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Phase Behavior in Blends of Asymmetrical Polyolefins

by

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requirements for the degree of

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in

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Committee in charge:

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Abstract

Phase Behavior in Asymmetrical Polymer Blends

by

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Polymer composites combine the physical properties of two or more distinct chemical species into a single material. Blends of two homopolymers, mixed homogeneously or structured on the nanoscale, are particularly useful nanocomposite materials because ordering occurs via thermodynamic equilibration rather than costly nanofabrication. However, the majority of homopolymer pairs are immiscible, leading to mechanically unstable materials. This work explores one route for compatibilizing two immiscible homopolymers (components A and B) via the addition of a tailored diblock copolymer surfactant (component A-C). The A-block of the copolymer was selected on the basis of having a neutral interaction with the A homopolymer, and the C-block had a favorable interaction with the B homopolymer. The favorable interaction between species B and C was first examined by preparing binary blends of B and C homopolymers. A detailed thermodynamic study explored the effects of blend composition and homopolymer chain length on the thermodynamic phase behavior of binary B/C blends. The results were used to design A/B/A-C ternary blends where the favorable interaction between homopolymer B and the C-block enabled the copolymer surfactant to efficiently stabilize the interface between nanoscale-ordered domains of A and B. The phase behavior of the resulting polymer nanocomposites was studied as a function of the composition of the blend and the chain lengths of the A and B homopolymers. These studies provide new insight into the tunability of of polymer nanocomposite materials by controlling parameters that have not been studied previously.

Polymer pairs that are miscible over a large range of chain lengths, N_B and N_C , are interesting to thermodynamic studies because the Flory-Huggins interaction parameter, χ , can be measured using scattering techniques and the theoretical framework of the Random Phase Approximation. Most tabulated χ values have been measured over a limited range of chain lengths small enough for the polymers to homogenize; such studies are largely constrained to the vicinity of $N_B \approx N_C$. This dissertation presents the most comprehensive study of χ to date for a single pair of homopolymers. Polyisobutylene (component B) and deuterated polybutadiene with 63 % 1,2 addition (component C) were selected for this study because they exhibit a large window of miscibility and may be tailored to cross the spinodal at experimentally accessible temperatures. Binary blends were designed across a range of values for N_B/N_C and the composition of the blend, ϕ_B , to study the effect of these parameters on the measured value, χ_{sc} . In addition to the strict temperature dependence presumed for χ , this study documented a composition and molecular weight dependence. The empirical expression for χ_{sc} , measured using small angle neutron scattering, was three times more dependent on composition then the expression for χ used to predict thermodynamic behavior. Despite this three-fold diminished dependence on $\phi_{\rm B}$, the composition-dependent χ profoundly affected the phase behavior of binary blends.

Binary B/C blends exhibited macrophase separation upon heating (above a threshold chain length), enabling experimental determination of the binodal and spinodal. These measured quantities were compared to predictions using Flory-Huggins Theory with the composition- and molecular weight-dependent χ . Phase diagrams are expected to be symmetric in the vicinity of $N_{\rm B} \approx N_{\rm C}$, with the critical point located at $\phi_{\rm B,crit} = 0.5$. However, both the measured and predicted phase diagrams were asymmetric in the vicinity of $N_{\rm B} \approx N_{\rm C}$, and increasingly symmetric as the value of $N_{\rm B}/N_{\rm C}$ was decreased. A range of values was studied for $N_{\rm B}/N_{\rm C} \leq 1$, and in all cases $\phi_{\rm B,crit} \geq 0.5$. This effect was shown to result from the combined effects of a composition-dependent χ and $N_{\rm B}/N_{\rm C}$ removed from values of 1. Remarkable agreement was obtained between the predicted phase diagrams and measured phase transitions, over a range of values for $N_{\rm B}/N_{\rm C}$ and $\phi_{\rm B}$, by accounting for the composition and molecular weight dependence of χ .

The miscibility of binary B/C blends was used as the basis for designing a diblock copolymer (component A-C) to order immiscible binary blends of polyisobutylene and deuterated polybutadiene with 89 % 1,2 addition (component A). The copolymer comprised one block chemically identical to component C (miscible in component B) and one block chemically identical to component A. This is in contrast to the majority of ternary blend studies which comprise A/B/A-B polymer systems with neutral interactions between each homopolymer and the corresponding block of the diblock copolymer. Ternary A/B/A-C blends exhibit a favorable interaction between the B homopolymer and C block, demonstrated by the miscibility of B/C blends. The A-C diblock copolymer surfactant can produce microstructures when added to A/B blends at much lower concentrations of copolymer than for an analagous A-B copolymer.

Previous studies have only considered the case $N_A \approx N_B$ and a symmetric diblock copolymer

 $(N_{\text{A-block}} \approx N_{\text{C-block}})$. In the present work, symmetric diblock copolymers were added to critical A/B blends. The values of $N_{\text{A}}/N_{\text{B}}$ were varied over two orders of magnitude. For each blend, the ratio of A:B was fixed by the Flory-Huggins Theory prediction for the critical point (which depends only on $N_{\text{A}}/N_{\text{B}}$), and a constant amount of copolymer was used for all blends. By creating blends with a wide range of values for $N_{\text{A}}/N_{\text{B}}$, the study accessed critical compositions, $\phi_{\text{A,crit}}$, well removed from the typical value of 0.5 (on a copolymer-free basis). The resulting phase behavior correlated directly with $N_{\text{A}}/N_{\text{B}}$, suggesting that the microstructures observed in a blend could be tuned not only by the conventional method of changing the amount of copolymer, but also by adjusting the ratio $N_{\text{A}}/N_{\text{B}}$.

Lamellar or microemulsion phases were observed over a temperature window for nearly all of the A/B/A-C blends studied. The former represent an ordered microphase and the latter a disordered microphase, each with unique applications. Previous work has attempted to distinguish the scattering profiles of lamellar phases from those of microemulsions by fitting both with the Teubner-Strey equation for microemulsions. The lamellar phase was judged to exist when the microemulsion fit did not capture the entire range of the scattering profile, otherwise the phase was presumed to be a microemulsion. This dissertation introduces the use of lamellar structure factor that fits scattering profiles unsuitable for the microemulsion fit. In addition, the lamellar fits include as adjustable parameters the size of each microdomain and corresponding interfacial width. These fit values agree quantitatively with independently generated predictions using self-consistent field theory, indicating a broad understanding of the physical parameters that affect thermodynamic behavior in the A/B/A-C system studied.

The composition of a blend, in particular the concentration of diblock copolymer, is known to affect the phase behavior, however most studies have only considered blends where equal amounts of A and B are blended with copolymer and $\phi_{A,crit} = 0.5$ (on a copolymer-free basis). This dissertation presents a study for which the concentration of diblock copolymer was fixed and the composition of the A and B homopolymers was systematically varied across a range of compositions including $\phi_{A,crit}$. The experiment corresponded to tracing the copolymer isopleth on a ternary phase prism. Theoretical groups have predicted a rich phase behavior along the isopleth for similar ternary systems, however, the observed phase behavior was quantitatively identical for all blends studied. Self-consistent field theory predictions agreed with fit values of the domain spacing and microdomain widths. There was no discernible correlation between ϕ_A and phase behavior. This finding, and that of the study with critical A/B/A-C blends, together suggest that N_A/N_B correlates strongly with the phase behavior of a blend, while ϕ_A does not. This relationship, captured by mean-field theory, provides a simple method for tuning the phase behavior of polymer nanocomposites without using additional surfactant.

Chapter 1

Introduction to Polymer Blends

Polymer blends comprise two or more distinct chemical species. The thermodynamic interactions between species can be tailored to produce a single-phase blend that is either homogeneous or microphase separated. Equilibrium microstructures, like lamellae and microemulsions, are of particular interest because they combine the desirable properties of the constituent polymer species into a mechanically stable composite material. Compatibilizing different polymer species at the micro- and nano-length scale remains a fundamental challenge in polymer science. This dissertation presents one route to the compatibilization of immiscible homopolymers. The interactions and phase behavior are studied for a miscible pair of polyolefins, and used to design a diblock copolymer surfactant. The diblock copolymer is added to blends of immiscible homopolymers to produce a microphase separated morphology. The thermodynamic behavior of both binary and ternary blends is explored with respect to molecular weight asymmetry (i.e. polymers with unequal molecular weights).

This chapter provides an introduction to the concepts and terminology used to describe binary and ternary blends. A historical review is presented for the use of diblock copolymer surfactants as compatibilizing agents. The last section of this chapter describes the model system of polyolefins used in this dissertation.

1.1 Binary blends

1.1.1. Thermodynamic phase behavior

The binary polymer blends studied comprise two different species of homopolymers, herein referred to as B and C. The homopolymers may either mix to form a single homogeneous phase, or macrophase separate to form coexisting B-rich and C-rich phases. The majority of polymer pairs do not mix homogeneously due to repulsive interactions between the chemical units of the constituent species. This dimensionless energy of interaction is quantized using the Flory-Huggins interaction parameter, χ . Flory-Huggins Theory describes the Gibbs free energy of mixing polymers on a lattice where each lattice site has *z* neighboring sites. A mean field interaction is presumed for all polymers on the lattice rather than computing interactions for each individual site. χ is defined by:

$$\chi = \frac{(z-2)}{kT} \left[w_{BC} - \frac{1}{2} (w_{BB} + w_{CC}) \right]$$
(1.1)

 w_{ij} is the energy required to place a unit of species i next to a unit of species j on the lattice. k is the Boltzmann constant and T is the temperature. Two neighboring lattice sites are occupied by the chemical units immediately before and after the unit of interest on the polymer chain, hence z - 2. It is assumed that there is no energy of interaction between units of the same chemical species and that polymer chains are infinite in length (i.e. no chain ends).

 w_{ij} is a difficult quantity to measure, however χ is directly related to experimentally determined quantities. The usual empirical form for χ is:

$$\chi = a + \frac{b}{T} \tag{1.2}$$

where *a* and *b* are both experimentally determined constants. The parameter *a* represents entropic contributions to χ which are not considered in eq. 1.1. The enthalpic contribution to χ is given by the parameter *b*. A priori, entropic considerations dominate the expression for χ at high temperatures. Entropy drives the blend towards mixing while enthalpy may drive either mixing or demixing, depending on the specific nature of chemical interactions between polymer units.

The length of the homopolymer chain (i.e. the number of lattice sites occupied by a single polymer molecule) affects the entropic contribution to the free energy of mixing. The relevant measure of chain length, N_i , is the number of lattice sites of volume v_0 occupied by a single polymer molecule of species i.

$$N_i = \frac{\hat{N}_i v_{i,mon}}{v_0} \tag{1.3}$$

The volume of a polymer chain is the product of the number of monomer units, \hat{N}_i , and the volume of each monomer unit, $v_{i,mon}$. Conserving the volume of a chain, this is equivalent to a chain of N_i units, each with volume v_0 . $v_0 = 0.1 \text{ nm}^3$ is used for all χ parameters and chain lengths described in this thesis. The normalization allows direct comparison of the chain lengths of homopolymers with different monomer volumes.

The majority of polymer blends exhibit an upper critical solution temperature (UCST), indicated by a positive value of b in eq. 1.2. UCST blends are homogeneous for any temperature above the critical temperature, and are macrophase separated within an envelope of temperatures below the critical temperature. Lower critical solution temperature (LCST) blends, identified by a negative value for b, are homogeneous below the critical temperature. A more general separated within an envelope of temperatures above the critical temperature. A more general phase diagram for binary blends can be established by selecting a different phase-space.

 χN is the meaningful thermodynamic parameter for the case of a symmetric binary blend where $N_{\rm B} = N_{\rm C} = N$. For both LCST and UCST blends $\chi N = 2$ at the critical point. Below $\chi N =$ 2 the blend is homogeneous, and above 2 the blend is macrophase separated within an envelope of χN values. For asymmetric blends $N_{\rm B} \neq N_{\rm C}$, and the thermodynamic parameter of interest is

of χN values. For asymmetric blends $N_{\rm B} \neq N_{\rm C}$, and the thermodynamic parameter of interest is $\chi N_{\rm AVE}$ where

$$N_{AVE} \equiv 4 \left[\frac{1}{N_B^{1/2}} + \frac{1}{N_C^{1/2}} \right]^{-2}$$
(1.4)

Phase diagrams are conventionally reported in the phase space of χN versus blend composition. Flory-Huggins theory predicts that for the simple case of $\chi(T)$, the critical composition depends only on $N_{\rm B}$ and $N_{\rm C}$.^{1,2} Blends prepared at the critical composition are used to measure χ because the magnitude of composition fluctuations is largest at the critical point. Scattering techniques, such as small angle neutron scattering (SANS), directly measure fluctuations and result in accurate measurements of χ . Measurements are limited to the homogeneous region of the phase diagram where Flory-Huggins Theory can be applied.

1.1.2. Composition and molecular weight-dependent χ

Two classes of blends are known to exhibit χ that is a function of both temperature and composition, $\phi_{\rm B}$: isotopic polymer pairs (i.e. the deuterated and hydrogenated analogues of a chemical species) and LCST blends. $\chi(T,\phi_B)$ has been measured for deuterated/hydrogenated pairs of polystyrene^{3,4}, polyvinyl ethylene⁵, polyethylene⁶, polybutadiene⁷⁻¹⁰, polyethyl butadiene¹¹, polydimethyl siloxane¹², as well as LCST blends of polystyrene/polyvinyl methylether^{13,14}, polyisobutylene/poly ethylene butenes¹⁵, polytetramethyl bisphenol A polycarbonate/polystyrene¹⁶, and polyisobutylene/polybutadiene with 63% 1,2 addition. The observed composition dependence derives from local effects that deviate from the Flory-Huggins mean field assumptions of structurally symmetric units on a lattice. The structural asymmetry of monomers (or normalized lattice units) results in biased monomer-monomer interactions. For the case of isotopic pairs, the difference in the bond lengths of the C-H bond and the C-D bond is sufficient asymmetry to drive a bias.¹⁹ The resulting local composition fluctuations, used to measure χ , are also biased towards the lowest energy configuration.⁶ However, the spatial bias of monomers that interact in preferential orientations cannot be decoupled from measurements based on scattering techniques. Application of the Flory-Huggins Theory to such measurements results in an observed composition dependence of χ . Equation-of-state models have replicated the empirical composition dependence of χ by accounting for monomer density fluctuations within a local fluid structure.²⁰⁻²⁴ Lattice theories^{10,25-27}, Monte Carlo simulations²⁸, and the polymer reference interaction model²⁹ have all confirmed that a composition-dependent χ can be derived from local structural asymmetry.

 χ is usually presumed to be independent of $N_{\rm B}$ and $N_{\rm C}$, as the former describes the enthalpic contribution to the free energy of mixing, and the latter two relate to the entropic contribution. The measurement of a χ parameter that depends on $N_{\rm AVE}$ has been observed for several LCST systems^{3,5,6,12,17,27} when χ is also dependent on composition. The functional dependence of χ can be written generally:

$$\chi(T, \phi_A, N_{AVE}) = f(T) + \frac{g(T, \phi_B)}{N_{AVE}}$$
(1.5)

In the limiting case $N_{AVE} \rightarrow \infty$ the mean-field behavior (i.e. χ is a function of *T* only) is recovered. Flory-Huggins Theory does not account for the entropy due to chain ends which becomes important for small polymers but vanishes in the limit of large N_{AVE} . Theories that account for fluctuations due to chain ends, such as that of Olvera de la Cruz et. al.²¹, predict the χ dependence of eq. 1.5.

The composition and molecular-weight dependences of χ described above represent empirically-inspired modifications to Flory-Huggins Theory. Despite the simplicity of the lattice model, Flory-Huggins Theory remains the starting point for all thermodynamic studies involving polymer blends because it can accurately predict phase behavior using a single, carefully measured, χ parameter.

1.2 Ternary Blends

1.2.1. Analogy to small-molecule blends

Ternary blends comprising two immiscible homopolymers, A and B, and a diblock copolymer surfactant can produce thermodynamically stable, microphase separated structures. Such materials find application to technologies involving controlled transport,³⁰⁻³³ however the production of diblock surfactant is expensive. The phase behavior of these systems is of technological impact as it can provide a low-surfactant route to ordered microstructures. These blends are thermodynamically analogous to oil/water mixtures with nonionic surfactants³⁴⁻⁴⁴ wherein the alkyl polyglycol ether portion of the surfactant exhibits attractive interactions with water. Thus homopolymer A is analogous to oil, homopolymer B is analogous to water, and the diblock copolymer behaves like the nonionic surfactant. The so-called "fish cut" phase diagram presents the phase behavior for oil/water/surfactant blends in the phase-space of *T* and the fraction of surfactant. It is analogous to the phase behavior observed for ternary polymer blends. Both ternary systems exhibit two and three-phase coexistence, ordered microstructures like lamellae and hexagonally packed cylinders, and disordered microemulsions. Increasing amounts of surfactant result in a larger temperature window for ordered phases.

Oil/water/surfactant studies have systematically varied the molecular weight of the oil to observe the effect of molecular weight on the type of microstructure formed.⁴²⁻⁴⁴ In these studies, the molecular weight of the hydrophilic phase is invariant because water is used. The molecular weights of both homopolymers, the oil- and the water-analogue, are controlled in polymer blends, providing an additional thermodynamic parameter for tuning polymer systems. Adjusting the ratio of the molecular weights of homopolymers A and B, known as the molecular weight asymmetry, may provide a route to microstructured blends that use low concentrations of surfactant.

1.2.2. Development of phase diagrams

Diblock copolymers were first tested as a surfactant for immiscible blends of homopolymers in 1967 by Riess et al.⁴⁵ In this and the majority of subsequent experiments, a symmetric blend of A and B homopolymers ($N_A = N_B$) was blended with a symmetric A-B diblock copolymer.^{10,46-63} In 1992 Holyst and Schick predicted that A-B diblock copolymers would only order an A/B binary blend at volume fractions of copolymer, $\phi_{diblock} > 0.5$.⁶⁴ While their prediction has not proven quantitative, the use of high concentrations of diblock copolymer is an intrinsic limitation of A/B/A-B systems. The use of an A-C diblock copolymer, where the C block is chosen to have favorable interactions with the B homopolymers.⁶⁵⁻⁷⁴ Despite this advantage, most theoretical and experimental work continues to pursue A/B/A-B systems because a single χ parameter can characterize all the interactions.

Flory-Huggins Theory may be extended to predict the one-phase region of multicomponent blends, however the utility is limited as the theory is not designed to differentiate between equilibrium phases that are microstructured and macrophase separated.

Shortly after the first experimental studies of ternary blends, new theories were developed for predicting the phase behavior. The first theoretical studies calculated the surface tension between the A and B phases when the junction of the A-B diblock copolymer was located at the interface.⁷⁵⁻⁷⁹ Leibler predicted a stable microemulsion phase by considering the curvature of such interfaces.⁷⁷ Noolandi and Hong used a mean-field approach to predict the concentration profiles of A and B through an emulsified interface in the presence of a non-interacting solvent.⁷⁹ Both groups showed that the entropic penalty associated with localizing a diblock copolymer at the A/B interface can be compensated by the enthalpic favorability of surrounding blocks with a compatible domain for a wide range of molecular weights.

The effect of molecular weight upon interfacial tension is pronounced in microstructured polymer blends.^{65,75-79} Homopolymers that are small relative to the diblock copolymer easily swell the copolymer domains, a phenomenon known as the wet brush regime. Large homopolymers cannot interpenetrate the stressed copolymer domains and separate from the copolymer, this is known as the dry brush regime. Roughly, the wet and dry brush regimes are delineated at $\alpha_i = 1$, where $\alpha_i = N_i/N$ for $i = \{A, B\}$, and N is the total length of the diblock copolymer.

The development of mean field self-consistent field theory (SCFT) enabled the prediction of ordered microphases. Janert and Schick generated the first theoretical phase diagrams for A/B/A-B blends allowing only lamellar microphases.^{80,81} They chose a homopolymer isopleth (i.e. fixed concentrations of A and B) and allowed the concentration of diblock copolymer to vary. They found that at high concentrations of copolymer a lamellar phase undergoes an unbinding transition wherein the lamellae continue to swell with increasing homopolymer concentrations of copolymer, i.e. the domain spacing diverges. At lower concentrations of copolymer, lamellar blends undergo macrophase separation.

In a series of landmark publications, Bates and coworkers reported the formation of microemulsions in symmetric A/B/A-B blends where $\chi_{AB}N$ for the diblock was around 10.5 and $\chi_{AB}N_A$ was in the vicinity of 2.0 for the binary blend without diblock.^{33,47,56,63,82-85} The pure binary blend undergoes a one-phase to two-phase transition at $\chi_{AB}N_A = 2$. The addition of copolymer slightly affects the location of this transition, mapping a "Scott line" of phase transitions in $\chi_{AB}N_A - \phi_{diblock}$ phase-space. The neat diblock copolymer undergoes an order-disorder transition (ODT) at $\chi_{AB}N = 10.5$; the location of the ODT changes with the addition of homopolymers. This line of ODT's meets the Scott line at an isotropic Lifshitz point, denoting the coexistence of a lamellar phase, a disordered phase, and macrophase separation.^{77,79,86-89} At the transition between lamellae and macrophase separation, fluctuations destroy the Lifshitz point, giving rise to a microemulsion channel.

While the effects of molecular weight asymmetry between A and B homopolymers is expected to significantly increase the window in which microemulsions are observed,^{21,88} only limited theoretical effort has been applied to this direction, and no previous experimental effort. This dissertation represents the first systematic study of the effects of α_i on phase behavior in ternary polymer blends.

1.3 Polymer systems

The binary blends studied comprise polyisobutylene (component B), and deuterated polybutadiene with 63 % 1,2 addition (component C). The ternary blends comprise deuterated polybutadiene with 89 % 1,2 addition (component A), polyisobutylene (component B), and a

hydrogenated polybutadiene with 89% 1,2 addition-*block*-polybutadiene with 63 % 1,2 addition (A-C). The deuterated homopolymer A is expected to behave identically to the hydrogenated A-block of the diblock copolymer, and likewise the deuterated homopolymer C behaves the same as the hydrogenated C-block. The Flory-Huggins χ interaction parameters were obtained from fits of the random phase approximation to SANS profiles from binary blends within the homogeneous window. χ_{BC} is negative over most of the experimental temperature window, signifying attractive interactions between components B and C. All other interactions are repulsive. The temperature dependences of χ_{AB} and χ_{AC} are reported in ref. ⁷⁰ and the composition and molecular weight dependence of χ_{BC} is reported in ref. ¹⁷. These values are summarized in footnote 90.

1.4 Dissertation outline

This dissertation describes the phase behavior in binary and ternary blends of polyolefins. Chapter 2 introduces the synthetic procedures used to make the polymers used, the polymer characterization techniques, and the SANS measurements used to study polymer blends. Chapter 3 describes the theory of polymer blends, beginning with the Flory-Huggins Theory and describing subsequent advances. The measurement of a composition and molecular weight-dependent χ_{BC} is the topic of Chapter 4. In Chapter 5 the phase behavior of asymmetric binary B/C blends is described in relation to the empirical form of χ_{BC} . Chapter 6 examines the phase behavior of A/B/A-C ternary blends in which A and B are asymmetric homopolymers blended at the Flory-Huggins critical composition (on a copolymer-free basis). Finally, Chapter 7 describes the phase behavior for a series of systematically-varied off-critical ternary blends with a constant asymmetry.

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- (90) Note. Temperatures are in K: $\chi_{AB} = 0.00034 + 3.94/T 817/T^2$; $\chi_{AC} = 0.00209 1.18/T + 747/T^2$; $\chi_{BC} = -0.00622 + 10.6/T 3040/T^2 + (-0.722 + 638/T 229000/T^2)(0.2 \phi_B)/N_{AVE,BC}$. Statistical Segment lengths: $l_A = 0.55$ nm; $l_B = 0.58$ nm; $l_C = 0.75$ nm.

Chapter 2

Experimental Methods

The synthesis of polyisobutylene and polybutadiene was carried out using cationic and anionic synthesis techniques and a high vacuum schlenk line. Polymers were characterized using gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), and a density gradient column. Binary and ternary polymer blends were prepared from the synthesized polymers. Blend structure was probed using small angle neutron scattering (SANS) and small angle light scattering (SALS).

2.1 Synthesis

2.1.1. Synthesis of TMPCl

2-chloro-2,4,4-trimethylpentane (TMPCl) was the initiator for polyisobutylene; it was synthesized¹ by slowly bubbling hydrogen chloride (HCl) gas through a solution of 2,4,4-trimethyl-1-pentene (TM1P) and dichloromethane (DCM) to chlorinate the double bond in TM1P (shown in Reaction scheme 2.1). The resulting solution was purified until only TMPCl remained. The synthetic setup is shown schematically in Figure 2.1

Reaction Scheme 2.1. Synthesis of TMPCl from TM1P and HCl



Figure 2.1. Schematic experimental setup for the synthesis of TMPCI.



2,2,4--trimethyl-1-pentene 99.9% was purchased from Sigma-Aldrich (T78409-100G). Fisher brand products included: HPLC grade dichloromethane 99.9% (D150-1), sulfuric acid 95% (7664-93-9), ACS grade crystalline sodium chloride 99.0% (7647-14-5), and calcium chloride 20 mesh for desiccators (C614-500).

The reaction was extremely sensitive to water in the DCM and only reached ~10 % completion without when the DCM was used as received. The conversion was ~97 % when the DCM was purified. The DCM was dried over crushed calcium hydride on a high vacuum schlenk line. The purification stage was free degassed once, hard degassed three times, and left stirring overnight. The DCM was then distilled into a clean reactor using dry ice/IPA to cool the reactor. The distilled DCM was transferred to an argon glovebox and 200 mL was added to a clean 250 mL round bottom flask with three ports. The ports were stoppered with rubber septa and the DCM was stored briefly in the glovebox while the rest of the setup was prepared.

The DCM flask was transferred from the glovebox to a hood with the septa still sealing all three ports. As quickly as possible, a very large stirbar was added to the flask along with 21 g of TM1P (used as received), and the center septum was replaced. The two side septa were removed and replaced with sealed connections to the experimental setup. The DCM flask was suspended in an ice bath atop a stir plate. A crystallization dish was used for the ice bath so that the stir plate magnetic field could turn the stirbar in the reactor flask. All the connections shown in Figure 2.1 were made with clear polypropylene tubing. Small glass pipettes were inserted into each end of the tubing (so that the plastic did not swell shut during the synthesis) and the pipette was introduced into a rubber septum in the ports of the flask. A small hole was punched into the septum to accommodate the pipette.

A 500 mL round bottom flask with three ports was filled two-thirds of the way with NaCl. 25 mL of sulfuric acid was charged to a buret and dripped very slowly (~ 3 drops /10 min) onto the salt to produce a continuous flow of HCl gas. The HCl gas was dried by passing it through a small column packed with anhydrous calcium chloride (CaCl₂) and then bubbled continuously into the solution of TM1P and DCM with stirring for nine hours at 0 °C. Excess gas was routed through a second column of anhydrous CaCl₂ and bubbled into a beaker with water to absorb the HCl. The second CaCl₂ column protected the reaction against water vapor diffusing from the waste beaker. The color of the reacting fluid changed from clear to pale yellow after 4.5 hours and became greenish-yellow after 5 hours. The color intensified through 7 hours of reaction, and did not change thereafter. During this time, the drip rate of sulfuric acid was carefully monitored to maintain a continuous stream of HCl bubbles into the reactor. Low flow rates were shown to cause low conversion.

The reacted mixture of TM1P, DCM, and the product TMPCl was purified on the high vacuum schlenk line. The mixture was transferred to a clean round bottom flask, free degassed once, and hard degassed once. The unreacted DCM was distilled into a waste flask, using ice water to cool the flask, for one hour. The cold source was switched to dry ice/IPA and DCM continued to distill off. The yellow color of the TMPCl flask intensified as DCM was removed. When the distillation slowed, the TMPCl flask was warmed with a room temperature water bath and the distillation was allowed to continue for three hours. The TMPCl flask was removed from the vacuum line, 10 g of crushed calcium hydride was added, the flask was returned to the vacuum line, free degassed once, hard degassed once, and stirred overnight. The TMPCl was hard degassed again using only the rotary vane pump, then a second time using the diffusion pump. The clean, dry, TMPCl was distilled into a clean reactor using liquid nitrogen to cool the reactor and room temperature water to warm the TMPCl stage. The distillation proceeded very

slowly and the distilled TMPCl was nearly clear with a slight peach-colored tinge. The purified TMPCl was stored and used in the glovebox. TMPCl is known to remain pure and effective for 4+ years of storage. NMR may be used to confirm the purity of TMPCl after long periods of disuse.

2.1.2. Synthesis of polyisobutylene

Polyisobutylene was synthesized in a solution of hexane and methylene chloride using TMPCl as the initiator, titanium (IV) chloride (TiCl₄) as the co-initiator, and the reaction was terminated with isopropanol (IPA) as shown in Reaction Scheme 2.2.

Reaction Scheme 2.2. Initiation, propagation, and termination of polyisobutylene



Polyisobutylene was synthesized cationically because the "living" center was a tertiary carbon stabilized by the electron density from neighboring carbon atoms.² TiCl₄ reacted reversibly with TMPCl to form the ion pair shown in Reaction scheme 2.2. The carbocation formed had a lifetime of ~10 ns, during which time it could react with the isobutylene double bond. TiCl₄ behaved as a Lewis acid, and would have reacted with any water present to commence an undesirable side reaction. A small amount of dimethyl phthalate (DMP) was placed in the reactor fluid prior to the addition of TiCl₄ to sequester unreacted water.³ However, DMP would have complexed with TiCl₄ if they had been added simultaneously to the reactor. Instead, the reactor was prepared with hexane, dichloromethane, DMP, and TMPCl. A small volume of isobutylene monomer was added to the reactor prior to the addition of TiCl₄. In the presence of monomer, the TiCl₄ reacted with TMPCl as desired to initiate the polymerization. Only a small amount of monomer was charged to the reactor during this step because the rate

constant for polymerization was highly dependent on the number of monomers added when the oligomers were less than 5 units long: $k_1 < k_2 < k_3 < k_4 < k_5 \cong k_p$. Longer chains would have grown more quickly and lead to a polydisperse product. By allowing a small amount of monomer to react completely, most of the chains reached 5 units in length, and subsequent growth was uniform amongst the chains. The resulting polymer was nearly monodisperse with a polydispersity index ≤ 1.04 .

Calculations:

The amount of isobutylene (IB) reacted is fixed by the volume of the reaction: 30 g IB per 0.431 L total solvent. Dimethyl phthalate (DMP) is used at a concentration of 1.5×10^{-3} mol/L, so it is also fixed by the volume of solvent used. The solvent is a mixture of 3:2 hexane:DCM. The target molecular weight of the product is used to calculate the moles of TMPCl needed, however the amount of TiCl₄ is based on kinetic considerations. The rate law for polymerization is given by⁴:

$$Rate = k_p [TMPCl] [IB] [TiCl_4]^2$$
(2.1)

The rate constant, k_p , is considered truly constant for oligomers of five or more units, so the rate is proportional to the concentrations of TMPCl and IB and the square of the concentration of TiCl₄. It was empirically determined that for [TMPCl][IB][TiCl₄]² = 3.41 × 10⁻¹⁵ mol⁴L⁻⁴ the polymerization goes to completion within 12 hours at dry ice/IPA temperature (-78 °C). Once the concentrations of IB and TMPCl have been fixed, the concentration of TiCl₄ is calculated from this equality. Physical properties of the chemicals used are listed in Table 2.1.

chemical	density (g/mL)	molecular weight (g/mol)
isobutylene	0.702 (-78 °C)	56.12
TMPCl	0.875 (20 °C)	148.7
DMP	1.19 (25 °C)	194.2
$TiCl_4$	1.73 (25 °C)	189.7
hexane	0.655 (25 °C)	86.18
hexane	0.735 (-78 °C)	86.18
DCM	1.33 (25 °C)	84.93
styrene	0.906 (20 °C)	104.2

Table 2.1. Physical properties of chemicals used for synthesizing polyisobutylene and polyisobutylene-*block*-polystyrene

Synthesis preparation:

The following chemicals were purchased from Sigma-Aldrich: a solution of 1.4 M secbutyllithium in cyclohexane (195596-100ML), titanium (IV) chloride 99.995 % (254312-10g), and a gas cylinder with isobutylene 99 % (295469-1kg). Burdick and Jackson brand products were ordered through VWR Labshop: ACS/HPLC grade methanol >99.9 % (BJAH230-4) and ACS/HPLC grade hexane >99.9 % (BJAH212-4). HPLC grade dichloromethane 99.9 % (D150-1) was purchased from Fisher. 2-chloro-2,4,4-trimethylpentane was synthesized as described in Section 2.1.1.

Prior to making polyisobutylene, TMPCl was synthesized as described above. Dimethyl phthalate (DMP) and isopropanol (IPA) were purified and stored in the glovebox, and a second stage for hexane purification was prepared (if one had not already been made). The DMP was purified by stirring 50 mL of DMP with 5 g of crushed calcium hydride in a small long-necked flask. The flask was attached to the vacuum line, free degassed, hard degassed, and left stirring overnight. The DMP was hard degassed with the diffusion pump, distilled into an ampoule or small reactor using dry ice/IPA to chill the cold stage, then stored in the glovebox. The IPA was purified in small quantities because it froze violently. Calcium hydride could not be used to dry the solvent because it would have reacted exothermically with IPA. 100 mL of IPA was added to a 1 L long-necked flask with a clean stirbar. The flask was attached to the vacuum line, free degassed once, hard degassed three times with the rotary vane pump, and hard degassed once with the diffusion pump. The IPA was distilled into a 250 mL clean reactor using dry ice/IPA to chill the reactor and leaving behind ~20 mL. The distilled IPA was stored in the glovebox. The second stage for hexane purification was made in a clean, torched 2 L reactor. 100 mL of 1.4 M sec-butyl lithium solution (in heptane) was added to the reactor in the glovebox. The reactor was transferred to the vacuum line, free degassed, hard degassed, and the hexane was distilled into a waste flask using liquid nitrogen to cool the flask. The reactor was then left open to the pump for 4 hours or until the pressure stopped decreasing. In a separate flask, 500 mL of hexane was added to 5 g of crushed calcium hydride. The hexane was free degassed, hard degassed three

times, and left stirring overnight. The hexane was hard degassed with the diffusion pump then distilled into the sec-butyllithium stage using dry ice/IPA to cool the reactor. The reactor was transferred to the glovebox and 25 g of diphenyl ethylene was slowly pipetted into the reactor with stirring. The sec-butyl lithium and diphenyl ethylene reacted exothermically, so they were added together slowly in the presence of excess hexane to serve as a heat transfer medium. The second stage was sealed with a valve and stored in a flame-proof cabinet outside the glove box. It was re-used for multiple purifications and terminated when the burgundy color began to fade.

Day 1:

The purification began for hexane, DCM, and IB. 500 mL of hexane was added to a 1L long-necked flask along with 5 g of crushed calcium hydride and a long stirbar. The hexane was free degassed once, hard degassed three times using the rotary vane pump, and left stirring overnight. 400 mL of DCM was added to a 1 L long-necked flask along with 4 g of calcium hydride and a large stirbar. The DCM was attached to the vacuum line, free degassed once, hard degassed three times using the rotary vane pump, and left stirring overnight. 50 - 100 mL of isobutylene was condensed into a 250 mL long-necked flask using dry ice/IPA to cool the flask. First, 2 g of crushed calcium hydride and a stirbar were added to the empty flask. Then the isobutylene regulator was connected to a polypropylene hose that was introduced into the flask just above the meniscus of the condensing isobutylene. The flask was placed in the dry ice/IPA bucket inside a hood, and the regulator was slowly opened until condensed isobutylene was seen to slowly drip from the tubing inside the flask. Once the desired amount of isobutylene had condensed within the flask (this took 30 - 60 minutes), the flask was immediately transferred to the vacuum line, free degassed once, and hard degassed three times using the rotary vane pump. Following each hard degas, the liquid nitrogen was removed from the flask for ~2 minutes. The flask was slowly returned to a dry ice/IPA bath while the isobutylene thawed. After degassing, the isobutylene was left stirring, in a dry ice/IPA bath for six hours. Overnight the flask was stored in a dewar packed with dry ice, but the solvent was not actively dried during this time because it could not be stirred due to the thickness of the dewar.

<u>Day 2:</u>

The hexane was hard degassed using the diffusion pump. The hexane second stage was placed on the vacuum line and hard degassed with the rotary vane pump then with the diffusion pump until the vacuum was $\sim 10^{-4}$ torr. The hexane was distilled into the second stage using dry ice/IPA to cool the second stage. The hexane was allowed to stir overnight. The DCM was hard degassed with the diffusion pump, and distilled into a second flask containing 4g of crushed calcium hydride and a stirbar, using dry ice/IPA to chill the second flask. The DCM was stirred overnight on the calcium hydride. The isobutylene was hard degassed with the diffusion pump and distilled into a second flask with 3 g of crushed calcium hydride and a stirbar using dry ice/IPA to chill the second flask with 3 g of crushed calcium hydride and a stirbar using dry ice/IPA to chill the second flask with 3 g of crushed calcium hydride and a stirbar using dry ice/IPA to chill the second flask with 3 g of crushed calcium hydride and a stirbar using dry ice/IPA to chill the second flask and salty ice water (-10 °C) to warm the isobutylene (water/ice/NaCl) to keep the flask below the boiling point of isobutylene at -6.6 °C). The isobutylene was stirred on calcium hydride for six hours at dry ice/IPA temperature, then stored overnight in a dewar packed with dry ice. A 1 L reactor with two 24/40 ports was prepared as synthesis vessel by marking lines on the outside where measured amounts of DI water correspond to the needed volumes of hexane and methylene chloride for the reaction. The

amount of hexane used was 20 mL less than the volume chosen for calculations, as a 20 mL aliquot was added to a separate ampoule with the TiCl₄. The reactor was marked and then placed in the oven to dry overnight.

<u>Day 3:</u>

The hexane was hard degassed with the diffusion pump. Then a clean ampoule was attached directly to the vacuum line, torched, and ~20 mL of hexane was distilled into the ampoule using dry ice/IPA to cool the ampoule. The ampoule was transferred into the glove box along with a 50 mL beaker, blunt tipped needed, 20 mL syringe, and a larger beaker for trash. The 20 mL of hexane was poured into the small beaker and the appropriate amount of titanium (IV) chloride (TiCl₄) was added with a pipette. The hexane/TiCl₄ solution was drawn into the syringe, the needle was locked into the luer fitting, and the solution was injected into the ampoule. All waste was placed into the large beaker, and Kimwipes were removed as they are flammable. The ampoule was transferred back to the vacuum line and hard degassed. Since the ampoule is so small, the valve was cold after freezing and care was taken to avoid breaking the valve by overtightening it. Carefully the valve was tightened and the ampoule was warmed to room temperature, at which point the valve was further tightened if necessary. The 1 L reactor with volume markings was attached to the line and torched under high vacuum. The side port was closed with a greased glass port cap and evacuated. The cap on the side port prevented oxygen from entering the vessel when the reactor was cooled. Failure to add a cap had resulted in a previous explosion.

The hexane was degassed with the diffusion pump and distilled into the reactor using dry ice/IPA. Next the DCM was degassed with the diffusion pump and distilled into the reactor using dry ice/IPA. The reactor and the degassed ampoule were transferred into the glove box along with vacuum grease and a vacuum port clamp. The DMP was added to reactor (with stirring), then the TMPCl, and then the degassed ampoule with hexane/TiCl₄ was attached to one port of the reactor, keeping grease away from the opening. The reactor was transferred to the vacuum line and hard degassed with the diffusion pump. The valve leading to the ampoule was opened so the space between the reactor and ampoule could be degassed. The isobutylene was hard degassed and distilled into a clean measuring ampoule using dry ice/IPA to cool the ampoule and warming the isobutylene with salty ice at -10 °C. The reactor. The vacuum line was closed to the isobutylene and the reactor was stirred for 5 minutes. The valve on the ampoule was opened to slowly allow the TiCl₄ solution to drain into the reactor. Dry ice/IPA cooled the reactor for 12 hours while the reaction proceeded.

Termination and purification:

Once the reaction was complete, the reactor volume was frozen, hard degassed, and thawed with dry ice/IPA. The distilled IPA was transferred from the glovebox to the vacuum line and hard degassed once. 5 mL of IPA were distilled into the reactor until the reacting fluid turned clear. At this point, the polyisobutylene was terminated and was removed from the vacuum line. The dissolved polymer was immediately precipitated in methanol and redissolved in hexane three times. The dissolved polyisobutylene was filtered with a 0.2 μ m Whatman filter, precipitated once more, and dried with nitrogen for two days. Finally the polymer was dried under vacuum at room temperature for one day, the temperature was raised to 150 °C for an additional day, and the polymer was stored in a freezer.

2.1.3. Synthesis of polyisobutylene-block-polystyrene

Polyisobutylene-*block*-polystyrene (PSIB) was synthesized cationically using TMPCl as the initiator.⁵ Polyisobutylene was the first block synthesized according to the procedure in section 2.1.2. Following the completed polymerization of PIB, purified styrene monomer was added to the reactor and the polystyrene block was allowed to react.

Styrene 99 % was purchased from Sigma-Aldrich (240869-100mL) and a solution of 1.0 M dibutylmagnesium in heptane (345113-100mL). The volume of styrene used was fixed by the desired molecular weight; the formula weight and density are given in Table 2.1.

Day 1 of styrene purification:

The purification of styrene took two days and was planned to coincide with the completion of the polyisobutylene block. 100 mL of styrene was placed in a 250 mL long-necked flask with 1 g of crushed calcium hydride and a stirbar. The styrene was free-degassed once, hard degassed three times, and stirred overnight. A second purification stage was prepared in the glovebox. 10 mL of 1.0 M dibutylmagnesium in heptane were added to a clean, torched 500 mL reactor. The reactor was transferred to the vacuum line, free degassed, and the heptane was distilled to a waste flask using dry ice/IPA to cool the empty flask. The pure dibutylmagnesium was left open to the vacuum pump overnight.

Day 2 of styrene purification:

The styrene was hard degassed once using the rotary vane pump, thawed, and degassed again using the diffusion pump. If the pressure did not drop to $\sim 10^{-4}$ torr within 5 minutes, the styrene was degassed an additional time to ensure an easy distillation. The thoroughly degassed styrene was distilled into the dibutylmagnesium stage using liquid nitrogen to cool the second stage. The styrene was left stirring overnight. A measuring ampoule was place on the schlenk line, torched, and evacuated overnight.

Day 3 of styrene purification and reaction:

The styrene was hard degassed using the diffusion pump, then distilled into the measuring ampoule using liquid nitrogen to cool the ampoule. Any extra styrene was distilled

off the dibutylmagnesium into a clean empty reactor and stored in the glovebox for up to a month. The reactor containing living polyisobutylene chains was frozen with liquid nitrogen and degassed. The reactor was returned to dry ice/IPA and the styrene was very slowly (~ 4 hours/30 mL of styrene) distilled into the reactor. The slow addition of styrene ensured a low poldispersity index. The reaction was allowed to proceed at -78 °C for 20 hours, and terminated by distilling in 5 mL of purified IPA. The diblock was purified and stored in the same way as the PIB homopolymer (see section 2.1.2).

2.1.4. Synthesis of polybutadiene

Polybutadiene was synthesized anionically from 1,3 butadiene in the presence of a solvent with controlled polarity. The butadiene monomer adds at both the 1,2 positions and the 1,4 positions, resulting in a random copolymer. Reaction schemes 2.3a and b show the initiation, propagation, and termination of 1,4 polybutadiene and 1,2 polybutadiene, respectively. The fraction of 1,2 addition is ~7 % in pure hexane and ~97 % in pure tetrahydrofuran (THF). For this study polybutadienes with either 89 % or 63 % 1,2 addition were synthesized. Previous work has established a calibration curve relating the fraction of 1,2 addition to both the concentration of initiator and the ratio of THF to initiator.⁶ Figure 2.2 shows the calibration for syntheses using 0.00053 M sec-butyllithium. The percent of 1,2 addition is highly sensitive to the ratio of THF:sec-butyllithium when the ratio is small, and insensitive at relatively high values of the ratio.

Reaction 2.3. Initiation, propagation, and termination of polybutadiene with (a) 1,4 addition and (b) 1,2 addition.





Figure 2.2. Percent of 1,2 addition as a function of THF:secbutyllithium ratio in the reacting fluid for polybutadienes synthesized using 0.00053 M secbutyllithium. Some data points are reproduced from Megan L. Robertson's Ph.D. Thesis.



Calculations and preparation:

For all reactions, the volume of hexane was chosen to be 500 mL at 20 °C and the concentration of sec-butyllithium was chosen to be 0.00053 M (calibration curves for additional concentrations are given in the Ph.D. dissertation of Megan L. Robertson⁶). For a targeted 89 % 1,2 addition the THF:sec-butyllithium ratio was chosen to be 240, and for 63 % 1,2 addition the ratio was 21.4. A target molecular weight was chosen for the polymer, and this, with the predetermined concentration of sec-butyllithium, set the mass of monomer to be used. The volume of THF added to hexane was taken into account as the total reactor volume for calculating the concentration of sec-butyllithium. The physical properties needed for calculations are listed in Table 2.2.

chemical	density (g/mL)	molecular weight (g/mol)
THF	0.888 (20 °C)	72.12
hexane	0.735 (-78 °C)	86.18
butadiene	0.650 (-4.5 °C)	56.10

Table 2.2. Characteristics of selected chemicals used for polybutadiene synthesis

A solution of 2.0 M n-butyllithium in cyclohexane (302120-100mL) was purchased from Sigma-Aldrich. Fisher supplied: Acros brand tetrahydrofuran ACS/HPLC grade 99.9 % (AC32697-0010) and MP Biomedicals Inc butylated hydroxytoluene (ICN10116290). Burdick and Jackson brand products were ordered through VWR Labshop: ACS/HPLC grade methanol >99.9 % (BJAH230-4), ACS/HPLC grade acetone > 99.9% (BJAH010-4), and ACS/HPLC grade hexane >99.9 % (BJAH212-4). 1,3-butadiene 99.8 % was purchased in a 2.8 lb gas cylinder from Praxair.

<u>Day 1:</u>

1,3-butadiene monomer was condensed into a long-necked flask containing a stirbar and 1 g of crushed calcium hydride for every 100 mL of butadiene. The monomer was directed from the cylinder through a column packed with neutral alumina and another column packed with molecular sieves while dry ice/IPA chilled the recipient flask. The butadiene was very briefly free degassed, hard degassed three times, and left stirring overnight. ~500 mL of hexane were dispensed from the still into a dried and torched 1 L reactor containing a clean stirbar. The hexane was free degassed on the line and hard degassed three times. A small reactor for THF was dried and torched, then opened to ambient conditions long enough to add calcium hydride (1 g of crushed calcium hydride per 100 mL of THF) and a clean stirbar. The reactor was returned to the vacuum line and evacuated for one hour. ~100 mL of THF was dispensed from the still into the reactor, free degassed once on the vacuum line, hard degassed three times, and left stirring overnight. Calcium hydride was not used with the hexane dispensed from the still because properly dispensed solvents contain less water than a flask open to the ambient with calcium hydride. The THF was placed on calcium hydride as a precaution against the possibility that the solvent still had dispensed THF with an high water content. The second purification

stage for THF, a sodium potassium alloy (NaK), was highly hygroscopic and a small amount of contaminant water could have caused a dangerous exothermic reaction. Any moisture introduced to the THF by the use of calcium hydride was removed in the second purification stage.

The second stages for the monomer and both solvents were prepared on the first day. A medium reactor was evacuated and torched, then transferred to the glovebox when cool. Inside the glovebox, 1 mL of 1.4 M n-butyllithium in heptane was added per 100 mL of butadiene monomer to be purified and a clean stirbar. The reactor was returned to the line and evacuated. The heptane was distilled into a waste flask, then the reactor was opened to vacuum until the pressure remained constant at ~10⁻⁴ torr. The second stage of hexane was prepared as described in section 2.1.2., transferred to the vacuum line, free degassed once, hard degassed three times, and allowed to stir overnight. The second stage for THF was a 2L reactor containing particles of sodium-potassium alloy. The THF second stage was reused until the blue color faded, and stored between syntheses in a flame-proof cabinet in the hood. The second stage was hard degassed three times and left stirring overnight. Due to the highly reactive metals, it was considered too dangerous to store in lab and the second stage was terminated in 2008.

<u>Day 2:</u>

The butadiene was hard degassed once, thawed, and hard degassed a second time using the diffusion pump. It was distilled into the reactor with n-butyllithium using dry ice/IPA to chill the empty reactor and salty ice water (-10 °C) to warm the monomer flask. The butadiene monomer was stirred for eight hours on dry ice/IPA then packed into a dewar with dry ice for overnight storage. The hexane was hard degassed once using the rotary vane pump, thawed, and hard degassed a second time using the diffusion pump. It was distilled into the second stage using dry ice/IPA to chill the cold stage, and left stirring overnight. The THF was hard degassed once, thawed, and hard degassed a second time using the diffusion pump. It was distilled into the second stage using dry ice/IPA to chill the reactor, and left stirring overnight. The reaction vessel was evacuated on the line overnight along with a measuring ampoule appropriately sized for butadiene. For 63 % 1,2 addition, a small reactor was evacuated overnight and for 89 % 1,2 addition a small measuring ampoule was evacuated overnight.

Day 3:

The reactor was torched and allowed to cool. The hexane was hard degassed with the diffusion pump and the appropriate amount was distilled into the reactor. The THF was hard degassed with the diffusion pump. The butadiene was warmed with salty ice water (-10 °C) while stirring for ten minutes. It was distilled into the measuring ampoule using dry ice/IPA to chill the ampoule. Any butadiene remaining in the n-butyllithium stage was immediately distilled into an empty flask for temporary storage on dry ice/IPA. Once butadiene has been heated on an organometallic purification stage it must be transferred entirely from that stage to prevent the possibility of a Trommsdorf reaction. The use of n-butyllithium (as opposed to secbutyllithium) and the low concentration were both chosen to mitigate the risk of an explosion.

For 63 % 1,2 addition: The small evacuated reactor was torched and allowed to cool. The THF was distilled into the reactor using dry ice/IPA to chill the cold stage. Both the large reactor

containing hexane and the small THF reactor were transferred to the glovebox. The appropriate amount of sec-butyllithium initiator was pipetted into the reactor with stirring, followed by the appropriate amount of THF. A clean stir bar was added to the reactor. The vessel was quickly transferred to the vacuum line, free degassed, and hard degassed. The reacting fluid was maintained cold for the duration of the synthesis to prevent the THF from reacting with the initiator. The THF and initiator were both added at room temperature in the glovebox because they are very dilute for 63 % 1,2 addition and do not react quickly. The reactor was hard degassed, being very careful to wait until all the solvent was frozen to avoid altering the THF:hexane ratio. The correct amount of butadiene was distilled into the reactor using dry ice/IPA to chill the reactor. The reactor was warmed with ice water and left stirring at 0 °C for 12 hours.

<u>For 89 % 1,2 addition</u>: The evacuated ampoule was torched and allowed to cool. The THF was distilled into the ampoule using dry ice/IPA to chill the cold stage. The large reactor containing hexane was transferred to the glovebox and the appropriate amount of sec-butyllithium initiator was pipetted into the reactor and a clean stir bar was added. The reactor was transferred to the vacuum line, free degassed, and hard degassed. The reacting fluid was maintained cold for the duration of the synthesis to prevent the THF from reacting with the initiator. The appropriate amount of THF was distilled from the measuring ampoule into the reactor using dry ice/IPA to chill the reactor. The correct amount of butadiene was distilled into the reactor using dry ice/IPA to chill the reactor. The reactor was warmed with ice water and left stirring at 0 °C for 12 hours.

Day 4 (both 63 and 89 % 1,2 addition):

The reactor was quickly transferred to the glovebox and the reaction was terminated with the addition of ~5 mL of IPA. If the reactor had been yellow-tinged, the termination step was complete when the fluid turned clear. However, if the reacting fluid was clear during the reaction, it was allowed to stir with IPA for 10 minutes to ensure complete termination. The polymer solution was precipitated into 1 L of 1:1 methanol/acetone and re-dissolved in hexane twice. After two precipitations, the re-dissolved polymer was filtered with a 0.2 μ m alumina filter. 0.5 mass % butylated hydroxytoluene was weighed into the hexane/polymer solution to protect the unsaturated polymer from oxidation. Then the solution was dried using filtered house nitrogen for ~ 1 week, then evacuated in a vacuum oven for one day at room temperature, one day at 90 °C, and the polymer was stored in a freezer.

2.1.5 Synthesis of polybutadiene (63 % 1,2 addition)-block-polybutadiene (89 % 1,2 addition)

The diblock was made by first synthesizing a polybutadiene with 63 % 1,2 addition as described above. Following the 12 hours of reaction, the reactor was quickly transferred to the glovebox, an aliquot was removed for characterization, and the reactor was rapidly returned to the vacuum line and hard degassed. THF was distilled into a measuring ampoule and the correct amount was distilled into the reactor using dry ice/IPA to chill the reactor. Butadiene for the second block was distilled into the reactor, and the reactor was again heated to 0 °C for 12 hours, then terminated with IPA.

2.1.6. Deuteration of polybutadiene

Polybutadiene was saturated using a Parr pressure reactor and a homogeneous nickelaluminum catalyst. Previously, a heterogeneous catalyst (5 % palladium on barium sulfate) was used to saturate lower molecular weight polymers in the range of 9.9 - 220 kg/mol.⁶ However the catalyst failed to saturate a 307 kg/mol polybutadiene because the pores were too small to accommodate the polymer. While the purification of polybutadiene saturated with the heterogeneous catalyst was accomplished in a day, the reaction often required several iterations to fully saturate the polymer and was entirely ineffectual for higher molecular weight polymers. The homogeneous catalyst saturated the polymer completely after just one reaction, however the subsequent purification took several days. A 1:3 ratio of nickel:aluminum was used.^{7,8}

High pressure saturation with the homogeneous catalyst:

Burdick and Jackson brand ACS/HPLC grade cyclohexane >99.9 % was purchased fromVWR Labshop (BJ053-4). 1 M triethylaluminum in hexanes (252662) and nickel (II) ethylhexanoate 15 mass % Ni (338184) were purchased from Aldrich. Cyclohexane (CH) for preparation of the catalyst was purified. About 500 mL of CH was added to a long-necked flask with 5 g of crushed calcium hydride and a stirbar. The CH was free degassed, hard degassed three times, and stirred overnight. It was distilled into a clean reactor using dry ice/IPA to cool the cold stage, then stored in the glovebox for up to one month. The nickel (II) ethylhexanoate was purchased in 25 mL units and diluted with an additional 25 mL of purified cyclohexane. The triethylaluminum solution was used as received. Characteristics of the chemicals are listed in Table 2.3.

Table 2.3 . Characteristics of the chemicals used to prepare the here	nomogeneous cat	alyst
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chemical	ho (g/mL)	molecular weight (g/mol)
nickel (II) ethyl-		
hexanoate	0.835 at 25 C	345.1
triethyl aluminum	0.960 at 25 C	114.16
cyclohexane	0.779 at 20 C	84.18

The BHT was stripped from the polybutadiene prior to saturation. 10 g of polymer was dissolved in ~600 mL of cyclohexane and stirred overnight. Filtered house nitrogen was blown

upon the solution until either the volume was halved or a skin of polymer formed at the surface of the solution. The concentrated solution was precipitated into a solution of 500 mL of acetone and 500 mL of methanol and stirred for two hours. The solvent was decanted, replaced with ~500 mL of fresh methanol and acetone (blended 1:1), and allowed to stir for another 2 hours. Again, the solvent was decanted and the polymer was dried under filtered nitrogen for several hours. The partially-dry polymer was then re-dissolved in cyclohexane and the entire process was repeated once. Following the second precipitation, the polymer was allowed to dry overnight under nitrogen, dissolved into 1 L of cyclohexane, and stirred overnight.

On the day of saturation, 100 mL of cyclohexane was added to the 1 L of dissolved polymer, and filtered house nitrogen was blown onto the stirred solution for one hour to remove as much oxygen as possible. The solution was quickly transferred to the pressure reactor, purged 3-5 times, pressurized to 200 psi with nitrogen, heated to 50 °C, and held for two hours. The pressure was observed to be stable during this time as a check for the proper assembly of the pressure fittings. The homogeneous catalyst was prepared in the glovebox during the reactor pressure test.

The three ported catalyst vessel was used to add the homogeneous catalyst to the pressure reactor without exposure to air. Inside the glovebox, 50 mL of degassed, distilled cyclohexane was charged to the catalyst vessel. The valves were all closed and the vessel was inverted to wet the septa with cyclohexane and test the seals. Next, 24.5 mL of the (1.23 M) nickel hexanoate solution were added and the vessel was gently shaken until the liquid was uniformly green. Finally, 90 mL of 1 M triethyl aluminum was very slowly pipetted into the solution. This resulted in a 1:3 ratio of nickel:aluminum. The reaction was exothermic and smoked if the triethylaluminum was added too quickly. The catalyst vessel was gently shaken until the entire contents were uniformly black. The solution was left in the glovebox for several minutes while the pressure reactor was prepared, but the catalyst was made freshly for each saturation performed.

The reactor was depressurized and cooled to room temperature in preparation for the catalyst. The catalyst vessel was attached to the reactor, and as much as possible the head space was purged with nitrogen making sure that the reactor was open to atmosphere to avoid pressurizing the reactor. A needle connected to filtered house nitrogen was inserted into one of the top septa on the catalyst vessel, and the house nitrogen was slowly turned on, pushing the catalyst into the vessel. Once the catalyst has been added, the vessel was sealed, pressurized to 300 psi with deuterium, heated to 80 °C, and allowed to react, with stirring, for 24 hours. The pressure sometimes dropped ~50 psi within the first hour of deuteration, in which case more deuterium was added to restore the pressure to 300 psi.

Purification:

Before opening the pressure vessel, a solution of 100 g of citric acid and 3 L of deionized water was stirred until the citric acid dissolved. The reacted polymer solution (~ 1 L in volume) was divided into two equal volumes and each volume was purified separately. The separated solutions were further diluted with 1 L of cyclohexane. Each purification beaker was placed on the strongest possible stirplate with the largest possible magnetic stirbar. As the solution stirred, 1.5 L of citric acid solution was added to each batch of polymer solution. The stirplate was adjusted so that the organic and aqueous phases were well mixed, and the solution was left to stir overnight. After stirring, the organic and aqueous phases were left for an hour to phase separate.

The aqueous phase was clear green and sank to the bottom of the beaker, the organic phase was slightly cloudy and grey. At the interface, a grey layer of opaque bubbles formed. Using house vacuum and a pipette attached to a waste flask, the aqueous phase was removed including the grey specks at the interface between the two phases. Another 1.5 L of fresh citric acid solution was added to the organic phase and the process was repeated. After the second separation, the organic phase, only slightly grey, was condensed in the Rotovap and precipitated into 1 L of 1:1 methanol:acetone. The polymer was dried under nitrogen, and dissolved into heptane. The solution was filtered with filter paper and a Buchner funnel. If any residual tint remained, the polymer was dried under nitrogen for several days, transferred to the vacuum oven for 24 hours of room temperature vacuum followed by 24 hours of vacuum at 90 °C. The dried polymer was stored in a freezer.

2.2 Characterization

2.2.1 Gel permeation chromatography (GPC)

Gel permeation chromatography separates a dilute polymer solution into fractions using separation columns. The fractions are measured to determine the number (M_n) and weight-averaged (M_w) molecular weight distributions as well as the polydispersity index. A Waters 2690 Separations Module was used to inject polymer samples into a Viscotek bank of four columns with a Viscotek TDA 302 triple detector array. THF was used as the mobile phase and the column bank was maintained isothermal at 25 °C. Omnisec software was used to analyze the data.

The refractive index increment, dn/dc, is specific to a polymer/solvent pair. A refractometer was used to measure the difference in the indices of refraction of pure THF and a solution of THF and polymer passing through the detector at any point in time. The dn/dc and concentration, c, were calculated based upon a known sample of polystyrene with dn/dc = 0.185 mL/g and $M_w = 80.7$ kg/mol.

The low angle light scattering detector was used to determine the weight-averaged molecular weight, M_w . Because the concentration of polymer injected was very low, the Rayleigh equation can be written in the limit of $c \rightarrow 0$:

$$\frac{Kc}{R_{\theta}} = \frac{1}{M_{w}}$$
(2.2)

The scattering signal, R_{θ} is directly proportional to the intensity measured by the detector at a given angle θ (which is extrapolated to 0), *c* is determined from the refractive index detector, and *K* is given by:

$$K = \frac{2\pi^2 n_0^2 (dn/dc)^2}{N_{av} \lambda^4}$$
(2.3)

The refractive index of the solvent, n_0 , is known, dn/dc is measured by the refractive index detector, N_{av} is Avogadro's constants, and λ is the wavelength of the laser used.

The inherent viscosity $[\eta]$ was measured using a viscometer detector and the universal calibration law of GPC gives:

$$\log M_{w,i}[\eta]_i = D_0 + D_1 V_e + D_2 V_e^2 + \dots$$
(2.4)

 $V_{\rm e}$ is the elution volume for the ith detector interval from the time the sample was injected.

Because the time intervals are very narrow, $M_{w,i} \cong M_{n,i}$. Hence the distributions for both M_w and M_n are detected independently, and from these distributions the polydispersity index is given by $PDI = M_w / M_n$.

2.2.2 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) was used to characterize the percent of 1,2 addition in polybutadienes, the percent of saturation, and the fractional conversion (and purity) of TMPCI. Figure 2.3 shows the NMR trace for a polybutadiene in which the areas of the two relevant peaks are given by Q and R. The fraction of 1,2 addition, f_{12} , is given by:

$$f_{12} = \frac{2R}{2Q+R}$$
(2.5)

Figure 2.3. NMR trace for a polybutadiene showing the chemical structures of the two monomer additions and the location and number of hydrogens contributing to each of the saturation peaks.



2.2.3 Density gradient column

The density of each polymer synthesized was measured with a Techne density gradient column. Methanol and ethylene glycol were the miscible liquids used to establish a density gradient (at 23 °C $\rho_{\text{methanol}} = 0.791$ and $\rho_{\text{ethylene glycol}} = 1.109$). The column was submerged in an isothermal water bath at 23 °C with temperature fluctuations < 0.1 °C. Glass beads of a known density were used to develop a linear calibration curve. Polymer samples were annealed at 90 °C overnight on a glass slide to remove any bubbles. The annealed samples were quickly frozen in

liquid nitrogen and cut into a suitable size while below the glass transition temperature (to prevent the introduction of bubbles). Polymer chunks were dropped into the column while still frozen and allowed to equilibrate for 3 - 4 hours. Measurements were repeated for each sample and the average value was reported. Densities between 0.88 and 0.96 g/mL were used, however densities outside of this range are accessible by altering the relative fractions of methanol and ethylene glycol used.

2.3 SANS analysis

2.3.1 Blend Preparation

Blend components were dissolved in hexane, partially dried under nitrogen, and precipitated in a 1:1 methanol/acetone mixture. Ultrahigh purity (>99.9%) solvents were used for all steps. The precipitated samples were transferred to a 1 mm-thick annular aluminum spacer with inner diameter 17 mm, placed on a ~1 mm-thick quartz disk, and dried under vacuum for two days. The temperature of the vacuum oven was raised to 90 °C and the samples were heated under vacuum for an additional day. A second piece of quartz was pressed onto the samples while they were slightly warm (~ 40 °C), and the perimeter of the sample was sealed with heat-proof epoxy, except for a 5 mm gap that was left open to allow the polymer to expand when heated. The thicknesses of both quartz windows were measured prior to making the sample using a micrometer, and the final thickness of the assembled sample was measured to determine the thickness of the actual scattering volume. The samples were annealed in the oven upright, with the gap at the top (this is the orientation in which it was placed in the SANS beamline), under vacuum at 90 °C for one hour. Samples were slowly quenched to room temperature and transferred to the SANS beamline for study.

2.3.2. SANS data acquisition

SANS measurements were made at the NG3 and NG7 beam lines at the National Institute of Standards and Technology Center for Neutron Research in Gaithersburg, Maryland. Scattering measurements were made with a beamstop blocking the primary beam and transmission measurements were made without a beamstop and a calibrated plexiglass attenuator protecting the detector. SANS standards were run for each beamline experiment in order to reduce the scattering data to absolute intensity. The entire set of standard measurements was repeated for each beam configuration used. Scattering profiles were collected during 5 minutes intervals for an incoherent standard, an empty cell, and a blocked beam measurement. Transmission profiles were collected during 3 minute intervals for the empty beam and the empty cell. Both the incoherent standard and the empty cell were brought to the beamline from lab. The incoherent standard was a hydrogenated polybutadiene [hPB63(10)] with 62 % 1,2 addition and a molecular weight of 9.90 kg/mol, and the empty cell was two quartz windows placed in a holder. A cadmium selenide block was provided by the NCNR for blocked beam measurements

Samples were placed in titanium holders (provided by the NCNR) rather than brass to avoid detectable levels of radioactivity in the holder. The high hydrogen content of polyolefin samples scatters neutrons into the brass holders, inducing temporary radioactivity. A sevenposition thermal stage was placed in the beamline, but only the center five positions were used for thermal experiments to avoid end cooling effects. Samples were checked for bubbles, and covered with a 14 mm cadmium mask (slightly smaller than the 17 mm diameter of the sample spacer to avoid reduced scattering volume due to misalignment). SANS profiles were collected for each sample using a five minute acquisition time. If a smaller cadmium mask was used to block bubbles, the acquisition time was increased until the scattering count reached ~ 10^6 .

Samples were placed into the beamline at room temperature and heated incrementally from 30 to 190 °C in steps of 20 °C. Each temperature step was followed by a ten minute anneal to allow the samples to equilibrate. Two ternary blends with relatively high molecular weight polymers were tested to verify that the 10 minute equilibration time for large temperature steps was sufficient to obtain reproducible SANS profiles that did not vary with time. These results are shown in Chapter 6. Fine temperature steps of 2 - 3 °C were used to resolve the temperature step, also shown to be adequate for equilibration. Transmission measurements were made at three temperatures across the temperature range for each sample. Three transmission at other temperatures. This optimized the use of beam time by minimizing the number of times the beam configuration was changed.

2.3.3. SANS data reduction

SANS data were corrected for background, empty cell, and transmission using the software package provided by NIST-NCNR.⁹ The profiles containing the empty beam transmission, empty cell scattering and transmission, and blocked beam scattering were placed in the same data folder as the sample files to be reduced. Transmissions were calculated for the empty cell and the sample files at the three temperatures for which transmission was measured. This was accomplished by using the NCNR protocol to link the empty beam transmission to all other transmission files, and then linking the transmission files with the scattering files. There was no scattering file for the empty beam nor a transmission file for the blocked beam standard. The file catalogue was refreshed after calculating transmissions in order to update the header of each file. Next a linear interpolation was performed between the measured transmission profiles were not measured. Both the calculated transmission and the sample thickness were patched to each sample scattering file. At each two-dimensional detector pixel, the measured intensity, *I*, was given by:

$$I = count \ rate \times counting \ time \tag{2.6}$$

I was measured for each sample, the empty cell, and the blocked beam background giving I_{sam} , I_{emp} , and I_{bgd} . The transmission of the sample, $T_{sam+cell}$ was calculated from the relation:

$$T_{sam+cell} = \frac{\Sigma_{sam}}{\Sigma_{empty beam}}$$
(2.7)
Where Σ_{sam} and $\Sigma_{\text{empty beam}}$ are the sums of pixel intensities within the areal footprint of the direct beam, measured using a transmission beam configuration, for the sample and empty beam, respectively. $T_{\text{sam+cell}}$ contains attenuation due to the empty cell because the sample is necessarily measured with quartz windows in place. The transmission for the empty cell, T_{emp} , was calculated similarly.

The scattering intensity of the sample (containing a contribution from the quartz windows) at each pixel, I_{sam} , was corrected to I_{cor} using:

$$I_{cor} = (I_{sam} - I_{bgd}) - \frac{T_{sam+cell}}{T_{emp}} (I_{emp} - I_{bgd})$$
(2.8)

The empty cell correction accounts not only for scattering due to the quartz windows, but also scattering due to air, windows, and collimation slits. The blocked beam background removes scattering due to stray neutrons and background radiation as well as the detector dark current.

The corrected intensity was calibrated with a detector sensitivity file (measured each beam cycle to determine the individual efficiencies of the pixels) to yield I_{cal} . The scattering cross section was calculated from I_{cal} :

$$\left(\frac{d\Sigma(q)}{d\Omega}\right)_{sam} = \frac{I_{cal}(q)}{\Phi A_{sam} d_{sam} \Delta \Omega \varepsilon t T_{sam+cell}}$$
(2.9)

where Φ is the incident neutron flux, A_{sam} is the scattering area, d_{sam} is the sample thickness, $\Delta\Omega$ is the solid angle of each pixel, ε is the detector efficiency, and t is the counting time. d_{sam} was measured for each sample as the thickness of the total sample less the quartz window thicknesses, and t was set for each run. The unknown quantities were measured from the empty beam transmission:

$$I_{empty beam} = \Phi A \Delta \Omega \varepsilon t T_{atten}$$
(2.10)

The transmission of the plexiglass attenuator, T_{atten} , is known from previous calibration with a standard. The angle-dependent scattering cross section of the sample was integrated azimuthally to render profiles of the absolute scattering intensity, I_{abs} , versus magnitude of the scattering vector, q. Here, $q = 4\pi \sin(\theta/2)/\lambda$ in which θ is the scattering angle and λ is the wavelength of incident neutrons. The contribution of incoherent scattering to I_{abs} was significant because the polyolefins studied contained a large fraction of hydrogen. The coherent intensity was calculated from:

$$I_{coh} = I_{abs} - I_{inc} \tag{2.11}$$

The incoherent contribution was calculated using the measured value of I_{abs} for the hydrogenated polymer standard.¹⁰

$$I_{inc} = \frac{I_{abs,std}}{\rho_{std}} \left[\sum_{H} \phi_{H} \rho_{H} + \sum_{D} \phi_{D} \rho_{D} \left(\frac{n_{H} - n_{D}}{n_{H}} \right) \left(\frac{M_{0,H}}{M_{0,H} + n_{D}} \right) \right]$$
(2.12)

 ρ_{std} , ρ_{H} , and ρ_{D} are the densities of the polymer standard, the hydrogenated species, and the deuterated species, respectively. ϕ_{H} and ϕ_{D} are the volume fractions of the hydrogenated and deuterated species. For polymer blends containing more than one hydrogenated or deuterated species, the quantities are summed over all species. $M_{0,\text{H}}$ is the molecular weight of a single hydrogenated monomer. For both polyisobutylene and polybutadiene the chemical repeat structure is C₄H₈ and $M_{0,\text{H}} = 56.1$ g/mol. n_{H} is the number of hydrogen atoms per monomer of the hydrogenated species, and is equal to 8 for both polyisobutylene and polybutadiene; n_{D} is the number of deuterium atoms per monomer unit for the deuterated species. The average number of deuterium atoms substituted into a polyolefin of the form $(\text{CH}_2)_x$ was determined by Krishnamoorti:¹¹

$$n_D = \frac{M_{0,H}(\rho_D / \rho_H - 1)}{1.01 + M_{0,H}(\rho_D / \rho_H)(\beta / 2x_H)}$$
(2.13)

 β is a constant value of 0.002 for polyolefins, x_H is the number of CH₂ repeat units in a monomer if the deuterated species had been hydrogenated (x = 4 for polybutadienes), and 1.01 is the difference in the masses of hydrogen and deuterium in g/mol.

The conformations of polymer chains give rise to a form factor contribution to the structural information contained within I_{coh} . This contribution is two orders of magnitude smaller than the lowest measured intensities for hydrogenated species, however, the form factor becomes important for deuterated species where the scattering contrast is large. The conformations of deuterated polymers were presumed to obey random walk statistics and the scattering from Gaussian coils is given by the Debye contribution to scattering:

$$I_{debye} = K_s v_{mon} N_{mon} \frac{2}{x^2} (\exp(-x) + x - 1)$$
(2.14)

The scattering contrast is given by K_s , the volume of a single chain is the product of v_{mon} and N_{mon} , and $x = q^2 R_{g,i}^2$ and $R_{g,i}^2 = N_i l_i^2/6$. $R_{g,i}$ is the radius of gyration for a chain of species i and l_i is the statistical segment length. I_{debye} was determined for each deuterated polymer by fitting the SANS profile of the neat sample with the adjustable parameters K and $R_{g,i}$. Table 2.4 combines older and more recent values for these parameters for each deuterated polybutadiene used in this study.

Table 2.4 . Parameters needed to calculate I_{debye} for deuterated polybutadienes with 89 and 63 %
1,2 addition. The values of K_s and R_g were fitted from a scattering profile of the neat sample,
and v_{mon} and N_{mon} were determined using a combination of GPC and density measurements.

Polymer	$K ({\rm cm}{\rm \AA}^3)^{-1}$	$R_{\rm g}$ Á	v_{mon} Å ³ at 23 °C	N _{mon}
dPB89(10)	5.48 x 10 ⁻⁶	30.99	107.9	180
dPB89(24)	1.45 x 10 ⁻⁵	50.5	107.9	429
dPB89(35)	8.89 x 10 ⁻⁶	52.41	107.8	625
dPB89(49)	6.12 x 10 ⁻⁶	68.07	107.9	866
dPB89(60)	1.29 x 10 ⁻⁵	75.99	107.9	1062
dPB89(66)	9.56 x 10 ⁻⁶	37.71	107.8	1172
dPB89(220)	8.28 x 10 ⁻⁶	89.77	108.0	3926
dPB63(10)	1.66 x 10 ⁻⁵	48.97	101.9	178.6
dPB63(58)	1.07 x 10 ⁻⁵	132.1	108.0	1037
dPB63(187)	1.98 x 10 ⁻⁵	142.9	107.7	3333

For many of the blends studied the q-dependent I_{debye} was used to correct the coherent data:

$$I(q) = I_{coh}(q) - I_{debve}(q)$$

$$(2.15)$$

The final intensity, I, was a q-dependent quantity that was used for structural analysis of each blend. The Debye correction was used for all binary blends studied. Unless otherwise noted, the Debye correction was also used for ternary blends. For the case of ternary blends with a lamellar structure, a form factor based on the RPA was used instead of I_{debye} if the data were fitted with a lamellar structure factor. Details of this correction are in chapter 6.

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Chapter 3

Theory of Polymer Blends

Polymer blends theory has conventionally relied upon the formalism of Flory-Huggins Theory. The Flory-Huggins interaction parameter, χ , is measured using scattering techniques, and used to predict the phase behavior of the spinodal and binodal for binary polymer blends. The multicomponent random phase approximation is used to predict the homogeneous phase window in ternary polymer blends.

3.1 Binary Blends

Miscibility in polymer blends is traditionally described using Flory-Huggins Theory.^{1,2} The dimensionless Gibbs free energy of mixing per volume is given by the Flory-Huggins Equation:

$$\frac{\Delta G v_0}{kT} = \frac{\phi_1 \ln \phi_1}{N_1} + \frac{(1 - \phi_1) \ln(1 - \phi_1)}{N_2} + \chi \phi_1 \phi_2$$
(3.1)

where v_0 is the volume of a single lattice site and is equal to 0.1 nm³, ϕ_1 is the volume fraction of species i in the blend, N_i is the number of repeat units of volume v_0 on a single chain of species i, and χ is the Flory-Huggins interaction parameter.

The chemical potential of blended species i is given, for a fixed temperature and composition, by the first derivative of the Gibbs free energy with respect to the number of molecules. Along an isotherm, two-phase coexistence is predicted at compositions ϕ_i^{I} and ϕ_i^{II} where the chemical potential for each species i is identical for both phases (I and II), and the free energy of the two coexisting phases is less than that of a single homogeneous phase. It is more convenient to differentiate eq. 3.1 with respect to the volume fraction of species i, such that the outer phase envelope is defined by:

$$\frac{\partial \Delta G}{\partial \phi_i}\Big|_{\phi_i^I} = \frac{\partial \Delta G}{\partial \phi_i}\Big|_{\phi_i^{II}}$$
(3.2)

Equation 3.2 is analogous to requiring that the chemical potential of species i is the same in phases I and II, however, $\frac{\partial \Delta G}{\partial \phi_i}$ is not identical to the chemical potential because eq. 3.1 was differentiated with respect to ϕ_i and not the number of molecules. Eq. 3.2 is solved at multiple temperatures to define a binodal curve, the outer phase envelope for two-phase behavior.

The limit of thermodynamic stability, the spinodal curve, is given by

$$\frac{\partial^2 \Delta G}{\partial \phi_i^2} = 0 \tag{3.3}$$

and the critical point is given by the simultaneous solution of eqs. 3.3 and 3.4:

$$\frac{\partial^3 \Delta G}{\partial \phi_i^3} = 0 \tag{3.4}$$

Flory-Huggins Theory (the combination of eqs. 3.1, 3.3, and 3.4) may be used to predict the volume fraction of species 1 at the critical point:

$$\phi_{1,crit,FHT} = \frac{1}{1 + (N_1 / N_2)^{1/2}}$$
(3.5)

For a symmetric polymer blend $N_1 = N_2$ and the critical composition occurs at $\phi_{1,\text{FHT}} = 0.5$. Eq. 3.5 is only valid if χ is independent of the composition of the blend, this is the case for many polymer pairs.

The measurement of a thermodynamically robust χ enables computation of the complete phase diagram for a binary polymer blend. Small angle neutron scattering (SANS) is commonly used to measure χ for polymer pairs because the coherent scattering intensity can be related to thermodynamically relevant quantities. Thermal fluctuations in the local composition of the blend are characterized by an effective interaction between homopolymer species, χ_{sc} . These fluctuations give rise to a spatially-dependent structure factor for the blend, S(q), that is described by the mean-field Random Phase Approximation (RPA):³

$$S(q) = \frac{1}{v_0} \left(\frac{1}{N_1 \phi_1 P_1(q)} + \frac{1}{N_2 \phi_2 P_2(q)} - 2\chi_{sc} \right)^{-1}$$
(3.6)

The single chain form factor for each homopolymer is given by the Debye function:

$$P_i(x) = \frac{2}{x^2} (\exp(-x) + x - 1)$$
(3.7)

with $x = q^2 R_{g,i}^2$ and $R_{g,i}^2 = N_i l_i^2/6$. $R_{g,i}$ is the radius of gyration for a chain of species i and l_i is the statistical segment length.

The static structure factor given by eq. 3.6 can be obtained from the measured coherent scattering intensity and the calculated scattering contrast:

$$I(q) = \Delta \rho^2 S(q) \tag{3.8}$$

where $\Delta \rho^2 = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2$ is the scattering contrast per unit volume. The scattering length of a

monomer of species i, b_i , is computed from the atomic composition of a monomer unit, and v_i , the monomer volume. When these quantities are known, the SANS intensity profile can be fitted with the RPA to extract a value for χ_{sc} as described in chapter 4.

The structure factor at zero scattering angle, S(0), is related to the second derivative of free energy:

$$S^{-1}(0) = \frac{\partial^2 (\Delta G / kT)}{\partial \phi_1^2}$$
(3.9)

At q = 0 the Debye function, P_i , is normalized to have a value of unity. Differentiating the Flory-Huggins free energy from equation 3.1 yields:

$$\frac{1}{S(0)} = \frac{1}{v_0} \left(\frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_2} - 2\chi_{sc} \right)$$
(3.10)

At the spinodal temperature, the correlation length between composition fluctuations diverges as the blend macrophase separates and the susceptibility, $S(0)^{-1}$, vanishes. The value of χ_{sc} at the spinodal is dependent upon the composition of the blend:

$$\chi_{s,sc} = \frac{1}{2} \left(\frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_2} \right)$$
(3.11)

so that eq. 3.10 may be rewritten to emphasize the relationship between the susceptibility and χ_{sc} .

$$\frac{1}{S(0)} = \frac{2}{v_0} \left(\chi_s - \chi_{sc} \right)$$
(3.12)

Experimental data must obey equation 3.12 for the RPA to be valid.

3.2 Composition-dependent χ parameters

 χ is usually presumed to be independent of composition and molecular weight with an empirical temperature dependence given by $\chi = A + \frac{B}{T}$. For this simple case, the measured value of χ_{sc} is identical to the thermodynamic parameter, χ , in eq. 3.1. It follows from eq. 3.12 that $S(0)^{-1} \sim |T_s|^1 - T^1|$. However, when χ_{sc} is a function of composition, it is no longer identical to χ , because the latter is also a function of composition. This compositional dependence must be taken into account when differentiating the Flory-Huggins Equation for free energy (eq. 3.1) to arrive at the relation between χ_{sc} and the static structure factor measured from scattering (eq. 3.9). Sanchez noted the discrepancy between χ and χ_{sc} and offered the following resolution:

$$\chi_{sc} = -\frac{1}{2} \frac{\partial^2 \left[\phi_1 (1 - \phi_1) \chi\right]}{\partial \phi_1^2}$$
(3.13)

Eq. 3.13 may be integrated to yield an expression for χ given a functional form of χ_{sc} , and solving for the constants of integration by requiring χ to be finite. An analogous solution was prescribed by Sanchez:

$$\chi = \frac{2}{(1-\phi_1)} \int_0^{1-\phi_1} (1-\phi_1) \chi_{sc}(\phi_1) d(1-\phi_1) + \frac{2}{\phi_1} \int_0^{\phi_1} (\phi_1) \chi_{sc}(\phi_1) d\phi_1$$
(3.14)

It is straightforward to show that χ depends linearly on ϕ_1 when χ_{sc} depends linearly on ϕ_1 .

3.3 Ternary Blends

Miscibility studies involving mixtures of three or more polymers requires the multicomponent Flory-Huggins Theory. For the ternary A/B/A-C blends studied here, the three polymer components are homopolymers A and B, represented by Ah and Bh, and the A-C diblock copolymer. The different chemical species comprising the blocks of A-C are referred to as Ab and Cb. The Helmholtz free energy of mixing per unit volume, f_m , is given by:

$$\frac{f_m v_0}{kT} = \sum_i \frac{\phi_i \ln \phi_i}{N_i} + \sum_{m,n} \phi_m \phi_n \chi_{mn} - \sum_{i,m,n} \frac{\phi_{i,m} \phi_{i,n}}{\phi_i} \chi_{m,n}$$
(3.15)

The index i refers to each of the three polymers, $i = \{Ah, Bh, A-C\}$ while m and n refer to each of the three chemical species, $m,n = \{A, B, C\}$. $\phi_{i,m}$ refers to the volume fraction of chemical species m comprising a chain of polymer i, and is zero-valued for homopolymers.

The coherent neutron scattering profile from an homogeneous multicomponent blend is given by the multicomponent random phase approximation^{3,5,6}:

$$I(q) = \boldsymbol{B}^T \underline{S}(q) \boldsymbol{B}$$
(3.16)

B is a column vector with elements that describe the difference in scattering length densities between species $j = \{Ah, Ab, Cb\}$ and the background species Bh:

$$\boldsymbol{B}_{j} = \frac{\boldsymbol{b}_{j}}{\boldsymbol{v}_{j}} - \frac{\boldsymbol{b}_{Bh}}{\boldsymbol{v}_{Bh}}$$
(3.17)

The structure factor matrix comprises contributions from the static structure factor matrix, $\underline{\underline{S}}^{0}(q)$, and the dynamic structure factor matrix, $\underline{\underline{V}}(q)$. The static structure factor gives the scattering from an homogeneous mixture of the three components in the absence of interactions, while the dynamic structure factor matrix describes the interactions between all components.

$$\underline{\underline{S}}(q) = \left[\underline{\underline{S}}^{0}(q)^{-1} + \underline{\underline{V}}(q)\right]^{-1}$$
(3.18)

The diagonal elements of the static structure factor are given by:

$$S_{jj}^{0}(q) = v_0 N_j \phi_j P_j(q)$$
(3.19)

 $P_j(q)$ is the Debye function (eq. 3.7), the form factor for a Gaussian chain. The off-diagonal elements of $\underline{\underline{S}}^0(q)$ are zero-valued for pairs of species belonging to different polymer chains and non-zero for pairs of species belonging to the same polymer chain (i.e. the copolymer):

$$S_{AbAh}^{0} = S_{CbAh}^{0} = S_{AhAb}^{0} = S_{AhCh}^{0} = 0$$
(3.20)

$$S_{AbCb}^{0} = S_{CbAb}^{0} = v_0 \left[N_{Ab} \phi_{Ab} N_{Cb} \phi_{Cb} \right]^{1/2} F_{Ab}(q) F_{Cb}(q)$$
(3.21)

and the F functions give the Debye function in the high q limit, at length scales for which intramolecular interactions are significant:

$$F_{j}(q) = 1 - \exp(-x_{j})$$
 (3.22)

The diagonal and off diagonal elements of the dynamic structure factor matrix are given by:

$$V_{jj} = \frac{1}{v_0} \left(\frac{1}{N_{Bh} \phi_{Bh} P_{Bh}(q)} - 2\chi_{jBh} \right)$$
(3.23)

$$V_{jk}(q) = \frac{1}{v_0} \left(\frac{1}{N_{Bh} \phi_{Bh} P_{Bh}(q)} - \chi_{jBh} - \chi_{kBh} + \chi_{jk} \right) \quad j \neq k$$
(3.24)

Eqs. 3.16 - 3.24 comprise the multicomponent random phase approximation, and can be used to predict the azimuthally integrated profile for coherent scattering. Within the homogeneous region, the profiles are continuous and may exhibit a correlation peak related to the presence of diblock copolymer. Outside the homogeneous window (macro- or micro-phase separated regions of phase behavior) the RPA predicts profiles with one or two poles. Figure 3.1 shows the RPA predictions for blend TB[19] (characterized in Chapter 6, Table 6.1) at selected temperatures. The main graph shows homogeneous profiles, with a high-q tail $I \sim q^{-2}$ due to

Debye behavior. The inset shows a lower temperature profile with two poles, indicating that the predicted phase is not homogeneous. Previous work suggested that RPA profiles with one pole indicate macrophase separation and those with two poles indicate microphase separation,⁷ however the RPA cannot be applied outside the homogeneous phase window. Figure 3.1 is a counterexample of this expectation: the RPA profile at 130 °C exhibits two poles, suggesting microphase ordering, but experiments confirm that the blend is macrophase separated over the entire region where RPA predicts two poles. Clearly, RPA is limited homogeneous phase predictions. Phases containing microphase ordering can be predicted using self-consistent field theory; this is done in Chapter 7.

Figure 3.1. Multicomponent Random Phase Approximation predicted profiles for blend TB[19] at selected temperatures. The inset depicts a temperature for which the blend is non-homogeneous, it employs linear axes.



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Chapter 4

Composition and Molecular Weight Dependence of χ for Asymmetric Binary Blends

SANS profiles were measured for a series of twenty-four binary blends comprising component B, polyisobutylene (PIB), and component C, deuterated polybutadiene with 63% 1,2 addition (dPB63). B/C blends are known to exhibit lower critical solution temperature (LCST) behavior. The measured values of χ_{sc} exhibited a dependence on both composition and molecular weight, a phenomenon previously observed in other LCST blends. Consequently, the "true" χ parameter, used with Flory-Huggins Theory to predict phase behavior, was calculated from an empirical expression for χ_{sc} .

4.1 Measurement of χ_{sc} using SANS

Miscibility in binary blends is limited to the regime where $\chi < 2/N_{AVE}$. Single-phase blends at the critical composition are best suited for measuring χ because of the presence of large concentration fluctuations, which, in turn, give rise to large SANS signals. In this regime, small changes in χ lead to large changes in predicted scattering using the random phase approximation (RPA). A majority of the values of χ in the literature are based on measurements obtained from a single polymer blend with a carefully chosen value of N_{AVE} in the vicinity of the critical point.¹⁻ ⁴ When χ is less than zero, single phase systems are obtained regardless of the values of ϕ_1 , N_1 , and N_2 . For blends that exhibit a lower critical solution temperature (LCST), χ increases with temperature, and if χ exceeds $2/N_{AVE}$, then the region of critical fluctuations can be accessed, and SANS can be used to measure χ .

Binary B/C blends were prepared using the methods outlined in Chapter 2 and the polymers listed in Table 4.1. Nine blends were prepared such that $\phi_B = \phi_{B,crit,FHT}$, and four of these blends exhibited a one-phase to two-phase transition within the window of experimental temperatures. The four B/C blends that phase separated were also studied at compositions removed from $\phi_{B,crit,FHT}$. All of the blends studied are characterized in Table 4.2. Blends are named BBX[yyy] where yyy is the asymmetry of the blend (N_B/N_C), "BB" indicates a binary blend, and X relates to the composition of the blend. The significance of X requires further explanation.

Three different expressions for χ have been reported for blends of PIB and dPB63: the first measurements presumed that χ was only a function of temperature⁵, the second χ contained both a temperature and composition dependence⁶, and the most recently reported expression for χ depends on temperature, composition, and molecular weight⁷. As the correct form of χ has evolved, so too the predicted critical composition has evolved because it depends on χ . When χ is only a function of temperature, regular Flory-Huggins Theory applies, and the critical composition, $\phi_{B,crit,FHT}$ is given by eq. 3.5. The nomenclature for this case is X = "F" (for "Flory-Huggins"). A revised prediction for the critical composition, $\phi_{B,crit,rev}$, was developed when χ was thought to depend only on temperature and composition. X = "C" when $\phi_B = \phi_{B,crit,rev}$ where

"C" refers to the composition dependence of χ . An anti-critical composition (X = "A") was also chosen for study, where ϕ_B is on the opposite side of the phase diagram and is given by $\phi_B = 1$ - $\phi_{B,crit,rev.}$ Finally, the most current expression for χ was used to predict the true (X = "T") critical point that is experimentally observed. The specific value of ϕ_B depends on the molecular weights of the homopolymers, however all blends with the same lettered value of X are expected to exhibit behavior in the same region of the phase diagram. When X is a number, the value gives the percent of component B in the blend.

	$M_{\rm w}^{\rm b}$				
polymer ^a	(kg/mol)	PDI	ho (g/mL)	Ν	$n_{\rm D}$
PIB(13)	12.5	1.04	0.9134	227	
PIB(45)	44.6	1.04	0.9140	810	
PIB(57)	56.8	1.02	0.9144	1031	
dPB63(10)	10.5	1.02	0.9125	191	3.44
dPB63(58)	62	1.01	0.9187	1120	3.65
dPB63(187)	197	1.02	0.9123	3589	3.04

 Table 4.1. Characterization of homopolymers

^aThe polymer name gives the species and the molecular weight in parentheses.

^bThe molecular weight, M_w , polydispersity index, *PDI*, and *N* were all determined using GPC. The density, ρ , and number of deuterium atoms per monomer, n_D , were determined using a density gradient column.

blend	В	С	$N_{\rm PIB}/N_{\rm PBD}$	$N_{\rm AVE}$	$\phi_{ m B}$
BBF[0.06]	PIB(13)	dPB63(187)	0.063	580	0.799
BBF[0.20]	PIB(13)	dPB63(58)	0.203	432	0.690
BBC[0.23]	PIB(45)	dPBD(187)	0.226	1489	0.272
BBT[0.23]	PIB(45)	dPBD(187)	0.226	1489	0.468
BBF[0.23]	PIB(45)	dPBD(187)	0.226	1489	0.678
BBA[0.23]	PIB(45)	dPBD(187)	0.226	1489	0.728
BBC[0.29]	PIB(57)	dPBD(187)	0.288	1750	0.238
BB30[0.29]	PIB(57)	dPBD(187)	0.288	1750	0.300
BBT[0.29]	PIB(57)	dPBD(187)	0.288	1750	0.439
BB50[0.29]	PIB(57)	dPBD(187)	0.288	1750	0.500
BB60[0.29]	PIB(57)	dPBD(187)	0.288	1750	0.600
BBF[0.29]	PIB(57)	dPBD(187)	0.288	1750	0.651
BBA[0.29]	PIB(57)	dPBD(187)	0.288	1750	0.762
BBC[0.72]	PIB(45)	dPBD(58)	0.723	947	0.267
BBT[0.72]	PIB(45)	dPBD(58)	0.723	947	0.370
BBF[0.72]	PIB(45)	dPBD(58)	0.723	947	0.540
BBA[0.72]	PIB(45)	dPBD(58)	0.723	947	0.733
BBC[0.92]	PIB(57)	dPBD(58)	0.921	1075	0.233
BBT[0.92]	PIB(57)	dPBD(58)	0.921	1075	0.340
BBF[0.92]	PIB(57)	dPBD(58)	0.921	1075	0.510
BBA[0.92]	PIB(57)	dPBD(58)	0.921	1075	0.767
BBF[1.19]	PIB(13)	dPB63(10)	1.189	208	0.478
BBF[4.24]	PIB(45)	dPB63(10)	4.241	346	0.327
BBF[5.40]	PIB(57)	dPB63(10)	5.402	373	0.301

Table 4.2. Characterization of Binary Blends

SANS profiles were measured for each blend at temperatures from 30 - 190 °C. The Debye form factor contribution of deuterated chains (eq. 3.7), was subtracted from the coherent intensity to render a corrected coherent SANS intensity profile, *I*. Data was obtained at two sample-to-detector distances to provide good statistics at both high and low-*q* values. The random phase approximation (RPA) was used to fit *I* using two adjustable parameters, χ_{sc} and α , sensitive to low and high-*q*, respectively. χ_{sc} is the Flory-Huggins interaction parameter measured from scattering experiments, and α is the fractional thermal expansion of the statistical segment lengths, $l_i(T)$, from a reference state; $\alpha = l_B(T)/l_{B,ref} = l_C(T)/l_{C,ref}$ with $l_{B,ref} = 0.58$ nm and $l_{C,ref} = 0.75$ nm. α enters the RPA through the Debye functions, $P_i(x)$, where *x* can be rewritten to illustrate the dependence on $\alpha x = q^2 R_{q,i}^2 = q^2 N_i \alpha_i^2 l_{i,ref}^2 / 6$

It is necessary to constrain components B and C to have the same value of α to prevent overfitting the SANS intensity profiles. The error in χ_{sc} introduced through this constraint is

very small because $\partial I / \partial \chi_{sc} \ll \partial I / \partial \alpha$ (i.e. χ_{sc} is a robust parameter). The monomer volumes are known to undergo thermal expansion according to⁸:

$$v_{i,mon} = v_{i,ref} \exp(\beta_i (T - T_{ref}))$$
(4.1)

where $\beta_{\rm B} = 0.0057 \text{ K}^{-1}$ and $\beta_{\rm C} = 0.0072 \text{ K}^{-1}$.

Figure 4.1 shows RPA fits to *I* for blend BBF[0.72] at selected temperatures. The profiles at and below 150 °C are consistent with a homogeneous phase, as indicated by the low-*q* intensity plateau. The SANS profile at 190 °C shows an up-turn in the low-*q* intensity consistent with the Porod Scattering Law $(I \sim q^{-4})$, indicating that the blend is macrophase separated. The RPA fits are shown to agree with the SANS profiles at both high and low *q* for all blends within the homogeneous phase window. Table 4.3 lists the fitting parameters χ_{sc} and α obtained from the RPA fits in Figure 4.1. All blends with $N_{AVE} \leq 580$ remained homogeneous in the window 30 - 190 °C while blends with $N_{AVE} \geq 947$ exhibited both homogeneous and macrophase

separated equilibrium behavior.

Figure 4.1. SANS intensity profiles for blend BBF[0.72] at selected temperatures. The profiles have been shifted 0 cm⁻¹ (30 °C), 700 cm⁻¹ (70 °C), 1500 cm⁻¹ (110 °C), 2400 cm⁻¹ (150 °C), and 4300 cm⁻¹ (190 °C). The solid lines are RPA fits to the data for blends within the homogeneous phase window.



T °C	χ	α
30	-0.00462	0.885
70	-0.00128	0.901
110	0.00065	0.909
150	0.00180	0.935

Table 4.3. χ_{sc} and α values for blend BBC[0.72] at selected temperatures

4.2. Determination of the composition dependence of χ_{sc} using Flory-Huggins critical blends

Initial studies of this system involved blends prepared with $\phi_B = \phi_{B,crit,FHT}$ (all blends with the prefix "BBF"). Critical blends were targeted for this experimental study because they pass directly through the critical point upon heating. The second order phase transition at the critical point, known as spinodal decomposition, is a continuous transition. In contrast, off-critical blends pass through the binodal into the metastable region where there is potential for kinetic trapping in the nucleation and growth regime. Critical blends circuit this potential problem as well as providing intense signals in the vicinity of the phase transition.

Figure 4.2 shows the measured values of χ_{sc} as a function of inverse temperature for blends BBF[5.40], BBF[0.72], and BBF[0.20]. It is clear that a linear $\chi_{sc} \sim 1/T$ relationship is not sufficient to describe the observed trends. It is also apparent that the measured values of χ_{sc} vary significantly between the three blends. While χ_{sc} is generally thought to be independent of the composition of homopolymers comprising a blend, such dependences have been observed in other LCST systems.^{1,9-11} It is not clear that the deviation in χ is due to ϕ_{B} because the blends in Figure 4.2 differ in value for ϕ_{B} , N_{B}/N_{C} , and N_{AVE} (see Table 4.2).

Figure 4.2. Measured values of χ_{sc} for selected blends: BBF[5.40](\diamond), BBF[0.72] (\bigcirc), and BBF[0.20] (\triangle).



Figures 4.3a-c examine in turn the dependence of χ_{sc} on ϕ_B , N_B/N_C , and N_{AVE} . In Figure 4.3a χ_{sc} is seen to change inversely with ϕ_B at all temperatures. Table 4.4a lists the results of fitting a linear trend line to the data. There is a correlation between ϕ_B and N_B/N_C for Flory-Huggins critical blends (stemming from eq. 3.5), consequently, the measured values for χ_{sc} also depend on N_B/N_C as shown in Figure 4.3b. Table 4.4b lists the results of power law fits to χ_{sc} vs N_B/N_C . Strictly based on eq. 3.5, $\phi_B \sim (N_B/N_C)^{-1/2}$ for Flory-Huggins critical blends, however the power law fits shown in Figure 4.3b appear to adequately capture the observed trends. χ_{sc} at 30 °C is plotted against N_{AVE} in Figure 4.3c. No trend between χ_{sc} and N_{AVE} is apparent at this temperature or any of the other temperatures studied.

Figure 4.3. Measured values of χ_{sc} for all Flory-Huggins critical blends at selected temperatures: 30 °C (\bullet), 70 °C (\triangleleft), and 110 °C (\diamond). (a) χ_{sc} plotted against ϕ_{B} , lines are linear fits to the data (b) χ_{sc} plotted against N_{B}/N_{C} , lines are power law fits to the data and (c) χ_{sc} plotted against N_{AVE} .





Table 4.4. Fitting parameters for all Flory-Huggins critical blends at selected temperatures: (a) $\chi_{sc} = a + b \phi_B$ and (b) $\chi_{sc} = y_0 + (N_B/N_C)^x$.

a			b		
<i>T</i> °C	а	b	T °C	Уо	x
30	0.002056	-0.01228	30	-1.0042	0.0014
70	0.003831	-0.00895	70	-1.0024	0.00124
110	0.004909	-0.00767	110	-1.001	0.00111

The values for the fitting parameter α are shown as a function of temperature for selected blends in Figure 4.4a. α remains nearly constant with temperature, suggesting that chain expansion is a negligible effect in the temperature window studied. In Figure 4.4b α is plotted against $\phi_{\rm B}$ at 30 °C. There is no correlation between α and $\phi_{\rm B}$ at any temperature.

Figure 4.4. Fitted values for α (a) as a function of temperature for selected Flory-Huggins critical blends: BBF[0.72] (\bigcirc), BBF[0.92] (\triangle), and BBF[0.29] (\square) (b) for all blends at 30 °C.





4.3 Determination of the molecular weight dependence of χ_{sc}

The critical composition given by eq. 3.5 is only accurate for a Flory-Huggins interaction parameter that is independent of composition. For polymer systems that exhibit a compositiondependent χ , the functional form of χ_{sc} (ϕ_B , T) must be known to calculate the "true"critical composition. The previous section demonstrates that χ is not a simple function of *T*, however the relative contributions of ϕ_B and N_B/N_C cannot be determined using only blends prepared at the Flory-Huggins critical composition. Off-critical blends enable the study of various compositions for a single fixed value of N_B/N_C . Four blends (those with $N_{AVE} \ge 947$) were chosen study at additional compositions.

Figure 4.5a shows the measured values of χ_{sc} for a series of blends based on BBF[0.29] whereby the same two homopolymers are blended at different concentrations. N_{AVE} has a constant value of 1750 for the blends shown, and ϕ_B varies from 0.238 – 0.762. There is a clear compositional dependence for χ_{sc} . In contrast, Figure 4.5b shows χ_{sc} plotted for five blends with similar values of ϕ_B and N_B/N_C ranging from 0.226 – 5.40. There is no deviation (outside of the error bars) in χ_{sc} measured across an order of magnitude of values for N_B/N_C . Clearly, χ_{sc} is a function of blend composition while any dependence on N_B/N_C is weak.

Figure 4.5. Measured values of χ_{sc} at 30 °C (a) for all blends with $N_{AVE} = 1750$ and (b) for blends BBC[0.72], BBC[0.23], BB30[0.29], BBF[5.40], and BBF[4.24] with ϕ_{B} ranging from 0.267 to 0.327.



Figure 4.6 shows the composition dependence of χ_{sc} for all blends studied, critical and off-critical. The abscissa was chosen to be $2\phi_B - 1$ rather than ϕ_B because it locates the reference point for symmetric blends along the ordinate. Blends tend to have lower values of χ_{sc} with increasing concentration of component B at all temperatures. However, it is not clear that the correlation between χ_{sc} and ϕ_B is linear as supposed in Figure 4.3a.

Figure 4.6. Measured values of χ_{sc} for all blends studied at selected temperatures: 30 °C (\bullet), 70 °C (\bullet), 110 °C (\bullet), 150 °C (\blacksquare). Solid lines are linear fits to the data.



Several composition-dependent χ_{sc} have also been found to demonstrate a molecular weight dependence^{3,7,12-15} of varying functional forms. Many empirical equations were fit to the data, and the lowest sum of squares error resulted from:

$$\chi_{sc} = A_{sc}(T) + B_{sc}(T) \frac{2\phi_B - 1}{N_{AVE}}$$
(4.2)

Figure 4.7a shows the least squares fit of eq. 4.2 to the measured values of χ_{sc} at 30 °C for all blends studied. A linear fit to the data is shown for comparison. Eq. 4.2 captures the observed deviation from linearity for many of the blends studied. The sum of squares error for a fit value of χ_{sc} is given by $\frac{1}{n} \sum_{n} (\chi_{sc} - \chi_{sc,fit})^2$ where *n* is the number of blends examined at a particular temperature (*n* changes with temperature because some blends macrophase separate). Figure 4.7b shows that the sum of squares error is significantly less for fits that take into account both ϕ_{B} and N_{AVE} (eq. 4.2) than for the linear fits to ϕ_{B} . The temperature dependence of the fitting parameters A_{sc} and B_{sc} is shown in Figure 4.7c. A quadratic fit to inverse temperature was necessary to capture the behavior of A_{sc} and B_{sc} . A least squares fit to the entire data set results in the following expression for χ_{sc} :

$$\chi_{sc} = -0.00622 + \frac{10.6}{T} - \frac{3040}{T^2} + \left[-2.17 + \frac{1910}{T} - \frac{687000}{T^2} \right] \frac{2\phi_B - 1}{N_{AVE}}$$
(4.3)

Figure 4.7. (a) χ_{sc} vs $2\phi_B - 1$ for all blends at 30 °C. Measured values of χ_{sc} (\bullet) are compared to those calculated from eq. 4.2 (\bigcirc). The dotted line is a visual aid, the solid line shows a linear fit to the measured data. (b) The sum of squares error is shown for linear fits of χ_{sc} to ϕ_B (\Box) and fits to eq. 4.2 (\triangle). (c) Temperature dependence of the fitting parameters A_{sc} (\blacktriangle)and B_{sc} (\blacksquare). Solid lines are quadratic fits to the data.





The inclusion of N_{AVE} in the expression for χ_{sc} is essential for fitting the data. Figure 4.8 shows a plot of χ_{sc} versus $(2\phi_{B}-1)/N_{AVE}$. The data when plotted in this manner are

approximately linear as expected. The least squares linear fits through the data in Figure 4.8 give additional estimates of A_{sc} and B_{sc} . In Table 4.5 the values of A_{sc} and B_{sc} from Figure 4.8 are compared to those calculated from eq. 4.3. There is good agreement between the two methods for estimating A_{sc} and B_{sc} .

Figure 4.8. Measured values of χ_{sc} all blends at selected temperatures: 30 °C (\bullet), 70 °C (\triangleleft), 110 °C (\bullet), and 150 °C (\blacksquare). Solid lines are linear fits to the data.



Table 4.5. Comparison of fitting parameters A_{sc} and B_{sc}

<i>T</i> °C	<i>A</i> _{sc} (Fig 4.8)	$A_{\rm sc}$ (eq. 4.3)	$B_{\rm sc}$ (Fig 4.8)	$B_{\rm sc}$ (eq. 4.3)
30	-0.00427	-0.00430	-3.29	-3.34
70	-0.00112	-0.00120	-2.41	-2.49
110	0.00078	0.00076	-1.81	-1.86

4.4 Correlation between χ_{sc} and χ

When χ_{sc} is dependent on composition it differs from the χ parameter used in the Flory-Huggins equation to predict phase behavior. The two parameters are interrelated by the derivatives of free energy as shown by Sanchez.¹⁶

$$\chi = \phi_2 \chi_{\mu 1} + \phi_1 \chi_{\mu 2} \tag{4.4}$$

where $\chi_{\mu 1}$ and $\chi_{\mu 2}$ are given by

$$\chi_{\mu 1} = \frac{2}{(1-\phi_{1})^{2}} \int_{0}^{\phi_{2}} (1-\phi_{1}^{'}) \chi_{sc} d(1-\phi_{1}^{'})$$

$$\chi_{\mu 2} = \frac{2}{\phi_{1}^{2}} \int_{0}^{\phi_{1}} \phi_{1}^{'} \chi_{sc} d\phi_{1}^{'}$$
(4.5 a and b)

It is straightforward to show that if χ_{sc} is a linear function of $(2\phi_B - 1)$ then χ is also a linear function of $(2\phi_B - 1)$. Employing eqs. 4.3 – 4.5 gives an expression for the "true" Flory-Huggins χ .

$$\chi = A_{sc}(T) + \frac{B_{sc}(T)}{3} \frac{2\phi_B - 1}{N_{AVE}}$$
(4.6)

Figure 4.9 shows χ_{sc} , $\chi_{\mu 1}$, $\chi_{\mu 2}$, and the "true" χ for the four blends studied where $N_{\rm B}/N_{\rm C} = 0.72$.

Figure 4.9. Measured values of χ_{sc} at 110 °C for all blends with $N_B/N_C = 0.72$ (\blacktriangle) along with $\chi_{\mu 1}$ (---), $\chi_{\mu 2}$ (···), and χ_{FH} (—).



From comparison of equations 4.3 and 4.6, it is apparent that the sole difference between the measured χ_{sc} and the thermodynamic χ is a factor of 3 multiplying the compositiondependent term. This has the effect of lessening the composition dependence of calculated quantities such as the binodal and spinodal relative to the more intense compositional dependence for measured values of χ_{sc} . The final expression is

$$\chi = -0.00622 + \frac{10.6}{T} - \frac{3040}{T^2} + \left[-0.722 + \frac{638}{T} - \frac{229000}{T^2} \right] \frac{2\phi_B - 1}{N_{AVE}}$$
(4.7)

Figure 4.10 compares the compositional dependences of χ_{sc} and χ , illustrating the diminished effect on the "true" χ . The modest effect of composition and molecular weight on χ profoundly affects the phase behavior of B/C blends. The phase behavior of B/C blends is the subject of Chapter 5.

Figure 4.10. Measured values of $\chi_{sc}(\bullet)$ and χ calculated from eq. 4.7 (\bigcirc) plotted against $2\phi_B - 1$ for all blends studied at 30 °C.



4.5 References

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Chapter 5

Phase Behavior in Asymmetric Binary Blends with a Composition and Molecular Weight-Dependent χ Parameter

SANS measurements were used to determine the binodal and spinodal temperatures for binary blends of component B, polyisobutylene (PIB), and component C, deuterated polybutadiene with 63% 1,2 addition (dPB63). The measured phase diagrams were compared to predictions generated using Flory-Huggins Theory with a composition- and molecular weight-dependent χ . The two most asymmetric blends exhibited the most symmetric phase diagrams as a consequence of the combined effects of molecular weight asymmetry and the composition dependence of χ .

5.1 Asymmetry in polymer blends and phase diagrams

The majority of studies using binary polymer blends have selected symmetric systems, those for which the two homopolymers have equal molecular weights.¹⁻¹¹ For this simple case, Flory-Huggins Theory^{12,13} predicts that $\phi_{B,crit,FHT} = 0.5$. The resulting phase diagram is symmetric about the critical composition. When $N_B/N_C < 1$, Flory-Huggins Theory predicts that $\phi_{B,crit,FHT} > 0.5$ to account for the disparity in chain volumes. In this way, molecular weight asymmetry leads directly to an asymmetrical phase diagram. However, the B/C polymer blends considered here are known to exhibit a composition- and molecular weight-dependent χ^{14} . For these blends, the critical composition does not depend solely on N_B/N_C , but on ϕ_B as well. The combination of these effects results in asymmetric phase diagrams.

This chapter examines the phase behavior for four pairs of asymmetric B/C homopolymers. Each pair comprises a series of blends (all with the same N_1 and N_2) across a range of compositions. The 19 blends studied, introduced in Chapter 4, were chosen because they exhibited a transition from one- to two-phase behavior in the experimental temperature window 30 - 190 °C. Characteristics of the blends are summarized in Table 5.1, full details are given in Table 4.2. The same blend nomenclature is used as in Chapter 4: BBX[yyy] where "BB" indicates a binary blend, X refers to the composition of the blend, and yyy is the value of $N_{\rm B}/N_{\rm C}$.

N_B/N_C	$N_{\rm AVE}$	$\phi_{\rm B}$ values studied ^a
0.921	1075	0.233 (C), 0. 339 (T), 0.510 (F), 0.767 (A)
0.723	947	0.267 (C), 0.369 (T), 0.540 (F), 0.733 (A)
0.288	1750	0.238 (C), 0.300 (30), 0.438 (T), 0.500 (50), 0.600 (60), 0.651 (F), 0.762 (A)
0.226	1489	0.272 (C), 0.467 (T), 0.678 (F), 0.728 (A)

Table 5.1. Summarized blend characteristics

^aThe quantity in parentheses is "X" according to the blend name nomenclature. A full discussion of the naming scheme is given in Chapter 4.

5.2 SANS measurements of phase behavior

SANS profiles were measured for each blend as the sample was heated from the onephase to the macrophase separated region. Profiles within the homogeneous phase window exhibited a plateau at low q values, indicating a single uniform phase. With the onset of macrophase separation there was an up-turn in the low q scattering consistent with the Porod Scattering Law ($I \sim q^{-4}$). The temperature at which this up-turn occurs, T_b , is expected to fall on the binodal for critical blends. For off-critical blends, however, the observed temperature of phase separation may be elevated from the binodal temperature due to nucleation barriers.

In the limit of $R_g^2 q^2 \ll 1$, the low-q scattering is described by the Ornstein-Zernike approximation:

$$S(q) = \frac{S(0)}{1 + \xi^2 q^2}$$
(5.1)

where ξ is the correlation length of composition fluctuations. The Ornstein-Zernike structure factor is related to the SANS intensity by $I(q) = \Delta \rho^2 S(q)$, where $\Delta \rho^2$ is a temperature dependent quantity because the monomer volumes change as $v_B = v_B(23 \text{ °C})\exp[5.7 \times 10^{-4}(T - 23 \text{ °C})]$ and $v_C = v_C(23 \text{ °C})\exp[7.2 \times 10^{-4}(T - 23 \text{ °C})]$. The monomer volumes at 23 °C are calculated from the measured density. Figure 5.1 shows the SANS profiles and Ornstein-Zernike fits for a critical blend, BBT[0.29], at temperatures near the transition from homogeneous to Porod scattering. The Ornstein-Zernike fitting parameters are listed in Table 5.2.

Figure 5.1: SANS profiles for blend BBT[0.29] at selected temperatures. Solid lines are Ornstein-Zernike fits to the low *q* data. Profiles are shifted 0 cm⁻¹ (100 °C), 14000 cm⁻¹ (112 °C), 29000 cm⁻¹ (118 °C), and 45000 cm⁻¹ (120 °C).



Table 5.2: Ornstein-Zernike fitting parameters for BBT[0.29]. These parameters correspond to the fits shown in Figure 5.1.

<i>T</i> °C	$S(0) \text{ nm}^3$	ξ nm
100	87.3	8.32
112	316	15.7
118	27800	146

The temperature at which a blend crosses the binodal curve, T_b , is determined in either of two ways using the Ornstein-Zernike fitting parameters. In the first case, illustrated by BBA[0.92] in Figure 5.2a, the susceptibility drops sharply before the phase transition. Large scale composition fluctuations presage the first-order phase transition, causing the sudden drop in susceptibility. The dotted line in Figure 5.2a is a linear fit to the susceptibilities measured at the highest temperatures for which the blend was homogeneous, the *x*-axis intercept is T_b . However, for many off-critical blends studied, the susceptibility dropped continually up to T_b , as illustrated by blend BBA[0.23] in Figure 5.2b. In this case, T_b was determined as the temperature halfway between the highest temperature that yielded an homogeneous blend and the lowest temperature that yielded a macrophase separated blend. The error in determining T_b by this method was only 1 or 2 °C because fine temperature scans were made in the vicinity of the phase transition to accurately determine T_b . Both methods of measuring T_b were applied to blends with a sharp drop in the susceptibility, and yielded the same results (within error).

Figure 5.2. Susceptibility versus inverse temperature for selected blends: (a) BBA[0.92] (\blacklozenge) and BBT[0.92] (\blacktriangle) and (b) BBA[0.23] series (\blacklozenge) and BBT[0.23] (\blacktriangle). Solid lines are quadratic fits to the data used to obtain T_s , the dashed line is a linear fit used to obtain T_b .





Figures 5.2a and b each show the critical and acritical compositions in a series of blends. As expected, both series show a continuous decrease in the susceptibility at the critical composition. The off-critical blends were prepared at similar compositions ($\phi_B = 0.767$ and 0.728 for 5.2a and b, respectively), however they exhibit different behaviors. The susceptibility for BBA[0.92] drops discontinuously at temperatures within 5 °C of the phase transition, the signature of a first-order phase transition, while the susceptibility of BBA[0.23] changes continuously through the phase transition.

The spinodal temperature, T_s , is also determined from the susceptibility. The measured χ_{sc} for B/C blends was shown to depend quadratically on 1/T, ¹⁴ leading to $S(0)^{-1} \propto a + b/T + c/T^2$ for fixed values of ϕ_1 and N_{AVE} . At the spinodal temperature the susceptibility vanishes. Figure 5.2 shows quadratic fits to the susceptibility versus 1/T for selected blends. The *x*-axis intercept of the quadratic fit, $S(0)^{-1} = 0$, occurs at T_s . While a quadratic dependence is not conventional, it should be noted that for this polymer system there is no basis upon which to expect a linear relationship between susceptibility and 1/T, and that linear fits result in significantly different values of T_s for off-critical blends. The quadratic formula is used to calculate T_s from the fitted parameters, and the error in T_s is propagated through this solution. The magnitude of the calculated error varies non-systematically from ~1 to 30 °C for all of the blends studied.

For any binary blend that obeys Flory-Huggins Theory, a plot of $v_0S(0)^{-1}$ vs $\chi_{s,sc} - \chi_{sc}$ should yield a straight line with a slope of 2 that intercepts the origin. χ_{sc} is calculated using the empirical form given by eq. 4.3 and $\chi_{s,sc}$ is calculated for each blend (using eq. 3.11) and by definition does not vary with temperature. The abscissa is a convenient choice for comparing blends with different values of ϕ_1 and N_{AVE} because it incorporates these dependences into a single parameter, χ_{sc} . Figure 5.3 shows $v_0S(0)^{-1}$ vs $\chi_{s,sc} - \chi_{sc}$ for all blends studied at temperatures near the phase transition. The data show scatter about a linear trend with a finite intercept that is ~10 % of the quantity $\chi_{s,sc} - \chi_{sc}$ and a slope of 1.88. The agreement is sufficient to confirm the amenability of these B/C blends to treatment by mean-field theory. **Figure 5.3**: $v_0 S(0)^{-1}$ vs $\chi_{s,sc} - \chi_{sc}$ for all blends at all temperatures for which a homogeneous phase was obtained. The solid line is a linear fit to the data.



The scatter in Figure 5.3 is likely to derive from uncertainties in the empirical expression used to calculate χ_{sc} . The effects of this uncertainty can be circuited by allowing $\chi_{s,sc}$ to become a fitting parameter. A plot of $\frac{1}{2}v_0S(0)^{-1}$ vs $-\chi_{sc}$ should yield a straight line of slope 1 that intercepts the y-axis at $\chi_{s,sc}$. Figure 5.4 shows these plots for the "true" critical blends at temperatures near the phase transition. Parameters for the linear fits shown in Figure 5.4 are listed in Table 5.3.

Figure 5.4: $\frac{1}{2}v_0 S(0)^{-1}$ vs $-\chi_{sc}$ for the "true" critical blend in each series: BBT[0.72] $\phi_{1,crit} = 0.369$ (•), BBT[0.92] $\phi_{1,crit} = 0.340$ (•), BBT[0.23] $\phi_{1,crit} = 0.468$ (•), BBT[0.29] $\phi_{1,crit} = 0.439$ (•). Solid lines are linear fits to the data.



Series	BBT[0.72]	BBT[0.92]	BBT[0.23]	BBT[0.29]
$\phi_{1,crit}$	0.369	0.339	0.468	0.439
intercept	0.00251	0.00216	0.00125	0.00100
slope	1.04	1.10	0.804	0.898

Table 5.3: Parameters for the linear fits to $\frac{1}{2}v_0S(0)^{-1}$ vs $-\chi_{sc}$ shown in Figure 5.4.

Figure 5.5 compares the fitted values of χ_s to theoretically predicted values (The fitted values of $\chi_{s,sc}$ had to be converted to χ_s for comparison). The values of T_s determined from quadratic fits to the susceptibility were also converted to χ_s for comparison. The measurements are in reasonable agreement with the prediction made using Flory-Huggins Theory.

Figure 5.5: $\chi_s N_{AVE}$ vs ϕ_B for all blends with $N_B/N_C = 0.29$ where χ_s is determined from: fit values of $\chi_{s,sc}$ (\bigcirc), measured values of T_s (\blacktriangle), and Flory-Huggins Theory (solid line).



5.3 Phase Diagrams

The "true" expression for χ (eq. 4.6) must be used with the Flory-Huggins Equation for the Gibb's free energy of mixing per unit volume to predict thermodynamic behavior. The first derivative of the Flory-Huggins expression with respect to composition gives a quantity analogous (but not identical) to chemical potential:

$$\frac{v_0}{kT}\frac{\partial\Delta G}{\partial\phi_B} = \frac{\ln\phi_B + 1}{N_B} + \frac{-\ln(1 - \phi_B) - 1}{N_C} + \left[A(T) + B(T)\frac{2\phi_B - 1}{N_{AVE}}\right] - 2\phi_B + \frac{2B(T)}{N_{AVE}}(\phi_B - \phi_B^2)$$
(5.2)

The binodal curve is the locus of points determined at each temperature using a common tangent line that touches the free energy curve at only two points, corresponding to the compositions of the two coexisting equilibrium phases. Figure 5.6 shows the free energy curves and common tangents for each of the series studied at selected temperatures. The two blend series with $N_B/N_C = 0.92$ and 0.72 have the lowest molecular weights of the four blend series studied. These blends exhibit two distinct coexisting phases at temperatures between the critical point and the experimental upper limit of 190 °C. In both cases the B-rich macrophase is lower in energy than the C-rich macrophase, resulting in an asymmetric free energy diagram. The two series with the highest molecular weights ($N_B/N_C = 0.23$ and 0.29) both have a maximum temperature for which a common tangent exists. Above this temperature, one of the local minima occurs at the extreme of the phase diagram, indicating that the two coexisting equilibrium phases are pure B and pure C. The C-rich phase is predicted to be lower in energy for both of these blends.

Figure 5.6: Free energy curves and common tangents at selected temperatures for the blend series with $N_{\rm B}/N_{\rm C}$ values of (a) 0.72, (b) 0.92, (c) 0.23, and (d) 0.29. The lowest temperature shown is the lowest temperature for which the common tangent algorithm converged on two distinct solutions.






The second derivative is zero-valued at the spinodal and both the second and third dervatives are zero-valued at the critical point:

$$\frac{v_0}{kT}\frac{\partial^2 \Delta G}{\partial \phi_1^2} = \frac{1}{N_1\phi_1} + \frac{1}{N_2(1-\phi_1)} + \frac{1-2\phi_1}{N_{AVE}} 6B(T) - 2A(T) = 0$$
(5.3)

$$\frac{v_0}{kT} \frac{\partial^3 \Delta G}{\partial \phi_1^3} = \frac{1}{N_1 \phi_1^2} + \frac{1}{N_2 (1 - \phi_1)^2} + \frac{12}{N_{AVE}} B(T) = 0$$
(5.4)

Figure 5.7a presents the measured spinodal curves for the blend series with $N_B/N_C = 0.29$ compared with spinodal curves calculated using three different expressions for χ : a strict temperature dependence for which $\chi(T) = -0.00527 + 10.3/T - 3168/T^2$ (from refs. 15,16), χ_{sc} (eq. 4.3) and the "true" χ (eq. 4.6). Because $\chi(T)$ is not a function of composition, it follows directly that the molecular weight asymmetry of the series components ($N_B/N_C = 0.29$) will result in a critical point on the B-rich side of the phase diagram. The simple dependence on N_B/N_C is not valid for either the "true" χ or χ_{sc} because both depend on the composition of the blend and the molecular weights of the homopolymers. When a composition-dependent χ parameter is used, the calculated spinodal curves show a critical point on the C-rich side of the phase diagram. The effect of using χ_{sc} (ϕ_B , N_{AVE} , T) to predict phase behavior is to shift the critical point to the

extreme left of the phase diagram and to exaggerate the compositional dependence of the spinodal curve. In contrast, the spinodal curve for the "true" $\chi(\phi_B, N_{AVE}, T)$ exhibits a critical point only moderately shifted from the center. The trends for the three different interaction parameters shown in Figure 5.7 are true for all of the blend series. It is clear that the "true" composition-dependent χ most accurately captures the experimentally observed phase behavior.

Figure 5.7. Measured values of χN_{AVE} at the spinodal (\bigcirc) and calculated spinodal curves for the blend series with $N_{B}/N_{C} = 0.29$: χ (T) ($-\cdot-$), χ_{sc} (ϕ_{B} , N_{AVE} , T) ($\cdot\cdot\cdot$), and the "true" $\chi(\phi_{B}, N_{AVE}, T)$ ($-\cdot$).



The measured values of $\chi_s N_{AVE}$ and $\chi_b N_{AVE}$ (χ_b is the value of the "true" χ at the binodal) for each blend series, determined from SANS data, are compared to the independently calculated spinodal and binodal curves in Figures 5.8. The "true" $\chi(\phi_l, N_{AVE}, T)$ is used for all calculations. The progression of figures from 5.8a to d corresponds to the progression of blend series from most symmetric to least symmetric. Figure 5.8a shows the nearly symmetric series with $N_B/N_C =$ 0.92 series. There is good agreement between the measured and calculated binodal curves. Near the critical point, the measured spinodal and binodal overlap, however, there is a large separation between the spinodal and binodal for extremely off-critical blends. The experimental phase diagram for the blend series with $N_B/N_C = 0.72$ in Figure 5.8b also shows a large separation

between the measured spinodal and binodal for off-critical blends. However, with increasing molecular weight asymmetry, the $N_{\rm B}/N_{\rm C} = 0.29$ series in Figure 5.8c shows overlapping values of $T_{\rm b}$ and $T_{\rm s}$ across the entire range of compositions. This is also true for the $N_{\rm B}/N_{\rm C} = 0.23$ series in Figure 5.8d, where the molecular weights of the components are the most different for all the series. The blends with the most asymmetric homopolymers exhibit overlapping spinodal and binodal curves across the entire range of compositions.

Figure 5.8. Phase diagrams showing the measured values of χN_{AVE} at the spinodal (\bigcirc) and χN_{AVE} at the binodal (\blacktriangle), and the calculated binodal (solid line) and spinodal (dotted line) for N_B/N_C values of (a) 0.92, (b) 0.72, (c) 0.29, and (d) 0.23.







While the effect of using blends with $N_{\rm B}/N_{\rm C} < 1$ is to shift the phase diagram towards the component B-rich side, this trend is opposed by the composition dependence of χ which shifts the critical point towards the component C-rich side of the phase diagram. Consequently, the opposing trends produce a nearly symmetric phase diagram when $N_{\rm B}/N_{\rm C}$ is well-removed from unity.

5.4 References

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Chapter 6

Critical Ternary Blends with Asymmetric Homopolymers

SANS measurements were used to determine the phase behavior for A/B/A-C blends where the diblock copolymer was near the order-disorder transition (ODT) and the binary mixture of homopolymers was near the critical point. Component A was deuterated polybutadiene with 89 % 1,2 addition (dPB89), component B was polyisobutylene (PIB), and component A-C was a linear diblock in which block A was hydrogenated polybutadiene with 89 % 1,2 addition (hPB89) and block C was hydrogenated polybutadiene with 63 % 1,2 addition (hPB63). Binary blends of A and B were prepared at the critical composition and constant amount of diblock copolymer was added to each blend. In one series of blends the segregation strength was held constant, and in a separate experiment the segregation strength was allowed to vary. Nearly all blends exhibited lamellar microstructures at low experimental temperatures. There was evidence for the formation of microemulsions in some of the blends at intermediate temperatures. The high temperature phase was not microstructured, blends either mixed homogeneously or macrophase separated. The high temperature behavior was observed to correlate strongly with N_A/N_B .

6.1 Critical ternary blends

Most previous work with ternary polymer blends has involved symmetric A-B diblock copolymers that have been added to symmetric mixtures of A and B homopolymers (i.e. N_A/N_B ≈ 1).¹⁻²² Bates et. al. reported the formation of microemulsions in symmetric A/B/A-B blends when the diblock copolymer used was near its ODT ($\chi N_{diblock} = 10.5$ for the diblock copolymer) and the binary blend of A and B homopolymer was near the critical point ($\chi N_A = \chi N_B = 2$ for the binary blend)^{2,12 21,23-27}. These experiments selected a fixed ratio ϕ_A/ϕ_B and varied the amount of diblock copolymer added to a blend, $\phi_{diblock}$. For small amounts of diblock copolymer, the ternary blend behavior was similar to that of a pure binary blend, and exhibited a critical point. For large amounts of diblock copolymer the ternary blend exhibited an ODT similar to that of the pure copolymer. At an intermediate value of $\phi_{diblock}$, where blend was transitioning between binary blend-like behavior and copolymer-like behavior, microemulsions were observed. These experiments were motivated by elegant theoretical predictions of an isotropic Lifshitz point (coexistence between an ordered microphase, homogeneous phase, and macrophase separation) in the vicinity of the observed microemulsion.²⁸⁻³³ Composition fluctuations destroyed the isotropic Lifshitz point, resulting in a microemulsion phase instead. Subsequent models have incorporated asymmetric homopolymers into phase behavior predictions^{34,35}, however, this is the first experimental study to employ asymmetrical homopolymers.

A series of ternary blends was prepared starting with 13 different A/B binary pairs for which the molecular weight asymmetry, N_A/N_B , varied from 0.17 to 18.7. Each of these pairs was prepared at $\phi_A = \phi_{A,crit,FHT}$. In contrast to the χ measured between components B and C (see Chapters 4 and 5), the χ between components A and B was found to be independent of composition or molecular weight³⁶, consequently the Flory-Huggins prediction of the critical point was presumed to be accurate. The resulting critical binary blends had compositions $\phi_{A,crit}$ ranging from 0.188 to 0.709 due to the range of molecular weight asymmetries. The same nearly-symmetric diblock copolymer ($N_{A-block} = 1509$, $N_{C-block} = 1257$) was added to each of these critical binary blends such that the overall composition of the blend comprised 40 % copolymer. In this way, the 13 ternary blends all occured along the isopleth $\phi_{diblock} = 0.4$, but with markedly different values of N_A , N_B , and ϕ_A . The copolymer was chosen because it exhibited an ODT within the range of experimental temperatures. SANS measurements have determined that the true ODT was 140 +/- 10 °C for the copolymer, not far from the prediction of (χN)_{diblock} = 10.5 at 128 °C (where $\chi_{diblock}$ is the interaction between A and C and $N_{diblock}$ is the sum over both blocks). The design of these ternary blends was expected to result in conditions near the theoretical isotropic Lifshitz point.

Table 6.1 lists the polymers used in this chapter, the blend characteristics are listed in Table 6.2. Blends are identified with the nomenclature TBF[yyy] where "TBF" indicates a ternary blend at the Flory-Huggins critical composition and yyy is the nominal value of N_A/N_B .

				ρ g/cm ³	
		$M_{ m w}$		(at 23	
polymer	N	kg/mol	PDI	°C)	n _D
dPB89(10)	195	10.6	1.01	0.902	2.54
dPB89(24)	463	25.3	1.01	0.9070	2.79
dPB89(35)	671	36.5	1.02	0.9037	2.56
dPB89(49)	935	50.9	1.02	0.9046	2.63
dPB89(60)	1146	62.3	1.01	0.9031	2.52
dPB89(66)	1264	69.9	1.02	0.9183	3.49
dPB89(220)	4237	230	1.02	0.9032	2.62
PIB(13)	227	12.5	1.04	0.9134	
PIB(19)	340	18.7	1.02	0.9131	
PIB(24)	437	24	1.05	0.9131	
PIB(43)	772	42.5	1.04	0.9135	
PIB(45)	811	44.6	1.04	0.9140	
PIB(57)	1032	56.8	1.02	0.9144	
PIB(64)	1162	64	1.02	0.9120	
PIB(98)	1778	97.9	1.02	0.9102	
hPB89-	1509 –	78.5 -			
hPB63	1267	65.4	1.01	0.8639	

 Table 6.1.
 Characterization of polymers

Blend	Binary Components	NAVE	N_A/N_B	$\phi_{A,crit}$	$\chi_{AB}N_{AVE}$
TBF[0.17]	dPB89(10)/PIB(64)	393	0.17	0.709	1.74 - 1.98
TBF[0.19]	dPB89(10)/PIB(57)	379	0.19	0.697	1.68 - 1.91
TBF[0.24]	dPB89(10)/PIB(45)	351	0.24	0.671	1.56 - 1.77
TBF[0.26]	dPB89(24)/PIB(98)	812	0.26	0.662	3.61 - 4.09
TBF[0.60]	dPB89(24)/PIB(43)	588	0.60	0.564	2.61 - 2.96
TBF[1.06]	dPB89(24)/PIB(24)	450	1.06	0.493	2.00 - 2.27
TBF[1.11]	dPB89(60)/PIB(57)	1087	1.11	0.487	4.83 - 5.48
TBF[1.15]	dPB89(49)/PIB(45)	870	1.15	0.482	3.87 - 4.38
TBF[1.36]	dPB89(24)/PIB(19)	394	1.36	0.461	1.75 - 1.99
TBF[2.96]	dPB89(35)/PIB(13)	363	2.96	0.368	1.61 - 1.83
TBF[3.72]	dPB89(66)/PIB(19)	590	3.72	0.342	2.62 - 2.97
TBF[4.11]	dPB89(49)/PIB(19)	407	4.11	0.330	1.81 - 2.05
TBF[18.7]	dPB89(220)/PIB(13)	599	18.67	0.188	2.66 - 3.02

Table 6.2. Characterization of blends

6.2 Constant Segregation Strength

Three blends were selected to have a nearly constant segregation strength ($\chi N_{AVE} \sim 2.63$) and largely varying molecular weight asymmetries: TBF[0.60], TBF[3.72], and TBF[18.7]. The phase behavior obtained from the asymmetric blends is compared with three previously-studied symmetric blends³⁷ that contain the same diblock copolymer at the same concentration and encompass $\chi_{AB}N_{AVE} \approx 2.7$.

6.2.1. SANS analysis

SANS measurements were made while the samples were heated from 30 - 90 °C in 10 °C increments, and from 90 - 190 °C in 20 °C increments. The samples were annealed for at least 10 minutes after each change in temperature. Selected samples were heated in 2 °C increments in the vicinity of an observed phase transition to resolve the transition temperature, these samples were annealed for 5 minutes after each temperature step. These anneal times were tested for some blends to verify thermal equilibration. In regimes where microphase separated states were observed, the scattering profiles obtained immediately after the temperature step were identical to those obtained following a short thermal anneal. In regimes where macrophase separation was observed, SANS profiles obtained after 10 min were slightly different from the early time data due to coarsening. These effects are discussed in the text for Figures 6.7b and 6.1b. In summary, the anneal times were adequate to determine the equilibrium phases of A/B/A-C blends.

SANS profiles obtained from TBF[18.7], shown in Figure 6.1a, exhibit scattering in two regimes, delineated at 140 +/- 10 °C. The scattering profiles below 140 °C exhibit a low-q upturn that is consistent with the Porod scattering law $(I \sim q^{-4})$, indicating macrophase separation.

The correlation peak at $q \sim 0.11 \text{ nm}^{-1}$ suggests that one of the macrophases is periodic. Above 140 °C the blend is single phase as indicated by the lack of a low-q up-turn in these data. Profiles were measured before and after short thermal anneals at selected temperatures, these profiles are shown in Figure 6.1b. At all temperatures the profile measured after a 10 minute thermal anneal overlaid the original profile. At 30 °C profiles were obtained every 5 minutes for 30 minutes and did not change within that time frame. This was taken as an indication of equilibrium phase behavior for this blend.

Figure 6.1. SANS intensity *I* versus scattering vector *q* for blend TB[18.7] at selected temperatures. (a) Profiles shifted vertically as follows: 5.6×10^6 cm⁻¹ (30 °C), 4.4×10^6 cm⁻¹ (70 °C), 2.8×10^6 cm⁻¹ (130 °C), 1.3×10^6 cm⁻¹ (150 °C), 0 cm⁻¹ (190 °C). (b) Profiles acquired before and after thermal annealing at selected temperatures: 30 °C offset 0 cm⁻¹: t = 0 (\triangleright), t = 30 min (\triangleright), 130 °C offset 300 cm⁻¹: t = 0 (\bigtriangledown), t = 10 min (\checkmark), and 170 °C offset 500 cm⁻¹: t = 0 (\triangleleft), t = 10 min(\blacktriangleleft). Lines connect the data points for visual clarity. (c) *I* versus *q* profiles from within the homogeneous phase window (markers) shown with the corresponding RPA predictions (lines connecting markers). The SANS and RPA profiles have been shifted as follows: 1000 cm⁻¹ (150 °C), 500 cm⁻¹ (170 °C), 0 cm⁻¹ (190 °C).





The SANS profiles from homogeneous blends were calculated independently using the multicomponent Random Phase Approximation (RPA)^{36,38,39}. Inputs to the RPA included the binary Flory-Huggins parameters describing monomer-monomer interactions between different

components and the statistical segment length of each species (homopolymers and blocks). Previously published values of these parameters³⁷ listed in ref. 40 were used to predict SANS profiles within the homogeneous window for blend TBF[18.7]. Attempts were made to extend the composition and molecular weight-dependent χ_{BC} established in Chapter 4 to ternary blends. The resulting phase predictions were within 5 % of those made using a strictly temperature-dependent χ_{BC} , so the composition dependence was ignored to minimize errors in χ_{BC} due to chain ends (χ_{BC} was measured using two homopolymers but was applied to the interaction between the block of a diblock copolymer and a homopolymer).

The RPA calculations for TBF[18.7] predict continuous profiles for temperatures ≥ 140 °C. Below 140 °C the calculated profiles contain a pole at finite q, indicating phase behavior outside of the homogeneous window. Figure 6.1c shows a comparison between RPA predictions and experimental SANS data. The $I \sim q^{-2}$ tail at high q is captured quantitatively by RPA, as is the value of q where I(q) turns over and approaches a plateau. The lack of quantitative agreement between the RPA calculations and experimental data in the high q regime indicates that the statistical segment length of at least one of the components is affected by the presence of the other components. In the experiments, the value of the low-q plateau decreases from 110 to 60 cm⁻¹ as the temperature is changed from 150 to 190 °C, while in the RPA calculations, the low-q plateau decreases from 170 to 92 cm⁻¹ in the same window. The departure between theory and experiment may derive from inaccuracies in the χ parameters used for the calculations. TBF[18.7] does not exhibit a single-phase microstructure in the temperature window 30 - 190 °C.

SANS data from blend TBF[3.72], shown in Figure 6.2a, are qualitatively different from those of TBF[18.7] discussed above. At low temperatures, the SANS profiles contain a welldefined scattering peak at $q^* = 0.107 \text{ nm}^{-1}$ and a shoulder at $2q^* = 0.214 \text{ nm}^{-1}$. Normalizing the ordered scattering profiles using a profile deep within the disordered state is model-free method for accentuating weak higher order peaks.⁴¹ The normalized profiles are obtained by dividing the *q*-dependent scattering intensity at a given temperature with the scattering intensity obtained at 190 °C. Structural information contained in the measured scattering profile is convoluted with the form factors of the polymer chains. Dividing out the profile obtained deep within the disordered state removes (or minimizes) the scattering contribution of the form factors, leaving structural scattering to dominate the normalized profile. The normalized profiles shown in Figure 6.2b were fit to a Gaussian with an exponential baseline to estimate the area under the $2q^*$ peaks, A_2 . A sharp decrease in A_2 is seen at 65 +/-5 °C, suggesting an ODT.

Figure 6.2. SANS data and analysis for blend TBF[3.72]. (a) SANS intensity *I* versus scattering vector *q*. Profiles shifted vertically as follows: 2.7×10^6 cm⁻¹ (30 °C), 2.0×10^6 cm⁻¹ (70 °C), 1.3×10^6 cm⁻¹ (110 °C), 6.8×10^5 cm⁻¹ (150 °C), 0 cm⁻¹ (190 °C). (b) Normalized SANS scattering profiles highlighting the 2*q** peak with the following vertical shifts: 400 (30 °C), 300 (40 °C), 200 (50 °C), 100 (60 °C), 0 (70 °C). The solid curves are Gaussian fits to the 2*q** peak and the exponentially decaying backgrounds. Inset: Integral of the 2*q** peak versus temperature.





The two-dimensional SANS scattering profiles for TBF[3.72] were azimuthally asymmetric at temperatures for which the blend was ordered (All of the SANS data from TBF[18.7] were azimuthally symmetric). Azimuthal asymmetry arises due to flow fields created during sample preparation, it reflects the presence of anisotropically ordered microstructures. Disordered samples scatter isotropically. Figure 6.3a shows the two-dimensional SANS data for TBF[3.72] at 30 °C, well within the lamellar ordered phase. The scattering ring of the primary peak exhibits two arcs of higher intensity opposite one another. In contrast, Figure 6.3b shows an isotropic scattering profile for TBF[3.72] well within the disordered phase at 190 °C. To quantify these differences, the integrated SANS intensity between q = 0.093 and 0.128 nm⁻¹ (in the vicinity of the primary peak) was determined as a function of azimuthal angle, α . The standard deviation of the data set, σ , was taken as a measure of azimuthal asymmetry. The results of this integration at 30 °C are shown in the inset of Figure 6.4. σ is plotted against temperature in Figure 6.4, dropping dramatically at 75 +/- 10 °C. The A_2 - and σ -based estimates of the ODT were in agreement (within error) or the A_2 -based estimate was below the σ -based estimate for all blends.



Figure 6.3. Two-dimensional SANS profiles for TBF[3.72] at (a) 30 °C and (b) 190 °C.

Figure 6.4. Azimuthal scattering asymmetry, σ , versus temperature for TBF[3.72]. The dotted line represents the transition between azimuthally asymmetric and symmetric scattering. Inset: integrated scattering intensity vs. azimuthal angle, α , at 30 °C.



The high temperature disordered phase was verified with multicomponent RPA calculations. These calculations indicated the presence of an homogeneous phase at temperatures above 150 °C, as shown in Figure 6.5. As with blend TBF[18.7], the RPA and measured SANS profiles agree qualitatively but not quantitatively.

Figure 6.5. SANS profiles for TBF[3.72] within the homogeneous phase window at 170 °C (+) and 190 °C (\blacktriangleright) and RPA predictions at the same temperatures, shown with lines connecting the markers. The profiles have been shifted as follows: 0 cm⁻¹ (170 °C) and 100 cm⁻¹ (190 °C).



In Figure 6.2 the presence of a shallow peak at $q = 0.11 \text{ nm}^{-1}$ in the SANS profiles between 80 and 150 °C suggests that the blend is microphase separated, however the microstructure are expected to be disordered because this temperature window is greater than the ODT. These observations are consistent with the microemulsion phase channel first observed by Bates et. al. Many studies have shown that SANS data from microemulsions can be fit to the Teubner-Strey equation⁴²:

$$I = \frac{1}{a + bq^2 + cq^4}$$
(6.1)

The scattering profiles for temperatures 80 - 150 °C were fitted with the Teubner-Strey equation and the results are shown in Figure 6.6. At 80 °C (and below) the low q data are not well fit by the Teubner-Strey equation because the $1q^*$ peak is too sharp, suggesting that the blend is lamellar at these temperatures. The fits from 110 - 150 °C are consistent with the Teubner-Strey equation, supporting the presence of a microemulsion in this temperature window. The fitted values of a, b, and c, summarized in Table 6.3, are similar to those reported in previous studies on microemulsions in symmetric A/B/A-C blends.^{43,44} The parameter b is negative when fit to the scattering profile of a microemulsion, and while b may be negative when fit to other microstructures, a positive value for b unambiguously identifies a structure that is not a microemulsion. The transition from a microemulsion to a homogeneous phase appears to be continuous as the peak at q = 0.11 nm⁻¹ fades to a monotonic scattering profile upon heating.

Scattering from the microemulsion phase was azimuthally symmetric, indicating the presence of randomly oriented microstructures even though the precursor phase from which it was formed contained a non-random collection of lamellar grains.

Figure 6.6. SANS scattering profiles for TBF[3.72] with Teubner-Strey fits to $1q^*: 80 \ ^\circ C (\blacktriangleright)$, 110 $^\circ C (\blacksquare)$, 130 $^\circ C (+)$, 150 $^\circ C (\diamondsuit)$.



Table 6.3. Teubner-Strey (TS) fitting parameters for blend TBF[3.72] at select temperatures

	Temperature in °C				
TS parameter	80	110	130	150	
a (cm)	0.019	0.023	0.023	0.023	
$b (cm \cdot nm^2)$	-2.39	-2.21	-1.71	-1.20	
c $(cm \cdot nm^4)$	89.3	83.6	71.9	60.6	

The scattering profiles for blend TBF[0.60] are shown in Figure 6.7a. At low temperatures the blend exhibits peaks at q^* , $2q^*$, and $3q^*$, consistent with a lamellar phase. At 122 ± 2 °C the blend macrophase separates as evidenced by the onset of Porod scattering. As was the case with TBF[3.72], the scattering from the lamellar phase is azimuthally asymmetric. The onset of Porod scattering coincides with the temperature at which σ decreases to a constant value for isotropic scattering. RPA calculations for TBF[0.60] indicate the absence of a homogeneous phase in the 30 - 190 °C window, consistent with experimental observations. Profiles were measured before and after a short thermal anneal to test for equilibrium behavior (Figure 6.7b). Within the lamellar phase window profiles overlap, however once the blend macrophase separates, the nonequilibrium effects of nucleation and growth cause the profiles to change with time.

Figure 6.7. SANS scattering profiles for blend TBF[0.60] (a) with the following shifts: 5×10^5 cm⁻¹ (30 °C), 3×10^5 cm⁻¹ (120 °C), 2×10^5 cm⁻¹ (122 °C), 9×10^4 cm⁻¹ (124 °C), 0 cm⁻¹ (190 °C). Solid lines are power laws with a slope of -4. (b) SANS profiles before and after short thermal anneals for selected temperatures: 80 °C offset 4500 cm⁻¹: t = 0 (\bigcirc), t = 10 min (\bullet), 120 °C offset 1500 cm⁻¹: t = 0 (\square), t = 5 min (\blacksquare), 122 °C offset 1000 cm⁻¹: t = 0 (\diamond), t = 5 min (\bullet), and 150 °C offset 0 cm⁻¹: t = 0 (\triangle), t = 10 min (\bullet).





6.2.2. Phase diagrams

Figure 6.8a shows the phase behavior of three nearly symmetric A/B/A-C blends measured previously³⁷, TBF[1.06], TBF[1.11], and TBF[1.15]. All of the symmetric blends exhibit a lamellar phase at low temperatures and macrophase separation at high temperatures. TBF[1.06] exhibits a microemulsion at intermediate temperatures. The lines in Figure 6.8a are used to obtain a best estimate of the phase behavior of symmetric blends with $\chi_{AB}N_{AVE} = 2.6$ (the same segregation strength as the asymmetric blends discussed above). **Figure 6.8.** Phase behavior denoted by hom: homogeneous phase, 2P: macrophase separated state, μ E: microemulsion, and lam: lamellae. (a) Phase transition temperatures as a function of segregation strength, $\chi_{AB}N_{AVE}$, for the symmetric blends TBF[1.06], TBF[1.11], and TBF[1.15]. (b) Phase transition temperatures for all blends with $\chi_{AB}N_{AVE} = 2.6$ as a function of N_A/N_B . Blends TBF[18.7], TBF[3.72], and TBF[0.60], are shown along with interpolated values for $N_A/N_B = 1$.





The phase behavior of the three asymmetrical blends is summarized in Figure 6.8b. An additional data point at $N_A/N_B = 1$ represents an interpolation for $\chi_{AB}N_{AVE} = 2.6$. At $N_A/N_B = 0.60$, the phase was lamellar at low temperatures and macrophase separated at high temperatures. Increasing N_A/N_B to 1.0 opened up a microemulsion window between the lamellar and macrophase separated states. Further increase of N_A/N_B to 3.72 resulted in lamellae at low temperatures, a microemulsion at intermediate temperatures, and a homogeneous phase at high temperatures. Finally increasing N_A/N_B to 18.7 led to macrophase separation at low temperatures and a homogeneous phase at high temperatures, i.e. periodic microphases are absent. Qualitatively different kinds of phase behavior were obtained at a fixed value of $\chi_{AB}N_{AVE}$ by simply altering the relative molecular weights of the homopolymers.

6.3. Nonconstant segregation strength

In total, thirteen A/B/A-C blends were studied for which the molecular weight of the diblock copolymer and its concentration in the blend were fixed. The previous section described the results for blends with a fixed segregation strength (χN_{AVE}) whereas the blends here vary N_A/N_B from 0.17 – 19 and N_{AVE} from from 351 – 1090. The resulting phase transitions were the same as those observed for the blends with constant segregation strength: all blends (except TBF[18.7]) were lamellar at low temperatures. Blends with $N_A/N_B > 1$ exhibited a homogeneous phase at elevated temperatures, and those with $N_A/N_B \leq 1$ exhibited macrophase separation upon heating. An exception was observed for the most asymmetrical blend studied, TBF[18.7], which transitioned from macrophase separated to homogeneous with heating. This is the only blend for which microphase ordering was not observed. Figure 6.9 summarizes the phase behavior for all blends studied in terms of χN_{AVE} vs N_A/N_B . The y-axis is a convenient choice for comparing

blends of the same homopolymer species and different molecular weights. The microemulsion channel, evident in Figure 6.8b, is too small to be labeled in $\chi_{AB}N_{AVE}$ phase space.

Figure 6.9. Phase behavior for all blends with $\phi_{\text{diblock}} = 0.4$ and $N_{\text{A-C}} = 1509 - 1257$. The symbols indicate the type of phase transition: lamellae to macrophase separated (•), lamellae to homogeneous (•), and macrophase separation to homogeneous (•). The annotation "2P" denotes macrophase separated, "hom" for homogeneous, and "lam" for lamellae. The solid lines connect the data points and dotted lines are drawn to approximate phase boundaries for visual clarity.



Figure 6.9 shows that $(\chi N_{AVE})_{crit}$ for ternary blends was often well-removed from the expectation of 2 for binary blends. The high temperature phase was strongly correlated with N_A/N_B , although microstructures were present at low temperatures across nearly the entire range of molecular weight asymmetries. Clearly, the parameter N_A/N_B offers the potential of tunable microstructures without the use of additional diblock copolymer. Because only critical blends were studied ($\phi_{A,crit,FHT} \sim N_A/N_B^{-1/2}$), it was unclear whether the observed correlation between N_A/N_B and phase behavior was due strictly to N_A/N_B or whether ϕ_A also contributed. This query is resolved in the following chapter.

6.4 References

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- (40) Note. Temperatures are in K: $\chi_{AB} = 0.00034 + 3.94/T 817/T^2$; $\chi_{AC} = 0.00209 1.18/T + 747/T^2$; $\chi_{BC} = -0.00527 + 10.3/T 3168/T^2$. Statistical Segment lengths: $l_A = 5.5$ Å; $l_B = 5.8$ Å; $l_C = 7.5$ Å.
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Chapter 7

Off-Critical Ternary Blends with Asymmetric Homopolymers

SANS measurements were used to determine the phase behavior for a series of A/B/A-C blends where ϕ_A varied from 0.1 to 0.5, but $\phi_{diblock}$ and N_A/N_B were fixed. Component A was deuterated polybutadiene with 89 % 1,2 addition (dPB89), component B was polyisobutylene (PIB), and component A-C was a linear diblock in which block A was hydrogenated polybutadiene with 89 % 1,2 addition (hPB89) and block C was hydrogenated polybutadiene with 63 % 1,2 addition (hPB63). Lamellar SANS profiles were fit using a model for randomly oriented lamellae described by Hosemann and Bagchi¹ to extract information about the A- and B-rich lamellae. The results of the analysis were found to agree with independently generated predictions calculated using self-consistent field theory (SCFT). Calculations based on the multicomponent RPA predicted a small homogeneous window that was not experimentally observed in any of the blends studied.

7.1 Introduction

The previous chapter did not resolve whether trends in the high temperature phase behavior of A/B/A-C blends were due to molecular weight asymmetry (N_A/N_B) or composition (ϕ_A) because the two parameters were coupled through the requirement of critical blending (eq. 3.5). This chapter relaxes the requirement for critical blending in order to decouple the effects of N_A/N_B and ϕ_A on phase behavior.

The three polymers used in blend TBF[0.60] (introduced in Chapter 6) were chosen as the basis for a series of off-critical blends. The A homopolymer was nearly 2/3 the length of the B homopolymer ($N_A/N_B = 0.60$), and the diblock copolymer was nearly symmetric ($N_{A-C} = 1509$ – 1257) with $f_A = 0.55$. $\phi_{diblock} = 0.400$ for all blends. The chain lengths of the homopolymers and diblock copolymer were chosen to lie nominally within the wet brush regime ($N_A/N_{A-C} =$ 0.17, $N_B/N_{A-C} = 0.28$). This is a regime wherein the homopolymer chain lengths are substantially smaller than that of the copolymer, and this enables penetration of the homopolymer chains into the diblock copolymer brush that lies between the A-rich and B-rich microphases.²⁻⁵

Table 7.1 characterizes the blends studied. The eight off-critical blends were named TBXX[0.60] where XX is the percent of A homopolymer in the blend and the critical blend was TBF[0.60] from the previous chapter. The total bulk fraction of component A in a blend, $\phi_{A,TOT}$ in Table 7.1, was the sum of contributions from the A homopolymer and the A-block of the copolymer (i.e. $\phi_{A,TOT} = \phi_A + f_A \phi_{diblock}$).

Table 7.1. Characterization of blends

Blend	ϕ_A	$\phi_{A, TOT}$	\$ A-dom	<i>d</i> (nm)
TB10[0.60]	0.100	0.318	0.359 - 0.431	59.9 - 74.7
TB15[0.60]	0.150	0.368	0.233 - 0.587	62.3 - 73.5
TB20[0.60]	0.200	0.418	0.297 - 0.357	63.2 - 74.2
TB25[0.60]	0.250	0.468	0.346 - 0.398	62.9 - 67.9
TB30[0.60]	0.300	0.518	0.587 - 0.636	63.2 - 76.2
TBF[0.60]	0.338	0.556	0.573 - 0.612	62.4 - 66.9
TB40[0.60]	0.400	0.618	0.599 - 0.621	64.7 - 70.6
TB45[0.60]	0.450	0.668	0.575 - 0.586	60.2 - 68.0
TB50[0.60]	0.500	0.718	0.567 - 0.600	5.64 - 6.72

7.2 SANS Phase Determination

Samples were placed into the SANS beamline at room temperature and heated incrementally from 30 to 190 °C. Each temperature step was followed by a ten minute anneal to allow the samples to equilibrate; previous work with this system has shown that this amount of time is sufficient to obtain reproducible SANS profiles that do not vary with time. Six of the blends (those with $\phi_A = 0.1$ - 0.338) were heated a second time from 110 to 130 °C in 2 °C increments to more accurately determine the temperatures of the phase transitions. These runs included a 5 minute anneal after each temperature step, shown to be adequate for equilibration after small temperature steps.

SANS profiles at selected temperatures are shown for blend TB40[0.60] in Figure 7.1. At 30 °C, the blend exhibits a primary scattering peak at $q = q^*$, and a higher order scattering peak at $q = 2q^*$, consistent with the scattering expected from a lamellar phase. The lamellar phase persists in blend TB40[0.60] until the temperature is increased to 120 °C. At higher temperatures the SANS profiles exhibit an up-turn in the low-q scattering consistent with the Porod Scattering Law ($I \sim q^{-4}$) indicating the onset of macrophase separation. The SANS profiles at 130 and 170 °C show a broad correlation peak at finite q in addition to Porod Scattering at low q, suggesting that one of the coexisting macrophases periodic. This phenomenon was previously documented by several groups.⁶⁻⁸ The SANS profiles for all nine blends listed in Table 7.1 were qualitatively similar to Figure 7.1: a microstructure correlation peak at low temperatures, and Porod scattering above 130 °C.

We tested the thermo-reversibility of the SANS profiles acquired for blend TB40[0.60] to ensure that the ten-minute anneal time after each temperature step was sufficient to attain thermal equilibrium. After obtaining the SANS profiles shown in Figure 1a, blend TB40[0.60] was allowed to cool to room temperature, then heated under vacuum at 90 °C for 24 hours. The sample was transferred immediately from the oven to the SANS heating stage, which had been preheated to 90 °C. The transfer took approximately one minute, and cooling was negligible because the sample was contained within a relatively large titanium sample holder. Figure 1b shows the SANS profiles obtained thereupon heating blend TB40[0.60] from 90 – 130 °C, then cooling the sample through the same temperature window, with a 10 minute anneal after each step change in temperature for both heating and cooling. The SANS profiles from Figure 1a are included in Figure 1b to compare data acquired at the same temperature and a different thermal history. The SANS profiles overlap upon heating the sample through the lamellar-to-macrophase separated transition and immediately cooling the sample back to lamellae, providing strong evidence that the data obtained represent thermal equilibrium. A ten-minute anneal time after each step in temperature appears adequate to obtain thermal equilibrium. However, the profiles obtained for different thermal histories varied slightly in intensity while retaining the same qualitative features and primary peak locations. The peaks are sharper for blend TB40[0.60] following a 24 hour anneal compared to a 1 hour anneal. The dependence of peak sharpness and intensity on the thermal history of the sample was found for all blends that were examined in multiple SANS runs. The widths of the SANS peaks are related to factors such as the extent of long range order (in the case of ordered microphases) which is known to depend on thermal history.

Figure 7.1: SANS intensity, *I*, versus scattering vector, *q* at selected temperatures for blend TB40[0.60]. (a) Thermal history is 1 hour anneal at 90 °C and slow cooling to room temperature. Profiles have been shifted vertically as follows: 30 °C (0 cm⁻¹), 110 °C (1.5×10^8 cm⁻¹), 120 °C (3.0×10^8 cm⁻¹), 130 °C (4.8×10^8 cm⁻¹), 170 °C (6.8×10^8 cm⁻¹). (b) Solid markers denote a thermohistory of 24 hours annealing time at 90 °C and no cooling. The sample was heated from 90 – 130 °C. Open markers denote the cooling run from 130 – 90 °C that was performed immediately after the heating run. The solid lines are duplicated from 1a, they denote a 1 hour anneal time at 90 °C and slow cool to room temperature. All profiles have been shifted as follows: 0 cm⁻¹ (90 °C), 3×10^6 cm⁻¹ (110 °C), and 6.5×10^6 cm⁻¹ (130 °C).





All of the samples exhibited azimuthally asymmetric scattering in the temperature window from 30 to ~120 °C. The presence of azimuthal asymmetry has been shown to result from the alignment of anisotropic microstructures during sample preparation.^{9,10} The integrated SANS intensity between q = 0.07 - 0.12 nm⁻¹, in the vicinity of the primary peak, was determined as a function of azimuthal angle, α , and the standard deviation of the data set, σ , was taken as a measure of azimuthal asymmetry. The results of this integration, obtained for TB25[0.60] at 30 °C, are shown in the inset of Figure 6.2, giving $\sigma = 0.471$. The temperature dependence of σ for blend TB25[0.60] is shown in the main graph of Figure 6.2. There is a twofold decrease in σ between 118 and 120 °C, in good agreement with the onset of macrophase separation inferred from the up-turn in the low-q scattering data. The σ -based measurement of the transition temperature from anisotropic to isotropic scattering was found to agree with the onset of macrophase separation for all blends studied.

Figure 7.2. Standard deviation, σ , of the SANS profiles integrated between q = 0.07 and 0.12 nm⁻¹ versus temperature for blend TB25[0.60]. The inset shows the integrated intensity versus azimuthal angle, α , at 30 °C.



7.3 Lamellar Structure Factor

The presence of a single scattering peak can, in principle, indicate the presence of a weakly ordered lamellar phase or a microemulsion. The intensity predicted by the Teubner-Strey Equation for microemulsions, $I_{\mu E}$, is given by¹¹:

$$I_{\mu E}(q) = \frac{1}{a + bq^2 + cq^4}$$
(7.1)

where the fitting parameter b is of particular interest as it is negative for the case of microemulsions.

The scattering profile from randomly oriented lamellae, I_{lam} , is given by¹²:

$$I_{lam}(q) = \frac{C_1}{q^4} f(q)$$
(7.2)

where C_1 is a constant that is related to the number of lamellae in the scattering volume and the average scattering contrast between the lamellae. The function f(q) is given by^{1,13}

$$f(q) = \frac{(1 - g_A)(1 - g_B)(1 - g_A g_B) + 2g_A(1 - \mathcal{G}_B^2)\sin^2\left(\frac{q\phi_{A-dom}}{2}\right) + 2g_B(1 - g_A^2)\sin^2\left(\frac{q\phi_{B-dom}}{2}\right)}{(1 - g_A g_B)^2 + 4g_A g_B \sin^2(qd/2)}$$

where

$$g_A = e^{-\frac{1}{2}\sigma_A^2 q^2}, \ g_B = e^{-\frac{1}{2}\sigma_B^2 q^2}$$
 (7.4a & b)

The parameters ϕ_{A-dom} and ϕ_{B-dom} refer to the volume fractions of the A- and B-rich lamellar microdomains ($\phi_{A-dom} + \phi_{B-dom} = 1$), *d* is the average overall domain spacing (the center-to-center distance between adjacent A-rich lamellae), and the widths of the A and B lamellae are assumed to follow a Gaussian distribution with a standard deviation of σ_A and σ_B . The form of eq. 7.2 assumes that lamellar grains are randomly oriented, which is clearly not true due to anisotropic scattering (Figure 7.2). However, it is expected that the prefactor C_1 can be used to account for the effects of nonrandom grain orientation. The SANS intensity profiles for all blends are fit with eqs. 7.2 - 7.4 using five adjustable parameters: C_1 , σ_A , σ_B , *d*, and ϕ_{A-dom} .

One of the difficulties with the expression for I_{lam} is that it is based on the assumption that the microphases themselves are unstructured. The Debye function gives the scattering intensity from chains in the melt configuration. A form factor based on the Debye scattering from each component is dominated by the contributions from A, the deuterated species. Such a form factor over-predicts the high-*q* scattering because the polymer chains in a lamellar microstructure are not random walks. In the lamellar phase, the A-rich microdomains comprise primarily of the homopolymer (Ah) and the A block of the diblock copolymer (Ab). The RPA computes a more appropriate form factor based on scattering from composition fluctuations in the A-rich microdomains:

$$I_{A,fluc}(q) = B^{2} \left(\frac{1}{N_{Ah} v_{Ah} \phi_{Ah} P_{Ah}(q)} + \frac{1}{N_{Ab} v_{Ab} \phi_{Ab} P_{Ab}(q)} \right)^{-1}$$
(7.5)

where *B* is the scattering contrast, related to the scattering length of species i, b_i , and monomer volume, v_i , as:

$$B = \frac{b_{hPBD}}{v_{hPBD}} - \frac{b_{dPBD}}{v_{dPBD}}$$
(7.6)

and $P_i(q)$ is the Debye function for species i. Eq. 7.5 is based on the assumption of ideal mixing in the A-rich domains. Eq. 7.5 neglects the contributions due to concentration fluctuations in the B-rich lamellae. The value of $I_{B,fluc}$ is estimated to be two orders of magnitude less than that of $I_{A,fluc}$ because both B and C chains are hydrogenated, with nearly identical scattering length densities.

The measured SANS intensity is simply a linear sum of contributions from the lamellar structure factor and the concentration fluctuations in the A-rich domains.

$$I(q) = I_{\text{lam}}(q) + I_{\text{A,fluc}}(q) \tag{7.7}$$

Figure 7.3 shows fits to I(q) for TB25[0.60] at 30 °C where just $I_{\text{lam}}(q)$ is used and also $I_{\text{lam}}(q) + I_{A,\text{fluc}}(q)$. In both cases, the lamellar fits were smeared with the instrument resolution function provided by the NCNR⁵⁹ to capture the width of the peaks. Both fits shown in Figure 7.3 have the same number of fitting parameters. It is clear that accounting for the fluctuations within the lamellae leads to a significant reduction in the deviation between the model and experiments.

Figure 7.3. SANS intensity, *I*, versus scattering vector, *q*, for blend TB25[0.60] at 30 °C (\bigcirc). The dashed curve is a fit of $I_{\text{lam}}(q)$ (eq. 7.2) and the full curve is a fit of $I_{\text{lam}}+I_{\text{A,fluc}}$ (eq. 7.7).



The detailed fitting of the lamellar structure factor was unnecessary for proving that TB25[0.60] at 30 °C forms a lamellar phase due to the presence of a shoulder at $q = 2q^*$. There were, however, several SANS profiles that only contained a primary peak. An example of this is shown in Figure 7.4 where I(q) for TB10[0.60] is shown at selected temperatures. A single scattering peak is seen at 30 °C. The profiles at 30 and 124 °C were obtained from the first SANS run after annealing the sample at 90 °C, while the profiles at 110, 118, and 122 °C were obtained from the second SANS run after annealing the sample at 190 °C. Figure 7.4a shows fits of $I_{\text{lam}}(q)$ through the data while Figure 7.4b shows the fits of $I_{\mu\text{E}}(q)$ through the same data set. It is evident that the $I_{\text{lam}}(q)$ fits are significantly better than those of $I_{\mu\text{E}}(q)$. The $I_{\text{lam}}(q)$ fits are consistent with the data when there is only one primary peak as is the case at 30 °C, as well as cases when both a primary peak and a shoulder at $2q^*$ are present, as is the case at 116 °C (Figure 7.4a) suggesting that a lamellar phase is present in TB10[0.60] at temperatures ≤ 120 °C.

Figure 7.4: SANS intensity, *I*, versus scattering vector, *q*, for blend TB10[0.60] at selected temperatures (markers) and solid-line fits to the data for (a) $I_{\text{lam}}(q)$ and (b) $I_{\mu\text{E}}(q)$. Intensity profiles in both figures were shifted for clarity: $6.0 \times 10^6 \text{ cm}^{-1}$ (124 °C), $4.4 \times 10^6 \text{ cm}^{-1}$ (122 °C), $3.0 \times 10^6 \text{ cm}^{-1}$ (116 °C), $1.6 \times 10^6 \text{ cm}^{-1}$ (110 °C), and 0 cm^{-1} (30 °C).





The fitted parameters obtained from sample TB10[0.60] at selected temperatures are given in Table 7.2 for the $I_{\text{lam}}(q)$ fits and Table 7.3 for the $I_{\mu E}(q)$ fits. The SANS profile for TB10[0.60] at 110 °C was for two distinct thermal histories. The domain spacings and σ values were similar for both thermal histories. In general, ϕ_{A-dom} is somewhat larger than the bulk value of component A in the blend, $\phi_{A,TOT} = 0.318$. The values of σ_A/d_A range from 0.01 to 0.07 and those for σ_B/d_B range from 0.10 to 0.16 indicating that the lamellar thicknesses vary around 10-20% in the sample. The fitted value of C_1 contains contributions from the scattering contrast and the number of lamellar stacks within the scattering volume, but has no particular significance.

	19	0 °C ann	90 °C anneal		
$T(^{\circ}C)$	110	118	122	30	110
$A x 10^{10} (\text{cm}^{-1} \text{nm}^{-4})$	3.592	3.49	3.32	5.10	2.53
$\phi_{A, TOT}$	0.412	0.356	0.344	0.431	0.359
$\sigma_{\!A}$ (nm)	4.53	4.94	6.18	0.969	5.45
$\sigma_{\!\scriptscriptstyle B} \ ({\rm nm})$	10.4	10.1	14.7	6.38	12.2
d (nm)	72.6	84.0	90.2	59.9	74.7

Table 7.2: SANS lamellar fitting parameters for blend TB10[0.60] at selected temperatures and two different annealing conditions.

Table 7.3. Teubner-Strey fitting parameters for blend TB10[0.60] at selected temperatures and two different annealing conditions.

	90 °C anneal	190 °C anneal		
$T(^{\circ}C)$	30	110	116	122
<i>a</i> (cm)	0.309	0.099	0.062	0.037
$b \ge 10^{-5} (\text{cm nm}^{-2})$	-5.51	-2.60	-2.09	-1.44
$c \ge 10^{-11} (\text{cm nm}^{-4})$	2.52	1.85	1.95	1.64

The above analysis was repeated on all of the blends studied. The data from 30 - 120 °C were consistent with the $I_{\text{lam}}(q)$ fits for all blends. The ranges of selected parameters obtained from the fits are listed in Table 7.1. For blends that were run twice, the fitting parameters from the second thermal history were found to be within the same ranges as those for the first run. In all cases, the fits with $I_{\text{lam}}(q)$ were significantly better than those with $I_{\mu\text{E}}(q)$. Previous studies of A/B/A-C mixtures^{7,8,14-20} assumed that samples with peaks that could

Previous studies of A/B/A-C mixtures^{7,6,14-20} assumed that samples with peaks that could not be fit with $I_{\mu E}(q)$ were lamellar. Here it is shown that scattering profiles that are inconsistent with $I_{\mu E}(q)$ fits are actually consistent with $I_{\text{lam}}(q)$ fits. This is especially important in cases where higher order peaks are not evident in the scattering profiles. The effect of instrument resolution is significant, and quantitative agreement between the model and experiments was not obtained without accounting for this effect.

7.4 Self-Consistent Field Theory

Theoretical predictions of equilibrium domain spacings were carried out using onedimensional SCFT calculations. The equations used in these calculations and our methods for solving the equations are given in ref 15. The program used was described in the Ph.D. dissertation of Dr. Benedict Reynolds²¹. Inputs to the SCFT calculations include the binary Flory-Huggins parameters describing monomer-monomer interactions and the statistical segment length of each species (homopolymers and blocks). Previously published values of these parameters¹⁹ are summarized in footnote 22. Calculations were limited to integral values of the box size used to coarse grain monomer interactions, introducing a maximum domain spacing error of 0.431 nm. This effect was shown to be negligible for the concentration profiles calculated. The Helmholtz free energy density was calculated for a range of box sizes, and the equilibrium domain spacing was determined from the minimum in the free energy curve. Figure 7.5 shows the SCFT free energy calculations for blend TB10[0.60] at selected temperatures. Below 139 °C, the profiles exhibited concave curvature (positive second derivative) at all box sizes. These profiles were fit with a parabola to determine the box size that gave the minimum free energy. The equilibrium domain spacing was given by d = 2 (minimum box size) $\Delta r v_0^{1/3}$ where Δr is a measure of the size of the box used for coarse graining. The data at 139 °C give the lowest temperature free energy profile that exhibits a monotonic decrease, indicating the loss of a periodic ordered microphase.

Figure 7.5. SCFT calculations of the dimensionless Helmholtz free energy for TB10[0.60] at selected temperatures. Solid lines are parabolic fits to the data.



The SCFT predictions for the equilibrium domain spacing in blends TB10[0.60], TBF[0.60], and TB50[0.60] were compared with the domain spacings measured using SANS in Figure 7.6. There was quantitative agreement between the measured and predicted data. At the extremities of the ϕ_A range studied (TB10[0.60] and TB50[0.60]) the domain spacing changed monotonically with temperature: increasing for TB10[0.60] and decreasing for TB50[0.60]. Trends were not monotonic for midrange values of ϕ_A where the system was transitioning between thermal swelling of the lamellar domains and thermal deswelling. The lamellar domain spacing determined by fitting a Gaussian curve to the primary scattering peak, q^* is shown for TBF[0.60] ($d = 2\pi q q^*$). The domain spacings calculated using this method varied by 2-5 nm from those determined by fitting a lamellar structure factor because they did not account for higher order peaks.
Figure 7.6. Lamellar domain spacings for selected blends across the experimental range of temperatures. Values obtained from fitting the SANS data with the lamellar structure factor (\blacksquare) are compared to values calculated using SCFT (\blacktriangle). For blend TBF[0.60], the lamellar domain spacing is also shown as calculated by $d = 2\pi q^*$, where q^* is determined from a Gaussian fit to the primary scattering peak (\Box). Lines are drawn between the data points for visual clarity.



The swelling and deswelling of the lamellar morphology lends itself to the interpretation of swollen diblock copolymer brushes with the A-C junction adsorbed at the interface between the A and B microdomains. Within a single A microdomain in the neat copolymer, two parallel brushes composed of A-block extend toward the center of the domain, emanating from the interface on either side of the microdomain. The chain ends of the A-block reside near the center of the domain to maintain a constant density across the microdomain, however there is an entropic penalty associated with localizing the chain ends in the center of the domain. The addition of homopolymer A enables the stretched copolymer chains to relax by preferentially locating at the center of the microdomain, fulfilling the incompressibility constraint. In the absence of enthalpic interactions (the χ parameter between deuterated and hydrogenated 89% 1,2 butadiene is so small that it may be neglected), the equilibrium distribution of homopolymer results from a balance of entropic driving forces. The A-block tends to contract away from the center of the microdomain to minimize stretching, while the A homopolymer tends to mix with the brush. These competing tendencies are affected by the relative molecular weights of the block and the homopolymer. The wet-brush regime, shown schematically in Figure 7.7a, occurs when the homopolymer chain length is much shorter than the A-block. Entropy favors mixing between the A-block and the A homopolymer, A homopolymer penetrates into the diblock brush, and the microdomain deswells. However, when the A-homopolymer is the same length or longer than the A-block, the dry-brush regime is observed, shown schematically in Figure 7.7b. Mixing is unfavorable between the brush and the homopolymer, so the homopolymer segregates to the center of the microdomain and the A-block of the copolymer relaxes to a near-random walk configuration close to the A-C junction. The segregation of the homopolymer away from the copolymer causes the microdomain to swell.

Figure 7.7. Schematics showing (a) the wet brush regime and (b) the dry brush regime for a single lamellar microdomain. The solid vertical lines represent the A-C junction interface, the solid black coils are homopolymers and the dotted lines are block copolymer brushes "anchored" to the A-C junction interface.



To better understand the observed trends in lamellar swelling and deswelling, SCFT concentration profiles were calculated for each component through a lamellar domain spacing. Figures 7.8a and b show the concentration of the components in the blends as a function of reduced distance, z/d, for TB10[0.60] at 30 and 130 °C, respectively. The B-rich domain, which is the larger domain in this blend, has a more uniform composition at 30 °C than at 130 °C. This can be seen by the distinct valley in the C-block concentration profile in the vicinity of z/d = 0.5 and the sharp peak in the B concentration in that region. This implies a transition from the wet brush regime at 30 °C to a dry brush regime at 130 °C. The driving force for this transition is clear. At low temperatures, χ_{BC} is negative and this promotes mixing between the B homopolymer and the C-block. This favorable interaction diminishes in magnitude with increasing temperature, resulting in an expulsion of the B chains from the brush. The SCFT profiles for TB10[0.60] provide a qualitative explanation for the observed trend in lamellar domain spacing.

Figure 7.8. SCFT lamellar concentration profiles for selected blends at selected temperatures: (a) TB10[0.60] at 30 °C, (b) TB10[0.60] at 130 °C, (c) TB50[0.60] at 30 °C, (d) TB50[0.60] at 98 °C. The volume fraction of each component is shown against z/d, the dimensionless distance through a single domain spacing. Homopolymer A is shown in solid black, homopolymer B is solid grey, block A is a broken black line, and block C is a broken grey line.





Figures 7.8c and d show the concentration profiles for TB50[0.60] at 30 and 98 °C (the highest temperature for which SCFT calculation converged), respectively. The A-rich domain, which is the larger domain in this blend, has a more uniform composition at 98 °C than at 30 °C. At 30 °C, the A homopolymer chains are being expelled from the A-block brush in spite of the fact that $N_A/N_{A-C} = 0.17$. In this case, increasing temperature causes a dry brush to wet brush transition and consequent deswelling of the lamellae. Since the interactions between the A-block and the A homopolymer are entropic (to a very good approximation, ignoring the effect of deuteration on thermodynamics)^{3,35,36,41} the observed temperature dependence arises from the other intermolecular interactions in the system. The mixing of A homopolymer chains seen in both A-rich and B-rich domains is driven by a decrease in χ_{AB} and χ_{AC} with increasing temperature.

The SCFT profiles may be used to determine the widths of the A and B microdomains. Because the polymers studied are in the weak segregation regime ($\chi N = 2.61$ to 2.96 for the A/B pair in the experimental temperature window 30 – 190 °C), the interfacial profiles of components A and B are broad. We define the interface between A-rich and B-rich domains to be located at the *z* value that is an arithmetic average of the *z* locations corresponding to the midpoint values in the concentration profiles of A and B, respectively. The distance between adjacent interfaces across an A-rich domain is z_A , allowing us to define $\phi_{A-dom} = z_A / d$. We define the interfacial width for each species following the work of Shull et al.^{23,24}:

$$\sigma_{i} = \frac{1}{2} \left(\phi_{i,\max} - \phi_{i,\min} \left| \frac{\partial \phi_{i}}{\partial z} \right|_{z_{avg}} \right]^{-1}$$
(7.8)

The index *i* is either species A or B and $\phi_{i,max}$ and $\phi_{i,min}$ are the maximum and minimum volume fractions of the components. In Figure 7.9 we show the overall domain spacing, *d*, as well as the microdomain spacings d_A and d_B for blend TB10[0.60]. Both A and B microdomains follow the same trend, in this case lamellar swelling. For all blends studied the microdomains both followed the same trend as the overall lamellar domain spacing at all temperatures.

Figure 7.9. SCFT predictions for the microdomain and overall domain spacings of TB10[0.60].



The results of the SCFT calculations are compared with experimental results based on fits of the SANS profiles to the lamellar structure factor. Figures 7.10a-d compare the SCFT predictions of ϕ_{A-dom} , σ_A , σ_B , and *d* at 30 °C with experimental measurements. The values for ϕ_{A-dom} in Figure 7.10a are plotted against the bulk fraction of component A, $\phi_{A,TOT}$. The line with slope of unity represents the expectation $\phi_{A-dom} = \phi_{A,TOT}$ in the limit of highly incompatible A/B

mixtures. SCFT predicts that ϕ_{A-dom} increases continuously with increasing $\phi_{A,TOT}$. In contrast, ϕ_{A-dom} obtained from fitting SANS data shows more of a step-like behavior, changing dramatically in the vicinity of $\phi_{A,TOT} = 0.6$ (between blends TBF[0.60] and TB40[0.60]). The trends observed for both SCFT and experiments were relatively invariant with temperature. Figures 7.10b and c show the dependence of σ_A and σ_B , respectively, on ϕ_A . Both SCFT and SANS indicate that the width of the A-interface increases with increasing ϕ_A . On the other hand, SANS results indicate that the width of the B-interface decreases with ϕ_A while SCFT predicts that the width of the B-interface in nearly independent of ϕ_A . Figure 7.10d shows that there is relatively good agreement between the equilibrium domain spacings predicted by SCFT and those measured experimentally. The lack of quantitative agreement between theory and experiment seen in Figure 7.10 may be due to a lack of uniqueness of the fitted parameters obtained from the SANS profiles or due to complexity of the thermodynamics of A/B/A-C mixtures that go beyond the simple mean-field theories used here.

Figure 7.10. Comparison of parameters at 30 °C calculated using SCFT (\blacktriangle) with those obtained by fitting the SANS data with a lamellar structure factor (\blacksquare). (a) ϕ_{A-dom} is plotted against the bulk fraction of component A in each blend, $\phi_{A,TOT}$. The solid line indicates x = y. (b) The interfacial widths of the B microdomains, σ_B , are plotted against ϕ_A for each blend. (c) The interfacial widths of the A microdomains, σ_A , are plotted against ϕ_A for each blend. (d) The domain spacing, *d*, is plotted against ϕ_A for each blend.





In addition, the SCFT calculations predict the surface tension between the A and B microdomains. Within the stability window for lamellae, the A-C diblock copolymer behaves as a surfactant and the interfacial tension vanishes. Figure 7.11 shows the interfacial tension across the lamellar stability window for blends TB10[0.60], TBF[0.60], and TB50[0.60]. Both TB10[0.60] and TB50[0.60] exhibit discontinuous maxima whereas the interfacial tension of

TB0.6 increases monotonically. Both TB10[0.60] and TBF[0.60] exhibit a temperature range for which γ is positive and SCFT converges upon a finite domain spacing for the lamellar microstructure. The value of γ is different for each blend at the temperature where SCFT no longer converges, suggesting limited utility or inaccuracy of the γ values predicted.

Figure 7.11. SCFT predictions for the dimensionless surface tension between the A and B microdomains across the lamellar stability windows of TB10[0.60], TBF[0.60], and TB50[0.60].



7.5 Phase behavior of the off-critical series

SCFT calculations were performed for each blend over a range of temperatures to determine the stability window of the lamellar phase. The predicted location of the phase boundary is the temperature T_{SCFT} , above which the calculated free energy density changes monotonically with domain spacing and does not exhibit a minimum. At temperatures above T_{SCFT} we use RPA to distinguish between one-phase and phase separated systems. The SANS profiles from homogeneous blends were calculated using the multicomponent Random Phase Approximation (RPA)^{15,25,26} using the same parameters as those used in the SCFT calculations.²² A homogeneous phase is predicted where the RPA calculations give SANS profiles without singularities. Outside the homogeneous window, RPA calculations contain poles indicating either microphase or macrophase separation. The phase behavior predicted using both the RPA and SCFT is compared to the experimentally determined behavior in Figure 7.12.

Figure 7.12: Phase transition temperature as a function of volume fraction of A homopolymer, ϕ_A . Markers represent the experimentally determined transitions from lamellae (lam) to macrophase separation (2P). The uniformly shaded region labeled "hom" represents phase space where the RPA predicts a single homogeneous phase, and the checkered region labeled "lam" is phase space where SCFT predicts a lamellar phase.



The experimental data are shown in Figure 7.12 with markers indicating the temperatures at which the onset of macrophase separation was observed by SANS. The region for which RPA predicts a homogeneous phase is shown along with the region for which SCFT predicts lamellae. There is a small region of overlap between the homogeneous region predicted by RPA and microphase separation predicted by SCFT. It is likely due to errors introduced in the coarse-graining used for the SCFT calculations. Figure 7.12 shows that the experimentally observed transitions from lamellae to macrophase separation are in quantitative agreement with SCFT/RPA calculations. The theoretical analysis predicts the existence of homogeneous windows for blends TB45[0.60] and TB50[0.60], but these were not seen in experiments. It is evident from Figure 7.12 that varying ϕ_A from 0.1 to 0.5 has no effect on the phase behavior of this A/B/A-C system. This behavior is unusual as both the structure of microphases and stability windows are usually strong functions of composition.^{4,5,27-29} This conclusion suggests that the observed phase behavior in Chapter 6 was due entirely to differences is N_A/N_B as the effect of composition is limited.

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- (22) Note. Temperatures are in K: $\chi_{AB} = 0.00034 + 3.94/T 817/T^2$; $\chi_{AC} = 0.00209 1.18/T + 747/T^2$; $\chi_{BC} = -0.00527 + 10.3/T 3168/T^2$. Statistical Segment lengths: $l_A = 5.5$ Å; $l_B = 5.8$ Å; $l_C = 7.5$ Å.
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Chapter 8

Dissertation Summary

The effects of molecular weight asymmetry and composition on phase behavior were studied for binary and ternary blends of polyolefins. The phase behavior in miscible pairs of B/C homopolymers was found to exhibit a strong dependence on ϕ_B and N_{AVE} , however no detectable dependence on N_B/N_C . Immiscible blends of A/B homopolymers compatibilized with an A-C diblock copolymer exhibited a strong dependence of phase behavior on N_A/N_B , however no dependence on ϕ_A . In both cases, the observed phase behavior was predicted from mean field theories using no adjustable parameters.

A series of twenty-four B/C binary blends was studied for values of $N_{\rm B}/N_{\rm C}$ ranging from 0.06 to 5.4. All blends exhibited a homogeneous phase window, and those for which $N_{\rm AVE} \ge$ 947 macrophase separated upon heating. SANS profiles measured within the homogeneous window were fitted with the RPA, allowing $\chi_{\rm sc}$ and α to be adjustable parameters. Each blend resulted in the measurement of a temperature dependent $\chi_{\rm sc}$ specific to the composition, $\phi_{\rm B}$, and $N_{\rm AVE}$ of the blend for which it was measured. By combining $\chi_{\rm sc}$ from each blend, an overall expression was developed for the composition- and molecular weight-dependence of $\chi_{\rm sc}$. As observed in other LCST polymer blends, $\chi_{\rm sc}$ was found to depend linearly on $\phi_{\rm B}$ and inversely on $N_{\rm AVE}$. The true thermodynamic χ was calculated from the expression for $\chi_{\rm sc}$, and retained the same form for the dependence on $N_{\rm AVE}$ and $\phi_{\rm B}$, however scaled down by a factor of 3. The final expression for χ agreed with the limiting case of infinite-length polymers for which a composition and molecular weight-independent χ is recovered.

The experimentally determined χ_{sc} was tested for consistency with the RPA, and shown to correlate linearly with susceptibility. The empirically determined χ parameter was used with Flory-Huggins Theory to predict the binodal and spinodal for four pairs of polymers, all with $N_{\rm B}/N_{\rm C}$ < 1. Flory-Huggins Theory with a composition-independent χ predicts that $\phi_{\rm B,crit}$ > 0.5 for all blends with $N_{\rm B}/N_{\rm C}$ < 1, however the opposite result was obtained from predictions, namely $\phi_{\text{B,crit}} < 0.5$ for all blends studied. The asymmetry of the predicted phase diagrams results from a combination of the composition dependence of χ (lowers the value of $\phi_{B,crit}$ for this system) and the molecular weight asymmetry (increases $\phi_{B,crit}$ for blends with $N_B/N_C > 1$). Extremely asymmetric homopolymers are predicted to exhibit nearly symmetric phase diagrams. The experimental spinodal was determined by fitting the susceptibility with an unprecedented quadratic dependence on 1/T, due to the measured temperature dependence of γ . The spinodal was determined as the temperature for which the susceptibility dropped off for blends exhibiting off-critical behavior and the temperature between those that gave SANS profiles for homogeneous and macrophase separation for blends exhibiting critical behavior. The experimentally measured spinodal and binodal were found to agree quantitatively with the predictions for most blends studied.

The phase behavior was studied for a series of thirteen A/B/A-C blends with values of N_A/N_B ranging from 0.17 to 19. All of the A/B blends were prepared at the critical composition predicted by Flory-Huggins Theory (on a block copolymer-free basis) and each contained 40 vol % of a symmetric diblock copolymer. SANS profiles were used to distinguish lamellae, microemulsions, homogeneous mixing, and macrophase separation. Three blends were designed

to have a constant value of N_{AVE} but largely varying values of N_A/N_B . Each of these blends exhibited distinctly different phase behavior, indicating the thermodynamic significance of N_A/N_B . The remaining 10 blends had varying values of N_{AVE} , but exhibited phase behavior that correlated with N_A/N_B . Blends with $N_A/N_B < 2$ tended to microstructure at low temperatures and macrophase separate upon heating, those for $N_A/N_B > 2$ were also microstructured at low temperatures, but they homogenized upon heating. The results provide strong evidence for a dependence of phase behavior upon N_A/N_B , however, because the blends studied were critical, the composition correlated with N_A/N_B , and the effects of composition and N_A/N_B were coupled in the observed phase behavior.

A series of eight off-critical A/B/A-C blends was prepared for compositions ranging from $\phi_A = 0.100$ to 0.500 and $N_A/N_B = 0.60$ fixed (i.e. the same three polymers were used for all blends). All of the blends exhibited quantitatively identical phase behavior: lamellae below 120 °C and macrophase separation at higher temperatures. This experiment clearly singled N_A/N_B as the important parameter in determining phase behavior. Scattering profiles within the microphase separated phase window were fitted with both a lamellar structure factor and a microemulsion structure factor. In all cases, the lamellar fits were significantly better than the microemulsion fits, so lamellae were judged to exist in these phase windows. Self-consistent field theory predictions were compared to the microdomain widths and interfacial thicknesses extracted from fits to the lamellar SANS data. Quantitative agreement between the theory and data support a broad physical understanding of the system parameters that control phase behavior.

Chapter 9

Appendices

9.1 List of Variables

 α_i = ratio of a temperature-dependent statistical segment length to a reference value for species i

 α = azimuthal angle of a scattering geometry

a, b, c, d, f, g = general constants or functions with a stated dependency

 A_2 = area under the second order peak of a lamellar scattering profile

 A_{sam} = scattering area of a sample

 β = a constant for polyolefins in the expression for $n_{\rm D}$

 β_i = thermal expansion coefficient for a monomer of species i

c = concentration

 $C_1 = \text{constant for lamellar fitting}$

d = domain spacing of lamellar microstructures

 d_i = thickness of an i-rich microdomain in a lamellae

 $d_{\rm sam}$ = thickness of a scattering sample

 $D_0, D_1, D_2 = virial coefficients$

 ε = detector efficiency

 ξ = correlation length of composition fluctuations

 $\eta = \text{viscosity}$

f = Helmholtz free energy of mixing per volume

 f_{12} = measured fraction of 1,2 addition for polyisobutylene

 f_i = volume fraction of a diblock copolymer comprising species i

 ΔG = The Gibbs free energy of mixing per unit volume

 I_i = scattered intensity for the sample i

i, j = indices referring to different polymer species

k =Boltzmann's constant

K =light scattering Rayleigh constant

 $K_{\rm s}$ = scattering contrast, units of m⁻⁴

 λ = wavelength

 l_i = statistical segment length for species i

 $M_{\rm n}$ = number-averaged molecular weight

 $M_{\rm w}$ = weight-averaged molecular weight

 $n_{\rm D}$ = number of deuterium atoms per C4 monomer unit

 n_0 = refractive index of a solvent

 \hat{N}_i = number of monomers comprising a chain of species i

 N_i = Number of reference volumes comprising a chain of species i

 $N_{\rm av}$ = Avogadro's constant

 N_{AVE} = a geometrical average of the homopolymer N_{A} and N_{B} in a blend PDI = polydispersity index

q = momentum transfer vector for scattering experiments

Q, R = integration areas from NMR signals

 $\rho_{\rm i}$ = density of species i

 $R_{\rm g}$ = radius of gyration of a polymer chain

 $R_{\theta} =$ light scattering signal

 σ = standard deviation of annularly integrated scattering profiles

 σ_i = standard deviation of the interfacial width for a lamellar microdomain of species i

 Σ_i = Sum of detector pixel signal for the sample i

S(q) = q-dependent structure factor for scattering data, a matrix for multicomponent blends $S_0(q) = q$ -dependent static structure factor, a matrix for multicomponent blends

t = time

T = temperature

 T_i = transmission of the sample i

 $T_{\rm ref}$ = reference temperature, 23 °C

 v_0 = reference volume defined at 0.1 nm³

 $v_{i,mon}$ = volume of a monomer of species i

 $v_{i,ref}$ = volume of a monomer of species i at the reference temperature, 23 °C

V(q) = q-dependent dynamic structure factor, a matrix for multicomponent blends

 $V_{\rm e}$ = elution volume

 w_{ij} = energy to place a monomer of species j next to a monomer of species i on a lattice

 ϕ_i = total volume fraction of species i in a blend

 $\phi_{i,m}$ = volume fraction of chemical species m comprising a polymer chain i

 $\phi_{i,crit}$ = volume fraction of species i in a blend at the "true" critical composition

 $\phi_{i,crit,FHT}$ = volume fraction of species i in a blend at the Flory-Huggins critical composition $\phi_{diblock}$ = total volume fraction of diblock copolymer in a ternary blend

 ϕ_{\min} = SCFT predicted minimum volume fraction of species i in a lamellar domain spacing ϕ_{\max} = SCFT predicted maximum volume fraction of species i in a lamellar domain spacing Φ = scattering flux

 χ = The "true" Flory-Huggins interaction parameter used to predict phase behavior

 $\chi_{i,j}$ = Specific value of χ between species i and j

 χ_s = The "true" Flory-Huggins interaction parameter at the spinodal temperature

 χ_{sc} = Flory-Huggins interaction parameter determined from scattering measurements

 $x_{\rm H}$ = number of equivalent CH₂ units comprising a monomer

 $x = q^2 R_{g,i}^2$, argument entered into the Debye function

 Ω = solid scattering angle

z = number of neighboring lattice sites on a Flory-Huggins lattice

 z_i = distance between adjacent interfaces for the i rich microdomain in a lamellar spacing

9.2. Inventory of Polyolefins

This list includes only the saturated A and B homopolymers and saturated A-C diblock copolymers. The Ph.D. Dissertation of Dr. Megan Robertson contains a complete listing of unsaturated polyolefins.

Dissertation	Lab	M_w			ρ	%1,2-	
Name	Name	(kg/mol)	PDI	N	(g/mL)	addition	$n_{\rm D}$
hPB89(10)	h12PBD17	10.1	1.01	195	0.8625	89.1	
dPB89(10)	d12PBD17	10.6	1.01	195	0.9020	89.1	2.54
hPB89(24)	h12PBD40	24.1	1.01	464	0.8636	90.4	
dPB89(24)	d12PBD40	25.3	1.01	464	0.9070	90.4	2.79
hPB89(27)	h12PBD34	~27	1.01			88.4	
dPB89(27)	d12PBD34		1.01			88.4	
hPB89(35)	h12PBD25	34.9	1.02	671	0.8639	90.1	
dPB89(35)	d12PBD25	36.5	1.02	671	0.9037	90.1	2.56
hPB89(49)	h12PBD27	48.6	1.02	935	0.8637	89.6	
dPB89(49)	d12PBD27	50.9	1.02	935	0.9046	89.6	2.63
hPB89(60)	h12PBD18	59.6	1.01	1146	0.8639	88.6	
dPB89(60)	d12PBD18	62.3	1.01	1146	0.9031	88.6	2.52
dPB89(66)	d12PBD36	69.9	1.02	1264	0.9183	86.8	3.49
hPB89(220)	h12PBD41	220.0	1.02	4240	0.8620	88.0	
dPB89(220)	d12PBD41	230.6	1.02	4240	0.9032	88.0	2.62
hPB89(310)	h12PBD47	307.1	1.05	5906	0.8633	88.0	
dPB89(310)	d12PBD47	329.5	1.05	5906	0.9032	88.0	2.62
hPB89(400)	h12PBD49	400.7	1.06	7707	0.8633	89.6	
dPB89(400)	d12PBD49		1.06	7707		89.6	

9.2.1. Polybutadiene homopolymers with 89 % 1,2 addition

9.2.2. Polybutadiene homopolymers with 63 % 1,2 addition

Dissertation		M_w			ρ	%1,2-	
Name	Lab Name	(kg/mol)	PDI	Ν	(g/mL)	addition	$n_{\rm D}$
hPB63(10)	h12PBD22	9.9	1.02	191	0.8593	61.6	
dPB63(10)	d12PBD22	10.5	1.02	191	0.9125	61.6	3.44
hPB63(58)	h12PBD33	58.2	1.01	1122	0.8620	66.0	
dPB63(58)	d12PBD33	62.0	1.01	1122	0.9187	66.0	3.65
hPB63(187)	h12PBD39	187.0	1.02	3591	0.8650	63.4	
dPB63(187)	d12PBD39	197.2	1.02	3591	0.9123	63.4	3.04

	Lab	M_w			ρ
Name	Name	(kg/mol)	PDI	N^*	(g/mL)
PIB(13)	PIB5	12.5	1.04	227	0.9134
PIB(19)	PIB6	18.7	1.02	340	0.9131
PIB(20)	PIB13	19.9	1.04	361	0.9158
PIB(21)	PIB11	~21			
PIB(43)	PIB9	42.5	1.02	773	0.9135
PIB(45)	PIB8	44.6	1.04	811	0.914
PIB(57)	PIB10	56.8	1.02	1032	0.9144
PIB(62)	PIB2	62.0	1.03	1127	0.9135
PIB(34)	PIB14	34.2	1.04	621	0.9122
PIB(64)	PIB15	64.0	1.02	1163	0.9120
PIB(37)	PIB17	37.1	1.00	674	0.9126
PIB(98)	PIB19	97.9	1.05	1778	0.9102
PIB(83)	PIB20	83.2	1.05	1511	0.9102

9.2.4. Polystyrene-block-polyisobutylene copolymers

Lab Name	M_w (kg/mol)	PDI	Ν	$f_{ m PS}$
SIB-1	3.4-32.9	1.03	59-599	0.09
SIB-2	2.0-35.7	>2	34-650	0.05

Dissertation	Lab Name	M_w	PDI	N	ρ	%1,2- addition	Ир	f
hPBPB (38-38)	hPBPB17	38.0- 38.4	1.01	731- 742	0.8629	90.0- 63.9		0.496
dPBPB (38-38)	dPBPB17	39.8- 40.2	1.01	731- 742	0.9047	90.0- 63.9	2.69	0.496
hPBPB (41-38)	hPBPB4	41.3- 37.6	1.01	794- 727	0.8633	91.9- 62.7		0.522
hPBPB (41-38)	dPBPB4	43.5- 39.6	1.01	794- 727	0.9098	91.9- 62.7	2.99	0.522
hPBPB (41-38)	hPBPB4	41.3- 37.6	1.01	794- 727	0.8633	91.9- 62.7		0.522
dPBPB (41-38)	dPBPB4	43.5- 39.6	1.01	794- 727	0.9098	91.9- 62.7	2.99	0.522
hPBPB (79-66)	hPBPB12	78.5- 65.4	1.01	1510- 1263	0.8639	89.7- 63.9		0.544
dPBPB (79-66)	dPBPB12	82.9- 69.0	1.01	1510- 1263	0.9122	89.7- 63.9	3.1	0.544
hPBPB (88-93)	hPBPB20	88.4- 92.9	1.02	1699- 1797	0.8629	89.9- 65.3		0.486
dPBPB (88-93)	dPBPB20	92.5- 97.3	1.02	1699- 1797	0.9035	89.9- 65.3	2.61	0.486
hPBPB (126-136)	hPBPB22	125.5- 135.9	1.03	2413- 2627	0.8627	88.1- 62.1		0.479
dPBPB (126-136)	dPBPB22	132.3- 143.2	1.03	2413- 2627	0.9093	88.1- 62.1	3.00	0.479
hPBPB (126-178)	hPBPB7	125.7- 178.3	1.02	2418- 3430	0.863	88.9- 62.5		0.412
hPBPB (240-192)	hPBPB18	240.0- 192.0	1.06	4614- 3712	0.8629	86.5- 61.5		0.554
dPBPB (240-192)	dPBPB18	253.6- 202.9	1.06	4614- 3712	0.912	86.5- 61.5	3.16	0.554

9.2.5. Polybutadiene (dPB89-b-dPB63) diblock copolymers

9.3 Inventory of Ternary Blends

Blend dissertation	Blend lab								Date of
name	name	$\phi_{\mathrm{A,crit\ FHT}}$	$\phi_{\rm A}$	$\phi_{\!\scriptscriptstyle m B}$	$\phi_{diblock}$	А	В	A-C	SANS
TBF[18.7]	H11	0.188	0.113	0.487	0.400	d12PBD41	PIB5	hPBPB12	Aug-08
	DB18	0.299	0.179	0.421	0.400	d12PBD41	PIB9	hPBPB17	May-09
	WB18	0.299	0.179	0.421	0.400	d12PBD41	PIB9	hPBPB20	May-09
	WB18-a	0.299	0.179	0.421	0.400	d12PBD41	PIB9	hPBPB12	Aug-09
	WB18-b	0.299	0.179	0.421	0.400	d12PBD41	PIB9	hPBPB7	Aug-09
	WB18-c	0.299	0.179	0.421	0.400	d12PBD41	PIB9	hPBPB18	Aug-09
	M20(50)	0.330	0.165	0.335	0.500	d12PBD27	PIB5	hPBPB12	Aug-08
	M20(45)	0.330	0.182	0.368	0.450	d12PBD27	PIB5	hPBPB12	Aug-08
TBF[4.11]	M20	0.330	0.198	0.402	0.400	d12PBD27	PIB5	hPBPB12	Aug-08
	M20(35)	0.330	0.215	0.435	0.350	d12PBD27	PIB5	hPBPB12	Aug-08
	M20(30)	0.330	0.231	0.469	0.300	d12PBD27	PIB5	hPBPB12	Aug-08
	M20(20)	0.330	0.216	0.584	0.200	d12PBD27	PIB5	hPBPB12	May-09
	M20(10)	0.330	0.271	0.629	0.100	d12PBD27	PIB5	hPBPB12	May-09
	M20(08)	0.330	0.304	0.616	0.080	d12PBD27	PIB5	hPBPB12	May-09
	M20(05)	0.330	0.314	0.636	0.050	d12PBD27	PIB5	hPBPB12	May-09
	M20(01)	0.330	0.327	0.663	0.010	d12PBD27	PIB5	hPBPB12	May-09
	H30d22	0.341	0.197	0.503	0.300	d12PBD36	PIB6	hPBPB22	Jul-09
	H30d07	0.341	0.217	0.483	0.300	d12PBD36	PIB6	hPBPB7	Jul-09
	H30d18	0.341	0.175	0.526	0.300	d12PBD36	PIB6	hPBPB18	Jul-09
TBF[3.72]	H20	0.342	0.205	0.395	0.400	d12PBD36	PIB6	hPBPB12	Aug-08
	AO40null	0.344	0.206	0.394	0.400	d12PBD41	PIB15	hPBPB12	Jul-09
	AO30lb	0.344	0.241	0.459	0.300	d12PBD41	PIB15	hPBPB22	Jul-09
	AO30mb	0.344	0.241	0.459	0.300	d12PBD41	PIB15	hPBPB7	Jul-09
	AO40hb	0.344	0.206	0.394	0.400	d12PBD41	PIB15	hPBPB18	Jul-09

Blend dissertation	Blend lab			,			Ð		Date of
name	name	$\phi_{\rm A, crit FHT}$	ϕ_{A}	$\phi_{ m B}$	$\phi_{diblock}$	A	В	A-C	SANS
	AO30ht	0.344	0.177	0.523	0.300	d12PBD41	PIB15	hPBPB18	Jul-09
	AO30hb	0.344	0.241	0.459	0.300	d12PBD41	PIB15	hPBPB18	Jul-09
TBF[2.96]	L22	0.368	0.221	0.379	0.400	d12PBD25	PIB5	hPBPB12	Aug-08
	RF30d04	0.383	0.226	0.474	0.300	d12PBD27	PIB13	hPBPB4	Jul-09
	RF30d22	0.383	0.239	0.461	0.300	d12PBD27	PIB13	hPBPB22	Jul-09
	RF30d07	0.383	0.259	0.441	0.300	d12PBD27	PIB13	hPBPB7	Jul-09
	H23(08)	0.383	0.353	0.567	0.080	d12PBD27	PIB13	hPBPB12	May-09
	H23(05)	0.383	0.364	0.586	0.050	d12PBD27	PIB13	hPBPB12	May-09
	H23(03)	0.383	0.372	0.598	0.030	d12PBD27	PIB13	hPBPB12	May-09
	H23(01)	0.383	0.380	0.610	0.010	d12PBD27	PIB13	hPBPB12	May-09
	RF30d18	0.383	0.217	0.483	0.300	d12PBD27	PIB13	hPBPB18	Jul-09
	DB24	0.394	0.236	0.364	0.400	d12PBD41	PIB19	hPBPB17	May-09
	WB24	0.394	0.236	0.364	0.400	d12PBD41	PIB19	hPBPB20	May-09
	DB23	0.394	0.236	0.364	0.400	d12PBD41	PIB19	hPBPB20	May-09
	WB24-b	0.394	0.236	0.364	0.400	d12PBD41	PIB19	hPBPB7	Jul-09
	WB24-c	0.394	0.236	0.364	0.400	d12PBD41	PIB19	hPBPB18	Jul-09
	CA71	0.457	0.274	0.326	0.400	d12PBD18	PIB8	hPBPB4	Apr-09
	CA72	0.459	0.276	0.324	0.400	d12PBD27	PIB17	hPBPB4	Apr-09
TBF[1.36]	M28	0.461	0.277	0.323	0.400	d12PBD40	PIB6	hPBPB12	Aug-08
	DB30	0.502	0.301	0.299	0.400	d12PBD18	PIB15	hPBPB17	May-09
	WB30	0.502	0.301	0.299	0.400	d12PBD18	PIB15	hPBPB20	May-09
	WB30d22	0.503	0.335	0.365	0.300	d12PBD18	PIB15	hPBPB22	Jul-09
	WB30d07	0.503	0.378	0.322	0.300	d12PBD18	PIB15	hPBPB7	Jul-09
	WB30d18	0.503	0.335	0.365	0.300	d12PBD18	PIB15	hPBPB18	Jul-09
	DB31	0.523	0.314	0.286	0.400	d12PBD27	PIB2	hPBPB17	May-09
	WB31	0.523	0.314	0.286	0.400	d12PBD27	PIB2	hPBPB20	May-09
	CA1.2(30)d12	0.528	0.369	0.331	0.300	d12PBD27	PIB15	hPBPB12	Aug-09

Blend dissertation	Blend lab								Date
name	name	$\phi_{\mathrm{A,crit\ FHT}}$	$\phi_{\! m A}$	$\phi_{\!\scriptscriptstyle m B}$	$\phi_{diblock}$	A	В	A-C	SAN
	CA1.2(30)d20	0.528	0.369	0.331	0.300	d12PBD27	PIB15	hPBPB20	Aug-
	CA1.3	0.537	0.322	0.278	0.400	d12PBD40	PIB14	hPBPB4	Apr-0
	CA1.3(30)	0.537	0.376	0.324	0.300	d12PBD40	PIB14	hPBPB4	Aug-
	CA1.3(30)d12	0.537	0.376	0.324	0.300	d12PBD40	PIB14	hPBPB12	Aug-
	DB33	0.543	0.326	0.274	0.400	d12PBD36	PIB19	hPBPB17	May-
	WB33	0.543	0.326	0.274	0.400	d12PBD36	PIB19	hPBPB20	May-
	WB33(35)	0.543	0.353	0.297	0.350	d12PBD36	PIB19	hPBPB20	Aug-
	WB33d22	0.543	0.326	0.274	0.400	d12PBD36	PIB19	hPBPB22	Aug-
	WB33d07	0.543	0.326	0.274	0.400	d12PBD36	PIB19	hPBPB7	Aug-
	WB33d18	0.543	0.326	0.274	0.400	d12PBD36	PIB19	hPBPB18	Aug
TBF[0.60]	H34	0.564	0.338	0.262	0.400	d12PBD40	PIB9	hPBPB12	Aug
TB10[0.60]	OC10	0.564	0.100	0.500	0.400	d12PBD40	PIB9	hPBPB12	Apr-
TB15[0.60]	OC15	0.564	0.150	0.450	0.400	d12PBD40	PIB9	hPBPB12	Apr-
TB20[0.60]	OC20	0.564	0.200	0.400	0.400	d12PBD40	PIB9	hPBPB12	May
TB25[0.60]	OC25	0.564	0.250	0.350	0.400	d12PBD40	PIB9	hPBPB12	Apr
TB30[0.60]	OC30	0.564	0.300	0.300	0.400	d12PBD40	PIB9	hPBPB12	May
TB40[0.60]	OC40	0.564	0.400	0.200	0.400	d12PBD40	PIB9	hPBPB12	May
TB45[0.60]	OC45	0.564	0.450	0.150	0.400	d12PBD40	PIB9	hPBPB12	Apr
TB50[0.60]	OC50	0.564	0.500	0.100	0.400	d12PBD40	PIB9	hPBPB12	Apr
	D22	0.564	0.338	0.262	0.400	d12PBD40	PIB9	hPBPB22	Apr
	TFA22	0.564	0.404	0.264	0.332	d12PBD40	PIB9	hPBPB22	Apr
	D07	0.564	0.338	0.262	0.400	d12PBD40	PIB9	hPBPB7	Apr
	TFA07	0.564	0.430	0.248	0.322	d12PBD40	PIB9	hPBPB7	Apr
	TFA07(25)	0.564	0.460	0.290	0.250	d12PBD40	PIB9	hPBPB7	Aug
	TFA07(20)	0.564	0.481	0.319	0.200	d12PBD40	PIB9	hPBPB7	Jul-
	TFA07(10)	0.564	0.522	0.378	0.100	d12PBD40	PIB9	hPBPB7	Aug
	TFA07(05)	0.564	0.543	0.407	0.050	d12PBD40	PIB9	hPBPB7	Aug

Blend dissertation name	Blend lab name	$\phi_{ m A,crit\ FHT}$	$\phi_{\rm A}$	$\phi_{\scriptscriptstyle m B}$	$\phi_{diblock}$	А	В	A-C	Date of SANS
	D18	0.564	0.338	0.262	0.400	d12PBD40	PIB9	hPBPB18	Apr-09
	TFA18	0.564	0.375	0.286	0.339	d12PBD40	PIB9	hPBPB18	Apr-09
	CA1.4	0.622	0.326	0.274	0.400	d12PBD36	PIB19	hPBPB4	Apr-09
	CA1.4d20	0.622	0.325	0.275	0.400	d12PBD36	PIB19	hPBPB20	Aug-09
TBF[0.26]	CA3.8	0.662	0.397	0.203	0.400	d12PBD40	PIB19	hPBPB12	Apr-09
TBF[0.24]	L40	0.671	0.403	0.197	0.400	d12PBD17	PIB8	hPBPB12	Aug-08
TBF[0.19]	L42	0.697	0.418	0.182	0.400	d12PBD17	PIB10	hPBPB12	Aug-08
TBF[0.17]	M43	0.709	0.426	0.174	0.400	d12PBD17	PIB15	hPBPB12	Aug-08