectively. The blends he prepared were spincast at room temperature for 24 hours and had compositions of 12/88 and 38/62. Dynamic mechanical testing proved that they were heterogeneous at 25°C. TEM revealed spherical inclusions of 1,2 PBD in a 1,4 PBD matrix, as shown in Figure VI.18 for the 38/62 blend. The inclusions ranged in size from 1µ to 50µ in these amorphous blends, whereas the degree of heterogeneity in the crystalline PBD blends we prepared by precipitation is not greater than 5µ to 10µ. Finer degrees of heterogeneity are obtained with precipitation because the blends drop out of solution nearly instantaneously. With spincasting, solvent is evaporated from the blend over the course of hours or days, thus phase separation in heterogeneous blends occurs to a greater extent than with the precipitation procedure, giving larger domains of the minor component. This observation was also reported by Qin et. al. [9] for precipitated versus spincast blends of polystyrene and low molecular weight PBD rubber.

To obtain a better measure of the degree of heterogeneity in our crystalline binary blends, we studied sulfur-stained TEM sections of 33/67, 50/50, and 67/33 precipitated, compression-molded blends and compared them to TEM sections of the homopolymers. Samples were prepared as described in Section IVD.5. In all of these blends, we observed the same 1000Å-spaced lamellar segments seen in Figure V.24b for trans 1,4 PBD homopolymer. Figures VI.19a and VI.19b display these formations in 50/50 and 33/67 sections. The quantity of segments approximately correlates with the amount of trans 1,4 PBD present per blend. Smaller 200Å-spaced lamellar segments, that we saw in Figure V.24a as being characteristic of s-1,2 PBD, were also evident in 50/50 and 33/67 blends. This feature is observable in Figure VI.19a.
Figure VI.8: TEM Micrograph of 38/62 Amorphous Binary Blend [8, 17]
Figure VI.7: Light Micrograph of 75/25 (1.2 PBD/1.4 PBD) Blend
(sample thickness: 10μ)
Generally, segments of the major blend component are more apparent than segments of the minor component, and regions of segments corresponding to the major component seem to be spaced approximately 0.5μ to 1μ apart. Therefore, domains of the minor component are approximately this size, assuming that the minor component fills the space between regions of the major component. In the light microscopy experiment discussed earlier in this section, trans 1,4 PBD domains ranged up to 5μ in a 75/25 blend. Based on all of the TEM and light micrographs, s-1,2 PBD domains are on the order of 0.2μ to 2μ when s-1,2 PBD constitutes less than 50% of the blend, and trans 1,4 PBD domains are between 0.5μ and 5μ when trans 1,4 PBD constitutes less than 50% of the blend.

SEM of freeze-fractured binary blends was also employed to elucidate heterogeneous blend morphology. We surmised that trans 1,4 PBD and s-1,2 PBD homopolymers differ in fracture behavior, especially at temperatures between the Tg's of the two materials. Since the Tg onsets for trans 1,4 PBD and s-1,2 PBD are about -85°C and 5°C respectively, as discussed in Sections VC.1 and VIB.2, we fractured precipitated, compression-molded blends in a dry ice/isopropanol/5% water bath at -40°C±7°C. Additionally, blends were fractured at approximately -160°C in liquid nitrogen. Blend compositions were as follows: 90/10, 67/33, 50/50, 33/67, and 10/90. Also, 100/0 and 0/100 homopolymer samples were examined. Fracture was accomplished by holding films 0.3-0.7 mm thick in the bath for approximately 30 seconds (until the bath stopped boiling around the sample), then quickly removing the sample from the bath and immediately snapping it in half. The samples may have warmed slightly between the time they were removed from the liquid nitrogen bath and the time the fracture was actually accomplished. Samples with trans 1,4 PBD content ≥67% that were fractured in the warmer bath had to be twisted in order to break them into two pieces. In all cases, the fractured surface ran parallel to the compression direction. Additional details concerning SEM operation are listed in Section IVD.5.

Figure VI.10 shows SEM micrographs of blends fractured at -160°C and Figure VI.11 shows micrographs of blends fractured at -40°C. For samples with more than 10% trans 1,4 PBD that were fractured at -160°C, fracture surfaces were relatively flat down to levels of 1μ in detail. This result is sensible since both blend components were below Tg when the fracture was imposed. A trans 1,4 PBD homopolymer sample and a 90/10 blend sample that were also
Figure VI.10: SEM Micrographs of Binary Blends Fractured at -160°C
Figure VI.11: SEM Micrographs of Binary Blends Fractured at -40°C
fractured at this temperature showed some rubbery tufts. With the samples fractured at -40°C, all blends showed elongated rubbery tufts except for the pure s-1,2 PBD homopolymer (100/0). Furthermore, the relative amount of elongated rubbery material increased with increasing trans 1,4 PBD content. Again, this result is appropriate since s-1,2 PBD is below its Tg at this fracture temperature. Unfortunately, however, the micrographs do not allow us to quantify or even approximate domain size of one PBD versus the other in these blends.

**VII. MECHANICAL PROPERTIES**

Instron stress-stain tensile data were obtained for binary blends with compositions 90/10, 67/33, 50/50, 33/67, and 10/90. All Instron testing was conducted at room temperature with "micro-dogbone" samples prepared as detailed in Section IVD.6. For each blend, the modulus, yield stress, percent elongation at break and stress at break are listed in Table VI.3 with precipitated homopolymer tensile data from Table V.14. These parameters are also plotted in Figures VI.12a through VI.12d as a function of trans 1,4 PBD content.

For the parameters measured, binary blend values fall between the homopolymer values, except in the case of the 10/90 blend which gave stress and percent elongation at break values greater than either homopolymer. Yield stress is weighted toward the more compliant trans 1,4 PBD component, as predicted from models of incompatible systems [10]. The modulus is linear as a function of trans 1,4 PBD content, though theory predicts the same response as that for yield stress. Percent elongation at break is slightly better than the weighted homopolymer combination, especially for the 10/90 blend. Stress at break is relatively linear, except again with the 10/90 sample which shows extreme property enhancement.

Permanent set indicates the equilibrium elongation to which a sample returned following tensile testing, as discussed in Section IVD.6. True rubber materials return to their original length, but crystalline or filled materials typically deform permanently and do not retract completely. Permanent set measurements are listed in Table VI.3 and plotted in Figure VI.12e with percent elongation at break data. S-1,2 PBD homopolymer retracts to a length slightly less than half its length at break, and trans 1,4 PBD homopolymer retracts to slightly more than half its length at break. Similarly, the permanent set
### Table VI.3: Binary Blend Tensile Properties

<table>
<thead>
<tr>
<th>composition</th>
<th>modulus (MPa)</th>
<th>yd stress (MPa)</th>
<th>% elong(brk)</th>
<th>stress(brk) (MPa)</th>
<th>perm set (brk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.2 / 1.4) crystalline PBD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>320</td>
<td>35</td>
<td>52%</td>
<td>48</td>
<td>20%</td>
</tr>
<tr>
<td>90/10</td>
<td>320</td>
<td>29</td>
<td>111%</td>
<td>61</td>
<td>40%</td>
</tr>
<tr>
<td>67/33</td>
<td>280</td>
<td>26</td>
<td>217%</td>
<td>80</td>
<td>60%</td>
</tr>
<tr>
<td>50/50</td>
<td>210</td>
<td>26</td>
<td>284%</td>
<td>79</td>
<td>120%</td>
</tr>
<tr>
<td>33/67</td>
<td>210</td>
<td>24</td>
<td>275%</td>
<td>101</td>
<td>160%</td>
</tr>
<tr>
<td>10/90</td>
<td>170</td>
<td>24</td>
<td>460%</td>
<td>240</td>
<td>280%</td>
</tr>
<tr>
<td>0/100</td>
<td>140</td>
<td>22</td>
<td>354%</td>
<td>163</td>
<td>200%</td>
</tr>
<tr>
<td>Wilfong's amorphous PBD [8]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>229</td>
<td>-</td>
<td>12%</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>38/62</td>
<td>10.7</td>
<td>-</td>
<td>25%</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>12/88</td>
<td>4.7</td>
<td>-</td>
<td>106%</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>0/100</td>
<td>2.7</td>
<td>-</td>
<td>45%</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>
Figure VI.12: Binary Blend Tensile Properties as a Function of Composition
length of the blends is about half their length at the break point and reflects the proportion of the two homopolymers present.

In Section VIC, we discussed the morphology of Wilfong's amorphous PBD blends. He also obtained stress-strain data for these homopolymers and blends, as shown in Figure VI.13a. The modulus, percent elongation at break and stress at break are included at the end of Table VI.3 and are plotted as a function of composition in Figures VI.13b, VI.13c, and VI.13d, respectively. The blend moduli fall far below the linear combination of homopolymer properties. As mentioned above, this response is appropriate for incompatible systems. The percent elongation and stress at break of the 38/62 blend are slightly less than the weighted homopolymer average. The properties at break for the 12/88 blend, however, are better than the weighted homopolymer average.

We showed earlier that the 12/88 amorphous PBD and 10/90 crystalline PBD blends are heterogeneous, thus the mechanical property enhancement in this composition range is quite interesting. Recall that at the end of Section VI.B.2, we also noticed a sharp increase in \( \%C_s \) for the 5/95 crystalline blend. Wilfong suggested that the 1,2 PBD component may act as a reinforcing filler. PBD blends in this composition range warrant further investigation in future projects, as does the "reinforcing filler" hypothesis. In the literature, blends of PE and PP exhibited a maximum in various mechanical parameters when PE content was approximately 10-25\%, but no convincing arguments were offered to explain why the enhancement occurred [11-13].

As mentioned earlier in this section, the modulus and mechanical properties at break in the crystalline PBD system are all near or better than the weighted average of the homopolymer values. This desirable mechanical behavior is likely due to the finer dispersion of phases achieved through precipitation as compared to the larger degrees of heterogeneity from alternative preparation techniques.

On the other hand, 67/33, 50/50, and 33/67 binary crystalline blends exhibited poor mechanical "integrity". I refer to the fact that specimens with these compositions split along the axis of tension prior to breaking perpendicular to the axis of tension. Figure VI.14 pictures this phenomenon for a 67/33 specimen. Out of three specimens per composition, one 67/33 specimen, one 33/67 specimen, and two 50/50 specimens fractured in this way. Such behavior is characteristic of oriented polymers in heterogeneous
VI.12c: Permanent Set

VI.13a: Stress-Strain Plots (Wilfong, [8])

Figure VI.13: Tensile Data for Wilfong's Amorphous Binary Blends
VI.13b: Modulus

VI.13c: Percent Elongation at Break

VI.13d: Stress at Break
Figure VI.14: 67/33 Blend Specimen that Fractured Along Axis of Tension
mixtures [14], thus we suspect that orientation was imposed on at least one of the components as tension was applied. In the literature, some heterogeneous binary crystalline blends are reinforced by influxes of one polymer between spherulites of the other [15, 16], but the type of fracture exhibited by our binary PBD system implies a lack of reinforcement.

VIE. SUMMARY OF HOMOPOLYMER BINARY BLEND CHARACTERIZATION

WAXS 2θ scans give distinct peaks for both components in binary blends of s-1,2 PBD and trans 1,4 PBD. DSC and light microscopy studies reveal two distinct melting points in every binary blend, i.e. one melting point per component. These results indicate that blends of s-1,2 PBD and trans 1,4 PBDs do not yield isomorphic or eutectic structures.

Plots of tan δ versus temperature show two recurring transitions in every blend sample. One of the transitions corresponds to the Tg of the trans 1,4 PBD component between -88ºC and -43ºC, the other transition corresponds to the Tg of the s-1,2 PBD component between 5ºC and 62ºC. The presence of one Tg per component signifies that the blends are heterogeneous at and below the Tg of s-1,2 PBD. In blends with a trans 1,4 PBD content greater than 66%, we observed an additional transition between -100º and -81ºC that corresponds to the Tg of cis 1,4 PBD or mixed cis+trans 1,4 PBD.

X-ray scattering studies imply that our binary blends are also heterogeneous in the melt. Amorphous halos of the melted blends comprise both amorphous peaks of trans 1,4 PBD and s-1,2 PBD homopolymer in the melt. These results verify the prediction of our thermodynamic model in Chapter III.

Blend melting points are slightly depressed from homopolymer values, as predicted by Burghardt [4] for immiscible crystalline binary polymer systems. Trans 1,4 PBD crystallization is influenced more adversely by the presence of the s-1,2 PBD component than vice-versa. For instance, blends with 5-10% trans 1,4 PBD gave Tt values that were 8º-11ºC lower than homopolymer Tt values whereas blends with 5-10% s-1,2 PBD gave Ts values only 2º-3ºC lower than homopolymer Ts values. Similarly, %Ct falls significantly as s-1,2 PBD is added to trans 1,4 PBD, but %Cs does not drop as trans 1,4 PBD is added s-1,2 PBD. Already-crystallized s-1,2 PBD chains may act as rigid barriers during subsequent crystallization of the trans 1,4 PBD.

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component. Such behavior may be true for any heterogeneous binary system where the component with the higher T_m crystallizes at a fast rate.

Light micrographs of precipitated (compression-molded) binary blends at a temperature between the homopolymer melting points reveal s-1,2 PBD spherulites about 1µ to 5µ in diameter surrounded by melted domains of trans 1,4 PBD about 1µ to 5µ in diameter.

In TEM micrographs of 67/33, 50/50, and 33/67 blends, we observed the same 1000Å-spaced segments found in micrographs of trans 1,4 PBD homopolymer. The quantity of segments correlates with the amount of trans 1,4 PBD present. In micrographs of 50/50 and 33/67 blends, we also distinguished the smaller 200Å-spaced segments characteristic of s-1,2 PBD homopolymer.

Wilfong [8] studied heterogeneous binary blends of amorphous 1,2 PBD (M_w=90k g/mol) and 1,4 PBD (M_w=100k g/mol). The blend compositions were 12/88 and 38/62 and they contained 1µ-50µ spherical macromdomains of 1,2 PBD in a matrix of 1,4 PBD. Macromdomains in the crystalline PBD blends we prepared by precipitation were not greater than 5µ-10µ in size. In general, finer degrees of heterogeneity can be achieved through precipitation than through spincoating because precipitation is a very quick process that does not allow for gross phase separation.

In Wilfong's amorphous PBD blends, the moduli and mechanical properties at break are well below the weighted average of the corresponding homopolymer properties, as expected of most incompatible systems. The exception is percent elongation at break of the 12/88 blend, which has a value greater than that of either amorphous homopolymer.

Tensile properties of crystalline binary blends of s-1,2 PBD and trans 1,4 PBD show the following trends: Modulus and yield stress decrease while stress and percent elongation at break and permanent set increase as a function of increased trans 1,4 PBD content. Mechanical properties at break exhibit a maximum with the 10/90 blend, otherwise blend data all fall between the homopolymer property values and are close to the weighted average of the corresponding homopolymer properties. The fact that our heterogeneous crystalline blends do not have mechanical properties inferior to those of the homopolymers is likely due to the relatively fine dispersion of phases achieved through precipitation. On the other hand, mechanical integrity of some of the 33/67, 50/50, and 67/33 specimens was poorer than that of the
homopolymers. These specimens split along the axis of tension prior to breaking at the axis perpendicular to the applied tension. Such behavior is characteristic of oriented polymers in heterogeneous mixtures, thus the tensile testing process may have imposed orientation in at least one of the components.

Finally, property enhancement in Wilfong's 12/88 amorphous PBD blend and in our 10/90 and 5/95 crystalline PBD blends suggests that the 1,2 PBD component acts as a reinforcing filler at these low concentrations. This phenomenon deserves further investigation.

**VIE. REFERENCES**


Chapter VII
CHARACTERIZATION OF BLENDS WITH DIBLOCK COPOLYMER

VIIA. DESCRIPTION OF THE DIBLOCK COPOLYMERS

VIIA.1. Reported Properties

Three amorphous diblock copolymers were used in our work. Two of the three diblocks were reported by Cohen and Wilfong [1] as having block molecular weights of 30k/50k g/mol (1,2/1,4 PBD) and 30k/200k g/mol. The 1,2 PBD blocks are said to be comprised of approximately 99% 1,2 PBD microstructure and the 1,4 PBD blocks are comprised of about 87% 1,4 PBD microstructure. As mentioned in Sections I.C and IV.A, the 30k/50k diblock is heterogeneous and the 30k/200k diblock is homogeneous at 25°C. The third diblock has block molecular weights of 60k/120k and is heterogeneous at 25°C.

VIIA.2. Structure Verification: GPC, $^1$H NMR and $^{13}$C NMR

GPC trials were performed on the 30k/50k and 30k/200k diblock copolymers in toluene at 25°C. For both materials, a single peak appeared which signifies that their blocked nature was retained.

To verify the relative proportion of 1,4 PBD to 1,2 PBD in the 30k/50k and 30k/200k diblock copolymers, $^1$H NMR data was obtained for the diblocks in toluene. Analysis subsequently showed that the 30k/50k has 41% 1,2 PBD content and the 30k/200k diblock has 20% 1,2 PBD content. Assuming no 1,4 PBD impurities in the 1,2 PBD block and no 1,2 PBD impurities in the 1,4 PBD block, we expect a 1,2 PBD content of 38% and 13% respectively for the 30k/50k and 30k/200k diblocks. Thus there is more 1,2 in the diblocks than is expected if each block is "pure" 1,2 PBD or 1,4 PBD. The observed 1,2 PBD content can be accounted for if the 1,2 PBD block is 95±5% 1,2 PBD (and 5% 1,4 PBD) and if the 1,4 PBD block is only 90±2% 1,4 PBD (and 10% 1,2 PBD). These values are within experimental error of the microstructures reported by Wilfong in Section VIIA.1. Similarly, in Section VB.2, s-1,2 PBD homopolymer was shown to have a microstructure of 95±3% 1,2 PBD and trans 1,4 PBD homopolymer was shown to have a microstructure of 91±6% 1,4 PBD.

$^{13}$C NMR data for the diblocks revealed 1,4 PBD cis and trans peaks at 27.3 and 32.5 ppm, respectively. The relative sizes of these peaks imply that the cis/trans ratio is 0.9 in the 30k/50k diblock and about 1.0 in the 30k/200k diblock. To determine tacticity in the 1,2 PBD blocks, peaks between 113-115
ppm were analyzed, as discussed in Section VB.3. The relative proportions for isotactic: atactic: syndiotactic 1,2 PBD are 28\%: 57\%: 15\% in the 30k/50k diblock. With the 30k/200k diblock, the three peaks were not sufficiently separable to obtain reliable percentage values, but clearly atactic content was greater than either isotactic or syndiotactic contents.

**VIIB. COMPOSITIONS OF BLENDS WITH DIBLOCK COPOLYMER**

Altogether, samples with forty-nine compositions were prepared for this thesis. The compositions are presented on ternary diagrams in Figure VII.1, where the apex of each diagram represents 100\% diblock and the points along the base represent binary blends of the two homopolymers. The compositions are labelled in similar ternary diagrams in Appendix A.1.

**VIIC. THERMAL PROPERTIES**

**VIIC.1. Glass Transitions**

Rheovibron-determined glass transition onsets and peaks were obtained for all of the ternary blends. Data for the complete ternary diagrams are given in Appendix A.2. As with binary blends of the two homopolymers, all blends that contain diblock copolymer plus both homopolymers exhibit at least two glass transitions - one corresponds to the 1,2 PBD component and one corresponds to the 1,4 PBD component. Thus these blends have distinct 1,2 PBD and 1,4 PBD phases.

Figures VII.2a and VII.2b depict some 1,2 PBD onset and peak temperatures in blends containing either 30k/50k or 30k/200k diblock. Figure VII.2c shows 1,4 PBD glass transition onset temperatures for various compositions. In all of these figures, a transition is always present for both the 1,2 PBD and 1,4 PBD components. Additionally, the peak and onset values are relatively constant and are comparable to the corresponding values for the homopolymers. Note that these results also apply to the left leg of the ternary diagrams where we have only s-1,2 PBD and diblock.

On the other hand, the peaks of the transitions on the right leg of the diagram, where we have only trans 1,4 PBD plus diblock, are not constant. With addition of homogeneous 30k/200k diblock, there seems to be only one T_g peak and it corresponds to 1,4 PBD. Though the onset of this transition is constant, the 1,4 PBD T_g peak value scales linearly with composition between the peak values of trans 1,4 PBD homopolymer and 100\% 30k/200k diblock. The
Figure VII.1: Compositions of Blend Samples
Figure VII.2: Tg Ternary Diagrams for Blends with 30k/50k or 30k/200k Diblock
tan $\delta$ curves for these blends are depicted in Figure VII.3b, and the $T_g$ peak temperatures are given in Figure VII.3c. These results suggest that mixing may occur between the trans 1,4 PBD and the homogeneous diblock.

In blends of trans 1,4 PBD and heterogeneous 30k/50k diblock, a peak corresponding to the 1,2 PBD block is definitely present when diblock content is $\geq$33%. A 1,2 PBD peak is probably also present in the blend with 10% 30k/50k diblock, though the tan $\delta$ curve is ambiguous. In general, the apparent 1,2 PBD peak value increases with increasing amounts of diblock and approaches the peak value of the 1,2 PBD block in 100% 30k/50k diblock. The onsets along this leg of the diagram correspond to 1,4 PBD onsets, so 1,4 PBD peaks are present but hidden by the response of the 1,2 PBD component. Tan $\delta$ curves for these blends are depicted in Figure VII.3a. The dependence of peak position with composition in blends of trans 1,4 PBD plus either 30k/200k or 30k/50k diblock clearly indicates that some type of interaction occurs between the diblocks and trans 1,4 PBD that does not also occur between the diblocks and s-1,2 PBD.

Finally, the transition between -100°C and -81°C that is present in two of the binary homopolymer blends, as discussed in Section VII.1, is also present in a few of the ternary blends. In addition, we observed small transitions at various other locations for a number of samples, but there is no obvious correlation between the additional minor transitions and sample composition. The locations of all transitions are included in Appendix A.2.

VIIC.2. Melting Point and Crystallinity Data

Trans 1,4 PBD melting points ($T_m$) in blends with diblock are given in Figure VII.4 for selected compositions, and s-1,2 PBD melting points ($T_s$) are given in Figure VII.5. General trends for the remaining blends are mapped out on the same diagrams. Arrows point in the direction of increasing value and dashed lines indicate values that are constant within experimental error. Melting point data for the complete ternary diagrams are presented in Appendix A.3.

Figures VII.4a and VII.4b show a 4°C melting point depression of the trans 1,4 PBD component as diblock is added to it, but this depression is less than that in binary blends of s-1,2 PBD and trans 1,4 PBD homopolymers. In Figures VII.5a and VII.5b, the s-1,2 PBD melting point is unchanged by addition of the 30k/200k diblock and is depressed by less than 4°C in the presence of high concentrations (>33%) of 30k/50k diblock. When more than 33% of a
VII.3a: Tan δ Curves with 30k/200k Diblock

VII.3b: Tan δ Curves with 30k/50k Diblock

Figure VII.3: Data for Blends with Trans 1,4 PBD plus Diblock
VII.3c: 1,4 PBD T_g Peaks with 30k/200k Diblock
VII.4a: Blends with 30k/50k Diblock    VII.4b: Blends with 30k/200k Diblock

Figure VII.4: $T_1$ Melting Point Ternary Diagrams

VII.5a: Blends with 30k/50k Diblock    VII.5b: Blends with 30k/200k Diblock

Figure VII.5: $T_s$ Melting Point Ternary Diagrams
blend is comprised of 60k/120k diblock, the s-1,2 PBD melting point is depressed about 5°C.

When miscibility occurs between a crystallizable polymer and a non-crystallizing polymer, melting point depression of the crystallizable homopolymer is predicted, as discussed in Section IIC.2. With our PBD system, the absence of more pronounced melting point depression of the crystalline components in the presence of amorphous diblock indicates that the diblocks do not interact with crystallites of the homopolymer components.

Percent-crystallinity of s-1,2 PBD and trans 1,4 PBD components, with respect to component mass, is relatively constant as diblock content increases. This result is evident in Figures VII.6a and VII.6b for the trans 1,4 PBD component and in Figures VII.7a and VII.7b for the s-1,2 PBD component. The exception is at a t/s ratio of 1/2. (The notation t/s refers to the ratio of trans 1,4 PBD to s-1,2 PBD.) Data for ternary blends along this composition line are given in Figures VII.6c and VII.7c. Recall that the 30k/200k diblock is homogeneous while the 30k/50k and 60k/120k diblocks are heterogeneous. Figure VII.6c depicts a slight increase in trans 1,4 PBD component crystallinity when a small amount (<10%) of heterogeneous diblock is present but a minor decrease when the same amount of homogeneous diblock is present. S-1,2 PBD component crystallinity in these blends is not significantly altered by small or large amounts of any of the diblocks, as depicted in Figure VII.7c.

The percent crystallinity data add further evidence that the diblocks interact in some way with the trans 1,4 PBD component but not with the s-1,2 PBD component. In addition, only a small amount of diblock is necessary to effect a change in the crystallinity of the trans 1,4 PBD component. Furthermore, at these small concentrations, the heterogeneous diblocks enhance trans 1,4 PBD crystallinity whereas the homogeneous diblock lowers trans 1,4 PBD crystallinity.

**VII D. MECHANICAL PROPERTIES**

A few samples containing 5% or less 30k/50k or 30k/200k diblock split along the axis of tension during Instron testing, as with the 67/33, 50/50, and 33/67 binary homopolymer blends discussed in Section VID. The samples with diblock that exhibited this behavior had compositions of 74/24/2 and 63/32/5 and are circled in Figure VII.8. Note that they all have trans 1,4 PBD/s-1,2 PBD ratios less than 1.0. Out of three specimens tested per composition, the number
VII.6a: Blends with 30k/50k Diblock

VII.6b: Blends with 30k/200k Diblock

Figure VII.6: Trans 1,4 PBD Crystallinity
VII.6c: 1/2 t/s Blends for Three Diblocks
VII.7a: Blends with 30k/50k Diblock

VII.7b: Blends with 30k/200k Diblock

Figure VII.7: S-1,2 PBD Crystallinity
VII.7c: 1/2 t/s Blends for Three Diblocks

Figure VII.8: Ternary Samples that Fractured Along Axis of Tension
[74/24/2 and 63/32/5 (s-1,2 PBD/trans 1,4 PBD/ amorphous diblock)]
of specimens that split this way is noted on these figures. Also, of the four compositions prepared that contain 60k/120k diblock, two specimens with composition 56/29/15 fractured in this manner, but specimens with composition 63/32/5 did not.

Presumably, the presence of significant amounts of rubbery material at higher diblock contents reduces interfacial stresses between the trans 1,4 PBD and s-1,2 PBD domains. Reduction of interfacial stress prevents heterogeneous crystalline regions from violently separating and propagating a fracture.

Tensile modulus and yield stress in blends with diblock are given in Figures VII.9a and VII.9b for selected compositions. As with the ternary diagrams of melting point data from above, general trends of the remaining blends are mapped out in these figures. Data for the complete ternary diagrams are given in Appendix A.4 for both modulus and yield stress.

In Figures VII.10a and VII.10b, tensile modulus is plotted as a function of diblock content for various trans 1,4 PBD/s-1,2 PBD ratios. In Figure VII.10c, the same parameter is plotted specifically for the t/s ratio of 1/2 so as to include data from blends with 60k/120k diblock. Similarly, yield stress is plotted in Figures VII.11a, VII.11b, and VII.11c. In all of these graphs, ternary blend values for modulus and yield stress are below the weighted average of the modulus and yield stress from the corresponding blends without diblock and pure diblock. As discussed in Section VID, this phenomenon is characteristic of heterogeneous systems and signifies the property dominance of the more yielding component. In this case, the diblock is the more yielding component. Even so, the mechanical properties drop very sharply as only a small amount of diblock is introduced. Thus, again, we see that a diblock content of less than 10% causes significant changes in blend properties. In addition, in Figure VII.10c, the drop in modulus is slightly more pronounced for blends with either of the two heterogeneous diblocks than it is for blends with the homogeneous diblock.

General trends for percent elongation at break and stress at break are shown in Figures VII.12a and VII.12b and Figures VII.13a and VII.13b, respectively. Data for the complete ternary diagrams of these parameters are given in Appendix A.5. Figures VII.14a and VII.14b portray the percent elongation at break as a function of diblock content for various t/s ratios. Stress at break is plotted in the same manner in Figures VII.15a and VII.15b.
Figure VII.9: Tensile Modulus and Yield Stress Ternary Diagrams for Blends with 30k/50k or 30k/200k Diblock
Figure VII.10: Tensile Modulus

VII.10a: Blends with 30k/50k Diblock
VII.10b: Blends with 30k/200k Diblock
VII.10c: 1/2 t/s Blends for Three Diblocks
Figure VII.11: Yield Stress

VII.11a: Blends with 30k/50k Diblock
VII.11b: Blends with 30k/200k Diblock
VII.11c: 1/2 t/s Blends for Three Diblocks
Figure VII.12: Percent Elongation at Break Ternary Diagrams

Figure VII.13: Stress at Break Ternary Diagrams
In Figure VII.14a, there is always a peak in percent elongation at break when 30k/50k diblock copolymer and trans 1,4 PBD are present together, and the peak occurs at 5-10% diblock content. This peak is not present in blends with t/s equal to 0/1, i.e. when diblock is added to only s-1,2 PBD homopolymer. In blends with 30k/200k diblock, as depicted in Figure VII.14b, a peak only occurs when the t/s ratio is 2/1. The results are basically the same for stress at break in Figures VII.15a and VII.15b.

Figures VII.14c and VII.14d show percent elongation at break for blends with a t/s ratio of 1/2. Data from blends with heterogeneous diblocks are plotted in Figure VII.14c and data from blends with homogeneous 30k/200k diblock are plotted in Figure VII.14d. Similarly, Figures VII.15c and VII.15d depict stress at break for blends with a t/s ratio of 1/2. For both properties, 5% heterogeneous diblock content clearly gives property enhancement, whereas low levels of homogeneous diblock are less effective.

Thus again, a small amount of diblock can significantly alter blend properties. In this latest case, properties at break were enhanced by diblock addition. Furthermore, the positive effects occur only when trans 1,4 PBD and diblock are present together, and the effects are again more pronounced with heterogeneous diblock than with homogeneous diblock.

Once diblock content exceeds 33%, percent elongation at break increases due to the overall high rubber content. Values for percent elongation and stress at break in such blends are slightly higher with the 30k/200k and 60/120k diblocks than with the 30k/50k diblock, probably due to the increase in total molecular weight.

VIIIE. SUMMARY AND DISCUSSION REGARDING BLENDS WITH AMORPHOUS DIBLOCK COPOLYMER

VIIIE.1. Effects of Adding Amorphous Diblock Copolymer

A number of significant effects result when diblock copolymer is added to blends of s-1,2 PBD and trans 1,4 PBD. First, all compositions that we studied are heterogeneous at room temperature, as determined by the presence of at least two glass transitions. One transition corresponds to 1,2 PBD and the second corresponds to 1,4 PBD. The only exception may be blends of 30k/200k diblock plus trans 1,4 PBD homopolymer.

Second, when the content of diblock is low, specifically ≤10%, some samples still fractured along the axis of tension during Instron tensile testing.
VII.14a. Blends with 30k/50k Diblock

VII.14b. Blends with 30k/200k Diblock

Figure VII.14: Percent Elongation at Break
VII.14c. 1/2 t/s Blends for Two Heterogeneous Diblocks

VII.14d. 1/2 t/s Blends for One Homogeneous Diblock
VII.15a. Blends with 30k/50k Diblock

VII.15b. Blends with 30k/200k Diblock

Figure VII.15: Stress at Break
VII.15c. 1/2 t/s Blends for Two Heterogeneous Diblocks

VII.15d. 1/2 t/s Blends for One Homogeneous Diblock
These samples have trans 1,4 PBD/s-1,2 PBD ratios less than 1.0. The fact that ternary blends with higher diblock contents did not fracture in this manner is understandable if the additional rubber content reduced interfacial stresses between domains of trans 1,4 PBD and s-1,2 PBD, and thus prevented the heterogeneous crystalline regions from violently separating and propagating such a fracture.

Third, mechanical properties were significantly altered by the addition of small amounts of diblock. Tensile modulus and yield stress dropped sharply in blends with only 5% diblock content, and stress and percent elongation at break peaked in value at low concentrations of diblock when trans 1,4 PBD was also present. Also, in t/s=1/2 blends with low diblock content, percent-crystallinity of the trans 1,4 PBD component deviated slightly from the norm. All of these results are not simply due to the presence of small amounts of any rubber since the phase behavior of the added diblock affected the degree of the observed phenomena, as is discussed in Section VII.E.2.

Fourth, there is some sort of interaction between the diblocks and trans 1,4 PBD that does not also occur between the diblocks and s-1,2 PBD. Glass transition peaks and onsets for both the 1,2 PBD and 1,4 PBD components were relatively constant in all blends, except when diblock was added to trans 1,4 PBD alone. In the latter case, Tg peak values for 1,4 PBD were dependent on sample composition. For the case of component crystallinities in t/s=1/2 blends, the trans 1,4 PBD component but not the s-1,2 PBD component was slightly altered by the presence of diblock in small amounts. Also, stress and percent elongation at break peaked in blends with low diblock content but only when the blends contained trans 1,4 PBD as well. Finally, interaction between the diblocks and trans 1,4 PBD may explain why ternary blends with more trans 1,4 PBD than s-1,2 PBD never fractured along the axis of tension, even with very low diblock contents.

VII.E.2. Addition of Heterogeneous versus Homogeneous Diblocks

In all cases where there was a difference in the effects of adding a heterogeneous versus a homogeneous diblock to s-1,2 PBD and/or trans 1,4 PBD, the effects were more pronounced with the heterogeneous diblocks. These cases are reviewed below.
In blends with 50\% or more heterogeneous diblock, the s-1,2 PBD melting point was depressed by 4°-5°C, but in the presence of homogeneous diblock, no significant melting point depression was observed at all.

The mechanical effects of low diblock content discussed in the Section VII.E.1 are all more pronounced with the 30k/50k and 60k/120k heterogeneous diblocks than with the 30k/200k homogeneous diblock. Tensile modulus dropped more sharply with heterogeneous diblock than with homogeneous diblock. A peak in percent elongation and stress at break occurred in more blends with heterogeneous 30k/50k diblock than with homogeneous 30k/200k diblock. For blends with a t/s ratio of 1/2, addition of heterogeneous diblock led to greater enhancement of mechanical properties at break than did addition of homogeneous diblock. Finally, the crystallinity of the trans 1,4 PBD component increased to a minor degree in the presence of heterogeneous diblock but decreased slightly in the presence of homogeneous diblock.

The two heterogeneous diblocks we studied have different block molecular weights as well as different ratios of block MWs, yet their impact on the blends was very similar.

**VII.E.3. Discussion and Proposed Morphologies**

In Chapters I and II, we discussed the relationship between molecular weight and a diblock's ability to compatibilize blends of two homopolymers. To summarize the relationship, homopolymers may be solubilized into diblock copolymer domains if the homopolymer MW's are less than the block MWs, especially when the homopolymer content is relatively low. When the block MW's are not equal, the homopolymer corresponding to the longer block is preferentially solubilized. Alternatively, diblocks may be solubilized into homopolymer domains if the diblock MWs are less than the corresponding homopolymer MW and if the diblock content is low.

Our blends of crystallizable PBD homopolymers plus amorphous PBD diblock copolymer are described better by the second category than by the first: The MWs of the blocks are less than or approximately equal to the MWs of the corresponding homopolymers, and blend properties are enhanced when diblock content is ≤10\%. The MW's of the two blocks in any of the diblocks we studied are not equal, and the block corresponding to the larger MW homopolymer seemed to interact preferentially with that homopolymer. Specifically, we concluded in Section VII.E.1 that there is a positive interaction
between the 1,4 PBD blocks (MW≤200k g/mol) and trans 1,4 PBD homopolymer (MW=425k g/mol) but no apparent interaction between the 1,2 PBD blocks (MW=30k-60k g/mol) and s-1,2 PBD homopolymer (MW=30k g/mol). We might have observed more interaction between the 1,2 PBD components if the 1,2 PBD block MWs had been smaller than the MW of the s-1,2 PBD homopolymer.

In general, melting points and crystallinities of s-1,2 PBD and trans 1,4 PBD components in blends with diblock copolymer were not lower than the melting points and crystallinities of the homopolymers. Thus diblock did not penetrate into the crystalline regions of either homopolymer component. Also, recall that all of the blends we tested were heterogeneous, except perhaps blends of only trans 1,4 PBD plus diblock. With these points in mind, morphologies for three categories of blends are proposed below. The categories are as follows: s-1,2 PBD plus diblock, trans 1,4 PBD plus diblock, and finally s-1,2 PBD plus trans 1,4 PBD plus diblock. For each of the categories, we suggest a morphology for low diblock content and for high diblock content. In some cases, we offer distinct morphologies for addition of heterogeneous versus homogeneous diblock copolymer.

In blends of s-1,2 PBD plus diblock copolymer, no property enhancement was observed at any composition. The diblock probably segregates from the homopolymer, leaving pools of diblock in a s-1,2 PBD matrix when diblock is the minor component or pools of s-1,2 PBD in a diblock matrix when diblock is the major component.

In Section VIIC.1, we concluded that glass transition peaks in blends of trans 1,4 PBD plus diblock depend on composition, and therefore there is some type of interaction between the diblocks and trans 1,4 PBD homopolymer. With addition of homogeneous 30k/200k diblock, the single Tg peak value scaled linearly between the peak values of the trans 1,4 PBD homopolymer and 100% 30k/200k diblock but there was no property enhancement at any composition. Perhaps, true miscibility occurs between this diblock and amorphous regions of the homopolymer. With addition of heterogeneous 30k/50k diblock on the other hand, the Tg peak corresponding to the 1,2 PBD block is distinct at most of the compositions and the mechanical properties in blends with 10% diblock are augmented. In this case, 1,4 PBD blocks may be mixing with amorphous regions of the homopolymer while 1,2 PBD blocks are excluded and forced to form their own phase, as depicted in Figure VII.16a. When diblock content is low, 1,2 PBD domains formed by the 1,2 PBD blocks may act as filler material to
give a response similar to that discussed in Section VID for 1,4 PBD homopolymers blended with small amounts of 1,2 PBD.

Finally, in ternary blends of both s-1,2 PBD and trans 1,4 PBD homopolymers plus diblock copolymer, mechanical properties were improved when homogeneous or heterogeneous diblock content was 5%-10%. Enhancement was more pronounced with the heterogeneous diblock copolymer. To achieve property enhancement, we needed slightly more diblock in blends with a trans 1,4 PBD/s-1,2 PBD (t/s) ratio of 2/1 than in blends with t/s=1/2. For example, 10% heterogeneous diblock content gave the best mechanical properties in t/s=2/1 blends, but only 5% heterogeneous diblock content gave the best mechanical results in t/s=1/2 blends. Correspondingly, the interfacial surface area between trans 1,4 PBD and s-1,2 PBD homopolymer domains is greater for t/s=2/1 blends than for t/s=1/2 blends since s-1,2 PBD inclusions are about 0.2μ-2μ in the former while trans 1,4 PBD inclusions are 0.5μ-5μ in the latter. These domain sizes were assigned in Section VIC. Interfacial surface area is dependent primarily on the size and distribution of homopolymer domains.

If diblock is located only at this interface in blends with enhanced mechanical properties, then 2%-20% of the interface is covered by diblock. This value is derived in Appendix B. Localization of diblock at the interface accounts for the more advantageous effects of heterogeneous diblock addition over homogeneous diblock addition. With heterogeneous copolymer, micro-phase separated 1,2 PBD blocks may be forced into s-1,2 PBD homopolymer domains, whereas with homogeneous diblock, the 1,2 PBD blocks are less likely to penetrate into s-1,2 PBD domains - unless heterogeneity is induced in the homogeneous diblock by the presence of homopolymer [2]. Figure VII.16b illustrates ternary blend morphology when diblock is located at the homopolymer interface. In ternary blends with higher than optimal amounts of diblock, the copolymer may form a thick rubber layer at the interface and/or segregate from the homopolymers into its own domains.

Another possibility for ternary blend morphology is that diblock solubilizes only in the trans 1,4 PBD component, as suggested above for blends of only trans 1,4 PBD plus diblock. If so, the improved properties must again be attributed to filler effects from 1,2 PBD block domains. This explanation does not account for property enhancement by homogeneous diblock unless the homogeneous diblock becomes heterogeneous with addition of
Figure VII.16: Proposed Morphologies for Blends with Diblock
homopolymer. And if micro-phase separation is so imposed on the homogeneous diblock, then we must explain why enhanced blends with 30k/50k diblock have slightly better properties than enhanced blends with the 30k/200k diblock. Thus, we feel that the ternary blend morphologies proposed in the previous paragraph are more consistent with the observed blend properties.

Considering that amorphous diblock copolymer did not alter homopolymer crystal structure in any of the blends, our suggested morphologies are not specific for systems with crystallizable homopolymers. They can be applied generally to heterogeneous systems with similar MW relationships, whether or not any of the homopolymer constituents have the ability to crystallize.

VIIF. REFERENCES
Chapter VIII
CONCLUSIONS AND FUTURE DIRECTIONS

VIII.A. SUMMARY OF MAJOR RESULTS AND CONCLUSIONS
VIII.A.1. Binary Blends of S-1,2 PBD and Trans 1,4 PBD Homopolymers

In Chapter VI, we showed that binary blends of the two crystalline PBD homopolymer isomers that we studied, s-1,2 PBD and trans 1,4 PBD, do not form isomorphic or eutectic systems. The MW of the trans 1,4 PBD component is approximately 425k g/mol and the MW of the s-1,2 PBD component is approximately 32.5k g/mol. For the full range of experimentally meaningful compositions and temperatures, the Flory-Huggins model in Chapter III predicts that the blends are heterogeneous. This prediction was verified by Rheovibron and x-ray experiments.

The average size of homopolymer domains is on the order of 1μ-5μ or less in crystalline blends of s-1,2 PBD and trans 1,4 PBD prepared by precipitation in a non-solvent. Blends of amorphous 1,2 PBD and 1,4 PBD that were spincast from solution at 25°C in an earlier work gave heterogeneous inclusions on the order of 1μ-50μ. Thus precipitation yields materials with smaller heterogeneous domains than those obtained by spincasting. Additionally, mechanical properties of the crystalline PBD blends are very near to the weighted average of their corresponding homopolymer values, whereas mechanical properties of the amorphous PBD blends are much lower than the weighted average of their corresponding homopolymer values. The more desirable mechanical behavior of the crystalline system is probably due to the finer dispersion of phases in those blends.

Not all of the binary crystalline PBD blends have reliable mechanical integrity: Tensile specimens from films with compositions of 67/33, 50/50, and 33/67 fractured along the axis of tension during Instron tensile tests. Such behavior is characteristic of oriented polymers in heterogeneous mixtures, thus we suspect that orientation was imposed on at least one of the components as tension was applied.

An unexpected positive result was observed in both the amorphous PBD and the crystalline PBD binary systems when 1,2 PBD content was approximately 10-12%. At this composition, percent elongation at break was much greater than that of either homopolymer that comprised the blends.
Also, there is a sharp increase in %C₅ for crystalline 5/95 PBD blends. Wilfong [1] suggests that the 1,2 PBD component acts as a reinforcing filler.

Blend melting points and component enthalpies are slightly depressed from homopolymer values, as predicted by Burghardt [2] for immiscible crystalline binary polymer systems. Trans 1,4 PBD crystallization is influenced more adversely by the presence of the s-1,2 PBD component than vice-versa. For instance, blends with 5-10% trans 1,4 PBD gave Tᵥ values that were 8°-11°C lower than homopolymer Tᵥ values whereas blends with 5-10% s-1,2 PBD gave Tₛ values only 2°-3°C lower than homopolymer Tₛ values. Similarly, %C₅ falls significantly as s-1,2 is added to trans 1,4 PBD, but %C₅ does not drop as trans 1,4 PBD is added s-1,2 PBD. Already-crystallized s-1,2 PBD chains may act as rigid barriers during subsequent crystallization of the trans 1,4 PBD component. Such behavior may be true for any heterogeneous binary system where the component with the higher Tₘ crystallizes at a fast rate.

VIIIA.2. Blends of S-1,2 PBD and Trans 1,4 PBD Homopolymers with Amorphous PBD Diblock Copolymer

We prepared blends of homopolymer(s) plus diblock with compositions as shown in Figure VII.1. All of the blends were heterogeneous at room temperature, with the possible exception of blends containing only trans 1,4 PBD plus diblock.

When diblock is present in ternary blends at concentrations of 10% or less, a number of significant results occur. Most importantly, mechanical properties are improved.

Also, there is clearly some sort of interaction between PBD diblock copolymer and trans 1,4 PBD that does not also occur between PBD diblock copolymer and s-1,2 PBD. The seeming absence of interaction between s-1,2 PBD homopolymer and diblock copolymer is probably because the MWs of the 1,2 PBD blocks are equal to or slightly greater than the MW of the s-1,2 PBD homopolymer.

Our results are not simply caused by the presence of small amounts of any rubber. In fact, the extent of the phenomena associated with diblock addition is dependent on whether the added diblock copolymer is thermodynamically heterogeneous or homogeneous. In all cases where there is a difference between heterogeneous diblock addition and homogeneous
diblock addition to s-1,2 PBD and/or trans 1,4 PBD, the effects are more pronounced with the heterogeneous diblocks.

We proposed various blend morphologies that take into account block and homopolymer MWs, thermal and mechanical property data, the preferred interaction of diblock with trans 1,4 PBD, and the greater effectiveness of heterogeneous diblocks over homogeneous diblocks. In ternary blends of both homopolymers plus diblock, the amount of diblock that gives optimal mechanical properties allows for 2%-20% coverage of the interfacial surface area between the two homopolymers.

VIII. GENERAL CONCLUSIONS

From our work with heterogeneous blends of polybutadienes, we can draw a number of general conclusions regarding the relationship between sample preparation, degree of heterogeneity, and the resulting blend properties, and regarding the role of amorphous diblock copolymer in a blend with two crystallizable homopolymers. The conclusions are listed below:

1) Precipitation gives a smaller degree of heterogeneity in blends than do other solvent mixing techniques. The finer dispersion of phases improves mechanical properties. For systems where properties are poor due to large domains of incompatible materials, precipitation may be successfully exploited to lower the degree of heterogeneity and thereby improve blend properties.

2) Heterogeneous blends of two crystallizable polymers can be advantageously manipulated by addition of amorphous diblock copolymer.

3) Furthermore, only a small amount of amorphous diblock is needed to obtain dramatic changes in mechanical properties. (Since amorphous diblock copolymers are easier and less costly to manufacture than diblock copolymers with two crystallizable blocks and since less diblock also means less cost, the commercial implications of our findings are also very important.)

4) Heterogeneous diblock copolymers seem to enhance blend properties to a greater extent than homogeneous diblocks.

5) In blends with enhanced properties, percent coverage of homopolymer interfacial surface area by diblock is about 2%-20%.

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Within this range, we can estimate a priori an effective diblock concentration for systems with a known degree of heterogeneity.

6) Finally, correlations in the literature regarding MW relationships in blends of homopolymer and diblock copolymer are applicable to our system of crystalline homopolymers plus amorphous diblock copolymer. Specifically, amorphous diblocks can be solubilized by appropriate crystalline homopolymers with MWs greater than the corresponding block, especially when the diblock content is low.

Since homopolymer crystalline structure was not altered by amorphous diblock addition, our conclusions are applicable to heterogeneous systems of amorphous homopolymers as well as crystalline ones.

VIIIIC. POTENTIAL AREAS FOR FURTHER STUDY

First, with regard to binary blends of 1,2 PBD and 1,4 PBD homopolymers, the property enhancement in Wilfong's 12/88 amorphous PBD blend and in our 10/90 and 5/95 crystalline PBD blends suggests that 1,2 PBD acts as a reinforcing filler at these low concentrations. PBD blends in this composition range warrant further investigation in future projects, as does the "reinforcing filler" hypothesis.

Second, we should test our conclusions in a second, different system of two crystallizable homopolymers plus amorphous diblock copolymer. But this time we should choose the system such that each copolymer block is compatible with its corresponding crystallizable homopolymer. Will we again find that a small amount of diblock achieves large changes in properties and will addition of heterogeneous diblock be more effective than addition of homogeneous diblock? Does our correlation between volume of diblock added and interfacial area of heterogeneous domains hold true?

Third, there are a number of questions that arose during the course of this research that either did not get answered or were not appropriate for our system. Some of the questions relate to binary blends of crystalline homopolymers and some relate to the conditions and extent to which diblock copolymers can emulsify blends of homopolymers, whether or not the homopolymers are crystalline. I list below a sampling of issues that deserve attention with appropriate blend systems and compositions.

Thermodynamic issues: For binary homopolymer blends where the heterogeneous-to-homogeneous transition temperature can be located, can
diblock addition - while the homopolymer blend is in the homogeneous state - allow the blend to retain its homogeneity once it reaches temperatures corresponding to the heterogeneous regime? If not, is the resulting degree of heterogeneity less than if diblock is added while the homopolymer blend is in a heterogeneous state?

Non-equilibrium issues: How does time affect degree of heterogeneity in an amorphous system, and at what point is an equilibrium morphology reached at various temperatures away from the binodal temperature? This question could be investigated with a phase-separated amorphous blend of homopolymers or with a phase-separated crystalline blend in the melt state. What, then, is the effect of diblock copolymer on the development of morphology with time at a given temperature? In addition, other processing and thermal history effects create a range of morphologies worth investigating. For example, we could ask if proven compatibilizers retain their compatibilizing potential when one or more of the blend components are subsequently oriented. Does the orienting process pull the compatibilizer from the interface, and if so what is the effect on the resulting degree of heterogeneity with time?

We also need to learn more about the role of crystallization kinetics and its effect on phase separation. In our work, we studied binary homopolymer blends where both components crystallized with very fast kinetics. We could also investigate the development of heterogeneity and the role of diblock copolymers in crystalline heterogeneous blends where one component crystallizes at a relatively fast rate and the second component crystallizes at a relatively slow rate. What are the implications of a system where the component with the higher crystallization temperature crystallizes much faster than the component with the lower crystallization temperature, and vice-versa?

Finally, in all of the situations suggested above, it is helpful to determine the relative effectiveness of heterogeneous diblocks versus homogeneous diblocks. By investigating these questions, we will greatly add to our understanding of heterogeneous polymer blends and the compatibilization capabilities of diblock copolymers, and thereby increase our ability to control the morphology and properties of blend materials.
REFERENCES

Appendix A

COMPLETE TERNARY DIAGRAMS

A.1 Final Weights and Degradation Levels of Prepared Films
A.2 Glass Transition Data
A.3 Melting Point Data
A.4 Tensile Modulus and Yield Stress Data
A.5 Data for Stress and Percent Elongation at Fracture

Preliminary Notes:

1) In the appendices that follow, diblock notation is in the form

   1,2 PBD block MW / 1,4 PBD block MW.

For example, 30k/50k refers to a diblock with a 1,2 PBD block of 30k g/mol and a 1,4
PBD block of 50k g/mol.

2) In Appendix A.1, blend notation is in the form

   % s-1,2 PBD / % trans 1,4 PBD / % diblock.

For example, 60/30/10 refers to a ternary blend with 60% s-1,2 PBD, 30% trans 1,4 PBD, and 10% diblock. Similarly, a 33/67/0 blend refers to a binary blend of 33% s-1,2 PBD and 67% trans 1,4 PBD. D-notations relate to visual levels of film degradation following compression-molding in the melt, as discussed in Section IVB.4.

3) Appendix A.2 includes values of both major and minor transitions observed during Rheovibron testing, as discussed in Section VIIC.1. Each vertical list of numbers corresponds to a single sample. For every transition, the peak and onset are both listed as follows:

   onset value (°C) / peak position (°C).

4) In Appendix A.3, the melting points of both the s-1,2 PBD and trans 1,4 PBD components are given, in that order. All values are in °C.

5) For each composition in Appendix A.4, first the modulus is listed and beneath it yield stress is listed. The values are all based on the average of the 2-3 specimens tested per composition, and the units are MPa.

6) In Appendix A.5, stress at break is listed above percent elongation at break. These values are based on the specimen from each composition that exhibited the highest values of percent elongation at break.

7) Original DSC scans, Rheovibron plots, and Instron stress-strain curves for all samples are not included here but are available from the author.
A.1: Final Weights and Degradation Levels of Prepared Films

Diblock
30k/50k

Syndie 1,2

Trans 1,4
A.2: Glass Transition Data

Diblock
30k/50k

Syndie 1,2

Trans 1,4
A.3: Melting Point Data

Diblock
30k/50k

Syndio 1,2

Trans 1,4
A.4: Tensile Modulus and Yield Stress Data

Diblock
30k/50k

Syndie 1,2

Trans 1,4
A.5: Data for Stress and Percent Elongation at Fracture
Appendix B
PERCENT COVERAGE OF INTERFACIAL SURFACE AREA BY DIBLOCK COPOLYMER

Given Data
1. The peaks in plots of percent elongation at break and stress at break as a function of diblock content occurred at the diblock contents listed below:

<table>
<thead>
<tr>
<th>t/s ratio in blend</th>
<th>% 30k/50k at peak</th>
<th>% 30k/200k at peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1/2</td>
<td>5% (same w/ 100k/100k)</td>
<td>0-5%</td>
</tr>
<tr>
<td>2/1</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>1/0</td>
<td>10%</td>
<td>-</td>
</tr>
</tbody>
</table>

2. Approximate domain sizes in binary blends of trans 1,4 PBD and s-1,2 PBD are as follows (from Section V): Trans 1,4 PBD domains when trans 1,4 PBD is the minor component are 0.5µ - 5µ. S-1,2 PBD domains when s-1,2 PBD is the minor component are 0.2µ - 2µ.

Calculations (based on 1g of polymer total in sample)
1. Total interfacial surface area in t/s = 1/2 and t/s = 2/1 blends:
   Assume that domain sizes do not change significantly as diblock is added to system and that domains are spherical in shape.

   If \( [N] \) = number of spheres of minor component in blend
   \( = \frac{\text{total volume of minor component}}{\text{(volume per sphere)}} \)
   \( = \frac{V_m}{(\pi d_s^3/6)} \), where \( d_s \) is the sphere diameter
   (B-1)

   and \( [S_{A_s}] \) = surface area per sphere
   \( = \pi d_s^2 \)  
   (B-2)

   then, \( S_{A_{total}} \) = total interfacial surface area
   \( = [N] [S_{A_s}] \)  
   (B-3)
   \( = \left( \frac{V_m}{(\pi d_s^3/6)} \right) \pi d_s^2 \)
   \( = 6V_m/d_s \)  
   (B-4)

   For example, in t/s = 1/2 blends, trans 1,4 PBD is the minor component. With a 1g total polymer basis, \( V_m = 0.33g \). Values for “\( d_s \)” range from 0.5µ - 5µ for trans 1,4 PBD, so we get

   \( S_{A_{total}} \) upper bound = 40,000 cm², \( S_{A_{total}} \) lower bound = 4,000 cm²
Similarly, in t/s = 2/1 blends, s-1,2 PBD is the minor component. \( V_m = 0.33g \) and "d_5" ranges from 0.2\( \mu \) - 2\( \mu \), so

\[ S_{A_{\text{total}}} \text{ upper bound} = 100,000 \text{ cm}^2, \quad S_{A_{\text{total}}} \text{ lower bound} = 10,000 \text{ cm}^2 \]

2. Surface Area of Diblock Copolymer at Interface:

The d-spacing, \( d_d \), of one diblock molecule must be on the order of the d-spacings of amorphous 1,4 PBD and 1,2 PBD homopolymers. Based on WAXS data in Section VB.4, \( d_d \) is thus about 5.5±1.0Å. Assuming that the diblock aligns at the homopolymer domain interface uncoiled and perpendicular to the plane of the surface, the surface area per diblock molecule at the interface is approximately \( d_d^2 \), or 30±10Å². [For reference, Siegmann (1979) lists transverse area per chain of polypropylene and polybutene as 35Å² and 45Å².]

For 1g of a blend with 5% diblock content, where the diblock has a total MW of 80k g/mol to 230k g/mol (as is the case for the 30k/50k and 30k/200k diblocks, respectively), we have

\[(0.05g/MW)(6\times10^{23} \text{ molecules/mole}) = 2.5\pm1.5 \times 10^{17} \text{ molecules of diblock.}\]

For 10% diblock content, we have 5.0±3.0 \( \times 10^{17} \) molecules of diblock.

Thus \( S_{A_d} \) = surface area covered by diblock

\[ = (30 \text{ Å}^2/\text{molecule})(\text{number of molecules for given blend}) \]

\[ = 750 \text{ cm}^2 \text{ for 5% diblock blends, and} \]

\[ = 1,500 \text{ cm}^2 \text{ for 10% diblock blends.} \]

The error associated with this calculation is on the order of 60% due to the range of diblock MWs.

3. Percent Coverage of Total Interfacial Surface Area by Diblock

We calculated above that blends with t/s = 1/2 have \( S_{A_{\text{total}}} \) values of 40,000 cm² to 4,000 cm² for 1g samples. Since 5% diblock gave maximal mechanical properties at break, we expect that only 750 cm² can be covered by diblock. Thus, diblock accounts for approximately 2%-20% of the total interfacial surface area in these blends.

Similarly, we can calculate percent coverage in blends with t/s = 2/1. Here, \( S_{A_{\text{total}}} \) is 100,000 cm² to 10,000 cm² for 1g samples. Ten percent heterogeneous diblock gave maximal mechanical properties at break, which corresponds to 1,500 cm² of the interface. Actually, these blends contain 0.9g, not 1.0g, total homopolymer, so actual \( S_{A_{\text{total}}} \) is about 0.9 times 100,000 cm² to
10,000 cm². With these numbers, diblock again accounts for approximately 2%-20% of the total interfacial surface area.