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Shaohua, Li

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THE STUDIES OF AROMATIC POLYIMIDES: SYNTHESIS, CHARACTERIZATION, AND THEIR RELATED BLENDS

&

THE INVESTIGATION OF LOCAL STRUCTURE OF POLYMER BLENDS BY SOLID-STATE NMR

A Dissertation Presented

by

SHAOHUA LI

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

Februray, 1995

Department of Polymer Science & Engineering
THE STUDIES OF AROMATIC POLYIMIDES: SYNTHESIS, CHARACTERIZATION, AND THEIR RELATED BLENDS

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ACKNOWLEDGMENTS

I would like to extend a special word of thanks to my advisor, Dr. Frank E. Karasz, for his financial support, encouragement, and patience throughout my graduate career. My deepest appreciation is also extended to the other members of my advisory committee, Dr. Robert W. Lenz and Dr. Paul M. Lahti.

My sincere thanks is also extended to Dr. David Rice, from whom I have learned so much about solid-state NMR. I treasured my many hours of discussion with him.

My sincere thanks is also extended to Victoria White and Nancy Lukaskiewicz for their generous help, and to all the other members of Dr. Karasz's group.
ABSTRACT

THE STUDIES OF AROMATIC POLYIMIDES: SYNTHESIS, CHARACTERIZATION, AND THEIR RELATED BLENDS

&

THE INVESTIGATION OF LOCAL STRUCTURE OF POLYMER BLENDS BY SOLID-STATE NMR

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Directed by: Professor Frank E. Karasz

This dissertation consists of the study of polyimides: their synthesis, characterization and blends, and the local structure of polymer blends by solid state NMR.

A series of polyimides and copolyimides from 3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride (BTDA), 3,3'-diaminodiphenyl sulfone (3DDS), and 4,4'-oxydianiline (4ODA) were synthesized and characterized. The solubilities of BTDA-3DDS/4ODA copolyimides were found to be strongly dependent on the copolymer compositions. The copolyimides became insoluble when the 4ODA content was higher than 40%. All the polyimides synthesized in this study, however, were soluble in acidic solvents such as trichloroacetic acid.

Dynamic mechanical thermal analysis showed that the segmental mobility of BTDA-3DDS/4ODA copolyimides increased with 3DDS content. From thermal expansivity measurements it was inferred that the segmental interaction in BTDA-
3DDS/4ODA copolymides decreased with 3DDS content. Infrared spectroscopy studies demonstrated that the segmental interaction in the copolymers was mainly due to the dipole–dipole interactions between the dianhydride units and the diamine units in polyimide chains. The strong electron donating effect of 4ODA resulted in a strong dipole–dipole interaction in high 4ODA content copolymides.

The dynamics of concentration fluctuation and the decomposition of the initial miscible phase during phase separation were studied by thermal analysis method for following blends: poly(BTDA-FDA)/poly(ethersulfone) (PES); DOW2080/PES; XU218/PES and poly(BTDA-3PDA)/PES. It was found that the dynamics of phase separation were strongly controlled by the chain diffusivity of polymers. The effect of chain diffusivity on the dynamics of phase separation can be described by its dependence on the glass superheating ($T_a - T_g$).

The spin diffusion of two-dimensional solid-state NMR was used to investigate the local structure of polymer blends of PPO/PS-d$_5$, PPO/PS-d$_5$, PS-d$_5$/PS-d$_3$, and PS/PVME. It was found that the local structure can be described by a Gaussian correlation model with a correlation length of 0.5 – 0.6 nm. The result suggested the existence of short-range ordering structure in these miscible blends.
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<td>BTDA</td>
<td>3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride</td>
</tr>
<tr>
<td>CHP</td>
<td>1-Cyclohexyl-2-pyrrolidinol</td>
</tr>
<tr>
<td>DCAA</td>
<td>Dichloroacetic acid</td>
</tr>
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<td>PMDA</td>
<td>Pyromellitic dianhydride</td>
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<td>Poly(2,6-dimethylphenylene oxide)</td>
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CHAPTER 1
SYNTHESIS AND CHARACTERIZATION OF
AROMATIC POLYIMIDES AND COPOLYIMIDES

1.1 Introduction

Much effort has been expended in developing new functional and structural materials for the electronic and aerospace industries. Due to increasing demands for high performance in extreme conditions, the materials are required to be light-weight, high strength and of high modulus, heat resistant and of good dimension stability. Nonconductivity and low dielectric constants are also required for many specific applications of these materials. Polymeric materials have been found to meet many of these requirements and have been used by the electronic and aerospace industries.¹

Polyimides can be used to meet the ever increasing demands of the aerospace and electronic industries because they are nonconductive, possess low dielectric constants, resist high temperatures, have high strength and high modulus. The electronic industry has used polyimides in its high-speed integrated multilevel circuits and packaging technologies.² The aerospace industry has used them in its space shuttles and aircraft.³ Indeed, polyimides have proved useful to the electronic industry and aerospace industry since early 1960's because of their outstanding properties and performance.³

Polyimides, however, are also known to be intractable materials. Many commercial polyimides are insoluble and infusible in their finished forms. As a result of these properties, the manufacturing and applications of polyimides are very limited and expensive.³ To obtain structural integrity, polyimides have to be fabricated through thousands of hours of continuous operation at 200 °C, hundreds of hours at 300 °C, and minutes at 500 °C. The procedures involved in this fabrication not only make the
materials very costly but also produce products of uneven quality.

To solve these problems, we need to understand what causes the intractability of polyimides. It was the goal of this study to investigate the molecular interactions and its dependence on the molecular structure of polyimide. This chapter will discuss the synthesis of a series of BTDA–3DDS/4ODA copolyimides.

1.1.1 Two Stage Polymerization

Polyimides are molecular chains containing heterocyclic ring systems of nitrogen, carbon, and oxygen atoms. The molecular fragment making up the imide structure is shown in Scheme 1.1. Traditionally, polyimides have been synthesized by the two-stage polymerization method, sometimes referred to as the solid-state curing method.\textsuperscript{4–10} In this method, the polyamic acid was cured at a high temperature into a polyimide. A typical reaction procedure is shown in Scheme 1.2.

The first step of aromatic polyimide synthesis is the preparation of the appropriate polyamic acid, which is usually performed as follows: To a solution of a known amount of the aromatic diamine in a suitable solvent, an equal molar amount of dry tetracarboxylic acid dianhydride is introduced in small portions, with stirring. The viscosity of the solution gradually increases as more dianhydride is added. High molecular weight polyamic acids are formed when the molar amount of dianhydride and the diamine are equal. Usually the dianhydride is added in excess (1–3% more dianhydride than diamine) to compensate for any loss of functionality in the dianhydride. The reaction is conducted at 10 to 50 °C. Aprotic solvents, such as \textit{N},\textit{N}-dimethylacetamide and \textit{N}-methyl-2-pyrrolidone, must be used so that both the reagents and the polyamic acids are soluble during the reaction.

When the diamine is in large excess, the reaction of diamine with dianhydride is
Scheme 1.1 Molecular structure of imide moiety.

rapid, and the formation of polyamic acid dominates. As the concentration of diamine decreases, however, the reaction tends to slow, and the side reactions assume more importance. Scheme 1.3 shows some mechanisms for the reaction of polyamic acids with other impurities.

Frost and Kesse studied the effect of water on the temporal viscosity of polyamic acid made from 4,4'-oxyphenylene diamine and pyromellitic dianhydride at 35 °C.\textsuperscript{11} They found that the decrease in viscosity in the anhydrous system was much smaller than that in systems containing some water. Their result is shown in Figure 1.1. However, other studies showed that at lower reaction temperatures (20 °C) the polymerization of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride with aromatic diamines was actually accelerated in the presence of small amounts of water. It was believed that water probably serves as a catalyst at low temperatures, whereas at high temperatures it leads to hydrolysis of the polyamic acids.

In the conventional two-stage polymerization procedure, the conversion of polyamic acid precursor into polyimides is performed by thermal treatment of the polyamic acid thin films at elevated temperatures. Intramolecular cyclization occurs as
Scheme 1.2 Scheme for the preparation of polyimides by the two-stage synthesis route.
Scheme 1.3 Side reactions in the synthesis of polyamic acids.\textsuperscript{9}
water is lost during curing. Step wise heating is usually employed for the removal of residual solvent. A typical procedure for the preparation of Kapton polyimides is:12–19

1. One hour at 70 °C
2. One hour at 100 °C
3. One hour at 200 °C
4. One hour at 300 °C

Infrared spectroscopy has been used to monitor the conversion reaction of a polyamic acid into a polyimides.14,15,20–26 Studies showed that the imidization proceeds by a fast cyclization reaction in the range of 160–180 °C, and is followed by a slower cyclization reaction.27 It was also found that the cyclization reaction ceases well short of the quantitative conversion.27–30 Figure 1.2 shows the conversion rate of imidization at various temperatures. It was believed that the conversion rate is determined by the stiffening of the polymer chains as conversion proceeds. There was also the possibility

Figure 1.1 Effect of water on the viscosity of 10% polyamic acid of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether at 35 °C.9
that the casting solvent assists the orientation needed for ring closure, thus its loss at high temperature retards the imidization.

Figure 1.2 Conversion rates of polyamic acids at various temperatures.\(^{21}\)

The molecular weight of the polyamic acid changes during the thermal treatment,\(^{31-35}\) as shown in Figure 1.3. First, a reduction of molecular weight is observed, probably as a result of the hydrolysis of polyamic acids by water produced from imidization. The molecular weight then increases again at high temperatures in the later stages of the curing.\(^{36}\)

The polyimides prepared in this fashion are usually insoluble and infusible in common organic solvents except in strong acidic solvents, such as sulfuric acid, nitric acid and trifluoroacetic acid.
1.1.2 "One-pot" Solution Polymerization

As a result of the inherent insolubility and infusibility of aromatic polyimides prepared by the two stage methods, many researchers have sought other alternatives. The "one-pot" solution polymerization method is one of the recent procedure employed to prepare soluble polyimides.\textsuperscript{37-48} This polymerization procedure is shown in Scheme 1.4. In an early study on the solution imidization of polyamic acid, the polyamic acid was converted into polyimide by refluxing in N-methyl-2-pyrrolidinone (NMP) at 200 °C.\textsuperscript{37} However, a severe degradation of the polyamic acid occurred during this process, and only very low molecular weight polyimide products were obtained. These researchers suggested that the presence of large quantities of water from the imidization reactions caused the hydrolytic degradation of the polyamic acid. If the water could be efficiently and immediately removed from the system, the hydrolytic degradation of polyamic acid could be avoided.

Many azeotropic systems have been used for the removal of water from the reaction solution. Takekoshi et al.\textsuperscript{39} successfully synthesized polyetherimide at moderate
Scheme 1.4 Scheme for the preparation of polyimides by the "one-pot" solution polymerization route.
temperatures of 160 - 180 °C by using toluene as the azeotropic agent. Summer et al.\textsuperscript{45} reported that the water from the cyclization can be effectively removed by using a 20% solution of cyclohexyl pyrrolidinone in NMP.\textsuperscript{46} Figure 1.4 shows the water content in NMP, CHP and a 20/80 mixed solution of NMP/CHP at various temperatures. Many of the polyimides synthesized in this studies were soluble in the mixed solvents, and nearly quantitative conversions of the polyamic acids was achieved by this method.

The synthesis of polyimides in m-cresol with azeotropic agents was also reported.\textsuperscript{49,50} Low molecular weight polyimides are usually obtained by this method for unreactive dianhydrides and diamines. However, high molecular weight polyimides could be obtained by directly polymerizing the unreactive pair of dianhydride and diamine by refluxing in m-cresol.

1.1.3 Other Polymerization Routes
1.1.3.1 Diisocyanate Polymerization

Polyimides can also be synthesized through the reaction of diisocyanates with dianhydrides, as showed in Scheme 1.5.\textsuperscript{51-55} The reaction is carried out in aprotic solvents such as N,N-Dimethylformamide (DMF) and Dimethylsulfone (DMSO) at 100 - 140 °C and is catalyzed by small amounts of water or other metallic alkoxides and alkali-metal lactamates.\textsuperscript{52,53} The presence of water was assumed to assist in the partial hydrolysis of isocyanate. The aromatic amines are then reacted with anhydrides.\textsuperscript{51} The reaction of dianhydride with diisocyanate was proposed by the formation of a seven-member ring as the intermediate.\textsuperscript{56-64} The intermediate loses carbon dioxide on heating.

The diisocyanate route usually produces polymers of low molecular weight, even though tractable polyimides have been prepared by this method. High molecular weight
polyimides were obtained with a mixture of tetracarboxylic acid and its dianhydride in molar ratios ranging from 1:7 to 1:4. Kakimoto et al. synthesized aromatic polyimides through the diisocyanate route and other routes.\textsuperscript{65} They reported that high molecular weight polyimides could be obtained in benzonitrile. However, these polyimides showed limited solubility in organic solvents. The authors suggested that cross-linking occurred during the polymerization and led to their insolubility in most solvents.

The diisocyanate route has been used for the commercial production of DOW2080 polyimides.\textsuperscript{64,65} The reaction has also been applied to synthesize polyamide-imides.\textsuperscript{64}
Scheme 1.5 Scheme for the preparation of polyimides by the diisocyanate route.
1.1.3.2 Nitro-Displacement Polymerization

The nucleophilic substitution reaction from bisphenoxide salts and aromatic dinitrobisimides can also be used for the synthesis of aromatic polyimides.\textsuperscript{66-69} The nitro-displacement polymerization reaction occurs under anhydrous conditions in aprotic solvents such as DMSO or DMF in combination with toluene or chlorobenzene at 40-60 °C.\textsuperscript{67} The reactivity of dinitrobisimides depends on the location of the nitro group. Usually the meta nitrobisimides give polyimides higher viscosity than do its para isomers. Many bisphenols are commercially available. Dinitrobisimides can be prepared in high yield by refluxing 3- or 4-nitrophthalic anhydride with the diamine in acetic acid.\textsuperscript{70}

Water can react with phenolate, so the presence of small amounts of water in the system may lead to an equilibrium with phenol. The formation of hydroxyl ion can also open the imide rings to generate the carboxylate, which deactivates the nitro group as a nucleophile and eventually stops the polymerization. Even under anhydrous conditions, only low to moderate molecular weight polyimides can be obtained.

1.2 Experimental

1.2.1 Reagents and Purifications

The preparation of polyimides in this study involves the reaction of dianhydrides and diamines. Dianhydrides are chemicals that are very reactive toward water and other reagents with free protons. The reaction of dianhydrides with these impurities in the reaction system leads to the loss of functionality in the dianhydride monomers and thus to the loss of the stoichiometry of the reaction reagents; consequently, such side reactions result in the termination of polymerization and the production of only low molecular
weight products. Because the solvents used (e.g. N,N-Dimethylacetamide (DMAc), and NMP) as well as the diamines are hydrophilic, water is usually the major impurity. To ensure a high molecular weight product in the synthesis of aromatic polyimides, most of the starting materials and solvents were carefully purified before use.

The monomer reagents were purified by various techniques unless they were obtained in a high degree of purity. Polymerization solvents were dried by various drying agents and distilled before use. In all the distillations, only the constant boiling middle fraction was collected and stored in a round bottom flask sealed with a rubber septum.

N,N-Dimethylacetamide (DMAc, Aldrich) was dried by stirring over crushed calcium hydride or barium oxide at room temperature for at least 8 hours. The dried solvent was then distilled under reduced pressure generated by a mechanical pump. The freshly distilled solvent was usually used immediately for polyimide polymerization. For long-term storage, the solvent was sealed with molecular sieve to avoid any potential moisture contamination.

N-Methyl-2-pyrrolidinone (NMP, Aldrich, spectrophotometric grade) was dried by stirring over crushed calcium hydride or barium oxide at room temperature for at least 8 hours. The dried solvent was then distilled under reduced pressure generated by a mechanical pump. Freshly distilled NMP was usually used for the polymerization. For long-term storage, the solvent was sealed with molecular sieve to avoid any possible contamination.

N-Cyclohexyl-2-pyrrolidinone (CHP, Aldrich, 99%) was stirred over crushed calcium hydride for at least one day. The dried solvent was then distilled under reduced pressure
generated by a mechanical pump. The distilled solvent was usually used immediately after distilled, or a molecular sieve was used to keep it anhydrous for long-term storage.

\( m \)-Cresol (Kodak, 99%) was stirred over barium oxide for at least 24 hours. The dried solvent was then stored at ambient temperature for several days to let inorganic particles fully precipitate. The clean solvent from the upper part of the flask was then transferred into another round bottom flask for further use.

2-methoxyethyl ether (Diglyme, Aldrich, spectrophotometric grade) was stirred over calcium hydride or barium oxide at ambient temperature for at least 8 hours. The dried solvent was then distilled under reduced pressure generated by a mechanical pump.

Benzophenone tetracarboxylic acid dianhydride (BTDA, Aldrich, 98%, mp 224-226 °C) was received as a white crystalline material. This BTDA was recrystallized as follows. To a 500-mL erlenmeyer flask was added 300 mL acetic anhydride (Kodak Chemicals), and the solvent was heated to 60 °C. At this temperature, as much BTDA as possible was added to obtain a saturated solution of BTDA in acetic anhydride. The clear, slightly yellowish solution was then allowed to cool to room temperature, at which large needle-like crystals of BTDA began to form. To induce the formation of BTDA crystals, the erlenmeyer flask was placed into an ice-water bath for 4-6 hours. The BTDA crystals were then obtained by filtering the solution through filter paper and washed with cooled acetic anhydride. The filtered materials were then dried at about 120 °C under vacuum for 24 hours. The pure BTDA monomer was stored under nitrogen.

BTDA was also obtained from CHRISKEV (99+%, mp > 225 °C) as a white, fine powder. This BTDA was highly purified and only needed to be dried in a vacuum oven at about 150 °C for 2-4 hours prior to polymerization. Experiments showed that polyimides
polymerized from this BTDA had no significant difference in molecular weight from those produced from by recrystallized BTDA.

4,4'-Oxydianiline  (4ODA, CHRISKEV, 99.5%, mp > 191.5 °C) was received as tan fine powder. This 4ODA was highly purified and was used as received.

3,3’-Diaminodiphenyl sulfone (3DDS, CHRISKEV, 99%, mp > 170 °C) was obtained as a fine white powder. This 3DDS monomer was highly purified and was used as received.

9,9’ Bis(4-aminophenyl) fluorene (FDA, CHRISKEV, 98%, mp > 237 °C) was received as a light brown powder. This FDA monomer was highly purified and was used as received.

1.2.2 Synthesis of Polyimides
1.2.2.1 Preparation of Poly(BTDA–3DDS)

To a 250-mL flask were added 6 g (24.16 mmol) of 3DDS and 7.798 g (24.200 mmol) of BTDA. The system was then purged with nitrogen and pumped to a 5-10 mm Hg vacuum alternatively several times before fresh DMAC was added. Solid concentration was kept at about 15%. The mixture was then stirred at room temperature under nitrogen for about 8 hours to allow the viscosity to build up.

Then to 25-mL cyclohexylpyrrolidinone preheated to 180 °C was added the synthesized polyamic acid through an addition funnel under nitrogen. The temperature was kept at 175 °C, and the reaction was allowed to proceed for 20 hours. At this temperature the water was effectively removed from the system by the flowing nitrogen gas. The dark viscous solution was then poured into a large amount of warm 50/50 mixture of 2-methoxyethyl ether/ethanone. The yellowish polyimide was precipitated
immediately and the mixture was stirred for another 5 hours. The polymer was then filtered and washed with a large amount of water, dried at 200 °C in vacuum for 5 days, and stored for future use.

1.2.2.2 Preparation of Poly(BTDA-4ODA)

The preparation of BTDA-4ODA polyamic acid is the same as for the BTDA-3DDS polyamic acid. Solution imidization of the BTDA-4ODA polyamic acid resulted in an early precipitation of the BTDA-4ODA polyimide. The slurry solution was stirred at 175 °C for 20 hours. Polyimide was obtained by precipitation into a large amount of water, filtered, and dried at 200 °C in vacuum for 5 days. The polyimide prepared by this method is insoluble, so to produce films of BTDA-4ODA polyimide, it was also prepared in the conventional two-step procedure. In the later preparation, the freshly synthesized BTDA-4ODA polyamic acid was cast onto an aluminum disk. Film was formed by evaporating the solvent at room temperature for 1 day. The film was annealed at first 150 °C in vacuum for 3 hours and then at 250 °C for 2 days.

1.2.2.3 Preparation of BTDA-3DDS/4ODA Copolymides

To a 250-mL flask were added 3 g (12.082 mmol) of 3DDS, 2.4193 g (12.082 mmol) of 4ODA, and 7.798 g (24.200 mmol) of BTDA. The reaction system was then purged with nitrogen and vacuumed several times before DMAC was added. The concentration was kept at about 15% solid. The reaction was allowed to proceed for 5 hr at room temperature under nitrogen. Solution imidization was then employed to obtain the polyimide as in BTDA-3DDS polyimide synthesis. The copolyimide with 60% 4ODA content precipitated from the solution after the reaction. Polymers were then poured into
a large amount of 50/50 diglyme/ethanone mixture, filtered, and washed with water. The polymers were dried at 220 °C in vacuum for 5 days.

1.2.3 Characterization of Polvimides

Intrinsic viscosity of the polymers that are soluble in DMAc were measured in DMAc with a concentration of about 0.1 g/dL at 30 °C. Intrinsic viscosity of the polymers that are not soluble in DMAc were measured in trichloroacetic acid (TCAA) with a concentration of about 0.1 g/dL at 65 °C. The glass transition temperatures and thermal gravimetry of the polymers were measured with a Perkin Elmer DSC 7 and with a heating rate of 40 °C/min and 10 °C/min, respectively. Dynamic mechanical thermal analysis (DMTA) was conducted with the Polymer Laboratory DMTA system and with a heating rate of 3 °C/min and a frequency of 1 Hz. Samples for the DMTA were prepared by compression molding at 300 – 325 °C, depending on the $T_g$ of the particular polymers, under vacuum. For the infusible polyimide of BTDA-4ODA, film was obtained by solid-state curing of the polyamic acid film.

1.3 Results and Discussion
1.3.1 Characterizations of BTDA-3DDS/4ODA Copolymides

The solution imidization was known to improve the solubility of aromatic polyimides relative to those prepared by its counterpart method, solid stage imidization.\textsuperscript{38-47,49-51} In this study, we adopted the synthesis procedure of Summers et al.\textsuperscript{45} for the imidization of polyamic acid. The cyclohexylpyrrolidinone (CHP)/NMP system has been shown to be a good medium for high temperature removal of the water,
Scheme 1.6 Molecular structures of BTDA-3DDS and BTDA-4ODA polyimides.
Figure 1.5 High-resolution $^{13}$C solid-state NMR spectra of BTDA-3DDS/4ODA copolymers.
which is generated by the cyclization reaction. We used DMAc instead of NMP in the
synthesis of polyamic acid because of the high boiling point of NMP. In all cases, a
yellowish powder was obtained and all the polymers were amorphous, as indicated by the
X-ray diffraction patterns (not shown here). Scheme 1.6 shows the molecular structure of
the two homopolymer polyimides, and Figure 1.5 shows the solid-state high-resolution $^{13}$C
NMR spectra of the polyimides. The chemical shift assignments are shown in Table 1.1.
Solution NMR spectra are not available because some of the copolymers are not soluble in
common solvents. The resonances are generally broad, and because all the carbons are
aromatic, many resonances overlapped.

Information about the sequence distribution can not be obtained from the spectra.
However, because the oxyphenylene diamine (4ODA) is much more reactive than
diaminodiphenylsulfone (3DDS), it is likely that most of the 4ODA forms dimers and
trimers with BTDA before 3DDS does, and then the dianhydride functional groups of
these dimers or trimers further react with the rest of the 3DDS diamine to form high
molecular weight polymers. Therefore, the polymer may be regarded as a copolymer that
falls between alternative and random copolymers.

<table>
<thead>
<tr>
<th>Table 1.1 Chemical shift assignments for BTDA-3DDS and BTDA-4ODA polyimides</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Chemical shift</th>
<th>Carbon No.</th>
<th>Chemical shift</th>
<th>Carbon No.</th>
</tr>
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<tbody>
<tr>
<td>203</td>
<td>1</td>
<td>203</td>
<td>1</td>
</tr>
<tr>
<td>175</td>
<td>2</td>
<td>174</td>
<td>2</td>
</tr>
<tr>
<td>160</td>
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<td>150</td>
<td>3</td>
</tr>
<tr>
<td>150</td>
<td>4</td>
<td>145</td>
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</tr>
<tr>
<td>145</td>
<td>5</td>
<td>135</td>
<td>5</td>
</tr>
<tr>
<td>135</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.2 Intrinsic viscosity of BTDA-3DDS/4ODA copolyimides

<table>
<thead>
<tr>
<th>Copolymer Composition BTDA-3DDS/4ODA(^{a})</th>
<th>Intrinsic Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>0.39(^{b})</td>
</tr>
<tr>
<td>90/10</td>
<td>0.35(^{b})</td>
</tr>
<tr>
<td>80/20</td>
<td>0.38(^{b})</td>
</tr>
<tr>
<td>60/40</td>
<td>0.60(^{c})</td>
</tr>
<tr>
<td>40/60</td>
<td>0.50(^{c})</td>
</tr>
<tr>
<td>0/100</td>
<td>0.36(^{c})</td>
</tr>
</tbody>
</table>

a. Ratio of 3DDS to 4ODA units.
b. Measured at 30 °C in DMAC.
c. Measured at 65 °C in trichloroacetic acid.

Table 1.2 gives the intrinsic viscosities of the polyimides. The molecular weight of the polyimides is generally higher when there is a higher content of 4ODA units. This finding is consistent with the high reactivity of 4ODA diamines and the more stable structure of its polyamic acid. The polymerization of BTDA and 4ODA produced the most viscous polyamic acid solution from the reaction system. The low viscosity of the BTDA-4ODA polyimide seen in Table 1.2 may be due to degradation during film formation in the air. The increase of molecular weight during the solid-state imidization is not seen. The BTDA-3DDS polyimide and the 90/10 BTDA-3DDS/4ODA copolymer are soluble in DMAc upon heating. However, BTDA-3DDS/4ODA copolyimides of 20–40% 4ODA units can only be swollen in boiling DMAc. Higher contents of 4ODA in the copolyimide result in completely insolubility in DMAc, even if the copolyimide is imidized by solution method. A transition of the solubility of the copolyimide in DMAc
was seen at compositions of about 20 - 30% 4ODA. In solvents with stronger interactions, such as dichloroacetic acid (DCAA), TCAA, and even nitric acid and sulfuric acid, all the copolymers are soluble. The results of the solubility and fusibility for BTDA-3DDS/4ODA copolyimides are summarized in Table 1.3. It was believed that the formation of hydrogen bonding of polyimides with these acids is the primarily responsible for their solubility in these acids. Conversely, DMF and DMAc do not provide any hydrogen bonding, and their interaction with the polyimides is probably weaker than that of the inter- and intramolecular interactions of the polyimides.

Table 1.3 Solubility and fusibility of BTDA-3DDS/4ODA copolyimides

<table>
<thead>
<tr>
<th>BTDA-3DDS/4ODA copolyimide compositiona</th>
<th>Solubilityb</th>
<th>Fusibilityc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMAC</td>
<td>NMP</td>
</tr>
<tr>
<td>100/0</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>90/10</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>80/20</td>
<td>p</td>
<td>p</td>
</tr>
<tr>
<td>60/40</td>
<td>p</td>
<td>p</td>
</tr>
<tr>
<td>40/60</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>0/100</td>
<td>I</td>
<td>I</td>
</tr>
</tbody>
</table>

a. Ratio of 3DDS to 4ODA units
b. With heating.
c. Compression molding at about 50 °C above the Tgs. If transparent films are obtained, it is defined as fusible.
d. Dichloroacetic acid.
e. Trichloroacetic acid.
f. s: soluble; p: partially soluble; I: insoluble.

Cross-linking and rigidity of the polyimide chains are considered to be the two major factors causing the insolubility of the aromatic polyimides. Intermolecular instead of intramolecular cyclization leads to the formation of a cross-linked network.
Intermolecular imidization also may occur in the solid-state reaction where each functional group is adjacent another function unit. Imidization in solution essentially eliminates the possibility of such cross-linking. Another factor is the rigidity and ordering of the polymer chain which limits the motion of the segments, which is refereed by the high glass transition temperature. Although BTDA-3DDS polyimide is soluble in DMAc, the solubility of BTDA-3DDS/4ODA copolymers in DMAc decreases as the content of 4ODA increases. However, all these polyimides are still soluble in stronger solvents that provide hydrogen bonding. The fact that the copolymers are still soluble in strong solvents refutes the hypothesis of cross-linking.

The fusibility of the copolymers is also shown in Table 1.3. The fusibility of the copolyimides is far better than their solubility even though a decrease of fusibility as 4ODA content increased was also observed. For all the polyimides except the BTDA-4ODA homopolymer, the polyimides are fusible above their T_g under high pressure of above 1,500 Kg/cm^2. Transparent films were obtained in this way for the measurement of DMTA. The polymers become only partially soluble in DMAc after compression molding but are still soluble in acid solvents.

Figure 1.6 shows the glass transition temperature of polyimides. The T_g s of the homopolyimides are consistent with the reported values. The T_g increases as a function of 4ODA content. However, the glass transition temperatures of the polyimides are very close: 268 °C and 283 °C for BTDA-3DDS and BTDA-4ODA, respectively. This relative closeness of T_g s implies a similar flexibility of the two molecular chains.

Figure 1.7 shows the dynamic mechanical response as a function of temperature for the polymers. Only the α transition is seen in the temperature range studied. The temperature of α transition is consistent to the T_g s as measured by DSC. However, the intensity of the loss tangent of the α relaxation decreases as 4ODA content increases. This finding provides an explanation for the decrease of solubility and fusibility with 4ODA
content as discussed above. The loss tangent is a measure of the energy dissipation of segmental motion at the glass–rubber transition. The decrease of segmental motion at higher temperature leads to high bulk viscosity and therefore difficulty in processing. The immobility of segments in BTDA–4ODA polyimide results in an inherent insolubility and infusibility. Increasing the 4ODA unit in the copolymer therefore decreases the segmental motion of the copolymers, and therefore decreases the solubility and the processability of...
Figure 1.7 Dynamic mechanical thermal analysis of BTDA-3DDS/4ODA copolyimides.
the polymers. Although the factor hindering for the motion of the BTDA-4ODA polyimide is not yet clear, it is probably due to the very strong intermolecular interactions of the polyimides.

1.3.2 Thermal Resistance of BTDA-3DDS/4ODA Copolyimides

Figure 1.8 shows the thermal gravimetry of both the polyimide homopolymers and their copolyimides. The thermal decomposition temperature of both polyimide homopolymers and their copolyimides are generally high, with the BTDA-4ODA polyimide decomposing at 575 °C under nitrogen and the polyimide homopolymer of BTDA-3DDS decomposing at 545 °C. The decomposition temperatures of the copolyimides are normally found between those of the polyimide homopolymers. However, the decomposition temperature of 10/90 and 20/80 BTDA-3DDS/4ODA copolymers are lower than those of the polyimide homopolymers, probably because of the low molecular weight oligomers.

1.4 Conclusions

Aromatic polyimides of BTDA-3DDS and BTDA-4ODA and their copolymers with high thermal resistance were synthesized by the solution imidization method. The insolubility and infusibility of the polyimides were studied. It was found that the poor solubility and fusibility of BTDA-4ODA polyimide was primarily due to the immobility of the segments. The lack of segmental motion of BTDA-4ODAD polyimide persisted even at high temperatures. The solubility of the polymer can be improved by copolymerizing it with a polyimides such as BTDA-3DDS polyimide that has high segmental mobility. The
Figure 1.8 TGA of BTDA–3DDS/4ODA copolyimides.

copolymer can retain the excellent solvent resistance of BTDA–4ODA polyimide while showing significant improvement in processibility. The thermal resistance of the copolyimide is determined by the structure of both components and by the copolymer composition.
1.5 References


2. Fegger, C., "Advanced Polymer Technology", a course provided at the University of Massachusetts, Amherst, 1991 and 1993.


2.1 Introduction

Recently many attempts have been made to improve the solubility and processibility of aromatic polyimides. Solubility of some polyimides has been reported to be improved by conducting the imidization in solutions.\textsuperscript{1-3} Polyimides with bulky structures were also reported to have better solubility.\textsuperscript{4-13} But though there has been progress in the development of soluble and processible polyimides, the mechanisms for the generally poor solubility and processibility of the materials, as well as the structure–property relation, have not been fully investigated. It was generally believed that imidization in the solid state caused a cross–linked structure in the polyimides, which resulted in their insolubility and infusibility.\textsuperscript{14-18}

High rigidity of the molecular chains of the aromatic polyimides was also assumed to be responsible for their poor solubility and processibility.\textsuperscript{19} But many polyimides that are not soluble in conventional organic solvents are soluble in strong acidic solvents such as sulfuric acid, without measurable loss of molecular weight. This contradictory result suggests that the poor solubility is not due to cross–linking.

As discussed in Chapter 1, the BTDA–3DDS polyimide homopolymer as synthesized is soluble in organic solvents such as DMAc and is melt–processable. The BTDA–4ODA polyimide homopolymer, however, is completely insoluble and infusible. For copolymers containing these two segmental units, solubility and fusibility decrease as the BTDA–4ODA content increases. Segmental mobility of homopolymeric BTDA–3DDS
and BTDA-4ODA polyimides and their copolyimides also decreases as BTDA-4ODA content increases. These results indicate a strong relation between the solubility, fusibility, and segmental mobility of BTDA-3DDS and BTDA-4ODA polyimides. The fact that both solubility and segmental mobility are correlated with BTDA-4ODA content of the copolymers suggests that both properties are controlled by a similar mechanism.

In this study, the segmental mobility of BTDA-3DDS/4ODA copolyimides is investigated by using dynamic mechanical thermal analysis (DMTA). The molecular interactions between chains of the BTDA-3DDS/4ODA polyimides is evaluated by using IR spectroscopy and thermal expansion coefficients measurements.

2.2 Methods and Materials

The BTDA-3DDS and BTDA-4ODA polyimide and copolyimide samples used in this study were synthesized by methods outlined in Chapter 1. The molecular structures of the two polymeric units, BTDA-3DDS and BTDA-4ODA, are shown in Scheme 1.6. The homopolymeric poly(BTDA-3DDS) and poly(BTDA-4ODA) and their copolyimides were synthesized through the solution imidization route. The poly(BTDA-4ODA) was prepared by solid-state imidization. Films of poly(BTDA-4ODA) were obtained by casting the corresponding polyamic acid solution onto a glass disk, followed by drying at room temperature for 1 day before curing in vacuum. All solution-synthesized copolyimides were molded into thick films by heating them to 350 °C in a vacuum and compressing at a pressure of about 2000 kg/cm². Films obtained by this method were normally 0.15 (±0.05) mm thick.

Dynamic mechanical thermal analysis measurements were conducted with a Polymer Laboratory DMTA apparatus, with a heating rate of 1-3 °C/min, depending on
the frequency range involved. The samples were purged with nitrogen during the experiment to prevent potential oxidation.

Thermal mechanical analysis (TMA) measurements were carried out in a Perkin Elmer Thermal Analysis System 4 under zero load. A heating rate of 1-3 °C/min was used, and the samples were purged with nitrogen.

The infrared spectroscopy of polyimides was carried out with a IBM System 30 IR spectrometer. Each spectrum were collected with 30 scans in nitrogen atmosphere. Samples were ground into a fine powder and mixed with KBr (about 1% concentration of sample). The powder mixtures were then compressed into transparent pellets for analysis.

2.3 Results and Discussion

2.3.1 Segmental Mobility of BTDA-3DDS/4ODA Copolymides

The relative segmental mobility of polymer chains in their viscoelastic state can be studied from the loss tangent of the α transitions. Figures 2.1 - 2.6 shows the loss tangents of the DMTA of poly(BTDA-3DDS) and poly(BTDA-4ODA) homopolymers and their copolymers at various frequencies. The peaks correspond to the α transitions of the materials. The β transitions, as reported by other authors in similar polyimide systems, were not visible in our results. The observed α transition temperatures are consistent with the DSC results shown in Figure 1.6. It was seen that the intensity of the α transition decreases as the BTDA-4ODA content increased. The intensity also slightly decreases with the frequencies.

The decrease in the segmental mobility has a profound effect on the melt processibility and solubility properties of the polyimides. The viscosity of polymers in their melt state is generally disproportional to the mobility of the polymer, as the
The following expression shows:\textsuperscript{21}

\[
[\eta] = \frac{1}{G_r \alpha M}
\]

where \(\alpha\) is the radius of the mobile species and \(M\) is the segmental mobility. The intensity of the \(\alpha\) transition is proportional to the total energy dissipation due to segmental motion; The energy dissipation of segmental motion is a function of segmental mobility and the number of segments. Therefore there are two possible mechanisms to explain the observed decrease in the intensity of the \(\alpha\) transitions: for systems with heterogeneous structure, the decrease in intensity of the \(\alpha\) transition reflects a decrease in the number of mobile segments; for systems with homogeneous structure, the decrease in intensity of the \(\alpha\) transition reflects a decrease in segmental mobility. A decrease of intensity of the \(\alpha\) transition as segmental mobility decreases has been reported for other polymers\textsuperscript{22} and have also been observed in dielectric studies of copolymers.\textsuperscript{23}

The segmental mobility of polymer chains at the \(\alpha\) transition is affected mainly by two parameters: chain flexibility and the segmental interaction. The segmental interaction determines the molecular friction as the segments creep against one another. The segmental interactions of poly(BTDA-3DDS) and poly(BTDA-4ODA) and their copolyimides will be discussed in the next section. The flexibility of the molecular chains essentially determines the size of the segments. The flexibilities of the polyimide chains of various structures have been calculated theoretically by Pavlova.\textsuperscript{5} These authors concluded that many aromatic polyimides with flexible bridging structures, such as ether or carbonyl linkages possess similar flexibilities. Their findings suggest that the flexibilities of the segments in poly(BTDA-3DDS) and poly(BTDA-4ODA) are approximately the same. Similar flexibilities for all the BTDA-3DDS/4ODA copolyimides was also supported by the observation of a weak dependence of their glass transition temperatures on composition. The glass transition temperature of the copolyimides
Figure 2.1 Loss tangents of BTDA-3DDS polyimide at various frequencies. ---, 0.3 Hz; --, 1 Hz; ---, 3 Hz; ----, 10 Hz.
Figure 2.2 Loss tangents of BTDA-3DDS/4ODA (90/10) copolyimide at various frequencies. ——, 0.3 Hz; — — —, 1 Hz; — — —, 3 Hz; — — — —, 10 Hz.
Figure 2.3 Loss tangents of BTDA-3DDS/4ODA (80/20) copolyimide at various frequencies. — —, 0.3 Hz; — — —, 1 Hz; — — — —, 3 Hz; — — — — —, 10 Hz.
Figure 2.4  Loss tangents of BTDA-3DDS/4ODA (60/40) copolyimide at various frequencies. — — , 0.3 Hz; — — — , 1 Hz; — — — — , 3 Hz; — — — — — , 10 Hz.
Figure 2.5 Loss tangents of BTDA-3DDS/4ODA (40/60) copolyimide at various frequencies. ——, 0.3 Hz; —•—, 1 Hz; —••—, 3 Hz; —•••—, 10 Hz.
Figure 2.6  Loss tangents of BTDA–4ODA polyimide at various frequencies. ---, 0.3 Hz; -- , 1 Hz; ---, 3 Hz; ---, 10 Hz.
mixture or to equilibrium concentration fluctuations. A systematic study with materials of different molecular weight is required to clarify this point.

Neutron scattering data for similar blends have suggested that there is a correlation length associated with long-range equilibrium concentration fluctuations. The distances are in the range of 2 nm (for a blend of perdeuterated polystyrene and a tetramethyl bisphenol-A polycarbonate)\(^7^6\) to 14 nm (for a mixture of protonated and deuterated polybutadiene).\(^7^6\) The implication of a correlation length is that the correlation function is monotonic and approximately exponential. It has been shown that the NMR data are consistent with a monotonic correlation function with a correlation length less than 1 nm. An exponential correlation function, with a comparable correlation length, decays to equilibrium much quicker at shorter-range than the Gaussian function, and would result in a faster initial spin-diffusion build-up. However, it is possible that the correlation length from Gaussian-type correlation function, which is consistent with the NMR data, is related to the scattering result. These latter distances are comparable, and this possibility is under investigation.

It is useful to compare other blends. These NMR data for PPO/PS are consistent with data of Kaplan\(^8^8\) and Caravatti et al.\(^4^3\) for the blend of PS and polyvinylmethyl ether (PVME), and we have produced similar data for PS/PVME with the heteronuclear method. Preliminary data have also been obtained for the mixture of ring deuterated polystyrene and chain deuterated polystyrene (PS\(_{6}/PS_{3}\)). Apart from the effects of deuteration, which should be small, for this blend \(\chi\) should be very close to zero. The NMR results for PS\(_{6}/PS_{3}\) are qualitatively similar to those of PPO/PS. In contrast for a blend of a polyimide and polybenzimidazole, where hydrogen bonding is present, spin diffusion correlation is at equilibrium within about 1 ms. Therefore, we suggest that the results which we obtain for PPO/PS may be typical for a blend with weakly interacting components.
increased only slightly as with the BTDA–4ODA content increased, as shown in Figure 1.6. The $T_g$ difference for the two homopolymers was only about 20 °C, a result suggesting that the two polyimide homopolymers have similar flexibilities.

The relative intensities of the $\alpha$ transition of the BTDA–3DDS/4ODA copolyimides and the homopolymers are listed in Table 2.1. The values have been normalized to the intensity of the poly(BTDA–3DDS) homopolymer to facilitate comparison. It is seen from Table 2.1 that the intensity of the $\alpha$ transition, and thus the segmental mobility of the BTDA–3DDS/4ODA copolyimides, was strongly dependent on copolymer composition. A 10% mole ratio of 3DDS/4ODS in the copolymer reduced the segmental mobility of the polyimide by about 50%. Further increases in BTDA–4ODA content in the copolymer further decreased segmental mobility. For the poly(BTDA–4ODA) homopolymer, the segmental mobility was reduced to only 9% of the value observed for the poly(BTDA–3DDS) homopolymer. This result suggests that segmental mobility of the BTDA–3DDS/4ODA copolyimides is greatly reduced by the presence of 4ODA units in the polyimide chain. This retarded segmental mobility thus results in the poor fusibility and solubility observed for the of the materials.

It is informative to study the activation energy of segmental motion at the $\alpha$ transition for BTDA–3DDS/4ODA copolyimides. This parameter can be calculated from data collected in multi-frequency experiments by using an Arrhenius equation. Figure 2.7 shows the activation energy of segmental motion at the $\alpha$ transition for the copolyimides as a function of copolymer composition. The activation energies of those BTDA–3DDS/4ODA copolyimides measured was higher than those of other linear polymers. An increase in the activation energy as BTDA–4ODA content increased was observed. The correlation is consistent with our previous conclusion that segmental mobility decreases as BTDA–4ODA content increases.
Figure 2.7 Activation energy of segmental motion for BTDA-3DDS/4ODA copolyimides as a function BTDA-4ODA content.
Table 2.1 Relative intensity of the α transition of the BTDA-3DDS/4ODA copolyimides.

<table>
<thead>
<tr>
<th>Copolyimide Composition&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Normalized Intensity&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>1.0</td>
</tr>
<tr>
<td>90/10</td>
<td>0.57</td>
</tr>
<tr>
<td>80/20</td>
<td>0.43</td>
</tr>
<tr>
<td>60/40</td>
<td>0.3</td>
</tr>
<tr>
<td>40/60</td>
<td>0.2</td>
</tr>
<tr>
<td>0/100</td>
<td>0.088</td>
</tr>
</tbody>
</table>

<sup>a</sup> Composition is expressed as the ratio of moles of BTDA-3DDS units to moles of BTDA-4ODA units.

<sup>b</sup> All the values are divided by the actually intensity of BTDA-3DDS polyimide.

We have seen that increasing the BTDA-4ODA content in the BTDA-3DDS/4ODA copolyimides reduced the segmental mobility of the polymers, assuming that the systems have homogeneous structures. If the structure of the system is inhomogeneous and the segments in each phase at the α transition undergo segmental motions with different relaxation times, the intensity of α transition of each phase is also related to the number of segments in the phase. The mechanisms of energy dissipation at the α transition can be studied by examining the relaxation of segmental motions. The loss tangent of α transition of polymers with a homogeneous structure can be expressed as

\[
\tan \delta \approx \frac{\omega \tau}{1 + \omega^2 \tau^2}
\]
where $\omega$ is the frequency of applied force and $\tau$ is the segmental relaxation time. For polymers with heterogeneous structure, the total loss tangent of $\alpha$ transition is the sum of loss tangent from all the phases, and

$$\tan \delta \propto \sum_{i=0}^{\infty} \frac{P_i \omega \tau_i}{1 + \omega^2 \tau_i^2},$$

where $P_i$ is the volume fraction of phase $i$. Thus, the mechanisms of segmental motion can be analyzed by the distribution of loss tangent of $\alpha$ transitions.

Figure 2.8 shows the normalized loss tangent and their related half–height width of $\alpha$ transition for the BTDA–3DDS/4ODA copolyimides as measured at a 1.0 Hz frequency. It was observed that the width of the $\alpha$ transition increased as BTDA–4ODA content increased. The poly(BTDA–3DDS) had the most narrow $\alpha$ transition and the poly(BTDA–4ODA) homopolymer had the widest. As BTDA–4ODA content increased, the loss tangent of $\alpha$ transition of the copolyimides broadened and shifted toward higher temperatures. The broadening of the $\alpha$ transition as BTDA–4ODA content increased indicates that the structure of the BTDA–3DDS/4ODA copolyimides becomes more heterogeneous as the BTDA–4ODA content increased. This inferences in turn suggests that the decrease in the intensity of the $\alpha$ transition correlated with increasing BTDA–4ODA content for BTDA–3DDS/4ODA copolyimide is attributable to the reduction in the absolute number of mobile segments. In other words, only a small portion of the polyimide segments are able to resonate with the applied force at the $\alpha$ transition. The large volume fraction of the immobile phase in the poly(BTDA–4ODA) makes that polymer insoluble and infusible.

The structure of other fully aromatic 4ODA–related polyimides (for instance, PMDA–4ODA based polyimide) has been studied by several investigators. It was found that this poly(PMDA–4ODA) possesses local ordering. Segmental aggregation in the polyimide resulted in abnormal dynamic mechanical properties. Other studies also showed a long range cooperative motion of the main chain associated with the glass
transition. Even if the structure of the segmental aggregation is still not very clear from their studies, we can speculate that similar segmental aggregation exists in poly(BTDA-4ODA) but is less likely in the poly(BTDA-3DDS). Therefore, the segmental motion in the homopolymer poly(BTDA-3DDS) above the glass transition temperature is less hindered than that in the homopolymer poly(BTDA-4ODA), in which most of the
segments form some kind of molecular aggregation. According to this notion, only a small number of segments in poly(BTDA-4ODA), i.e., those not aggregated, would be able to participate in the cooperative, large-scale micro-brownian-type motion. As the BTDA-4ODA content increases in the copolymers, the segments of the polymer main chains are more and more likely to associate with one another, and this aggregation leads to increasingly smaller numbers of free segments that can respond at the glass transition temperature.

The forgiving conclusions are based on the results of studies of molecular motion and the thermal properties of the polymers. However, the dependence of segmental aggregation on the BTDA-4ODA structural unit suggests that the molecular structure is responsible for the segmental aggregation. Wide angle X-ray diffraction and small angle X-ray scattering studies have shown that the polyimide poly(PMDA-4ODA) has a zigzag stack morphology,27–30,32 This structure is probably due to the electron-donating ability of the 4ODA group and the electron-accepting ability of the BTDA group. Thus when molecular chains stack parallel to one another, they form an intermolecular charge transfer complex. The strong segmental aggregation in poly(BTDA-4ODA) prevents most of the segments from participating in large scale brownian motion in their viscoelastic state, and this constraint is responsible for the infusibility of the material. 3DDS has a weak electron-donating ability, so molecular aggregation in homopolymers of this compound is unlikely. Because segmental aggregation in poly(BTDA-3DDS) is very weak or absent in its viscoelastic state, most of the segments of the polymer can undergo large scale brownian motion, a capability resulting in enhanced solubility and thermal processibility in its viscoelastic state.
2.3.2 Segmental Interaction in BTDA-3DDS/4ODA Copolyimides

We have seen that both the segmental mobility and the number of mobile segments of the BTDA-3DDS/4ODA copolyimide decreased as BTDA-4ODA content increased. It is believed that the hindrance in the segmental motion with different molecular structure is the result of intermolecular interaction and coupling. For organic solids like polymers, molecular interaction is mainly attributable to the Van der Waals force, which is related to the linear thermal expansion coefficient \(^{14}\) (see Appendix):

\[
\alpha = -\frac{3d}{2B^2N_n}C_v
\]

where \(B\) and \(C\) are the Lanner-Jones repulsive force constant and attractive force constant, respectively. \(C_v\) is the specific heat capacity, \(N\) is Avogadro's number, and \(n\) is the coordination number.

Figure 2.9 shows the linear thermal expansion coefficients of BTDA-3DDS/4ODA copolyimides at their viscoelastic state as a function of copolymer composition. It is seen that the thermal expansivity of the polymers decreased as the BTDA-4ODA content increased, a result indicating that there is an increase in intermolecular interaction as the BTDA-4ODA content increased.

Although the thermal expansion coefficients suggested a stronger molecular interaction at higher BTDA-4ODA content, they did not reveal the molecular origin of this interaction. The mechanism of the segmental interaction can be investigated by spectroscopy studies. Figure 2.10 shows the transmittance band of carbonyl asymmetrical stretching vibration. A gradual shift of the frequencies to lower wavenumber is seen for higher content of 4ODA structure, a result indicating a weakening of the carbonyl double bond as a result of charge coupling with other groups. The total shift is about 4 cm\(^{-1}\) from poly(BTDA-3DDS) homopolymer to poly(BTDA-4ODA) homopolymer.
Figure 2.9  Linear thermal expansion coefficients of BTDA-3DDS/4ODA copolyimides above their $T_g$'s as a function of BTDA-4ODA content.
As discussed above, higher content of 4ODA structure leads to more intense molecular interaction. This interaction may be due to the dipole-dipole electron coupling between the electron-deficient carbonyl group and the electron abundant phenyl ring of the amine component. The coupling interaction of poly(PMDA-4ODA) and poly(BTDA-4ODA) polyimides were also reported by fluorescence spectroscopic studies. The
presence of the ether group in the diamine component would enhance the electron density of the phenyl ring of the diamine component, and result in a stronger interaction. On the other hand, the sulfone group in the 3DDS structure is a electron-withdrawing group and would lower the electron density, thereby resulting in a weaker interaction.

2.4 Conclusion

We can conclude that the stronger dipole–dipole interaction of BTDA–4ODA segments results in a heterogeneous structure of BTDA–3DDS/4ODA copolyimides with a larger fraction of immobile segments. The strong segmental interaction also reduces the segmental mobility of the copolyimides at their viscoelastic state. The low volume fraction of the mobile phase and the weak segmental mobility at BTDA–3DDS/4ODA copolyimides with high BTDA–4ODA content are responsible for the poor solubility and processibility of the materials. The molecular interaction can be estimated from the thermal expansion of the polymers. The strong intermolecular interaction is probably due to the formation of charge coupling resulting from the electron–donating ability of 4ODA group and the electron–accepting ability of the BTDA group.

2.5 References


2.6 APPENDIX

The intermolecular interaction of organic solids can be described by the Lennard-Jones equation:^^

\[ E = \frac{B}{R^{12}} - \frac{C}{R^6} \]  

(2.1)

where \( B \) is the repulsive force constant, \( C \) is the attractive force constant, and \( R \) is the distance. Because the different forces follow different power laws, the potential energy well is asymmetric. The asymmetric potential energy well can also be expressed by a Taylor expansion series as:^^

\[ E = B'R^2 + C'R^3 + \ldots \]  

(2.2)

For the first approximation, we can assume that the cubic term is sufficient to match the potential energy well:

\[ E = B'R^2 + C'R^3 \]  

(2.3)

Then the linear thermal expansion coefficient \( \alpha \) can be obtained as:^^

\[ \alpha = \frac{3C'}{2B'^2N_n} C_v \]  

(2.4)

where \( B' \) and \( C' \) are constants similar to the constants in equation (2.1). \( N \) is Avogadro's number, \( n \) is the coordination number, and \( C_v \) is the specific heat capacity.

The molecular interaction in the polymeric solids can also be treated by the equation of state, which has been successfully applied to the glassy polymers and polymer blends.^^ For particles with an intermolecular energy of the van der Waals type, the partition function \( Z \) can be expressed as,

where \( g \) is the geometry factor, \( v \) is the particle volume, \( v^* \) is the reduced particle volume.
\[ Z = Z_{\text{comb}} \left[ \xi \left( \frac{1}{v^3} - \frac{1}{\nu^3} \right)^3 \right]^{\text{rcn}} \frac{n}{2\pi kT} \]  

(2.5)

\( \xi \) is the surface area, \( \xi \) the degrees of freedom, \( n \) the number of particles, and \( \sigma \) is the interaction energy constant. Equation (2.5) is usually written in the reduced form, and

\[ Z = Z_{\text{comb}} \left( \frac{g}{\nu^3} \right)^{\text{rcn}} \left( \frac{1}{\nu^3} - 1 \right)^{\text{rcn}} \frac{n}{\nu^3 T} \]  

(2.6)

and the equation of state:

\[ \bar{p} \frac{\bar{v}}{T} = \frac{1}{\frac{\bar{v}^3 - 1}{\bar{v}} T} \]  

(2.7)

where the reduced parameters are:

\[ \bar{v} = \frac{v}{\nu^*} \]  

(2.8)

\[ T = \frac{T}{T^*} = \frac{2\nu^* cRT}{s\eta} \]  

(2.9)

\[ \bar{p} = \frac{p}{\nu^*} = \frac{2p\nu^*^2}{s\eta} \]  

(2.10)

Experimentally, the reduced volume can be obtained through the thermal expansivity at \( p=0 \) by means of the expression:

\[ \frac{1}{\bar{v}^3} = 1 + \left( \frac{\alpha T}{3 \left( 1 + \alpha T \right)} \right) \]  

(2.11)

By substituting equations (2.9), (2.10) and (2.11) into equation (2.7) and keeping the lower order terms, the interaction energy can be estimated as a first approximation:

For a specific temperature region, the above expression can be simplified to
\[ s\eta = \frac{6vcr}{\alpha} \left( 1 + \alpha T \right) \]  

\[ s\eta = 6 \frac{vcr}{\alpha} \]  

i.e., the intermolecular interaction energy is proportional to the reciprocal of the volume thermal expansion coefficient. This result is exactly the same as that derived from the energy well model, as discussed above.
3.1 Introduction

Blending is still the most widely accepted method used to modify properties of the polymeric materials. The properties of the blends usually depend on the miscibility and the domain structure of the materials. Because most of the thermoplastic materials are generally processed in their melt states, phase separation usually occurs for blends that have LCST below the processing temperature. The studies of phase separation of polymer blends will provide information for understanding and controlling the morphology and structure of materials. There are also academic interests for studying phase separation. Many of the theoretical predictions can be tested in polymeric systems in which the high viscosity of polymers allows phase separation processes to be measured.

The theory of spinodal decomposition was introduced by Cahn and Hilliard\textsuperscript{1-4} for small molecules of liquids, metal alloys, and glasses. In a metastable region, where the concentration fluctuation everywhere is very small, the Cahn–Hilliard theory predicts an exponential decay of the structure factor. However, for polymeric blends, it is usually found that the linear Cahn–Hilliard theory does not explain experimental observation even in the early stage of phase separation\textsuperscript{5-7}. Even though many modifications have been tried in an effort to correct the discrepancies,\textsuperscript{8-13} little consideration has been given to the diffusivity of polymer segments.\textsuperscript{14}

For small molecular systems, each molecular species possesses a very high mobility, and the phase separation process is primarily determined by thermodynamic driving.
forces. As molecular weight increases, the diffusivity of polymer chains decreases and thus becomes increasingly important in the dynamics of phase separation. For polymeric systems in which molecular chains are entangled with one another, molecular chain diffusivity is highly dependent on the state of the polymers. Polymer segments are frozen in their glass state, but undergo reptation in their viscoelastic state. When phase separation of polymer blends occurs at temperatures above their T_g, the chain diffusivity is greatly dependent on the temperature, and thus may strongly affect the diffusion process in phase separation. Thus, it is necessary to consider the role of the chain diffusivity in the dynamics of phase separation of polymer blends.

Most early studies of the dynamics of phase separation of polymer blends assumed a constant mobility of the diffusion species$^{15-18}$. This assumption is approximately valid only for blends with wide miscibility windows$^{23,24}$, i.e., where the LCSTs of the blends are much higher than the glass transition temperatures. We have recently found that blends of polyimides with polyethersulfone show either a very narrow miscibility window above the common glassy transition of the blends$^{21-24}$ or the LCST far below the glassy transition temperature of the blends$^{21}$. The narrow miscibility window of polyimide/polyethersulfone blends will result in a strong effect on the dynamic behavior of phase separation. In this study, the dynamics of phase separation of several polyimide/polyethersulfone blends are studied by using thermal analysis. The deviation from the Cahn–Hilliard theory will be examined by a chain-diffusivity controlled mechanism of phase separation.

3.2 Methods

Polyimide XU218 was obtained as a yellowish powder from Gibar Gagy Co. The polymer has an intrinsic viscosity of 0.63 dL/s as measured in DMAC at 35 °C and a glass transition temperature of 150 °C.
3.3 Theoretical Background

The stability of a homogeneous phase in a binary mixture is determined by the second derivative of the free energy, \( f \) with respect of concentration \( C \). If \( \frac{\partial^2 f}{\partial C^2} < 0 \), the phase is unstable; if \( \frac{\partial^2 f}{\partial C^2} > 0 \), the phase is metastable. The concentration at \( \frac{\partial^2 f}{\partial C^2} = 0 \) is called the spinodal. If the mixture is quenched into the metastable region, it will undergo spinodal decomposition driven by a thermodynamic energy force. The theory of spinodal decomposition was first introduced by Cahn and Hilliard\(^1\) and predicts an exponential growth of concentration fluctuation of phase separation. By expressing the concentration fluctuation as a Fourier series, the time dependence of concentration of a phase at position \( X \), \( C(X,t) \), is given as:

\[
C(X,t) - C(X,0) = \sum_{l=0}^{\infty} e^{R_{CH}(\beta_l) t} [A(\beta_l) \cos(\beta_l X)]
\]

(3.1)

where \( t \) is the time, \( A \) and \( \beta \) are structural parameters. The rate constant of concentration fluctuation, \( R_{CH} \), is given as:

\[
R_{CH}(\beta) = -M \frac{\partial^2 f}{\partial C^2} \beta^2 - 2 M \kappa \beta^4
\]

(3.2)

where \( M \) is diffusivity constant of polymer chains and \( \kappa \) is the interfacial energy parameter. Equation (3.2) describes the concentration changes of a fixed domain (at a fixed position \( X \)). It is seen that the Cahn–Hilliard rate constant \( R_{CH}(\beta) \) is a function of chain diffusivity, \( M \), and the thermodynamic energy \( \frac{\partial^2 f}{\partial C^2} \), which are functions of concentration.

One common assumption in the application of the Cahn–Hilliard theory is constant chain diffusivity. This assumption may be valid for small molecular mixtures, metallic alloys, and glasses.\(^{26-28}\) However, when applied to polymer systems, most studies found
that the Cahn–Hilliard theory does not accurately predict dynamic behavior even at the early stages of phase separation for polymer mixtures. Much consideration has been given to the concentration dependence of thermodynamic energy, and modifications of Cahn–Hilliard’s linear theory and newer theories have been reported. These can be found in the work of Cook,\textsuperscript{8} Langer,\textsuperscript{10} Kawasaki,\textsuperscript{11} and recently Furukawa\textsuperscript{12}.

To study the mechanisms for the nonlinearity in the dynamics of phase separation of polymer blends, one needs to take into account the time dependence of diffusivity of polymer chains in each phase. The diffusivity of polymer chains consisting of \( N \) segments with bond length \( b \) and a friction constant \( \xi \) in a miscible phase in their viscoelastic state can be described by the reptation model\textsuperscript{29}:

\[
D_s = \frac{k_B T \alpha^2}{N^2 \xi b^2} \tag{3.3}
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \alpha \) is the step length of a primitive chain, and \( b \) is the effective bond length. Because segmental brownian motion of polymer chains ceases below the glass transition temperature, the dependence of polymer chain diffusivity may be expressed as a function of the glass superheating \( (T_a - T_g) \), where \( T_a \) is the annealing temperature. Equation (3.3) can be rewritten as

\[
D_s \propto k_B (T_a - T_g) \tag{3.4}
\]

The chain diffusivity of polymers during phase separation is a dynamic parameter that changes as the \( T_g \) changes with time.\textsuperscript{30} Equation (3.1) can then be rewritten as

\[
C(X,t) - C(X,0) = e^{H_{CH}(T_a - T_g(t))t} \cos(\beta X) - e^{H_{CH}(T_a - T_g(t))t} \cos(\beta X)
\]

where \( T_g(t) \) is the glass transition temperature of phase at position \( X \) at time \( t \). Equation
(3.5) describes the changes of the concentration fluctuation during phase separation of polymer blends with the time–dependent chain diffusivity represented by the reptation model.

The above derivation considers the concentration changes at a fixed position X. Similarly one can derive the changes of probability of finding a certain concentration within the system. Following an approach similar to that in Cahn–Hilliard theory, the probability of finding a certain concentration, \( P(C,t) \), is given as

\[
P(C,t) = \sum_{i=0}^{\infty} e^{H(B_i)t} [A(B_i) \cos(B_i C)]
\]  

(3.6)

where \( A \) and \( B \) are structural parameters. The rate constant of the decomposition of a miscible phase, \( R'_d \), is given by

\[
R(B) = -M_0^2 \frac{\partial^2 f}{\partial C^2} CB^2 - 2M_0 CB^4
\]  

(3.7)

Note that \( R' \) is measured at a fixed concentration; thus \( R' \) is independent of the concentration.

We have discussed the different approaches for the dynamics of phase separation of polymer blends. The simple Cahn–Hilliard theory as given in equation (3.1) describes the concentration changes of a fixed phase with a constant chain diffusivity. The dynamics of phase separation with a time–dependent chain diffusivity can be represented by a reptation model, as expressed in equation (3.3). Equation (3.6) reveals the dynamics of the decomposition of a homogeneous phase at a fixed concentration. Because the latter describes the dynamics at a fixed concentration, the rate constant is not affected by the concentration during phase separation. The above approaches will be used to analyze the dynamics of phase separation of several polyimide/poly(ethersulfone) blends.
3.4 Results and Discussion

3.4.1 Poly(BTDA-FDA)/Poly(ethersulfone) Blends

A few assumptions and approximations must be made to use the thermal analysis for the study of dynamics of phase separation of polymer blends. First, the mole concentration of the blends can be approximated by a linear function of glass transition temperature:

\[ T_g = T_g^i + (T_g^A - T_g^B) m_i \]  \hspace{1cm} (3.8)

where \( T_g \) is the common glass transition temperature of the blend, \( T_g^i \) and \( m_i \) are the glass transition temperature and the concentration of pure \( i \)-th polymer, respectively. Thus the concentration changes during phase separation can be obtained by measuring the changes of glass transition temperatures. Equation (3.8) can be derived from the two-parameter empirical Expression of Wood.\(^{31}\) Figure 3.1 shows the glass transition temperature of miscible poly(BTDA-FDA)/PES blends as a function of poly(BTDA-FDA) weight fraction. The solid line is the best fit using the Equation of Wood.\(^{31}\) It is seen that the line fairly represented the experimental data. This linear relationship will also be used for other blend systems in this study.

Secondly, assuming that the polymer segments at a given concentration of a miscible state undergo glass transition with the same mechanism, and neglecting the overlap of glass transition, the volume fraction of the materials with a given \( T_g \) can be approximated by the intensity of glass transition. Thus the relative volume fraction of the material with a \( T_g \) at the peak position of the DSC derivative can be represented by the peak intensity.

Figure 3.2 shows the derivatives of DSC curves at various blend compositions annealed for 10 minutes. Phase separation occurred for samples annealed at temperatures
above their glass transition temperatures. The blends became cloudy after annealing, indicating the occurrence of phase separation. For blends of 10/90 and 20/80 compositions, only the peak for the PES abundance phase is visible due to the little amount of materials in the polyimide abundance phase after phase separation. The peak temperature shifts toward the glass transition temperature of PES as the annealing temperature increased. For blends of compositions from 30/70 - 70/30, multiple peaks

Figure 3.1 Glass transition temperatures of poly(BTDA-FDA)/PES blends as a function of composition.
were seen for annealed samples. A peak at the temperature near the $T_g$ of PES gradually emerged, and the peak for the polyimide abundance phase moves toward the annealing temperature as the annealing temperature increased, whereas the intensity at the temperature of initial miscible phase decreased. The temperature of peak for the PES abundance phase is relatively fixed but the intensity increased as the annealing temperature increased. This result inferred that the PES abundance phase had a relatively fixed concentration. Increasing the annealing temperature only increased the volume fraction of the PES abundance phase. For the poly(benzoimidazole–fluorenone) abundant phase, increasing the annealing temperature increased the polyimide concentration of the phase, a result indicating that the phase separation was not in equilibrium. The 90/10 poly(benzoimidazole–fluorenone)/PES blend was similar to that of 10/90 and 20/80 blends where only one peak was seen.

The dynamic pattern of the DSC derivatives can be understood from the phase diagram depicted in Figure 3.3. It is believed that the poly(benzoimidazole–fluorenone)/PES blends possesses a LCST curve below the glass transition temperatures. Thus the blends undergo phase separation when annealing at above the glass transition temperature. As discussed above, the glass transition temperature of the blend in a miscible state is a linear function of concentration. Such the shift of $T_g$'s of each phase indicates the change of concentration during phase separation. The relative volume fraction of the material with a $T_g$ at the peak position can be represented by the peak intensity of the DSC derivative. The decrease of the peak intensity at the glass transition temperature of the unannealed samples with increasing annealing temperature indicates the decomposition of original miscible phase.

The phase separation does not reach the spinodal points immediately. Instead, many intermediate phases with a spectrum of compositions are formed as the original miscible phase decomposes. A two-phases model may be used to describe these multi-
Figure 3.2 Derivatives of DSC traces for poly(BTDA-FDA)/PES blends annealed for 10 minutes at various temperatures. (continued next page)
Figure 3.2 (continued)

10/90: (a) Unannealed; (b) 230 °C; (c) 240 °C; (d) 250 °C; (e) 260 °C; (f) 400 °C.
20/80: (a) Unannealed; (b) 255 °C; (c) 265 °C; (d) 275 °C; (e) 285 °C; (f) 295 °C; (g) 400 °C.
30/70: (a) Unannealed; (b) 275 °C; (c) 285 °C; (d) 295 °C; (e) 305 °C; (f) 400 °C.
40/60: (a) Unannealed; (b) 285 °C; (c) 295 °C; (d) 305 °C; (e) 315 °C.
50/50: (a) Unannealed; (b) 290 °C; (c) 300 °C; (d) 310 °C; (e) 320 °C.
60/40: (a) Unannealed; (b) 310 °C; (c) 320 °C; (d) 330 °C; (e) 340 °C.
70/30: (a) Unannealed; (b) 320 °C; (c) 330 °C; (d) 340 °C; (e) 350 °C; (f) 400 °C.
90/10: (a) Unannealed; (b) 340 °C; (c) 350 °C; (d) 360 °C; (e) 370 °C.

phases structure in which concentration of each phase can be estimated by the glass transition temperatures of the peaks in the DSC derivatives. It is seen that for the annealed samples, the glass transition temperatures of the blends are a function of annealing temperature. For the PES abundant phase, in general increasing the annealing temperature only slightly decreases the glass transition temperature of PES abundant phase but significantly increases the peak intensity, indicating the concentration of the phase is closed to equilibrium. The glass transition temperature of the poly(BTDA-FDA) abundant phase approaches the annealing temperature. Increasing the annealing temperature increases the glass transition temperature of the poly(BTDA-FDA) abundant phase. This suggests that the spinodal point is not reached. The composition of the poly(BTDA-FDA) abundant phase is determined by the glass transition temperature of the phase. As the glass transition temperature approaches the annealing temperature, phase separation ceases.

The relevant mechanisms are depicted in Figure 3.3. For PES abundant phase, the annealing temperature is much higher than its glass transition temperatures, and thus the spinodal point can quickly reached. Increasing the annealing temperature can only result in formation of more materials in the PES abundant phase. For poly(BTDA-FDA) abundant phase, the its glass transition temperature is above the spinodal point, and thus the phase concentration is controlled by the glass transition temperature. As depicted by equation (3.3), the rate constant of phase separation is a function of glass superheating.
$$T_a - T_g$$: Thus when the glass transition temperature reaches the annealing temperature, the chain diffusivity is very small and therefore the rate constant approaches zero.

We have discussed the phase separation mechanisms for poly(BTDA-FDA)/PES blends quantitatively. Qualitative analysis was not attempted because the broad distribution in the peak intensities of the DSC derivatives. The latter was probably due to the large difference in the glass transition temperatures of the two homopolymers. Thus
phase separation occurs continuously when the $T_g$'s were measured by DSC. This problem is insignificant for blends with a smaller difference in glass transition temperatures.

3.4.2 DOW2080/Poly(ethersulfone) Blends

The miscibility of these blends has been reported by this laboratory. Single $T_g$'s were observed for all compositions through DSC measurement. The blends show an apparent LCST behavior below the glass transition temperatures. Thus, when annealed at temperatures above their glass transition temperatures, phase separation occurs.

Figure 3.4 shows the derivatives of the DSC traces as a function of annealing time for samples of the 50/50 weight ratio DOW2080/PES blend annealed at 290°C and 300°C. The unannealed sample possessed a single narrow peak at a temperature of 257°C, as seen in the DSC derivative curve. The glass transition temperature, $T_g=257°C$, was associated with the initial miscible phase of the blend and thus the intensity at $T_g=257°C$ reflects the relative volume fraction of the initial miscible blends. For samples annealed at both temperatures, the peak became broadened and gradually split into two peaks at longer annealing times. A higher annealing temperature apparently resulted in a more complete of phase separation. The intensity at the temperature of $T_g=257°C$, the glass transition temperature of unannealed sample, decreases as the annealing time increased, indicating the decomposition of the initial miscible phase.

As seen with the poly(BTDA-FDA)/PES blends, the phase separation of DOW2080/PES did not reach the spinodal points immediately. As the initial miscible phase decomposes, many intermediate phases with a spectrum of compositions are formed. This result is demonstrated by the emergence of two broad peaks as the annealing time increased. The positions of the two peaks also moved further apart as annealing time lengthened, a result indicating the continuous changes of concentration in both phases.
Figure 3.4 Derivatives of the DSC traces for samples of the 50/50 DOW2080/PES blend annealed at: (a) 290 °C for various time. (A) 0 min; (B) 1 min; (C) 2 min; (D) 4 min; (E) 8 min; (F) 20 min. (b) 300 °C for various time. (A) 0 min; (B) 0.5 min; (C) 1 min; (D) 2 min; (E) 3 min; (F) 4 min; (G) 8 min.
If the multiphase structure of the phase separated blends can be represented by a two-phase model, each peak temperature represents the glass transition temperature of the phase in the blend. Figure 3.5 shows the logarithmic plots of the glass transition temperatures of both phases as a function of time for samples of the 50/50 DOW2080/PES blend annealed at 290 °C and 300 °C. The Cahn–Hilliard decomposition rate, as given in equation (2), can be calculated from the slope of the plots. It is seen that the phase separation proceeded rapidly at the beginning, but slowed rather abruptly after several minutes. Increasing the annealing temperature increased the initial rate of phase separation. The time dependence of the phase separation rate suggests that the phase separation did not follow the Cahn–Hilliard theory.

The nonlinear dynamics of phase separation may be caused by the time dependence of chain diffusivity and the thermodynamic driving force. The effect of chain diffusivity in the phase separation can be examined by using equation 3.4. Figures 3.6a and 3.6b show the logarithmic plots of the glass transition temperatures of both phases of the blends annealed at 290 °C and 300 °C as a function of superheating, \((T_a - T_g)t\), where \(T_a\) is the annealing temperature and \(T_g\) is the glass transition temperature of the DOW2080–abundant phase. Since the superheating is larger for PES abundance phase than that for the DOW2080 abundance phase, the overall rate constant is controlled by the chain diffusivity in the DOW2080 abundant phase. Thus only the superheating from the DOW2080 abundance phase is considered. Only data with relatively large superheating \((T_a - T_g)\) are presented in the figures because the use of \(T_g^s\) in the final state to calculate the chain diffusivity might overestimate its dynamic dependence on the glass transition temperature.

It is seen that linear relations were obtained for samples annealed at both temperatures. The rate constants as obtained from the slopes for samples annealed at 290 °C were 0.035 and 0.037 for the PES-abundant phase and DOW2080 phase, respectively.
Figure 3.5 Plots of ln\((T_g - T^\circ)\) as a function of time for samples of the 50/50 DOW2080/PES blend annealed at: (a) 290 °C. (b) 300 °C. Filled triangle: PES abundant phase; open triangle: XU218 abundant phase.
Figure 3.6 Plots of $\ln(T_g - T_0)$ as a function of $(T_a - T_g)t$ for samples of the 50/50 DOW2080/PES blend annealed at: (a) 290 °C. (b) 300 °C. Filled triangle: PES abundant phase; open triangle: XU218 abundant phase.
For samples annealed at 300°C, the corresponding rate constants were 0.038 and 0.039. Good agreement were seen for the rate constants calculated from both phases. The rate constants for samples annealed at 300°C were slightly higher than those for samples annealed at 290°C, although the difference is well within the experimental error of about 15%. Because the time dependence of chain diffusivity has been taken into account in the plots, the rate constants obtained from the slopes can only be affected by the time dependence of thermodynamic driving force. Thus, the linear relation suggests that the thermodynamic driving force is nearly constant throughout phase separation. In other words, the time dependence of the phase separation rate of the 50/50 DOW2080/PES blend is mainly the result of the chain diffusivity of polymers.

To further reveal the effects of various mechanisms in the dynamics of phase separation for the 50/50 DOW2080/PES blend, one can also examine the dynamics of decomposition of the initial miscible phase. Figure 3.7 shows logarithmic plots of the heat flow rate in the DSC derivatives of the original miscible phase as a function of time for samples annealed at 290°C and 300°C. The use of the derivative intensity for the volume fraction of materials might slightly overestimated the volume fraction for the initial period due to the overlap of glass transitions. Linear relations were obtained for the initial stages of phase separation. At the later stages, the curves leveled off as the annealing time increased. A higher annealing temperature did not significantly affect the rate constant, but increased the extent of phase separation.

The independence of the initial decomposition rate constant on annealing temperature indicates that the decomposition of the initial miscible phase is relatively independent of the formation of new phases during phase separation. The decomposition rates of the original phase were nearly the same for both annealing temperatures. At the later stages the decomposition rate of the initial miscible phase slowed down.

The deviation from a straight line at the later stage was not clear. The impreciseness of using the intensity of the glass transition of a phase to represent its
Figure 3.7 Plots of LN(dC_p/dT) at T_g = 257 °C as a function of annealing time for samples of the 50/50 DOW2080/PES blend. Filled triangle: annealed at 290 °C; open triangle: annealed at 300 °C.

volume fraction makes the judgement difficult. The glass transition of polymer chains is a dynamic process, and thus the intensity of the transition takes a certain width. Fluctuations in concentration and structures of each individual phase will further broaden the distribution of the intensity. Thus, for systems containing a spectrum of phase domains, there will be an extensive overlap in the intensity of glass transitions. This
overlap might be very significant when the intensity of the phase is low. There might be other mechanisms of phase separation that lead to the deviation from linearity such as the nucleation mechanism.

3.4.3 XU218/Poly(ethersulfone) Blend

The XU218/PES blends behave differently from the two blends already discussed earlier. The XU218/PES blends showed a single \( T_g \) and a narrow miscibility window above their \( T_g \).  

Figures 3.8a and 3.8b show the derivative of the DSC traces for samples of the 50/50 XU218/PES blend annealed at 290\(^\circ\)C and 304\(^\circ\)C. Single peak was observed for the unannealed sample. For annealed samples, the intensity at the glass transition temperature, \( T_g = 263\)^\(\circ\)C decreased, a result indicating the decomposition of the original miscible phase. The single peak broadened and separated into two peaks as the annealing time increased. The shift of the peak temperature with time indicates a change in the concentration of each phase. The glass transition temperatures of the blends were used to monitor the concentration fluctuation, as was done for the DOW2080/PES blends.

Figures 3.9a and 3.9b show the logarithmic plots of the glass transition temperatures of both phases for samples of the 50/50 XU218/PES blend annealed at 290\(^\circ\)C and 304\(^\circ\)C as a function of time. The Cahn–Hilliard rate constants can be obtained from the slopes of the plots. Like in the 50/50 DOW2080/PES blend, this blend showed a fast initial phase separation rate for samples annealed at both temperatures. The phase separation slowed down in samples annealed for longer periods. The decrease in the rate constant at the later stages was more significant in the sample annealed at the higher temperature. Obviously, the phase separation kinetics do not follow the Cahn–Hilliard theory.
Figure 3.8 Derivatives of DSC traces for samples of the 50/50 XU218/PES blend annealed at two temperatures. Above: annealed at 290 °C, (a) 30 min; (b) 1 min; (c) 2 min; (d) 4 min; (e) 8 min. Bottom: annealed at 304 °C, (a) 30 min; (b) 1 min; (c) 3 min; (d) 4 min; (e) 8 min; (f) 10 min. Each trace represents the average of data from two to four runs.
Figure 3.9 Plots of \( \ln(T_g - T_g^0) \) as a function of time for samples of the 50/50 XU218/PES blend annealed at (a) 290 °C. (b) 304 °C. Filled triangle: PES abundant phase; open triangle: XU218 abundant phase.
The deviation from the Cahn–Hilliard theory may be caused by the time dependence of chain diffusivity and free energy. We have seen that, for the 50/50 DOW2080/PES blend, the time dependence of chain diffusivity is a major contribution to the deviation. The contribution of time dependence of the chain diffusivity can be investigated by examining the dependence of rate constant on the glass transition temperature as depicted in equation (4). Figures 3.10a and 3.10b show the logarithmic plots of glass transition temperatures of both phases for samples of the 50/50 XU218/PES blend annealed at 290°C and 300°C as a function of \((T_a - T_g)t\). A linear relationship was observed for samples annealed at 290°C and 304°C. This result suggests that the phases separation was controlled only by the chain diffusivity, i.e., thermodinamic driving force is relatively time independent. Both phases showed a rate constant of 0.046 from the slopes for annealing at 290°C. The rate constants from the initial slopes of the plots for samples annealed at 304°C are 0.042 and 0.045 for the PES-abundant phase and XU218-abundant phase, respectively. Thus it can be concluded that for XU218/PES blends the nonlinear dynamics of phase separation are attributable to the time dependence of chain diffusivity for small concentration fluctuations. For large concentrations, the time dependence of free energy also contributes to the deviation from the Cahn–Hilliard theory.

The mechanisms of phase decomposition of the XU218/PES blends can also be investigated by examining the decomposition rate of the original miscible phase. Figure 3.11 shows the logarithmic plots of the intensity (heat flow rate) of the DSC derivative for the original miscible phase as a function of time for samples annealed at 290°C and 304°C. The decomposition rate constants of the original miscible phase can be obtained from the slopes. The rate constants were 0.20 for annealing at 290°C and 0.43 for annealing at 304°C. Because these rate constants were measured at a fixed concentration, the thermodynamic driving force was a constant; thus, the higher decomposition rate of the
Figure 3.10 Plots of $\ln(T_g - T_g^0)$ as a function of $(T_g - T_g^0)t$ for samples of the 50/50 XU218/PES blend annealed at: (a) 290 °C, (b) 300 °C. Open triangle: PES abundant phase; filled triangle: XU218 abundant phase.
Figure 3.11 Plots of $\ln(dC_p/dT)$ at $T_g = 263^\circ C$ as a function of annealing time for samples of the 50/50 XU218/PES blend. Filled triangle: annealed at 290 °C; open triangle: annealed at 304 °C.

Miscible phase at higher annealing temperatures is probably due to the higher chain diffusivity.
3.4.4 Poly(BTDA-3PDA)/Poly(ethersulfone) Blend

The miscibility of the poly(BTDA-3PDA)/PES blends and their phase diagram are not as well understood as those already discussed. Single $T_g$s were observed for blends of all the compositions at ambient temperatures as measured by DSC, an observation indicating an apparent miscibility of the blend. When annealed above their glass transition temperatures, phase separation occurred. Figure 3.12 shows the derivatives of the DSC traces for the 50/50 poly(BTDA-3PDA)/PES blend annealed at 290°C as a function of time. It can be seen that the intensity of the original miscible phase decreased as annealing time increased, a result indicating the decomposition of the original miscible phase. A PES-abundant phase and a poly(BTDA-3PDA) abundant phase were formed as the original miscible phase decomposed, as seen by the emergence of two new peaks at longer annealing times. The glass transition temperature of the PES-abundant phase decreases, whereas the glass transition temperature of the poly(BTDA-3PDA)-abundant phase increased as annealing time increased, a result indicating the increase in concentration fluctuation.

To examine the effect of each mechanism on the dynamics of phase separation for the 50/50 poly(BTDA-3PDA)/PES blend, one can first analyze the overall time dependence of the phase separation rate, using equation (1). Figure 3.13 shows the logarithmic plots of the glass transition temperatures of the two phases as a function of annealing time. Like the other polyimide/PES blends, the phase separation proceeded at an initially fast rate, and slowed at longer annealing times. The time dependence of the rate of phase separation indicates that the phase separation in poly(BTDA-3PDA)/PES blend does not follows a Cahn–Hilliard mechanism.

To depict how the time-dependent rate of phase separation is affected by different mechanisms, one can examine its diffusivity dependence as revealed by equation
Figure 3.12 Derivatives of DSC traces for samples of the 50/50 poly(BTDA-3PDA)/PES blend annealed at 290 °C for various times. (a) unannealed; (b) 1'; (c) 2'; (d) 4'; (e) 9'; (f) 42'; (g) 270'; (h) 1200'; (i) 2400'.

Figure 3.14 shows the logarithmic plots of glass transition temperature of both phases for samples of the 50/50 poly(BTDA-3PDA)/PES blend as a function of \((T_a - T_g)\). Linear relations were observed for both phases. The slopes were 0.004 and 0.005 for the PES-abundant phase and poly(BTDA-3PDA)-abundant phase, respectively. This result indicates the effect of chain diffusivity of the poly(BTDA-3PDA)-abundant phase on
Figure 3.13 Plots of $\ln(T_g - T_g^0)$ as a function of time for samples of the 50/50 poly(BTDA-3PDA)/PES blend annealed at 290 °C. Filled triangle: PES abundant phase; open triangle: XU218 abundant phase.

Figure 3.14 Plots of $\ln(T_g - T_g^0)$ as a function of $(T_a - T_g)t$ for samples of the 50/50 poly(BTDA-3PDA)/PES blend annealed at 290 °C. Open triangle: PES abundant phase; filled triangle: poly(BTDA-3PDA) abundant phase.
One can examine the effect of the spinodal mechanism on the dynamics of phase separation by using equation (3.3). Figure 3.15 shows the logarithmic plots of intensity (heat flow rate in the DSC traces) of the original miscible phase as a function of annealing time. Linearity was observed only for a short period. For longer annealing times, the plot became nonlinear. The reason for this irregular behavior is not yet clear. It may be due to a secondary mechanism for the phase decomposition at the later stages, for example, nucleation of phase formation.31

3.5 Conclusion

We have analyzed the dynamics of phase separation for several polyimide/Poly(ethersulfone) blend systems by using thermal analysis method. Two properties of the blends during phase separation were measured by this thermal analysis method: the concentration fluctuations as indicated by the glass transition temperatures (concentration evolution of phase separation), and the volume fraction of the initial miscible phase (decomposition of original miscible phase). It was found that the dynamics of the concentration evolution of the systems studied did not follow the Cahn–Hilliard linear theory. Analysis of the time dependence of the glass transition temperatures of the blends suggested that the change of chain diffusivity during phase separation was the primary mechanism responsible for the deviation from the Cahn–Hilliard linear theory.

When phase separation occurred, the initial miscible phase decomposed into a PES abundant phase and a polyimide abundant phase. As the concentration fluctuation increased, the glass transition temperature of the PES abundant phase decreased, approaching the value that corresponds to the spinodal point of the PES abundant phase, whereas the glass transition temperature of the polyimide abundant phase increased,
Figure 3.15 Logarithmic plots of the heat flow rate in the DSC traces, \( \frac{dC_p}{dT} \), at the temperature of \( T_s = 270 \) °C, as a function of annealing time for samples of the 50/50 poly(BTDA-3PDA)/PES blend annealed at 290 °C.

approaching the value that corresponds to the spinodal point of polyimide abundant phase.

The increase of the glass transition temperature of the polyimide abundant phase affects the chain diffusivity, as can be explained by the decreases in free volume. The effect of glass transition temperature on the chain diffusivity can be described by its dependence on the glass superheating, \( (T_a - T_g) \), as depicted by the reptation model. The small
superheating makes the polyimide/PES blends particularly sensitive to the chain diffusivity. The apparent rate constants do not significantly depend on the annealing temperature. The changes of free energy with concentration fluctuation is insignificant in contributing to the nonlinear dynamics in the concentration evolution of phase separation. The decomposition of the original miscible phase follows a different dynamics during phase separation. In general the dynamics in the early stage can be described by a linear function as predicted by the statistical theory. At late stage, the experimental result deviates from the theory. As the intensity of the glass transition in the DSC derivatives becomes a poor representation of the volume fraction of original miscible phase, the reason for deviation is still not clear. Other type of experiments are necessary for further investigation. For 50/50 DOW2080/PES blend, increasing the annealing temperature does not affect the apparent rate constant, but increases the extent of phase separation. For 50/50 XU218/PES blend, increasing the annealing temperature increases both the apparent rate constant and the extent of phase separation.

3.6 References

23. Liang, K., Grebowicz, J., Valles, E., Karasz, F. E., and MacKnight, W. J.,
CHAPTER 4
THE LOCAL STRUCTURE OF MISCIBLE POLYMER BLENDS

4.1 Introduction

The miscibility of Polymeric blends can usually be diagnosed by their single \( T_g \) and transparency.\(^1,2,3\) These criteria, even though practical, only imply a homogeneity on a scale of tens of nanometers or larger.\(^4-8\) The local structure of such miscible blends on a shorter scale, on the other hand, is less understood. Despite the lack of knowledge about the fine structure, many theoretical works of polymer blends were explicitly or implicitly derived on the assumptions of totally homogenous segmental mixing.\(^9-11\) Although this assumption may be entirely reasonable for small molecule mixtures, it is questionable for high polymers.

4.1.1 Local Structure of Miscible Polymer Blends

Many attempts have been made to investigate the local structures of miscible polymer blends\(^{12-16}\). The Ornstein–Zernike approximation, which assumes a random phase structure, provides a methodology to calculate the correlation length of concentration fluctuation from Small Angle Neutron Scattering\(^{17-19}\):

\[
S(q) = \frac{S(q = 0)}{1 + \xi^2(T, \phi) q^2}
\]

where the structure correlation length, \( \xi \), is a function of both the interaction parameters and blend compositions:

\[
\xi^2(T, \phi) = \frac{b^2}{36} \left[ \phi_A \phi_B (x_A - x_B) \right]^1
\]
and $b_i$ is the statistical segment length (persistent length) of the $i$th component in the blend.

In the vicinity of the phase separation temperature, both $S(q)$ and $\xi(T,\phi)$ may follow the scaling law:

$$S(0,T,\phi) \propto |T - T_c|^{-1}$$

$$\xi(\phi) \propto |T - T_c|^{-\frac{1}{2}}$$

It was found that most miscible polymer blends have correlation lengths from 30 to 150 Å. Table 4.1 lists the correlation lengths of some commonly known miscible polymer blends. The correlation length of many miscible polymer blends are both composition and temperature dependent. However, their dependencies on the composition and the temperature are found not to always follow the theoretical predictions as shown by equation 4.2 and equation 4.6. The picture and the physical nature of the correlation length of miscible polymer blends remain unclear today and innovative methods for the studies of local structure of polymer blends are needed to supplement results of other experiments such as SANS.

4.1.2 Recent Advance in Theories of Polymer Blends

The development of theoretical foundations for polymeric blend structure is not as well established as for small molecular mixtures. The local structure of small molecular mixture have been studied. It was found that the clusters structure of small molecule mixture is approximately of the size of the molecule itself as shown in Figure 4.1 by the correlation functions. Each molecule in the mixture is surrounded by other unlike molecules. It was also found that the local structure of the mixture is also
Table 4.1 Correlation lengths and interaction parameters of some miscible polymer blends

<table>
<thead>
<tr>
<th>polymer blends</th>
<th>correlation length (Å)</th>
<th>interaction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-H/PB-D</td>
<td>100-141 $^{63}$</td>
<td>-3.0x10^{-3} - +0.0</td>
</tr>
<tr>
<td>PS-d/PVME</td>
<td>25-100 $^{15}$</td>
<td>-1.3x10^{-2} - -0.0</td>
</tr>
<tr>
<td>PS-H/PS-D</td>
<td>82 $^{14}$</td>
<td>-2.5x10^{-5}</td>
</tr>
<tr>
<td>PS-D/TMBP</td>
<td>21 $^{12}$</td>
<td>-2.8x10^{-2}</td>
</tr>
</tbody>
</table>

dependent on the interaction of the molecules and the molecular structure of each component.$^{21}$

Polymers differ from small molecules by the connectivity of segments, which dramatically reduces the entropy of mixing.$^{10}$ The small entropy of mixing renders a strong effect of molecular interaction on the local structure. Unless the interaction parameter $\chi$ is very small or negative, immiscible blends are usually obtained. The connectivity of polymers greatly limits the dispersion of polymer segments among other unlike species, resulting in abnormal structure behavior from low molecular weight molecule mixing. De Gennes has shown that the segmental density fluctuation decreases as $1/r$ in the regime of $b << r < R_g$ for polymer chains,$^{11}$ where $b$ is the Kuhn length and $R_g$ the radius of gyration. Recently Schweizer and Curro applied the "Reference Interaction Site Model" theory to polymer blends.$^{31-35}$ They predicted a critical-like correlation of structure associated with the large scale weak fluctuations of the polymer chain concentration. A nonmonatomic correlation function was obtained on a scale of radius of the gyration length. Figure 4.2 shows the structural correlation function for a blend in comparison with the tangent hard-sphere blend.
Figure 4.1a Pair-distribution function $g(R)$ for a water(W)-methanal(M) mixture with $X_M = 0.125$; $n$ is the integrated coordination number at the distance indicated by the arrow.

Figure 4.1b The angular distribution functions $H_D(R)$ at 50/50 mixture for various dipole moments.$^{21}$
The structural correlation function of bimodal blend $\Delta G = G_{AA} + G_{BB} - 2G_{AB}$ as a function of interchain site distance $r$ normalized by the statistical segment length $\sigma_A$.

4.1.3 Recent Advance in Spin Diffusion Studies of Polymer Blends by Solid State NMR

Solid state NMR spin diffusion has been used to study the inhomogeneity of polymer blends for over a decade.\cite{36-43} Inhomogeneity in the scale of nanometers in miscible blends of PPO/PS has been found by the non-linearity of the proton $T_1(\rho)$ decay.\cite{36,37} Kaplan has studied the miscibility of PS/PVME blend by measuring the two dimensional proton correlated spectra of the blends.\cite{88} A recent development of spin diffusion studies of polymer blends was summarized by Vanderhart.\cite{44} However, few studies were reported to investigate the detail structure of the inhomogeneity of the miscible polymeric blends.
4.2 Theoretical Background of Spin Diffusion

In principle, the dipolar interaction between individual spins with well-defined energy levels, induces several kinds of transitions at a certain rate, \( W \): flip of one spin only, flips of both spins in the same direction, opposite flips of the two spins. Only the last one is important in a very strong applied field. For spins \( 1/2 \), the spin flips do not change the populations. Thus the mutual flips will have the effect of suppressing local differences in spin "temperatures" (spin magnetization) by a transport process which is usually called "spin diffusion". The rate of spin diffusion depends on the structure of the spin distributions. Thus spin diffusion can be used to determine the structure heterogeneity of the materials.

4.2.1 Characterization of Spin Diffusion Correlation

Spin-diffusion mixing curves\(^{38,40-43} \) are calculated from the diffusion equation, which for one dimension is\(^{53} \)

\[
\frac{\partial M_A(x,\tau)}{\partial \tau} = D \frac{\partial^2 M_A(x,\tau)}{\partial x^2} \tag{1}
\]

where \( M_A(x,\tau) \) is the \(^1\)H magnetization density at position \( x \) contributed by spins A (the respective protons are labeled A, B etc.), \( D \) is the spin-diffusion coefficient and \( \tau \) is the spin-diffusion mixing time. Usually \( \tau \) is much shorter than the spin-lattice relaxation time \( T_1 \), and therefore the total \(^1\)H magnetization density at a given position \( x \) is a constant, that is, \( M_A(x,\tau) + M_B(x,\tau) = 1 \), and

\[
\int_{-\infty}^{\infty} M_A(x,\tau) \, dx = \text{const}
\]
\[
\int_{-\infty}^{\infty} M_B(x, r) \, dx = \text{const}
\]

In general \(M_A(x, r)\) follows the following equation:\(^{73}\)

\[
M_A(x, r) = \frac{1}{\sqrt{4\pi Dr}} \int_{-\infty}^{\infty} M_A(x', 0) \, e^{-\frac{(x-x')^2}{4Dr}} \, dx'.
\] \( (2) \)

For equation \((4.2)\), no assumptions are made about the initial conditions. The initial value of \(M_A(x, r)\), \(M_A(x, 0)\), is equal to the probability density function of spin A, \(P_A(x)\). This approach is similar to that employed by Cheung and Gerstein\(^{42}\) and recently by Spiess\(^{38}\).

At later times magnetization that is initially associated with spin A diffuses to other positions according to equation \((4.2)\). The total \(^1\)H magnetization of spin A transferred into spin B through spin diffusion (the build-up curve of spin diffusion) in the 2D experiment, \(Q_{AB}(r)\), is obtained by integration of the product of \(M_A(x, r)\) and \(P_B(x)\), the probability density function of spin B, and therefore

\[
Q_{AB}(r) = \int_{-\infty}^{\infty} P_B(x) M_A(x, r) \, dx
\] \( (3) \)

In using equations \((4.1)\) and \((4.2)\) we neglect the effect of differences in the \(^1\)H density per segment on the rate of spin diffusion and on the buildup curve. The diffusion constant \(D\) is determined from the average \(^1\)H density of the blend. These are the usual assumptions made when modeling domain size with spin–diffusion data.\(^{38,40-43}\)

For the homonuclear experiment,\(^{43}\) the protons of segments A and B should have unique chemical shifts. For HETCOR, because the protons from one segment are detected indirectly through the resonance of their attached \(^{13}\)C, only one \(^1\)H chemical shift must be found uniquely in a separate component.
For materials which possess domain structure, theoretical mixing curves $Q_{AB}(\tau)$ are usually obtained by modeling the domain structure, either through numerical solution of equations (4.1) and (4.2)\textsuperscript{52} or analytically with the Fourier method of Cheung and Gerstein.\textsuperscript{42} The use of numerical method requires that one specify a particular segmental concentration profile (i.e. the domain size, shape, and repeat distance). We note that this approach does not easily represent the random nature of the size and placement of domains and thus the interpretation of the shape of a particular concentration profile must be qualitative. Cheung and Gerstein\textsuperscript{42} do incorporate this random character and model the blend with two distributions, one of domain size and a second of values of the interdomain spacings. When this method is used to represent domain structure with three dimensions, one must still supply information about the domain-shape, and there is an implicit assumption that domains have a cubic structure. For miscible blend that may contain no domain structure at all, we require a simpler method for analysis of the data which does not require the a priori assumption of the existence of domains. This approach, using a single correlation function, is shown below.

### 4.2.2 The Segmental Heteropair Correlation Function

The buildup curve $Q_{AB}(\tau)$ is related to the spin heteropair correlation function,

$$G_{AB}(X) = \int_{-\infty}^{\infty} P_B(x)P_A(x + X)dx$$  \hspace{1cm} (3)

where $G_{AB}(X)$ is defined as the mean probability density fluctuation of the system containing spins A and B in a spatial scale of X. Thus

where $d$ is the dimensionality. Equation (4.5) is obtained directly by substitution of equation (4.2) into equation (4.3). Also, it might be noted that calculation of spin-diffusion correlation for a one-dimensional periodic concentration profile is formally
\[
Q_{AB}(r) \propto \frac{1}{(4\pi Dr)^{d/2}} \left[ \int_{-\infty}^{\infty} G_{AB}(X) \exp \left[ -\frac{X^2}{4Dr} \right] dX \right]^d
\]  

(4)

similar to the calculation of a time-correlation function for isotropic rotational diffusion about a bond, a calculation that is commonly employed in the characterization of NMR relaxation data. The two correlation functions can be viewed similarly when "correlation time" is replaced by "correlation length" in the static case.

For a particular concentration profile the correlation function and this profile are equivalent solutions to equations (4.1) and (4.2). However, \( G_{AB}(X) \) can also be interpreted more broadly as an ensemble average over a distribution of random concentration profiles. Equations (4.4) and (4.5) (which are one-dimensional) can also represent three dimensions when diffusion is isotropic and \( G_{AB}(X) \) is replaced by a radial correlation function \( G_{AB}(R) \), where \( R \) is the radial distance.

All the information that is available from the spin diffusion experiment is contained in \( G_{AB}(R) \) and its associated experimental uncertainty. This function can be considered to be experimental data—with the assumption that the diffusion equation is a good representation of the multiple dipolar interactions in a heterogeneous blend. \( G_{AB}(R) \) can also be compared with correlation functions from other experimental data, for example from neutron scattering experiments or dilute-spin double resonance NMR experiments, or it might be compared with theory.

For this study, we take two approaches to the analysis of data. First the uncertainty of \( G_{AB}(R) \) is obtained by modeling the solution to equations (4.4) and (5). It will be seen that in one dimensional spin diffusion a simple function without periodicity, such as a Gaussian, is inconsistent with the experimental data. A cosine with a Gaussian decay is the simplest function which correctly represents the data. In three dimensional spin diffusion, a simple Gaussian decay is consistent with the data. In a second approach
theoretical functions $G_{AB}(R)$ are obtained from a lattice simulation of the blend using Monte Carlo methods, and equations (4.4) and (4.5) used to calculate $Q_{AB}(\tau)$. This approach shows the relationship between the correlation function and the interaction parameter, $\chi$, that is obtained from the lattice calculations. The output of the Monte Carlo calculation is the function $G_{AB}(n)(n = 0 \text{ to } 10)$ between segments separated by $n$ lattice sites; $G_{AB}(R) = G_{AB}(nl)$ for $|n(l/2)| < X |(n+1)(l/2)|$. The value of $l$ is the lattice spacing and is a parameter in the calculation. Integration yields a sum of error function curves:

$$
\begin{align*}
Q_{AB}(\tau) & \propto G_{AB}(\infty) - \sum_{n=1}^{10} \left[ G_{AB}(n+1) - G_{AB}(n-1) \right] \text{erf} \left[ \frac{n}{\sqrt{4Dr}} \right] \\
\end{align*}
$$

Equation (4.6) also illustrates the argument about periodicity. If $G_{AB}(R)$ decays monotonically to equilibrium, then $Q_{AB}(\tau)$ is a positive sum of error function curves. Such a function is distinguished by a rapid initial buildup followed by a slow decay to equilibrium, which appropriately describes the three dimensional spin diffusion. However, an alternating positive and negative slope, resulting from periodic character in $G_{AB}(R)$, leads to alternate subtraction of error–function curves. The result is a more rapid approach to equilibrium, which for one dimension spin diffusion is consistent with experimental data. It should also be noted that $G_{AB}(R)$ can also be readily modeled with the assumptions of Cheung and Gerstein. They note that a more rapid approach to equilibrium can be obtained by specifying a distribution of finite domains spacings. We find that for one dimensional spin diffusion specification of a minimum finite domain spacing introduces periodicity into the correlation function.
4.3 Experiments

4.3.1 Materials

The polymers used in this study were polystyrene-d5 (Cambridge isotope, MW=50,000, T_g=105 °C). Poly(2,6-dimethylphenylene oxide) (Scientific Polymeric Products, Inc. MW=27,000, T_g=210 °C), poly(vivymethylether) (Scientific Polymer Products, Inc. MW=130,000, T_g=-34 °C) and polystyrene-d3 (MW=225,000, T_g=109 °C) (the later was synthesized by Lotus, Inc.). The deuterated polymers have deuterium content higher than 98%. The PPO/PS-d5 blends and the PS/PVME blends were prepared by the dissolving proper amount of materials in toluene and followed by film casting at room temperature. The isotopic polystyrene blends were prepared by dissolving the appropriate amount of polymers in chloroform and followed by film casting at room temperature. The films were then dried at about 100 °C in vacuum for complete removal of the residual solvent. The blend samples prepared in this way are transparent and possess single glass transition temperatures as observed by DSC. The dried materials were then ground into fine powder in liquid nitrogen on a Spex freeze mill and then packed into the NMR rotor for measurement. PPO/PS-d5 50/50 blend was also annealed at 245 °C for 30 hours under vacuum to further assure the thermodynamic equilibrium of mixing. Little degradation of the sample was observed under this condition. One of the 65.5/34.5 PVME/PS blend was annealed at 145 °C for 30 minutes under vacuum and then quenched to room temperature for measurements. The samples and their conditions of preparation are listed in Table 4.2.
4.3.2 Solid State NMR Experiments

Solid state two dimensional (2D) NMR spectra of spin diffusion were conducted with a Bruker MRL 300 NMR spectrometer ($^1$H, 300 Mhz and $^{13}$C, 75 Mhz) using a HETCO pulse sequences under magic angle spinning (MAS) condition. The spinning rate was around 4.5 KHz. The Pulse sequence is shown in Figure 4.3

The pulse sequences basically consist of four time periods: the excitation, the evolution, the mixing and the detection. During the $^1$H evolution period, 0 to 63 cycles of the multiple pulse $^1$H decoupling sequence (BLEW−12)$^{59}$ (012232010032 with $^+X=0$, $^+Y=1$, $^−X=2$, and $^−Y=3$, $^{13}$C and $^1$H 90° pulse =4.0 µs, F1 dwell=4.0x12=48.0 µs) were applied synchronously with (BB−12)$^{60}$ (21202210212) $^{13}$C decoupling to suppress the $^{13}$C−$^1$H dipolar interaction. A 63° tilt pulse and a 90° selection pulse rotated the appropriate phase of $^1$H magnetization to the z axis, and these were followed by a delay, $\tau$, for spin diffusion mixing$^{61}$. After the mixing period, a 90° pulse was applied to $^1$H to rotate the appropriate phase of $^1$H magnetization back to the x axis for Hartman−Han match of cross polarization with $^{13}$C. The cross polarization was carried out with a WIN−24 pulse sequences (3033031011101323121121 for both $^1$H and $^{13}$C). The $^{13}$C detection (64 spectra, 1024 points, 1024 transients, spectral width=22.7 KHz) was followed with the $^1$H decoupling. Time proportional phase incrementation (TPPI)$^{62}$ was implemented to obtain pure-phase spectra in the F1 dimension, with 90° advancement of the phase of the selection pulse, the $^1$H phases of WIM−24, and the receiver. Other detailed experimental conditions are reported elsewhere$^{45}$.

The two-dimensional HETCO spectra were processed on the Aspect 3000 computer of the MSL−300 spectrometer or through use of FELIX−PC off line. Exponential line broadening was used in both dimensions, and the data was zero filled in the $^1$H dimension to yield a 1024x1024 data matrix. Proton peak intensities were obtained from individual
Figure 4.3 The HETCOR pulse sequences used for the measurements of two dimensional spin diffusion solid state NMR spectra.
slices and were verified with deconvolution using a Lorentzian–Gaussian line-shape simulation program supplied with the MSL–300 instrument.

The correlation functions of polymer blends were obtained through curve fitting of $^1$H intensity data to the minimization of the sum of the square of the residuals. The spin diffusion constant of the polymer blends can be estimated from the following relation:

$$ D \propto \omega^2 a^2 $$

(4.13)

where $\omega$ is the second moment of NMR line shape, which is related to the spin–spin relaxation time, and $a$ is the lattice coordinator. If the NMR line shapes are assumed the same for the polymer blends in this study, then the spin diffusion coefficients of the polymer blends can be estimated from their dependence on the lattice coordinate $a$. The spin diffusion coefficients of some organic materials have been measured.$^{42,44,64}$ A value of $6.2 \times 10^{-12}$ cm/s was reported for alkanes.$^{42}$ Values of spin diffusion coefficients from $6.7–8.3 \times 10^{-12}$ cm/s were estimated for various polyethylene and polypropylene.$^{44}$ A value of $6.2 \times 10^{-12}$ cm/s was also reported for polyethylene.$^{64}$ If a value of $6.6 \times 10^{-12}$ cm/s was assumed for low density of polyethylene, and by taking into account the dependence of $a^2$, the spin diffusion coefficients of the polymer blends can be taken as the average of the two components. The values of the spin diffusion coefficients thus estimated are listed in Table 4.2.

4.4 Results and Discussion

4.4.1 PPO/PS–d5 and PPO/PS–d3 Blends

The proton spin diffusion under the current experimental conditions allows the observation of spin magnetization energy to transfer from aromatic protons to aliphatic
Table 4.2 The spin diffusion coefficients of the blends used in this study.

<table>
<thead>
<tr>
<th>Samples</th>
<th>D (x10^{-12} cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO/PS-d5 50/50</td>
<td>3.4</td>
</tr>
<tr>
<td>PPO/PS-d3 50/50</td>
<td>3.8</td>
</tr>
<tr>
<td>PS-d5/PS-d3 75/25</td>
<td>3.2</td>
</tr>
<tr>
<td>PS-d5/PS-d3 50/50</td>
<td>2.9</td>
</tr>
<tr>
<td>PS-d5/PS-d3 25/75</td>
<td>2.7</td>
</tr>
<tr>
<td>PS/PVME 65.5/34.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Figure 4.4 Diagram of the expected spin-diffusion mixing for a PPO/PS-d5 mixture. Intrasegmental spin diffusion between the PPO aromatic and methyl protons is rapid ($\tau_{\text{equilibrium}} < 0.3$ ms). PS-d5 can obtain aromatic correlation only from a heterocontact with PPO.
Figure 4.5 2D HETCOR spectra of PPO/PS-\(d_5\) 50 wt% obtained with spin-diffusion mixing periods (a) \(\tau = 0.3\) ms and (b) \(\tau = 10.0\) ms. \(^{13}\)C resonances 1 (118 ppm) and 2 (113 ppm) are PPO aromatic carbons, resonance 3 (35 to 50 ppm) contains the two PS-\(d_5\) aliphatic carbons; and resonance 4 (17 ppm) contains the PPO methyl carbons. PS-\(d_5\) aromatic carbons (127 ppm) are absent because of deuteration.
protons, and vice versa. Thus if the polymers in the blends are selectively
deuterated to contain only one type of the protons, the spin diffusion from one polymer
chain to the other can be observed. The spin diffusion between aliphatic protons and
aromatic protons in the PPO/PS-d5 blends is schematically shown in Figure 4.4. The PS is
aromatically deuterated so that it contains only the aliphatic protons, while PPO contains
both the aliphatic protons and aromatic protons. In the mixing period, the aromatic
protons in PPO segments exchange magnetization with both the aliphatic protons within
the PPO segments and with those in the PS-d5 segments simultaneously. Strictly speaking,
the density correlation function to be calculated from this experiment is the density
correlation function of protons, which is different from the segmental density correlation
function. If the intrasegmental spin diffusion is fast enough to be negligible, the
segmental density correlation function can be approximated by the proton density
correlation function. VanderHart reported that the intrasegmental spin diffusion reaches
95% of the equilibrium value. Thus the proton density correlation function may be a good
representation of the segmental density correlation function.

4.4.1.1 NMR Spectra of PS-d5/PPO (50 wt%)

Figure 4.5 contains a 2D $^{13}\text{C}$-$^1\text{H}$ HETCOR spectrum of PPO/PS, obtained with the
pulse sequence of Figure 4.3 and with a short dipolar mixing time (0.3 ms). The horizontal
axis (F2) corresponds to the $^{13}\text{C}$ chemical shift range (-5 to 205 ppm), and the vertical axis
(F1) corresponds to the $^1\text{H}$ chemical shift range (-6.0 to 14 ppm). Horizontal ($^{13}\text{C}$) and
vertical ($^1\text{H}$) projections are shown above and to the left. Contour spots in the spectrum
result from both heteronuclear and homonuclear correlations. Heteronuclear correlation
occurs between $^{13}\text{C}$-$^1\text{H}$ pairs coupled by the through-space $^{13}\text{C}$-$^1\text{H}$ dipolar interaction.
These contours are also present in a pure HETCOR spectrum of the blend. Additional
contours result from spin-diffusion (\(^{1}H-{^{13}}H\)) coupling of other protons with the proton of the primary \(^{13}C-{^{1}}H\) pair, when \(\tau > 0.0\) (Figure 4.3), and the intensity of these contours depends on the mixing time, \(\tau\). The interaction between dissimilar chains is apparent as the correlation between a \(^{1}H\) resonance of one chain and a \(^{13}C\) resonance of the second.

The four \(^{13}C\) resonances of protonated carbons are labeled 1–4 in Figure 4.5 and are of particular interest for the study of \(^{1}H\) spin diffusion. These include the protonated aromatic carbons (113 and 118 ppm) and the methyl carbons (17 ppm) of PPO.\(^{45}\) The aliphatic carbons of PS are found in a broad band between 35 and 50 ppm. The resonance of the protonated aromatic carbons of PS (127 ppm) is diminished (as expected) due to deuteration. The less intense correlations for the nonprotonated carbons are also evident in the \(^{13}C\) projection of Figure 4.5, but they have intensities below the lowest contour level of Figure 4.5.

Figure 4.6 provides a schematic explanation of the observed \(^{1}H\) correlations in Figure 4.5 and Figure 4.5. For a mixing time of \(\tau = 0.0\) s (spectrum not shown), a pure HETCOR spectrum results, and \(^{13}C\) resonances are correlated only with their directly attached protons. Aromatic \(^{13}C\) resonances have \(^{1}H\) correlations at about 7.0 ppm, and aliphatic \(^{13}C\) resonances have \(^{1}H\) correlations at 2.0 ppm. For the value \(\tau = 0.3\) ms (Figure 4.5), the \(^{13}C\) resonances of PPO show strong correlation with both aromatic and aliphatic protons, whereas the \(^{13}C\) resonance of PS shows predominantly an aliphatic correlation. The shortest aromatic–proton to methyl–proton distance for a single segment of PPO is about \(r_{HH} = 0.25\) nm, so intrasegmental spin diffusion nearly completely mixes the aromatic and aliphatic protons of this segment within the 0.3–ms mixing time. Spin diffusion between PPO segments or across the ring of one segment might require a longer time, but the equilibrium intensity (\(I_{\text{aliphatic}}/I_{\text{aromatic}} = 3.0\)) should not change. For PS–d\(_5\), because of deuteration, intrasegmental spin diffusion cannot mix aromatic and aliphatic
Figure 4.6 Curves of aromatic $^1$H intensity ($^1$H, 7.0 ppm) correlated with (a) the aromatic $^{13}$C of PPO (resonances 1 of Figure 4.2) and (b) the aliphatic $^{13}$C of PS-$d_5$ (resonance 3). O represent data for a film as cast; □ represent data for a film annealed at 245 °C. The solid curve of (b) is a best fit to a sum of two exponential functions as described in text, $k_1 = 7.0 \times 10^3 \pm 1 \times 10^3 \text{ s}^{-1}$; $k_2 = 5.5 \times 10^2 \pm 1 \times 10^2 \text{ s}^{-1}$; $a_1 = 0.51 \pm 0.05$; standard deviation = ±5%.
intensities. An aromatic $^1$H correlation with the aliphatic carbons of PS can only come from a heterosegmental contact, and this mixing occurs more slowly.

For $\tau = 10.0$ ms (Figure 4.5), interchain mixing due to spin diffusion is nearly complete. Spectra obtained with a greater mixing time show the same result within experimental error ($\pm 5\%$), and for $\tau = 10$ ms, the intensities should be within $< 10\%$ of the true equilibrium values. The $^1$H correlation patterns ("slices") of each of the $^{13}$C resonances are similar to one another (within $10\%$) and similar to the total $^1$H projection. In each slice the ratio of aliphatic to aromatic intensity should be determined by the total $^1$H composition ($I_{\text{aliphatic}}/I_{\text{aromatic}} = \sim 21\%$ aromatic intensity). The experimental equilibrium is close to this value (20–22% aromatic intensity). The deviation probably results from an uncertainty of the composition or to a systematic error in the curve fitting of $^1$H slices, which should not affect the observed rate of buildup.

In an earlier study of PPO/PS by Schaefer and coworkers, measurements of the $^1$H rotating frame spin lattice relaxation time $T_{1\rho}$ were used to characterize the equilibrium spin–diffusion mixing time. It was shown that equilibrium was obtained in less than 25.0 ms (equal to the average $T_{1\rho}$ of the blend). Nonlinearity of the $T_{1\rho}$ decay curve suggested that some partially phase-separated PS was present. The equilibrium mixing time for the present data is consistent with the previous study and is a shorter value ($\tau = 10.0$ ms).

Because all slices have the same intensity at equilibrium, the blend must be homogeneous within a radius of spin diffusion determined by 10 ms (roughly 2.1 nm), and a significant amount of phase-separated PS cannot be present on this scale. Deuteration might account for the difference, but we suggest instead that the nonlinearity may in fact be related to the mechanism of $T_{1\rho}$ relaxation.
4.4.1.2 Spin-Diffusion Correlation Data for PPO/PS-d<sub>5</sub>

Panels a and b of Figure 4.6 are plots of intensity versus mixing time, τ, for two selected correlations of the 50 wt% PS/PPO blend. Figure 4.6a is a plot of the fractional aromatic <sup>1</sup>H intensity (7.0 ppm) associated with one of the aromatic <sup>13</sup>C resonances (118 ppm) of PPO. Figure 4.6 shows the fractional aromatic <sup>1</sup>H intensity (7.0 ppm) of the aliphatic <sup>13</sup>C resonance (30 to 40 ppm) of PS-d<sub>5</sub>. Each point is obtained from a separate 2D experiment with the indicated value of τ. In Figure 4.6 the initial PPO aromatic <sup>1</sup>H measured intensity (τ = 0.0, no mixing) is 1.0 (off-scale), as predicted. In Figure 4.6 the initial PS-d<sub>5</sub> aromatic intensity is 0.0. Both sets of data approach the equilibrium value of 20 to 22% noted above; for τ = 10 ms the intensities are about 2% apart. PPO aromatic protons (Figure 4.6) rapidly reach equilibrium with their own methyl protons (τ < 0.3 ms). For larger mixing times, there is a slower approach to equilibrium that can be attributed to mixing with the additional aliphatic protons of PS-d<sub>5</sub>. The initial intensity of Figure 4.6 is 29% (τ = 0.3 ms), and it is followed by a subsequent decay to the equilibrium value, 22%.

For the aliphatic protons of PS-d<sub>5</sub> (Figure 4.6), due to interchain spin diffusion, is present, only the slower decay because PS-d<sub>5</sub> contains no aromatic protons. The approach to equilibrium is clearly nonexponential; 50% of the equilibrium value is attained before 0.3 ms but a substantially greater time is required for full equilibrium. The solid curve in Figure 4.6 is an empirical fit to a sum of two exponential functions I(τ) = M<sub>A</sub>(∞)[1 - a<sub>1</sub>exp(-k<sub>1</sub>τ) - (1 - a<sub>1</sub>)exp(-k<sub>2</sub>τ)] (parameters are shown in the caption), and this function adequately describes the data within the experimental uncertainty.

Figure 4.6b contains points from the two PPO/PS samples. The circles were obtained for a film cast directly from chloroform, and the squares were obtained after annealing film above the glass transition. The two curves are similar within the experimental uncertainty, although it might be noted that the annealed sample shows a
slightly faster buildup, an effect that could result from a more intimate mixing. Otherwise, annealing has no substantial effect on the interchain interaction, and the solvent-temperature protocol used to prepare the samples appears to provide an equilibrium blend.

Two approaches can be used to analyze the data qualitatively. Figure 4.7 shows a plot of intensity versus the square root of time for the data of Figure 4.6, which is a usual method for presentation of spin-diffusion data.\(^{44}\) When domains are present, the radius \(r_d\) is determined from the initial slope \(s\) of such a plot

\[
\frac{1}{s} \times \left( \frac{4D}{3} \right)
\]

where \(D\) is the spin-diffusion constant. A spin-diffusion constant \(D = 6.2 \times 10^{-12} \text{ cm}^2/\text{s}\) has been reported for alkanes. A value of \(3.4 \times 10^{-12} \text{ cm}^2/\text{s}\) is calculated for this blend, taking into account the square proton-proton distance dependence of \(D\) and the deuteration.\(^{53}\) The two slopes evident in Figure 4.7 differ by a factor of about 2. The initial slope suggests \(r_d = 0.84 \text{ nm}\), and the second slope (were it to depend on a second set of domains) would lead to \(r_d = 30.3 \text{ nm}\). These domain sizes are greater than the average distance between segments (\(1 \sim 0.5 \text{ nm}\)),\(^{84}\) though clustering of PS-d\(_5\) segments in domains should be limited in size to the first and second coordination shells. Equation (7) is applicable only for an isolated, linear extended domain, so the above distances should be considered approximate.

The initial buildup of Figure 4.7 also allows estimation of the closest spacing associated with an individual heterocontact. Simpson et al.\(^{85}\) have used the 2D HETCOR method to observe intrasegmental dipolar mixing rates for model compounds with known bond lengths. They found empirically that \(k = G/r_{HH}^3\), where \(k\) is a first-order rate constant and \(G = 2.5 \times 10^{-19} \text{ cm}^3/\text{s}\) is a constant of proportionality, a number that is consistent with the expected strength of the \(^1\text{H}-^1\text{H}\) dipolar interaction and other
Figure 4.7 Plot of aromatic $^1\text{H}$ intensity versus the $\tau^{1/2}$ for the data of Figure 4b. The two slopes provide values of the PS-d$_5$ domain size.
measurements of intramolecular spin diffusion. Using this equation, the initial buildup rate \( k_1 = 7.0 \times 10^3 \) (Figure 4.7) implies \( r_{HH} = 0.33 \) nm between the protons of PPO and PS segments in adjacent lattice sites. This distance is a reasonable number for a close contact between protons on adjacent segments. If the remainder of the decay (\( r_{HH} = 0.77 \) nm) were attributed to PS-\( d_5 \) segments in clusters involving more than one lattice site, the weighing constant \( (a_1 = 0.51) \) associated with the two exponential functions might suggest that roughly 50% of the contacts between lattice sites are heterocontacts. This method is based on a \( 1/r^3 \) dependence and should underestimate distances that are affected by spin diffusion. Although these different methods of estimating domain structure depend on different models, they both provide a consistent picture of nearly randomly mixed chains with a "domain" or cluster radius between 0.8 and 30 nm.

4.4.1.3 Determination of the Heteropair Correlation Function

Recently Cifra et al. have presented a model for interchain interactions based upon energy minimization of a cubic lattice, using Monte Carlo methods.\(^6\)–\(^8\) This calculation provides a simple form of molecular modeling of the blend which can be compared with NMR data. The result of the Monte Carlo calculation is a correlation function for heterocontacts\(^6\) which describes the probability \( G_{AB}(n) \) of a PPO/PS pair in adjacent or related lattice sites at distance \( n, (n < 10) \). Cifra et al. relate the correlation function to the segmental interaction parameter, \( \chi \), by specifying a reduced interaction energy between segments. The spin-diffusion mixing can be calculated directly from \( G_{AB}(n) \) (see THEORETICAL). For this calculation, one must specify a lattice spacing \( (l = 0.5 \) nm) and the spin diffusion constant \( (D = 3.4 \times 10^{-12}) \). The ratio \( 1/D^{1/2} \) is a parameter in the calculation. Except for specification of this parameter, all assumptions about chain mixing derive from the lattice calculation.
Figure 4.8a Calculated one-dimensional spin diffusion buildup curves for the three model correlation functions. Curves IG) Best fit using Gaussian function; IC): Best fit using cosine function; ICG): Best fit using a cosine Gaussian correlation function.

Figure 4.8 show the calculated curves using several correlation functions for both one dimension and three dimension spin diffusion in comparison to the experimental data. The one-dimensional spin diffusion is relevant to lamellar structure of domains where the lateral spin diffusion may be negligible. The curves using Gaussian and cosine correlation function (curves IG, and IC Figure 4.8 do not provide as good a fit as that calculated on
Calculated three dimensional spin diffusion buildup curves for the three correlation models. Curves 3C) Best fit using cosine function; 3G) Best fit using Gaussian function; 3CG) Best fit using a cosine Gaussian function. Curves for two large, negative the basis of the cosine Gaussian correlation function (curve 1CG). The same is true of the curve using the cosine correlation function (curve 3C, Figure 4.8) in three dimensions spin diffusion. Only the curves using a simple Gaussian and a cosine Gaussian correlation functions (curve 3G and 3CG, Figure 4.8) adequately represent the experimental data.
Figure 4.9 shows a comparison of the several model correlation functions (—) with the best fit parameters derived from the NMR data for one and three dimensional spin diffusion. A set of four theoretical correlation functions $G_{AB}(n)$, from Monte Carlo simulation, obtained from reference 6, are also shown (--). The lattice spacing $l = 0.5$ nm converts the units of the abscissa from lattice-site (top) to length (bottom). The individual curves correspond to four values of the reduced segmental interaction energy, $\epsilon'_{AB}$, $\epsilon'_{AB} = \epsilon_{AB}/kT$ where $\epsilon_{AB}$ is the interaction energy between segments. The usual interaction parameter, $x$, can be related to $\epsilon_{AB}$ through $x_{AB} = (z - 2)\epsilon_{AB}/kT$, where $z = 6$ is the coordination number for the three dimensional cubic lattice. For the Monte Carlo calculation, chains of 22 segments of the two types were placed on a $22 \times 22 \times 22$ cubic lattice. The total interaction energy was minimized and $G_{AB}(n)$ was calculated from the final conformation. The condition $\epsilon'_{AB} = 0.0$ corresponds to athermal mixing (curve mc3). Values of $\epsilon'_{AB}$ (strong interaction, curves mc1 and mc2) and a positive value (immiscibility: phase separation) of $\epsilon'_{A}$ (curve mc4) are also shown.

The model correlation functions (—) reasonably represents the best fits to the experimental spin-diffusion curve through equations (4) and (5). Parameters and their uncertainties are shown in Table 1. Curve 1cg (figure 4.9) was obtained from one-dimensional spin diffusion fitting (curve 1CG, figure 4.8a) and is essentially a cosine function with a Gaussian decay in the amplitude. The correlation function slightly overshoots the equilibrium blend composition, which might imply a partial phase separation of the two chains or alternating fluctuations of concentration. Curve 3g and 3cg are obtained from three-dimensional spin diffusion fits (curves 3G and 3CG, Figure 4.9). In contrast to that of one-dimensional spin diffusion, the correlation functions of three-dimensional spin diffusion fitting curves decay monotonically to the equilibrium, suggesting a higher degree of randomness in the local structure. It is also seen that in this
Figure 4.9 Theoretical heteropair correlation functions $G_{AB}(n)$ for 50 mol% blend (ref. 6) obtained from a Monte Carlo calculation on a $22 \times 22 \times 22$ cubic lattice (---) for $\epsilon'_{AB} = -1.5$ (□), -0.5 (○), 0.0 (■), and 0.3 (△). Three experimental correlation functions $G_{AB}(R)$ (— 1cg, 3g, and 3cg) obtained from the data of Figure 4b. Parameters are shown in Table 1. These curves establish the probable ± error of $G_{AB}(R)$.

In this case both functions are essentially of the same shape, indicating the insignificance of the periodicity in the cosine function of curve 3cg.

The modeling process described can be viewed simply to represent the experimental uncertainty of $G_{AB}(R)$. In this case, examination of Figure 4.10 shows
the experimental probability of a heterocontact in the first coordination shell \( G_{AB}(1) = 0.25 \) to \( 0.35 \). One can compare these values with \( G_{AB}(1) \) predicted by the lattice calculation and it can be seen that \(-0.5 < \epsilon'_{AB} < 0.0\). Interpolation suggests a value of \( \epsilon'_{AB} = -0.1 \) to \(-0.2\). A value of \( \chi = -0.1 \) has been estimated for the PPO/PS blend\(^{44} \) suggesting that for the cubic lattice \( \epsilon'_{AB} = -0.025 \). This is good agreement given the uncertainty of both the lattice calculation and the experimental measurement, though the lattice calculation based upon \( \chi \) appears to underestimate the experimental number of heterocontacts. To obtain a correlation function consistent with strong mixing, \( \epsilon'_{AB} = -1.5 \), would require that \( l \) increase by a factor of \( 1.4 - 2.0 (l = 0.7 \) to \( 1.0 \) nm) or \( D \) decrease by a factor of two to four (\( D = 0.9 \times 10^{-12} \) to \( 1.7 \times 10^{-12} \text{cm}^2/\text{s}\)). The larger value of \( l \) would be inconsistent with the X-ray scattering data for polystyrene\(^{84} \) and the density of the blend. The smaller values of \( D \) are also unlikely. However, one possibility should be considered, i.e., that a particular geometry of the deuterated phenylene ring PS-d\(_5\) may effectively shield \(^1\text{H}-^1\text{H} \) contacts. In this case our estimate of \( D \) would be high and our estimate of the number of heterocontacts too low. At present, details of the geometry of interaction between PPO and PS are unknown, though experiments with different deuterium-labeled blend components or rotor-driven \(^{13}\text{C} \) spin diffusion experiments\(^{77} \) (with \(^{13}\text{C} \) labeled materials) could potentially provide an answer to this question. Also, it has been suggested that a directionally specific interaction can increase the number of heterocontacts associated with a particular interaction energy.\(^{86} \) The lattice calculations shown here do not include this effect. Therefore, we conclude that this experiment probably provides a minimum estimate of the number of heterocontacts.

For the second lattice site, \( G_{AB}(2) \), curve 1cg indicates that in one dimension structure \( G_{AB}(2) \) is already influenced by the periodic character of the correlation function. The lattice calculation fails to predict any concentration fluctuation with the large period of curves 3cg. This disagreement may simply exclude the existence of any
lamellar structure of domains in the blend. Curves 3c and 3g indicate that a less than 10% concentration fluctuation is remained within the second coordination shell. The high segmental miscibility is consistent with the lattice prediction of \(-0.5 < \epsilon'_{AB} < 0.0\).

Figure 4.10 shows the reverse comparison, that is between theoretical three-dimensional spin diffusion build-up curves \(Q_{AB}(r)\) (derived from the correlation functions of Cifra et al.) and the experimental data. The conclusions are similar to those of Figure 4.10. It can be seen that the overall slope of the data is consistent with \(-0.5 < \epsilon'_{AB} < 0.0\).

However, the initial data build up more slowly than the theoretical predictions. The deviation is explained by the steeper initial decay in the theoretical correlation functions that are derived from the lattice calculation.

It is useful to examine the type of clustering of segments implied by the NMR data. Neglecting chain ends, for the cubic lattice model two of the six coordination sites in the first coordination shell must contain the adjacent PS segments. Therefore, a value of \(G_{AB}(1) = 0.28\) for \(\epsilon'_{AB} = 0.0\) corresponds to 42% occupancy of the remaining sites by PPO. This value is in fact quite close to the equilibrium composition of the blend, a value that might be expected for an interaction energy of zero and no chain connectivity. The difference could be associated with the loss of entropy associated with the molar masses of these model chains with \(N = 22\) segments. The molar masses for the PPO and PS used in this study are higher, 10,000 and 50,000 respectively (\(\sim\)100 to 500 segments). An even lower entropy of mixing (and fewer heterocontacts) might be expected. Because the experimental NMR data are quite consistent with the calculations with \(\epsilon'_{AB} \sim 0\) and \(N = 22\), it is suggested that molar mass does not strongly influence these results. In the extreme, if phase separated on a cubic lattice, the single polymer chains of this study would occupy domains with a radius of 2.5 to 4 segments. Heterocontacts would be found only at the interfaces and would be insignificant in number \((G_{AB}(1) = 0.09\) to 0.06). Clearly, the NMR data are inconsistent with this picture. If the structure is ideally
Figure 4.10  Theoretical curves, $Q_{AB}(r)$, obtained from the curves $Q_{AB}(n)$ of Figure 7 (curves mc1, mc2, mc3 and mc4) with the assumption that equilibrium intensity is 0.20. The solid and dotted lines are for three-dimensional and one-dimensional spin diffusion, respectively. The data of Figure 4b (O).

random, the correlation function would follow an exponential form. It is possible that the Gaussian type correlation function noted in this study might be attributed to residual memory of the phase separated chains that survive the protocol used to cast and anneal the
mixture or to equilibrium concentration fluctuations. A systematic study with materials of different molecular weight is required to clarify this point.

Neutron scattering data for similar blends have suggested that there is a correlation length associated with long-range equilibrium concentration fluctuations. The distances are in the range of 2 nm (for a blend of perdeuterated polystyrene and a tetramethyl bisphenol–A polycarbonate) to 14 nm (for a mixture of protonated and deuterated polybutadiene). The implication of a correlation length is that the correlation function is monotonic and approximately exponential. It has been shown that the NMR data are consistent with a monotonic correlation function with a correlation length less than 1 nm. An exponential correlation function, with a comparable correlation length, decays to equilibrium much quicker at shorter-range than the Gaussian function, and would result in a faster initial spin-diffusion build-up. However, it is possible that the correlation length from Gaussian-type correlation function, which is consistent with the NMR data, is related to the scattering result. These latter distances are comparable, and this possibility is under investigation.

It is useful to compare other blends. These NMR data for PPO/PS are consistent with data of Kaplan and Caravatti et al. for the blend of PS and polyvinylmethyl ether (PVME), and we have produced similar data for PS/PVME with the heteronuclear method. Preliminary data have also been obtained for the mixture of ring deuterated polystyrene and chain deuterated polystyrene (PS–d₅/PS–d₃). Apart from the effects of deuteration, which should be small, for this blend $\chi$ should be very close to zero. The NMR results for PS–d₅ and PS–d₃ are qualitatively similar to those of PPO/PS. In contrast for a blend of a polyimide and polybenzimidazole, where hydrogen bonding is present, spin diffusion correlation is at equilibrium within about 1 ms. Therefore, we suggest that the results which we obtain for PPO/PS may be typical for a blend with weakly interacting components.
4.4.2 PS-d5/PS-d3 Blends: Composition Dependence

Isotopic polymer blends consist of a special class of blends in which molecular interaction can be considered zero. This is of great theoretical interest since in athermal blends the molecular behavior of the polymer chains is driven only by entropy of mixing. The blends of hydrogenated polystyrene and deuterated polystyrene have been studied by many researchers.\textsuperscript{14,54,56,66–70} It will be interesting to study the local structures of this isotopic blend.

Figure 4.11 shows the two-dimensional heterogenous nuclear correlation spectrum of a 50/50 wt\% PS-d\textsubscript{5}/PS-d\textsubscript{3} blend at two mixing times, 0.3 ms and 10 ms. The spin diffusion time (mixing time), $t$, determines the spatial range of spin diffusion, illustrated by the following relation:\textsuperscript{44}

$$<r^2>^{1/2} = \sqrt{\frac{4}{3}Dt} \quad (4.4)$$

where $<r^2>^{1/2}$ is the root mean square spin diffusion length and $D$ is the spin diffusion constant. At zero time, no diffusion occurs, and the proton signals observed in the HETCOR spectrum are only associated with the respective directly attached carbons. For finite spin diffusion times, the proton signals are also associated with protons attached to more distant carbons. As discussed earlier, a spin can diffuse over average segmental distances for these polymers in times of the order of 0.3 ms. Thus the HETCOR spectrum at $t=0.3$ ms corresponds to spin diffusion at the segmental level (Figure 4.1a) A spin diffusion time at either too short or too long a scale would not properly represent the segmental miscibility which is of interest. If there is no contact between unlike segments in the two polymers, as will occur in a fully ordered structure, there can be no spin diffusion between protons in the two polymers at a spin diffusion time on this time scale. It is seen from the spectrum in Figure 4.1a that there can only be very weak energy
Figure 4.11 Two dimensional HETCOR spectra for the sample of the 50/50 PS-d$_5$/PS-d$_3$ blend. (a) $\tau = 0.3$ ms; (b) $\tau = 10$ ms.
transfer between the aromatic protons of PS-\(d_3\) located at 7 ppm and the aliphatic protons of PS-\(d_5\) at 2 ppm since it is not visible above background noise. This indicates that the numbers of heterosegmental contacts at the segmental scale is small.

The HETCOR spectrum at a mixing time \(t=10\) ms is taken as an extreme in which spin diffusion is well equilibrated. This is evidenced by the observation that the same ratios of aromatic to aliphatic proton signal intensities are reached at 43 ppm and 127 ppm in the \(^{13}\)C spectrum.

The form of the correlation function depends on the type of structure. A simple exponential correlation function was suggested by Debye for materials of totally random structure.\(^{46}\) Similar correlation functions have also been used in neutron scattering calculations.\(^{47,19}\) A structure with local cluster characters may be represented by a Gaussian correlation function, which illustrates a relatively high correlation at short distances and ordered structures may be simply described by a periodic function such as the cosine. More complicated structures may be represented by a combination of the above functions. In this study, several forms of correlation functions were used to test different possible structures.

Figure 4.12 shows the best fit correlation intensities as a function of mixing time based on several structural models, for the 50/50 PS-\(d_3\)/PS-\(d_5\) blend. The relevant parameters and the corresponding correlation functions are listed in Table 4.3. As discussed earlier, an exponential correlation represents a homogeneous structure which inevitably results in a rapid build up in spin diffusion. The best fit curve based on the exponential model is shown in Figure 4.12 (long dashed line). It is seen that the initial build up is about 20-40% faster than the experimental data, a disagreement outside the experimental error of ±5%. Similarly, a cosine correlation structure provides a poor fit of the spin diffusion data, with a deviation of 15% from the experimental data. The failure of both the exponential and the cosine forms as a correlation function excludes the
possibilities of both a randomness of structure and a long range ordering in this 50/50 PS-d$_3$/PS-d$_5$ blend.

The best fits using the Gaussian and the cosine Gaussian correlation functions are shown by the solid and dotted dashed lines in Figure 4.12. It is seen that both curves fit the entire spin diffusion data well. The simulations using the cosine Gaussian correlation function can also correctly describe the spin diffusion data for the 25-75 PS-d$_5$/PS-d$_3$ and 75/25 PS-d$_5$/PS-d$_3$ blends. The results are shown in Figures 4.13 and Figure 4.14.

The best fit Gaussian and cosine Gaussian correlation functions for the PS-d$_5$/PS-d$_3$ data of various composition are shown in Figure 4.15. Note that both functions are virtually the same in terms of their best fits. The loss of periodicity of the cosine Gaussian correlation function suggests that a long range ordering is not consistent with the spin diffusion data. A short range ordered structure in the blend is implied by the Gaussian type correlation function.

It is useful to examine the concentration fluctuations of the short range ordered structure of the blend at the segmental level. The proton density fluctuation at the segmental level can be characterized by the correlation on the segmental scale, $G_{AA}(R_{\text{segment}})$. For polystyrene $R_{\text{segment}}$ is on a scale of 0.6 nm. The $G_{AA}(R_{\text{segment}})$ value ranges from 1.0 for a fully ordered structure to 0.0 for a completely random structure. Table I lists the characteristic values of $G_{AA}(R_{\text{segment}})$ for the three compositions of PS-d$_5$/PS-d$_3$ blends. It is seen that the 50/50 PS-d$_5$/PS-d$_3$ blends have a proton density fluctuation magnitude $G_{AA}(l_{\text{segment}})$ of 0.68. The corresponding values for the 25/75 and 75/25 blends on the same scale are 0.61 and 0.65. These high magnitudes of proton density fluctuation again indicate that the number of heterosegmental contacts of the isotopic PS-d$_5$/PS-d$_3$ blends are small and the mixing at the segmental level is not completely homogeneous. This conclusion is consistent with the weak spin diffusion
The aromatic to aliphatic proton correlation intensity at 40 ppm $^{13}$C resonance as a function of mixing time for the samples of the 50/50 P S-d$_5$/PS-d$_3$. The lines are the best fits from various structural correlation models. Solid: Gaussian; long dashed: cosine Gaussian; short dashed: exponential; Dotted dashed: cosine.

intensity in the HETCOR spectrum at $\tau=0.3$ ms, as shown in Figure 4.11a. The dependence of difference are within the experimental error.

The local ordered structure of the blends can be characterized by the correlation length. The correlation lengths of PS-d$_5$/PS-d$_3$ blend are also listed in Table I. It is seen
Figure 4.13 The aromatic to aliphatic proton diffusion intensity as a function of mixing time for the sample of the 25/75 PS-d₅/PS-d₃ blend. Solid line: the best fit from the cosine Gaussian correlation function.

Figure 4.14 Aromatic to aliphatic proton correlation intensity as a function of mixing time for the sample of 75/25 PS-d₅/PS-d₃ blend. The solid line is the best fit calculated from the cosine Gaussian correlation model.
that correlation length ranges at a scale of about 0.8 - 0.9 nm depending on the blend composition. Again, the apparent composition dependence of the domain size is not significant considering the experimental error.

The experimental observation of a locally ordered structure in miscible polymer blends has been postulated in earlier investigations for PPO/PS-d₅ blend. However,
recent theoretical models also support this concept. As noted, Curro and Schweizer applied the Reference Interaction Site Model Integral theory (RISM) to polymer blends. They predicted that a weak local fluctuation can exist in athermal polymer blends. The Monte Carlo simulation by Cifra et al. implies that athermal polymer blends have a tendency toward segmental segregation on a scale of 4 to 5 repeat units. In other words, athermal blends are not completely randomized on the segmental scale. Larger scale concentration fluctuations with correlation lengths of the order of 8 nm have been reported by SANS for isotopic polystyrene blends. This larger scale concentration fluctuation is not observed from the spin diffusion experiments.

The studies of the local structure of polymer blends were extended to the PPO/PS-d$_3$ system, for which the macroscopic miscibility parameters are well known. Figure 4.14 shows the time dependence of the correlated intensity as well as the calculated spin diffusion curve for the 50/50 PPO/PS-d$_3$ blend. The results are listed in Table I. The PPO/PS-d$_3$ blend differs from the PS-d$_3$/PS-d$_5$ blend in that in the former the PPO chains contain both aromatic and aliphatic protons. Proton spin diffusion can occur within the PPO polymer chains as well as between PPO and PS-d$_3$ segments. However, because the dipole-dipole interaction of protons is proportional to the cube of the distance, spin diffusion from adjacent protons on the same polymer chain is much faster than any intermolecular spin diffusion. As discussed earlier, it takes less than 0.3 ms to reach equilibrium for intramolecular spin diffusion. Therefore it can be assumed that the protons in the PPO segments have reached equilibrium before they "communicate" with protons of the PS-d$_3$ segments.

Figure 4.15 also shows the correlation function for the PPO/PS-d$_3$ blend. As in the case of the PS-d$_3$/PS-d$_5$ blend, simulation with a simple Gaussian correlation function does not fit the experimental data, whereas simulations using a cosine Gaussian function gave a satisfactory fit. The relevant parameters from the best fits are listed in Table I.
The mean square proton density fluctuation at the segmental scale, \( <G_{AA}(R_{\text{segmental}}) > \), is 0.34, much lower than that found for the PS-d\(_5\)/PS-d\(_5\) blend. The higher degree of segmental mixing for the former is also seen by the much greater spin diffusion energy transfer at a mixing time of 0.3 ms (Figure 4.14). The weak segmental fluctuation in the PPO/PS-d\(_3\) blends can be explained by their difference in segmental dimensions. Even though both systems are found to be miscible by the criterion of single \( T_g \)'s, there is evidence that the partial deuteration of polystyrene results in a small unfavorable interaction with a hydrogenated polystyrene chain,\(^{14,54,58,62,63}\) and this leads to macroscopic phase separation for isotopic polystyrene blends of high enough molecular weight.\(^{56}\) This result may well extend to isotopic mixtures studied here. Though the effect of deuteration of polystyrene in PPO blends has not been examined, the favorable interaction of the PPO chain with protonated polystyrene is well established.\(^{57}\) It is probably this favorable interaction that results in a weaker concentration density fluctuation and, hence, the weaker magnetization density fluctuation. It is also possible that the lower molecular weight of PPO used here would favor the miscibility in PPO/PS-d\(_3\) compared to PS-d\(_5\)/PS-d\(_3\). The spin diffusion data were collected for PS-d\(_5\)/PS-d\(_3\) blends as similar to the PPO/PS-d\(_5\) blends.

4.4.3 65.5/34.5 PS/PVME Blend

The unannealed 65.5/34.5 PS/PVME films are transparent, and have a single glass transition temperature of about 50 °C. This allows the cross-polarization in the NMR measurement at ambient temperature. When annealed at 140 °C, the films become cloudy and show two glass transition temperatures in DSC.

Figure 4.16 shows the aliphatic to aromatic proton correlation function at 127 ppm \(^{13}\)C resonance (aromatic carbons of PS) as a function of mixing time for both the
unannealed (open circles) and annealed samples (filled circles). For phase separated blends the signals represented only the PS abundant phase, signals from the PVME abundant phase were too weak due to the inefficiency of cross-polarization. It is seen that for the annealed sample the final proton correlation intensity was about 15% lower than that of unannealed sample. If the final proton correlation intensity of the unannealed sample is taken as the equilibrium spin diffusion correlation intensity, the low value of correlation intensity indicated that the aromatic protons in PS can only partially "communicate" with the aliphatic protons in PVME. This result inferred that presence of doamin structure that is larger than the spin diffusion distance.

The spin diffusion data for both the unannealed and annealed samples were fitted with a two phase cosine Gaussian correlation structural model. The best fits are also shown in Figure 4.16.

The corresponding correlation functions are shown in Figure 4.17. At short range, the correlation functions decay as a Gaussian. The correlation function for the unannealed sample quickly a small value at about 1.0 nm. For the annealed sample, the correlation function levels off, also at about 1.0 nm. This result suggests that short range segmental aggregation is present for both the unannealed and annealed samples. The perseverance of local segmental aggregation for the annealed samples may be explained by existence of two miscible phases in the system. It is seen from the phase diagram\(^5\) that PVME abundant phase contains about 90% of PVME while the second phase contains about 75% of the PS. Because the PVME abundant phase is not observable under the experimental condition, only the PS abundant phase is observed.

The long range structures of the annealed sample displayed significant different for that of the unannealed sample. For the unannealed sample, the correlation function quickly converges, a result indicating the loss of correlation in concentration fluctuation. For the annealed sample, the correlation function levels off after 1.0 nm, and maintains at a
certain value, a structure of long range ordering. This result reflects the fact that spin diffusion cannot reach equilibrium even after a long mixing time.

The fact that the local ordering exists in both the miscible and phase separated blends is important. Along with the results from other miscible blends discussed in earlier
Figure 4.17 The proton correlation functions calculated from the best fit of the spin diffusion data in Figure 4.16 for samples of the 65.5/34.5 PS/PVME blend. The correlation function is based on a two-phase cosine Gaussian correlation model.
sections, it seems that the local ordering is a universal phenomena of polymer blends. Since small molecular mixtures do not have such local ordering, it may be speculated that the local ordering is due to the connectivity of long polymer chains. Unlike small molecules, which have very high degree of freedom in generating a large number of microscopic states, the connectivity greatly reduces the conformational entropy, which is characterized by the radius of gyration, and entropy of mixing, which cause phase separation for many polymer blends. Recently, by applying the Reference interaction site model integral theory to polymer blends, Curro, et al. have shown that the connectivity of long polymer chains, besides the global radius of gyration, also causes a short range and molecular weight independent fluctuation in a range of the screened Coulomb potential. The local ordering may be responsible for this short range fluctuation.

The minimum size for homogeneity of concentration fluctuation was given by the length at which the fluctuation becomes unrelated. These correlation lengths, which are relatively long range, may be closely related to the correlation lengths obtained by small angle neutron scattering. It is seen that they are quantitatively in agreement with the reported values as seen in Table 4.1. Our result suggests that while the short range structure can be roughly described by the periodicity of the cosine function, the correlation length from SANS describes the long range structure of the blends.

4.5 Summary

A novel NMR spin diffusion technique has been used to study the local structure of several miscible polymer blends, PPO/PS-d5, PPO/PS-d3, PS-d5/PS-d3 and PS/PVME. The correlation functions of the proton density functions were calculated from the best fits of the experimental data, using various structural models.
It is found that for one-dimensional spin diffusion, a cosine Gaussian correlation function gave a good fit of the experimental data. For three-dimensional spin diffusion, a simple Gaussian correlation function provides a best fit of the experimental data. The assumption of one-dimensional spin diffusion is not very realistic since it requires a lamellar morphology, resulting in periodicity in the correlation function.

Annealing of PPO/PS-d5 blends does not significantly alter the local ordering, even though annealing may seem to reduce the fluctuation in the segmental level. Deuteration of aromatic carbons in polystyrene may result in stronger local ordering. Slightly larger local ordering was seen for PS-d5/PS-d3 blends, indicating a less favorable local environment in PS-d5/PS-d3 blends. The local ordering was observed for three different compositions of the blends. This may suggest that short range ordering is a phenomenon of local property. Local ordering was found to exist in both the miscible and phase separated blends. The structure of the local ordering in both the miscible and phase separated blends were very similar, which again proves that short range is only sensitive to local environment. The short range local ordering exists in both miscible and phase separated blends. The relative long range correlation length, which may be closely related to the correlation length of small angle neutron scattering, described the miscibilities in the macroscopic level.

NMR spin diffusion has proved to be a powerful tool for the analysis of local structure of polymer blends. However, some comments must be made. The domain sizes calculated were determined by the assumption of constant spin diffusion coefficients, which were calculated based on the measured value of polyethylene. There is also speculation about intrasegmental spin diffusions, e.g. the proton spin diffusion within a segment takes place within 300 ms. Solid evidence is needed to verify the assumptions.
The discussion in chapter 4 presents a new approach for the study of the structure of polymer blends. While the results are very interesting, they have not been predicted by any contemporary theories or observed by experimental methods. Therefore much work remains to be done. One of the questions that is asked most frequently has to do with local ordering structure: is it determined by the properties of chain molecules or is it an artificial result from instrumentation or other computer manipulations? Since local ordering is not observed for homopolymers, the later must be rejected. To answer the first part of the question, however, more evidence is needed. The investigation of the structure of mixture of small molecules and low molecular weight oligomers will be very constructive. The experiments with small molecules or oligomers will be technically quite difficult since low temperatures are required for cross-polarization. The temperature dependence of spin diffusion rate and other parameters must be considered before the results are compared. Secondly, model polymers with known structure, such as block copolymers and random copolymers should be employed for the investigation of local ordering structures. This will help compare results from spin diffusion and other experimental methods. Other experimental evidence may be very necessary, for instance, from small angle neutron angle scattering or high resolution electron microscopy.
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89. The space occupied by a deuterated PS repeat unit can be calculated through the density:
\[ d = \frac{M}{(N_A V)} \]

Where \( d \) is the macroscopic density, \( N_A \) is the Avogadro's Number, \( V \) is the segmental volume. Taking \( d = 1.116 \text{ g/cm}^3 \), \( M = 104 \text{ g/mol} \), then the radius of the repeat unit \( l = 0.3 \text{ nm} \).
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The space occupied by a deuterated PS repeat unit can be calculated through the density:

\[ 104/(6.0222\times10^{23}\text{V})=1.116^{[55]}/(10^{8})^{3}, \text{then } V^{1/3}=5.37 \text{ A.} \]


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