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Thermodynamics and Phase Behavior of Miscible Polymer Blends in the Presence of Supercritical Carbon Dioxide

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Thermodynamics and Phase Behavior of Miscible Polymer Blends in the Presence of Supercritical Carbon Dioxide

by

Nicholas Philip Young

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemical Engineering in the Graduate Division of the University of California, Berkeley

Committee in charge:

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By Nicholas Philip Young
Abstract

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Professor Nitash P. Balsara, Chair

The design of environmentally-benign polymer processing techniques is an area of growing interest, motivated by the desire to reduce the emission of volatile organic compounds. Recently, supercritical carbon dioxide (scCO₂) has gained traction as a viable candidate to process polymers both as a solvent and diluent. The focus of this work was to elucidate the nature of the interactions between scCO₂ and polymers in order to provide rational insight into the molecular interactions which result in the unexpected mixing thermodynamics in one such system. The work also provides insight into the nature of pairwise thermodynamic interactions in multicomponent polymer-polymer-diluent blends, and the effect of these interactions on the phase behavior of the mixture.

In order to quantify the strength of interactions in the multicomponent system, the binary mixtures were characterized individually in addition to the ternary blend. Quantitative analysis of was made tractable through the use of a model miscible polymer blend containing styrene-acrylonitrile copolymer (SAN) and poly(methyl methacrylate) (dPMMA), a mixture which has been considered for a variety of practical applications. In the case of both individual polymers, scCO₂ is known to behave as a diluent, wherein the extent of polymer swelling depends on both temperature and pressure. The solubility of scCO₂ in each polymer as a function of temperature and pressure was characterized elsewhere. The SAN-dPMMA blend clearly exhibited lower critical solution temperature behavior, forming homogeneous mixtures at low temperatures and phase separating at elevated temperature. These measurements allowed the determination of the Flory-Huggins interaction parameter $\chi_{23}$ for SAN (species 2) and dPMMA (species 3) as a function of temperature at ambient pressure, in the absence of scCO₂ (species 1).

Characterization of the phase behavior of the multicomponent (ternary) mixture was also carried out by SANS. An in situ SANS environment was developed to allow measurement of blend
miscibility in the presence of scCO$_2$. The pressure-temperature phase behavior of the system could be mapped by approaching the point of phase separation by spinodal decomposition through pressure increases at constant temperature. For a roughly symmetric mixture of SAN and dPMMA, the temperature at which phase separation occurred could be decreased by over 125 °C. The extent to which the phase behavior of the multicomponent system could be tuned motivated further investigation into the interactions present within the homogeneous mixtures.

Analysis of the SANS results for homogeneous mixtures was undertaken using a new multicomponent formalism of the random phase approximation theory. The scattering profiles obtained from the scCO$_2$-SAN-dPMMA system could be predicted with reasonable success. The success of the theoretical predictions was facilitated by directly employing the interactions found in the binary experiments. Exploitation of the condition of homogeneity with respect to chemical potential allowed determination of interaction parameters for scCO$_2$-SAN and scCO$_2$-dPMMA within the multicomponent mixture ($\chi_{12}$ and $\chi_{13}$, respectively). Studying this system over a large range of the supercritical regime yielded insight on the nature of interactions in the system. Near the critical point of scCO$_2$, $\chi_{12}$ and $\chi_{13}$ increase monotonically as a function of pressure. Conversely, at elevated temperature away from the critical point, the interaction parameters are found to go through a minimum as a pressure increases. Analysis of the critical phenomenon associated with scCO$_2$ suggests that the observed dependence of $\chi_{12}$ and $\chi_{13}$ on pressure are related to the magnitude of scCO$_2$ density fluctuations and the proximity of the system to the so-called density fluctuation ridge. By tuning the system parameters of the multicomponent mixture, the phase behavior can be altered through the balance of pairwise interactions been the constituent species. The presence of scCO$_2$ in the mixtures appears to eliminate the existence of the metastable state that epitomizes most polymer-polymer mixtures. Thus it is shown that knowledge of the individual pairwise interactions in such multicomponent mixtures can greatly influence the resulting phase behavior, and provide insight into the design of improved functional materials with decreased environmental impacts.
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1 Introduction

1.1 Polymer Blend Thermodynamics

Mixtures of high-molecular weight polymers have been studied for decades due to the plethora of desirable different properties inherent to the pure molecules, as well as the ability to optimize the behavior of the resulting composite materials. [1, 2, 3, 4, 5] Binary and multicomponent polymer blends have found use in nearly all aspects of modern technology, from commodity materials such as thermoplastic elastomers and high-impact plastics to incorporation in devices for energy generation and storage, water purification, and biofuel processing. In each case, the physical properties of these materials, and thus the performance in any application of interest, depend fundamentally on the structural characteristics at the molecular scale. The extent to which a given mixture is homogeneous or phase-separated dramatically affects its behavior. Ultimately, the thermodynamic interactions between the components of a mixture are the defining criteria for the morphological characteristics of any polymer blend.

Owing to the extensive utilization of polymer blends in technological advancements, considerable effort has been dedicated to determining the governing rules for the design of these mixtures. In spite of the tremendous advances which have been realized over the course of several decades, the analysis of thermodynamic considerations relevant to polymer blends invariably centers on the simple, deceptively powerful formalism which has long defined the field of polymer science: the Flory-Huggins Theory (FHT). Since the introduction of the lattice-based theory to describe polymer-solvent mixtures, the theory has been recast in numerous approaches; however, its efficacy in describing the most crucial underlying aspects governing polymer thermodynamics using a single interaction parameter, $\chi$, remains unchanged. The plurality of techniques available to measure $\chi$ experimentally, coupled with the success found in predicting phase behavior with the FHT, make this an invaluable platform for understanding polymer mixtures.

The simplest case to consider is a binary polymer blend, consisting of two species of chemically-distinct polymers, which can be referred to generically as A and B. As in any binary mixture, the polymers can exist in either of two conditions: a homogeneously mixed single phase, or a phase-separated state wherein coexistent, macroscopic (on the order of $10^3$ nm or greater) domains are found to be enriched in species A or species B. A multitude of phase behaviors have been observed in binary polymer blends, illustrating the complex interplay of dependencies that control mixing. Due to the variety of different important parameters at play in any given blend, it is necessary to begin the consideration of the relevant thermodynamics with a tractable model system. To accomplish this goal, a lattice model is used to account for the configurational entropy of the mixture, as is shown schematically in Figure 1.1. [6] From this model, a relationship can be determined to equate the tendency for a given pair of polymers to mix. Using the familiar definition of free energy of mixing, the lattice can be used to relate miscibility to the defining characteristics of the molecules and their interactions. Summation of the energies of nearest-neighbor interactions gives the energy of the mixture.
Figure 1.1. Lattice model of a polymer blend.
Schematic diagram showing arrangement of A (blue) and B (green) segments with lattice sites of size \( v_0 \) equal to that of one segment of either polymer.

**Flory-Huggins Theory**

The Gibbs free energy of mixing, \( \Delta G_m \), is given by:

\[
\Delta G_m = -T \Delta S_m + \Delta H_m
\]

(1)

where \( \Delta S_m \) is the entropy of mixing, \( \Delta H_m \) is the enthalpy of mixing, and \( T \) is the absolute temperature. A polymer molecule is approximated as a chain of identical segments. Each segment occupies a volume, \( v_0 \), which is equal to the volume of a lattice site, and the chain consists of \( N_i \) total segments, connected linearly. In the binary blend case, polymer A has \( N_A \) segments and polymer B has \( N_B \) segments.

In FHT, the entropy of mixing, \( \Delta S_m \) is given by:

\[
\Delta S_m = -k_B v_0 \left( \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right)
\]

(2)

where \( k_B \) is the Boltzmann constant and \( \phi_i \) is the volume fraction of polymer \( i \). Since the value of \( \ln \phi_i \) is always negative, the entropic contribution to \( \Delta G_m \) will always promote miscibility, which is due to the increased number of possible configurations that a given chain can exhibit when the two components are mixed.

The second contribution to \( \Delta G_m \) is related to the interactions between individual segments. FHT assumes no volume change upon mixing (\( \Delta V_m = 0 \)). If the interactions are considered for each possible type of segment pairs (A-A, B-B, and A-B), each pair has an interaction energy \(-\varepsilon_{ij}\), and a given configuration of chains has \( N_{ij} \) contacts between segments \( i \) and \( j \), leading to an overall energy of:
Under the assumption of a homogeneous state, the probability that a given lattice site is occupied by a segment of A or B is just equal to the volume fraction of that segment. For a lattice where each site has \( z \) neighboring sites, each species has \( N_{ii} = zN\phi_i/2 \) self-contacts, and the remainder of \( N_t \) total contacts are cross-contacts. \( \Delta H_m \) can then be approximated as:

\[
\Delta H_m = \phi_A\phi_B\chi_{AB}k_BT
\]

where a dimensionless interaction energy parameter \( \chi_{AB} \) for each segment is defined in terms of the pairwise interaction energies \( -\varepsilon_{ij} \):

\[
\chi_{AB} = \frac{z-2}{k_BT}\left(\varepsilon_{AB} - \frac{1}{2}\varepsilon_{AA} - \frac{1}{2}\varepsilon_{BB}\right)
\]

with \( z - 2 \) number of contacts to account for the connectivity of each chain. Here it is assumed that there is no interaction energy between neighboring segments on a chain and that chain ends can be ignored. Thus it can be seen that a positive value of \( \chi_{AB} \) suppresses miscibility. The majority of polymer pairs exhibit \( \chi_{AB} \) values that are positive in the experimentally observable range of conditions, due to repulsion between dissimilar segments related to van der Waals forces.

The Flory-Huggins equation was derived by Flory [7] and Huggins [8] independently, for the case polymer-solvent mixtures, and then generalized to include polymer blends by Scott. [9] The focus of this theory is the previously described development of \( \Delta S_m \) and \( \Delta H_m \) into a central expression for \( \Delta G_m \). This can be written in dimensionless form:

\[
\frac{\Delta G_m v_0}{k_BT} = \frac{\phi_A\ln\phi_A}{N_A} + \frac{\phi_B\ln\phi_B}{N_B} + \chi_{AB}\phi_A\phi_B
\]

The original derivation of FHT for polymers mixed with a low-molecular weight component (i.e. solvent molecules) can be recovered by replacing \( N_B \) with unity in equation 6. The strict definition of FHT utilizes \( \chi_{AB} \), the Flory-Huggins parameter, depending solely on \( T \). However, it has been shown extensively in the literature that a variety of other aspects of blends affect \( \chi_{AB} \), including chain structure, specific monomer interactions, and compressibility (\( \Delta V_m \neq 0 \)). This gives rise to complicated dependencies of \( \chi_{AB} \) on \( N_t \) and \( \phi_i \), as well as on other state variables such as the pressure, \( P \). It is important to note that the imposition of a lattice model onto real polymer chains requires the use of chain length defined in terms of effective degree of polymerization. The actual degree of polymerization, \( \hat{N}_i \), can be related \( N_i \) using the volume of each monomer, \( v_{l,mon} \):
The value of $v_{i,\text{mon}}$ is temperature-dependent, since it is related to the polymer density ($v_{i,\text{mon}} = M_{i,\text{mon}} / \rho(T)$, where $\rho(T)$ is the density of the polymer of interest and $M_{i,\text{mon}}$ is the monomer molecular weight). Using a standard size for $v_0$ allows comparison between $\chi_{AB}$ parameters for any system, regardless of monomer size or shape. The choice of $v_0$ value is arbitrary, but reports in the literature often use 0.1 nm$^3$ as a standard reference volume $v_0$. FHT can be generalized to multicomponent mixtures with arbitrary number of species as such:

$$\frac{\Delta G_m}{k_B T} = \sum_i \frac{\phi_i \ln \phi_i}{N_i} + \sum_{i \neq j} \chi_{ij} \phi_i \phi_j$$

(8)

**Thermodynamic Relationships for Polymer Blends**

Understanding the phase behavior of polymer blends using FHT relies on classical thermodynamic relationships. The defining features of the phase diagram for a binary mixture are the spinodal and binodal curves, and the critical point. The nature of these characteristics depends most crucially on the interaction parameter, $\chi_{AB}$. The spinodal curve represents the limit of thermodynamic stability for a single-phase mixture, while the binodal curve establishes the extent of the stable, homogeneous region of the phase diagram. By quantifying the dependence of these conditions, the extent of single-phase and phase-separated regions of the phase diagram can be mapped out.

The most common empirical form given for $\chi_{AB}(T)$ is as follows:

$$\chi_{AB}(T) = a + \frac{b}{T}$$

(9)

In this form $a$ and $b$ are experimentally determined constants. It is usually assumed that $a$ is due to local entropic considerations not captured by equation 2, while $b$ results from enthalpic factors (equation 4). Thus for the simplest case wherein $\chi_{AB}$ varies inversely with $T$, $a$ and $b$ have values greater than zero. This type of dependence is far from universal, however. [10] The two most general classes of blend behavior are defined in relation to the form of $\chi_{AB}(T)$. In the more common case, where $b$ is positive and thus $\chi_{AB}$ decreases with $T$, the polymer mixture will exist in the phase-separated state at low $T$ and becomes homogeneous as $T$ is increased. This is referred to as upper critical solution temperature, or UCST, phase behavior. The converse case, in which $\chi_{AB}$ increases with $T$, (i.e. $b$ is negative) results in lower critical solution (LCST) phase behavior. In this case the polymer mixture is homogeneous at low $T$ and phase separated upon heating. A variety of alternative behaviors are also possible, including the presence or absence of both LCST and UCST transitions in the experimentally accessible temperature window.

The spinodal condition, or the limit of stability of the homogeneous mixture, is defined as:
\[
\frac{\partial^2 \Delta G_m}{\partial \phi_A^2} = 0
\]  

Taking the second derivative of equation 6 (FHT) with respect to \( \phi_A \), and noting that \( \phi_B = 1 - \phi_A \), the spinodal condition reduces to:

\[
\chi_{AB}(T) = \frac{1}{2} \left( \frac{1}{N_A \phi_A} + \frac{1}{N_B \phi_B} \right)
\]  

Equation 11 assumes that, as mentioned previously, \( \chi_{AB} \) is a function of \( T \) only, and not \( \phi_A \). A more general expression requires knowledge of the dependence of \( \chi_{AB} \) on \( \phi_A \), which is difficult to obtain \textit{a priori}. The spinodal curve delineates the regime of the phase diagram where fluctuations in concentration or density are not suppressed and instead result in phase separation. Depending on the nature of transition (LCST or UCST), the spinodal curve is concave up or concave down on the \( T - \phi \) phase diagram. Regardless, the region enclosed by the curve represents the condition of unstable fluctuations, while the region outside of the curve defines where fluctuations are metastable (at a local free energy minimum) or completely stable (universal free energy minimum).

The binodal condition can also be obtained using FHT, in combination with the definition of thermodynamic equilibrium. In order for two phases to coexist in equilibrium, the chemical potential of each species must be equal in the two phases. This condition is obtained according to the definition of chemical potential, as the first derivative of \( \Delta G_m \) with respect to \( n_i \) for two phases, I and II (where \( n_i \) is the number of chains of species \( i \)):

\[
\frac{\partial \Delta G_m}{\partial n_A^I} = \frac{\partial \Delta G_m}{\partial n_A^II}
\]

\[
\frac{\partial \Delta G_m}{\partial n_B^I} = \frac{\partial \Delta G_m}{\partial n_B^II}
\]

At a given condition in the two-phase region, there will exist a concentration of species \( i \) in phases I and II, specifically \( \phi_i^I \) and \( \phi_i^II \), so that both expressions of equation 12 are satisfied. Substituting equation 6 into equation 12 gives
\[
\ln \left( \frac{\phi_A^I}{\phi_A^H} \right) + (\phi_A^H - \phi_A^I) \left( 1 - \frac{N_A}{N_B} \right) + \chi_{AB}(T)N_A \left[ (1 - \phi_A^I)^2 - (1 - \phi_A^H)^2 \right] = 0
\]

\[
\ln \left( \frac{1 - \phi_A^I}{1 - \phi_A^H} \right) + (\phi_A^I - \phi_A^H) \left( 1 - \frac{N_B}{N_A} \right) + \chi_{AB}(T)N_B \left[ (\phi_A^I)^2 - (\phi_A^H)^2 \right] = 0
\]

These expressions yield the boundary for the region where the homogeneous state is stable.

The critical point is obtained at the particular \( T \) and \( \phi \) where the spinodal and binodal curves meet. This implies that the condition can be determined explicitly from the coincident minimum of these curves, corresponding to the solution of equation 10 and equation 14:

\[
\frac{\partial^3 \Delta G^m}{\partial \phi_A^3} = 0
\]

The critical composition \( \phi_c \) thus obtained is:

\[
\phi_{A,c} = \frac{1}{1 + \sqrt{N_A/N_B}}
\]

Combining equations 11 and 15, an expression for \( \chi_{AB} \) at the critical point can be obtained:

\[
\chi_{AB,c} = \frac{1}{2} \left( \frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2
\]

Equation 17 is the basis for the definition of an average chain length for the two species, \( N_{ave} \):

\[
N_{ave} = 4 \left( \frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2
\]

This relation demonstrates the relation for determining phase separation, \( \chi_{AB,c}N_{ave} = 2 \). Frequently, binary polymer blend phase diagrams are represented with the \( \chi_{AB,c}N_{ave} - \phi \) phase space in place of the \( T - \phi \) phase space.

The typical features of the \( T - \phi \) phase space for a UCST binary polymer blend are shown schematically in Figure 1.2. In the single-phase regime, outside of the binodal envelope, the homogeneous phase is stable. Within the spinodal envelope is the two-phase regime where fluctuations on concentration do not decay spontaneously. This phenomenon results in phase
separation by a mechanism called spinodal decomposition. Between the binodal and spinodal curves lies the metastable region. In this region the phase separated mixture is obtained at equilibrium. However, a phase transition from single-phase to two-phase states requires crossing of a nucleation barrier. It is thus possible to observe a homogeneous mixture in this region for a time period that depends on the height of the barrier. Finally, the critical point is represented as the locus of the binodal and spinodal curves.

Figure 1.2. Typical UCST-type phase diagram of a binary polymer blend. Schematic representation of a typical binary polymer blend $T - \phi$ phase diagram for a mixture demonstrating UCST phase behavior.

Flory-Huggins Theory has long proven its value in the understanding of the phase behavior of binary and multicomponent mixtures. In spite of the relative simplicity of the basis for its derivation, it remains a crucial facet of the understanding of polymer blend thermodynamics. As such, it continues to possess high priority for use in the analysis of both model and commercially-relevant composite polymeric materials.

1.2 Polymer – Supercritical Carbon Dioxide Mixtures

Supercritical carbon dioxide (scCO$_2$) has been investigated extensively in recent years as an environmentally benign option for the synthesis and processing of polymers. [11] Owing mostly to its accessible critical point (critical temperature $T_{c,\text{CO}_2} = 30.9 \, ^\circ\text{C}$ and critical pressure $P_{c,\text{CO}_2} = 7.38 \, \text{MPa}$), scCO$_2$ has a unique set of properties, enabling its widespread use. Temperature and pressure can tune the physical properties of scCO$_2$, including density, viscosity, and diffusivity, over a wide range of values. As an example of this behavior, Figure 1.3 shows the dependence of scCO$_2$ density $\rho_{\text{CO}_2}$ on $P$ for a range of $T$ in the supercritical regime, calculated from the equation of state of Span and Wagner. [12] A key result of this characteristic is that the solvent quality of scCO$_2$ with many solutes of practical interest can be adjusted to obtain the desired behavior. The efficacy of scCO$_2$ for polymer processing has been established
in applications including organic photovoltaics, [13] supercapacitors, [14] and foams for various purposes. [15, 16, 17, 18]

![Figure 1.3. P-\(\rho\)-T phase behavior of scCO\(_2\).](image)

Pressure-density-temperature phase behavior in the supercritical regime: 7.4 MPa ≤ \(P\) ≤ 40 MPa and 35 °C ≤ \(T\) ≤ 100 °C. [12]

In spite of these developments, relatively little effort has been dedicated to elucidation of the underlying thermodynamic behavior of scCO\(_2\) with polymers, particularly in the case of multicomponent mixtures. Melnichenko considered the phase behavior of polymers dissolved in scCO\(_2\) in an attempt to quantify the solvent quality of supercritical fluids. [19] Watkins \textit{et al.} and Spontak \textit{et al.} explored the influence of supercritical fluid diluents on the location of phase boundaries for several polymer blends and block copolymers, and attempted to quantify the effect of these compressible components as plasticizing agents. [20, 21, 22, 23, 24, 25] Efforts have been made to develop an understanding of the relationship between scCO\(_2\) concentration and effective interaction parameters between the constituent polymer chains or blocks. Depending on the miscibility of the neat blend system, the introduction of a supercritical diluent has been shown to improve mixing in blends exhibiting upper critical solution temperature (UCST) behavior, and diminish mixing in lower critical solution temperature (LCST) blends. However, these analyses fail to acknowledge the multicomponent nature of these systems. The goal of this work is to quantify the thermodynamic interactions in a representative multicomponent mixture of practical interest: styrene-acrylonitrile random copolymer and poly(methyl methacrylate).

Mixtures of SAN and PMMA (in the absence of scCO\(_2\)) have been studied at great length due to the tunable miscibility of the polymers and the exemplary mechanical properties that the blends possess. For copolymers containing 10% – 30% acrylonitrile by weight, the blends exhibit LCST behavior at experimentally accessible temperatures. [26] Outside of that composition window, the polymers are immiscible. The existence of this limited miscibility has
been attributed to the strong repulsion between styrene and acrylonitrile, overwhelming the repulsive interaction that either experiences with PMMA. This general phenomenon has been observed in many mixtures of copolymers with homopolymers [27] as well as with small molecules, [28] and is often referred to as the “copolymer effect” or “intramolecular repulsion”.

1.3 Dissertation Outline

The remainder of the dissertation is outlined as follows. Chapter 2 describes the experimental methods used throughout this work, including polymer synthesis, characterization, and the chosen methods for probing scCO₂-polymer interactions. In Chapter 3 the thermodynamic interactions and phase behavior of multicomponent mixtures containing scCO₂ and two polymers are investigated by small-angle neutron scattering (SANS). We describe the derivation of a new formalism of the multicomponent random phase approximation to interpret SANS data applicable to systems relevant to this work. The effect of temperature, pressure, and scCO₂ density on the strength of interactions in this system are evaluated to provide insight into the complex phase behavior of the system, and are discussed within the context of fundamental behavior of supercritical fluids. Chapter 4 provides a summary of the work and possible routes forward to develop better understanding these systems of growing commercial interest.
2 Experimental Methods†

To facilitate the clear application of thermodynamic relations to analyze data obtained throughout this study, the use of model polymers with narrow molecular weight distribution (polydispersity index PDI = $M_w / M_n$, where $M_w$ is the weight-averaged molecular weight and $M_n$ is the number averaged molecular weight) was paramount. All scattering experiments used the deuterated form of PMMA (dPMMA) in order to take advantage of the significant increase in neutron scattering contrast obtained for deuterium-containing species, as described below. In commercial applications, SAN is prepared by conventional free radical polymerization (FRP). Polymers obtained by this approach are not suited for fundamental thermodynamic studies because the samples have large PDI. Controlled radical polymerization (CRP) techniques enable the synthesis of samples with narrow molecular weight distributions. Atom transfer radical polymerization (ATRP) is one of the most widely used controlled polymerization methods. However, it has been shown that only low molecular weight SAN copolymers can be prepared by this method and that it requires relatively large quantities of copper catalysts. [29, 30] A related synthetic method called activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) requires much lower concentrations of the copper catalyst. [31] The reduced concentration of catalyst suppresses undesired side reactions between growing radicals and copper species, enabling the preparation of high molecular weight SAN copolymers with narrow molecular weight distributions. [32] This method was used to prepare all SAN copolymers studied in this dissertation.

2.1 Polymer Synthesis and Characteristics

dPMMA with low PDI was purchased from Polymer Source (Montreal, Canada). The molecular characteristics of dPMMA studied in this work are summarized in Table 2.1.

<table>
<thead>
<tr>
<th>Table 2.1. dPMMA Homopolymer Characteristics</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kg/mol)</th>
<th>PDI</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dPMMA185</td>
<td>185</td>
<td>1.03</td>
<td>2619</td>
</tr>
</tbody>
</table>

Monodisperse (or nearly so) styrene-acrylonitrile copolymer (SAN) is not easily obtained commercially, so its synthesis was performed by controlled radical polymerization techniques. The synthetic details are outside the scope of this thesis, and so will be described briefly here. For comparison, a SAN copolymer synthesized by FRP was supplied by The Dow Chemical Company (Midland, MI).

†Adapted with permission from Macromolecules 2013, 46, 6345-6356. Sebnem Inceoglu, Nicholas P. Young, Andrew J. Jackson, Steven R. Kline, Stéphane Costeux, Nitash P. Balsara, “Effect of Supercritical Carbon Dioxide on the Thermodynamics of Model Blends of Styrene-Acrylonitrile Copolymer and Poly(methyl methacrylate) Studied by Small-Angle Neutron Scattering.” Copyright 2013 American Chemical Society.
Materials

Styrene (S, 99.9%), deuterated styrene (dS, 98%), acrylonitrile (AN, >99%), tin (II) 2-ethylhexanoate (Sn(EH)$_2$, 95%), Tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN), copper (II) chloride (CuCl$_2$, 99.9%), ethyl 2-bromo isobutyrate (EBiB, 98%), anisole (99%), and deuterated chloroform (CDCl$_3$) were purchased from Sigma-Aldrich (St. Louis, MO). Tetrahydrofuran (THF, 99.9%) and methanol (99.9%) were purchased from Acros (Pittsburgh, PA), and benzene (99.9%) was purchased from OmniSolv (Salisbury, NC). Both styrene and acrylonitrile monomers were passed through a basic alumina column to remove inhibitors and then purged with argon for thirty minutes. All other chemicals were used as received.

Synthesis of styrene-acrylonitrile copolymer

A styrene-acrylonitrile “random” copolymer was synthesized via ARGET ATRP. [32] In reality the SAN copolymer obtained by this approach is a statistical copolymer and we have not characterized sequence distributions in our sample. The chemical structure of SAN is shown in Figure 2.1. Styrene (13.3 mL, 116 mmol), acrylonitrile (10 mL, 153 mmol) and anisole (10 mL) were added to a dry Schlenk flask. Argon was bubbled through the Schlenk flask for fifteen minutes. Then the initiator, EBiB (12 µL, 81.7 µmol), and a solution of CuCl$_2$ (0.0074 g, 55 µmol)/Me$_6$TREN (10 µL, 35.5 µmol) complex in degassed anisole (5 mL) was added. After stirring the mixture under argon for ten minutes, a purged solution of Sn(EH)$_2$ (17 µL, 52.4 µmol) and Me$_6$TREN (3 µL, 10.6 µmol) in anisole (5 mL) was added. The sealed flask was placed in thermostated oil bath at 80 °C. Samples were taken at timed intervals and analyzed by gel permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped at the desired $M_n$ by opening the flask and diluting with THF. The resulting polymers were isolated from catalyst by passing the reaction mixture through a neutral alumina column and performing two precipitations in methanol. The product was dried under vacuum at 60 °C. The polymers were redissolved at five weight percent solids in a benzene-THF mixture (90%-10% v-v), freeze-dried in a lyophilizer (Millrock LD85, Kingston, NY), and dried under vacuum at 90 °C for six days to remove benzene. Proton nuclear magnetic spectroscopy ($^1$H NMR) measurements were carried out to determine the weight fraction of acrylonitrile in the SAN copolymer, $w_{AN}$. The obtained copolymer was named following the nomenclature SANXX(yy), where $XX = M_n$ in kg/mol and $yy = w_{AN}$, the weight percentage of acrylonitrile (100·$w_{AN}$). The characteristics of SAN polymers that were used to carry out the work described in this thesis are summarized in Table 2.2.
Figure 2.1. Molecular structure of SAN and dPMMA. (a) Styrene-acrylonitrile random copolymer structure. Carbon atoms of SAN are labeled for NMR analysis (see text). (b) Deuterated poly(methyl methacrylate) structure.

Table 2.2. SAN Copolymer Characteristics

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kg/mol)</th>
<th>$PDI$</th>
<th>$w_{AN}$</th>
<th>$N$</th>
<th>Synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAN74(26)</td>
<td>74</td>
<td>1.17</td>
<td>0.26</td>
<td>0.25</td>
<td>1492</td>
</tr>
<tr>
<td>SAN44(18)</td>
<td>44</td>
<td>2.34</td>
<td>0.18</td>
<td>-</td>
<td>1785</td>
</tr>
</tbody>
</table>

Through this manuscript, the components will be referred to according to the following numerical nomenclature: 1 = scCO$_2$, 2 = SAN, 3 = dPMMA (or equivalently hydrogenous PMMA). The monomer molecular weight $M_{0,i}$ are $M_{0,S} = 104.15$ g / mol, $M_{0,AN} = 53.06$ g / mol, and $M_{0,3} = 108.17$ g / mol. The monomer volume $v_i$ at a reference temperature $T_{\text{ref}} = 413.15$ K and a reference pressure $P_{\text{ref}} = 0.1$ MPa are $v_S = 0.179$ nm$^3$, $v_{AN} = 0.0819$ nm$^3$, [33] and $v_3 = 0.149$ nm$^3$. [10] The dependence of $v_i$ on temperature ($T$) is obtained from the thermal expansion coefficient, $d \ln v_i / dT$, for which we use an approximate value of $7 \times 10^{-4}$ K$^{-1}$. [10] We ignore the heterogeneous nature of the SAN copolymer and obtain average $M_{0,SAN}$ and $v_{SAN}$ from the mass and volume averages of the constituent values, respectively. For the statistical segment length $l_i$ of species $i$, a reference value was used at the reference conditions. The reference value for dPMMA has been tabulated ($l_{3,\text{ref}} = 0.54$ nm) but we were unable to find any instance of this value reported for SAN and thus reported it for the first time in ref [34] ($l_{2,\text{ref}} = 0.54$ nm).

2.2 Polymer Blend Preparation

SAN/dPMMA blends were prepared by drop casting. Predetermined quantities of dPMMA125 and SAN74(26) polymers needed to achieve the desired blend composition were dissolved in THF (~0.2 g/mL) and stirred for two days to obtain a homogeneous solution. The volume fraction of component $i$ in the scCO$_2$-free polymer mixture is $\phi_{i,0}$ (for example, $\phi_{1,0} = 0$, $\phi_{2,0} = 0.539$, and $\phi_{3,0} = 0.461$). The volume fraction was determined using the $\rho_i$ in the amorphous state at $T = T_{\text{ref}} = 413$ K and $P = P_{\text{ref}} = 0.1$ MPa, and the weight fraction $w_i$, of the components in a given mixture. The density of dPMMA at $T_{\text{ref}}$ and $P_{\text{ref}}$ is 1.205 g/cm$^3$. [10] The density of SAN copolymer at $T_{\text{ref}}$ and $P_{\text{ref}}$ is 1.054 g/cm$^3$. [33] Films were prepared by slowly drop casting the solution inside O-rings (McMaster Compressible FEP-Encapsulated Silicone O-Rings: nominal thickness = 1/16", Santa Fe Springs, CA) to avoid the formation of air bubbles and subsequently dried in ambient atmosphere for four days and under vacuum at room
temperature for two days. The thickness of the films was controlled between 80 and 200 μm by varying the quantity of solution dropped into the O-ring spacer. We present data from one particular blend which contained 46 volume percent dPMMA.

2.3 Polymer Characterization

_Gel Permeation Chromatography (GPC)_

GPC measurements were carried out to obtain $M_n$ and $PDI$ were obtained using a Malvern Instruments Viscotek TDA 302 GPC system that has a guard column, a set of four Viscotek columns (300 mm × 7.8 mm, T-3000, T-4000, T-5000 and T-6000 columns) and a refractive index detector, with THF eluent (flow rate of 1 mL / min, 35 °C). The instrument was calibrated with polystyrene standards (Agilent Easivials PS-M). Intrinsic viscosity measurements were used to estimate the absolute molecular weights of SAN and dPMMA samples used in this study. Commercially-supplied SAN44(18) was analyzed only by this system, and thus its molecular weight is only an estimate.

Figure 2.2 shows typical chromatograph traces obtained from SAN copolymers using the Viscotek TDA 302 system. The figure contains the trace for SAN74(26), synthesized by ARGET ATRP for this work, and SAN44(18), synthesized by FRP at Dow. It is evident in Figure 2.2 that the polymer synthesized by ARGET ATRP has significantly narrower molecular weight distribution than that of the commercial sample.

![Figure 2.2. GPC chromatograph of SAN copolymers. Representative GPC traces comparing $M_n$ and PDI of SAN74(26) (black solid line), prepared in this work by ARGET ATRP, with a commercially-available SAN copolymer, SAN44(18) (red solid line), synthesized by FRP.](image-url)
In order to more accurately obtain measurements of absolute molecular weight, a second set of GPC experiments were carried out as well. In this case polymers were analyzed by a Malvern Instruments Viscotek TDA 305 GPC system with a single T-6000M column using triple detection via refractive index, viscosity, and light scattering. The system used THF as eluent at 30 °C with a flow rate of 1 mL / min. The instrument was calibrated using a single narrow-PDI polystyrene standard with $M_w = 105,268$ g / mol, intrinsic viscosity $\eta = 0.481$ dL / g, and refractive index increment $dn / dc = 0.185$. The use of triple detection to obtain absolute molecular weight for a given polymer is preferred for accuracy compared with molecular weight determination by way of a calibration curve. Details of the absolute molecular weight measurement are given in reference [35]. Results from these analyses are summarized in Table 2.2.

**Fourier-Transform Infrared (FT-IR) Spectroscopy**

A Fourier-transform infrared (FT-IR) spectrometer (Thermo Scientific Nicolet™ 6700), equipped with attenuated total reflection and a germanium crystal, was used to detect the presence of cyano (–C≡N) group in SAN. Data were collected using OMNIC™ spectroscopy software.

FT-IR spectra of SAN74(26) and SAN44(18) are shown in Figure 2.3. A spectrum obtained from the polystyrene homopolymer PS48 is also shown as a reference. Both SAN77(26) and SAN44(18) have a clear absorption peak at approximately 2236 cm$^{-1}$ indicating the presence of cyano groups. [36] In contrast, the spectrum of PS48 is featureless in the range 2800 cm$^{-1}$ to 2000 cm$^{-1}$.
Figure 2.3. FT-IR spectra of SAN copolymers and PS homopolymer. Representative FT-IR spectra showing –C≡N stretching absorption signatures (2236 cm\(^{-1}\)) to indicate presence of acrylonitrile in ARGET ATRP–synthesized SAN74(26) (black solid line), and as well as SAN44(18) (red solid line). Homopolymer PS48 (blue solid line) has no absorption in the relevant wavenumber range. Spectra are shifted vertically for clarity.

*Nuclear Magnetic Resonance (NMR) Spectroscopy*

Three methods were used to quantify the SAN copolymer composition: \(^1\)H NMR, \(^{13}\)C NMR, and elemental analysis. \(^1\)H NMR measurement was conducted on 400 MHz Bruker AVB400 spectrometer using CDCl\(_3\) solutions with a polymer concentration of \(\sim 5\) mg/mL. Distinguishing between SAN74(26) and PS48 using \(^1\)H NMR is difficult. The unique chemical shifts of the acrylonitrile groups overlap with those of the hydrocarbon backbone of PS (see Figure 2.4). One estimate of the copolymer composition was found by comparing the area of all backbone peaks (0.5 ppm – 3.0 ppm) with that of the aromatic peak area (6.4 ppm – 7.4 ppm). By this methodology, the copolymer is estimated to have \(w_{AN} = 0.26\).
Representative $^1$H NMR spectra of SAN74(26) and PS48 showing the close correspondence in features between SAN and PS. The peak areas corresponding to the polymer backbone (0.5 ppm – 3.0 ppm) are compared to the peak areas corresponding to the styrenic aromatic group (6.4 ppm – 7.4 ppm) to calculate the copolymer composition.

$^{13}$C NMR spectroscopy was used to obtain unique signatures of styrene and acrylonitrile groups in SAN. [37] The measurement was performed on Bruker BioSpin 900 MHz spectrometer with a polymer concentration of ~360 mg/mL at 50 °C for 24 hours. Spectra were analyzed to determine copolymer composition. The aromatic carbon atoms forming the phenyl group of styrene have $^{13}$C NMR chemical shifts between 120 ppm and 145 ppm, while the nitrile carbon has a chemical shift at 120 ppm. Finally, the backbone carbon atoms have shifts in the 20 ppm – 60 ppm range. In Figure 2.1, the carbon atoms of SAN are labeled as $X_y$, where $X$ refers to the group of related carbon atoms and $y$ represents our numbering scheme. Figure 2.5 shows the $^{13}$C NMR spectrum of SAN74(26), with peaks labeled according to nomenclature of Figure 2.1. By this methodology, the copolymer is estimated to have $w_{AN} = 0.25$. 
Representative $^{13}$C NMR spectrum of SAN74(26). The peaks assignments are based on the structure of SAN shown in Figure 2.1. The peak areas are used in conjunction with the known carbon group ratios to determine the copolymer composition. The peak marked X represents the chemical shift associate with the solvent, deuterated chloroform.

**Elemental Analysis**

Elemental analysis was carried out using the CHN combustion methodology by Elemental Analysis Incorporated (Lexington, KY) to provide the elemental composition of SAN74(26) in terms of atom weight fraction $w_i$, where $i$ refers to carbon, hydrogen and nitrogen. Measurement yielded the weight fractions of carbon, hydrogen, and nitrogen: $w_C = 0.85$, $w_H = 0.071$, and $w_N = 0.073$. By this methodology, the copolymer is estimated to have $w_{AN} = 0.28$.

The close agreement in $w_{AN}$ measurements obtained from $^1$H NMR, $^{13}$C NMR, and elemental analysis provides compelling evidence that the copolymer is well-characterized. Since the different techniques provided quantifications in good agreement with each other, the remainder of SAN copolymers were characterized solely by $^1$H NMR for simplicity. The results of these measurements are summarized in Table 2.2.

**Differential Scanning Calorimetry (DSC)**

DSC experiments were performed on a Thermal Advantage Q200 calorimeter at the Molecular Foundry, Lawrence Berkeley National Laboratory. Samples were sealed in aluminum hermetic pans. DSC scans consisted of two heating/cooling cycles and were conducted over the range $0 \, ^\circ\text{C} - 150 \, ^\circ\text{C}$ at a rate of $10 \, ^\circ\text{C}/\text{min}$. The glass transition temperatures ($T_g$) for SAN74(26), dPMMA185, and a blend of the two containing a volume fraction of dPMMA $\phi_{dPMMA} = 0.46$ are from the inflection point of the transition in the second heating run.
Table 2.3 provides an overview of the results of DSC experiments on SAN74(26), dPMMA125, and the blend. The $T_g$ of a homogeneous blend can be estimated using the Fox equation:

$$\frac{1}{T_{g,\text{blend}}} = \frac{w_2}{T_{g,2}} + \frac{w_3}{T_{g,3}}$$  \hspace{1cm} (18)

In equation 18, $T_{g,i}$ and $w_i$ refer to the is the $T_g$ and weight fraction of each component in the blend. The predicted $T_g$ of the blend using equation 18 is $(120 \pm 4) \, ^\circ C$, which is consistent with the value reported in Table 2.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ ($^\circ C$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAN77(26)</td>
<td>113 ± 2</td>
</tr>
<tr>
<td>dPMMA125</td>
<td>126 ± 4</td>
</tr>
<tr>
<td>Blend</td>
<td>115 ± 3</td>
</tr>
</tbody>
</table>

### 2.4 Supercritical Carbon Dioxide Uptake

The uptake of scCO$_2$ by neat SAN copolymers and hydrogenous poly(methyl methacrylate) (hPMMA) was measured gravimetrically by at Dow Chemical Company. [34, 38] CO$_2$ solubility from magnetic suspension balance experiments at pressures up to 14 MPa and multiple temperatures were fitted with the PC-SAFT equation of state to allow extrapolation to higher pressures. The results of these experiments were reported as solubility of scCO$_2$, $w_{1,i}$, in each polymer as a function of $P$ for isothermal conditions for $35 \, ^\circ C \leq T \leq 105 \, ^\circ C$. A summary of the results are shown in Figure 2.6. It is evident that $w_{1,3}$ is significantly greater than $w_{1,2}$ at low $T$. As $T$ increases, the difference in solubility decreases and at $100 \, ^\circ C$, $w_{1,2}$ surpasses $w_{1,3}$ for $P > 30$ MPa. Dow noted that the solubility of scCO$_2$ in SAN and PMMA is independent of $M_n$ and PDI in the ranges of interest. We use the data in Figure 2.6 to interpret SANS data from scCO$_2$/SAN/dPMMA mixtures, neglecting the possible effect of deuteration on the solubility.
Figure 2.6. scCO$_2$ solubility in SAN and PMMA. Supercritical carbon dioxide solubility in (a) SAN copolymer ($w_{AN} = 0.26$) and (b) poly(methyl methacrylate), as a function of $P$ at for $35 \, ^\circ\text{C} \leq T \leq 100 \, ^\circ\text{C}$. Solubility is expressed as weight fraction $w_{1-i}$, where scCO$_2 = 1$, SAN = 2, and dPMMA = 3.

2.5 Small Angle Neutron Scattering

SANS measurements were carried out on the NG3 and NG7 beamlines at the National Institute of Standards and Technology Center for Neutron Research (NCNR) in Gaithersburg, MD. Measurements were first performed at ambient $P$ ($P \approx 0.1 \, \text{MPa}$) to quantify the $T$-dependent miscibility of the binary polymer blend. For ambient $P$ experiments, samples were
studied at $T = 60 \, ^\circ C$, $100 \, ^\circ C$, $120 \, ^\circ C$, and $140 \, ^\circ C$ by heating in the beamline using a seven-sample $T$-control stage, excluding the end positions. Samples were held for at least 30 min at each $T$ prior to commencing measurements to ensure equilibration. Raw data were corrected for detector sensitivity, [39] background and empty cell scattering contributions, incoherent scattering, and coherent scattering from the pure dPMMA. [40] Data were azimuthally integrated to obtain absolute scattering intensity, $I$, as a function of the scattering vector, $q$, where $q = (4\pi/\lambda) \sin(\theta/2)$, $\lambda$ is the incident neutron beam wavelength (0.6 nm), and $\theta$ is the scattering angle. For some ambient $P$ experiments sample-to-detector distances of 1.33 m and 5 m were used, and the data were combined to access the range $0.133 \, nm^{-1} \leq q \leq 1.838 \, nm^{-1}$.

scCO$_2$ was added to the blend using a modified high-$P$ sample environment provided by NCNR. Modifications to the high-$P$ sample cell and housing devised specifically to enable experiments with scCO$_2$. A manually-driven piston was connected to a liquid CO$_2$ cylinder. Tygon tubing was wrapped around the barrel of the piston to enable heating and cooling of the piston chamber. Liquid CO$_2$ was loaded into the piston at 5 $^\circ C$. The piston was isolated and heated to 50 $^\circ C$. Compression of the contents of the piston results in a phase transformation from liquid CO$_2$ to scCO$_2$. The scCO$_2$ was delivered to the polymer blend sample cell using high-$P$ tubing (High Pressure Equipment Company, Erie, PA). The assembly was connected via the high-$P$ tubing to the piston, and the procedure for adding scCO$_2$ to the sample was initiated. The sample cell comprised two sapphire windows separated by a 1/16” Viton O-ring. Films of the binary polymer blend were secured within the O-ring and sandwiched between the sapphire windows. The films, with $t \approx 100 \, \mu m$, filled approximately 10% of the sample cell volume. This allowed the remainder of the volume to be filled with scCO$_2$ at the given $T$ and $P$, which acted as a reservoir to swell the film as conditions were systematically varied. This construction was secured within a stainless steel cell housing that could be connected to the scCO$_2$ source. In this manner, scCO$_2$ could be introduced to the blend. A digital $P$-reader was used to monitor the $P$ of the scCO$_2$ reservoir in contact with the blend. The same sample cell, housing, and $T$-control stage were used in the absence and presence of scCO$_2$. The blend was thermally equilibrated at the desired $T$ set point for at least 30 min prior to addition of scCO$_2$ and the sample cell was flushed with CO$_2$ vapor before pressurization by opening a valve in series with the cell. The valve was then closed and the piston was adjusted to obtain the desired $P$.

SANS data were obtained using the following protocol: upon reaching the desired $P$, a series of three two-minute runs was commenced, followed by a three-minute transmission run. This series of runs was repeated one time, for a total of twelve minutes of scattering data collection. If time-independent scattering profiles were obtained, the scCO$_2$ $P$ was increased to the next value and the process was repeated. In some cases, especially near the point of phase separation, the sequence of scattering and transmission runs would be repeated more than twice until equilibrium scattering profiles were obtained or clear evidence of phase separation was observed. All scCO$_2$ experiments were conducted using a sample-to-detector distance of 5 m, to obtain a $q$ range of $0.133 \, nm^{-1} \leq q \leq 0.886 \, nm^{-1}$. Data reduction and processing was performed in an identical manner to that for the ambient $P$ experiments.

Neutron scattering contrast between two species of a mixture $i$ and $j$, $B_{ij}$, is defined:
\[ B_{ij} = \frac{b_i}{v_i} - \frac{b_j}{v_j} \]  \hspace{1cm} (19)

where \( b_i \) representing the scattering length of component \( i \), and the ratio for each species is the scattering length density (SLD). For neutron scattering of polymers, the SLD is defined for a monomer, allowing the \( b_i \) to be calculated from the atomic composition:

\[ b_i = \sum_{k}^{m} b_{c_k} \]  \hspace{1cm} (20)

In equation 20, \( b_{c_k} \) is the bound coherent scattering length of the \( k \)th atom in a molecule of \( m \) atoms. The values of \( b_{c_k} \) are tabulated for both pure isotopes as well as the natural abundance of the elements, [41] and a calculator is made available by NCNR on the web. [42] A crucial advantage of the SANS technique is the ability to vary SLD through isotopic variation. Unlike other scattering techniques such as small-angle X-ray scattering, \( b_i \) has no correlation with atomic number. This is especially useful in the case of polymers, where there is a large difference in the value of \( b_c \) between the \(^1\)H and \(^2\)H (deuterium, D) isotopes of hydrogen. For reference, the values of \( b_c \) for the relevant elements are given in Table 2.4, at the natural isotopic abundance (with the exception of pure D). It is clear that the substitution of D for H in a polymer has a significant effect on the SLD of molecule.

<table>
<thead>
<tr>
<th>Element</th>
<th>( b_c \times 10^{-6} \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-3.739</td>
</tr>
<tr>
<td>D</td>
<td>6.671</td>
</tr>
<tr>
<td>C</td>
<td>6.646</td>
</tr>
<tr>
<td>N</td>
<td>9.360</td>
</tr>
<tr>
<td>O</td>
<td>5.803</td>
</tr>
</tbody>
</table>

Table 2.4. Bound Coherent Neutron Scattering Lengths

Using the above tabulated \( b_c \) and the value of \( v_i \) given for SAN (with \( w_{AN} = 0.26 \)) and dPMMA, we can illustrate the effect of deuteration on SLD, and thus \( B_{ij} \). The values of SLD calculate at \( T_{ref} \) are listed in Table 2.5 for SAN and dPMMA. The value for hPMMA is also given to illustrate the value of using the deuterated form of PMMA for neutron scattering experiments.
Table 2.5. Neutron Scattering Length Density of SAN and PMMA

<table>
<thead>
<tr>
<th>Polymer</th>
<th>SLD (× 10⁻⁴ nm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAN</td>
<td>2.208</td>
</tr>
<tr>
<td>hPMMA</td>
<td>1.002</td>
</tr>
<tr>
<td>dPMMA</td>
<td>6.591</td>
</tr>
</tbody>
</table>

It is clear from Table 2.5 that a significant advantage is obtained by using dPMMA in tandem with SAN in scattering experiments, with an increase in $B_{ij}$ by a factor of approximately 3.6 compared with SAN-hPMMA. It is worth noting that the density of the polymers is not expected to vary significantly in the $P$ range of interest to this work (see Figure 2.6). Thus the polymer SLD is roughly independent of $P$. Conversely, $\rho_{CO_2}$ clearly depends strongly on $P$ (Figure 1.3). In Figure 2.7, SLD of dPMMA, SAN (with $w_{AN} = 0.26$), and sc$CO_2$ are presented as a function of $P$ in the range $7.4 \text{ MPa} \leq P \leq 40 \text{ MPa}$ at $T = 40 \degree C$. In this range it can be seen that the SLD of SAN and sc$CO_2$ are nearly equal and much less than that of dPMMA. Thus it is expected in SANS experiments that the scattering intensity will come primarily from the contrast between dPMMA and the other components. Qualitatively similar results are obtained at other $T$ investigated in this work.

![Figure 2.7. Pressure-dependence of SLD.](image)

SLD of dPMMA, SAN ($w_{AN} = 0.26$), and sc$CO_2$ as a function of $P$, at $T = 40 \degree C$, for $7.4 \text{ MPa} \leq P \leq 40$. 
3 Thermodynamic Interactions and Phase Behavior of scCO$_2$ – SAN – dPMMA Multicomponent Mixtures†

ABSTRACT

Quantitative analysis of small-angle neutron scattering data from homogenous multicomponent mixtures of scCO$_2$, SAN, and dPMMA was performed for the first time. Homogeneous ternary mixtures phase separated as $P$ was increased at constant $T$. Phase separation pressure $P_s$ was a non-monotonic function of $T$ with a minimum at $T = 60$ °C. A formalism of the multicomponent RPA was derived to obtain a simple expression to describe SANS profiles. The scCO$_2$-free binary blend was studied to determine the $T$-dependence of the polymer-polymer interaction parameter. scCO$_2$ uptake data for each polymer was used to relate scCO$_2$-polymer interaction parameters in the multicomponent blend. Comparisons between SANS profiles from multicomponent mixtures and the RPA expression provided an estimate of the interaction parameter between scCO$_2$ and SAN ($\chi_{12}$) and scCO$_2$ and dPMMA ($\chi_{13}$). $\chi_{12}$ and $\chi_{13}$ follow complicated behavior with respect to $T$ and $P$ but are shown to collapse onto a straight line when plotted as a function of $\rho_{\text{CO}_2}$.

3.1 Introduction

The goal of this work is to use SANS to quantify the thermodynamic interactions in ternary mixtures of scCO$_2$, SAN and dPMMA. We probed the pairwise interactions of these components using model polymers to obtain robust thermodynamic parameters. By combining the RPA theory for multicomponent mixtures of polymers with information on the solubility of scCO$_2$ in both neat SAN and PMMA, we obtained quantitative understanding of the thermodynamics of these multicomponent mixtures, and demonstrated the ability to adjust the limits of the homogeneous phase window drastically.

3.2 Materials and Experimental Methods

The work described in this chapter utilized the materials and methods described in Chapter 2. Specifically, experiments were performed using the polymers dPMMA185 and SAN74(26), for which the characteristics are listed in Table 2.1 and Table 2.2, respectively.

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†Adapted with permission from Macromolecules 2013, 46, 6345-6356. Sebnem Inceoglu, Nicholas P. Young, Andrew J. Jackson, Steven R. Kline, Stéphane Costeux, Nitash P. Balsara, “Effect of Supercritical Carbon Dioxide on the Thermodynamics of Model Blends of Styrene-Acrylonitrile Copolymer and Poly(methyl methacrylate) Studied by Small-Angle Neutron Scattering.” Copyright 2013 American Chemical Society.
3.3 Theory of Scattering from Homogeneous Mixtures

RPA theory has been used extensively to analyze the coherent scattering intensity, \( I(q) \), from a homogeneous mixture of polymers, with and without small molecule diluents. [43] The most general form of the expression is given by equation 21: [44]

\[
I(q) = B^T S(q) B
\]

(21)

For our system with three components, the multicomponent structure factor \( S(q) \) is a 2 by 2 matrix with elements \( S_{ij} \) that describe the correlations between components \( i \) and \( j \). Component 3, which we arbitrarily define as dPMMA, is considered the “background” component. The correlations between the other components (i.e., scCO\(_2\) and SAN) and dPMMA are thus the source of the scattering intensity measured experimentally. Elements of the column vector \( B \), which quantifies the scattering contrast between components, are the neutron scattering contrast \( B_{ij} \), defined in equation 19. The definition of matrix \( S(q) \), illustrates the additive contributions of correlations in the absence and presence of interactions:

\[
S(q) = \left[ S^*(q)^{-1} + V(q) \right]^{-1}
\]

(22)

The ideal structure factor matrix, \( S^*(q) \), contains information on the correlations between components in the absence of thermodynamic interactions. The matrix consists of the following elements:

\[
S^*_{ii}(q) = N_i \phi_i P_i(q) \quad (i = 1, 2)
\]

(23)

\[
S^*_{ij}(q) = 0 \quad (i \neq j)
\]

(24)

Correlations between monomers along a given chain are represented by the partial structure factor \( S^*_{ii}(q) \), which is based on the single-component form factor for each component of the mixture as given by the Debye function for flexible chains:

\[
P_i(q) = \frac{2}{u_i^2 \left[ \exp(-u_i) + u_i - 1 \right]}
\]

(25)

where \( u_i = q^2 \cdot (R_{gi})^2 \) and the radius of gyration for a chain of species \( i \) is \( R_{gi} = N_i \cdot l_i / 6^{1/2} \). \( N_1 \) is taken to be unity, and \( P_i(q) = 1 \) at all values of \( q \) due to the lack of connectivity between the scCO\(_2\) molecules. The interaction matrix \( V(q) \) is given by:
Equations 21 – 27 are derived on the assumption that $\delta \phi_1(r) + \delta \phi_2(r) + \delta \phi_3(r) = 0$ at each $T$ and $P$ ($r$ is an arbitrary position in the blend and $\delta \phi(r)$ is the local fluctuation in the volume fraction of component $i$ at $r$). RPA expressions derived under this assumption are sometimes called “incompressible” RPA. It is routine to employ this assumption in analysis of SANS data at atmospheric pressure. In reference, it has been argued that the validity of this assumption increases with increasing pressure. [45] We use RPA expressions to analyze our data regardless of $T$ and $P$. SANS profiles as a function of $T$ and $P$ from single-phase binary (SAN and dPMMA) and multicomponent (scCO$_2$, SAN, and dPMMA) mixtures were used to obtain $\chi_{ij}$ and $l_i$ by performing non-linear least-squares fits of the RPA expression. Rather than fitting the data by varying $l_2$ and $l_3$ independently, a multiplicative constant $\alpha$ is used to adjust both simultaneously: [45, 46]

$$l_i(T, P) = \alpha_i(T, P) \chi_{i, \text{ref}} (i = 2, 3)$$

Thus $\alpha$ can be considered an average expansion factor for SAN and dPMMA that quantifies the effect of $T$ and $P$ on chain configuration.

Combining equations 21 – 27 yields the primary result of this section: the expression for $I(q)$ for the multicomponent mixtures of interest:

$$I(q) = B_1^2 S_{11}(q) + 2B_1B_2 S_{12}(q) + B_2^2 S_{22}(q)$$

$$S_{11}(q) = \frac{1}{S_{22}^0 + V_{22}}$$

$$S_{22}(q) = \frac{1}{S_{11}^0 + V_{11}}$$

$$S_{11}(q) = \left( \frac{1}{S_{11}^0 + V_{11}} \right) \cdot \left( \frac{1}{S_{22}^0 + V_{22}} \right) - V_{12}^2$$

$$S_{22}(q) = \left( \frac{1}{S_{11}^0 + V_{11}} \right) \cdot \left( \frac{1}{S_{22}^0 + V_{22}} \right) - V_{12}^2$$
\[
S_{12}(q) = \frac{-V_{12}}{\left( \frac{1}{S_{11}^0} + V_{11} \right) \cdot \left( \frac{1}{S_{22}^0} + V_{22} \right) - V_{12}^2} \quad (32)
\]

It is implicit in equations 21 – 27 that the free energy of mixing per unit volume \(\Delta G_m\) for a mixture of a diluent (component 1) and two polymers (components 2 and 3) is given by the Flory-Huggins Theory, modified from the multicomponent formalism in equation (8):

\[
\frac{\Delta G_m}{k_B T} = \frac{\phi_1 \ln \phi_1}{v_1} + \frac{\phi_2 \ln \phi_2}{v_2 N_2} + \frac{\phi_3 \ln \phi_3}{v_3 N_3} + \frac{\chi_{12} \phi_1 \phi_2}{v_0} + \frac{\chi_{13} \phi_1 \phi_3}{v_0} + \frac{\chi_{23} \phi_2 \phi_3}{v_0} \quad (33)
\]

Expressions for \(\Delta G_m\) for a scCO\(_2\)/polymer mixture can be obtained from equation (33 setting either \(\phi_2\) or \(\phi_3\) = 0. The expression thus obtained is:

\[
\frac{\Delta G_{m,1-i}}{k_B T} = \frac{\phi_{1-i} \ln \phi_{1-i}}{v_1} + \frac{(1 - \phi_{1-i}) \ln(1 - \phi_{1-i})}{v_i N_i} + \frac{\chi_{1i} \phi_{1-i} (1 - \phi_{1-i})}{v_0} \quad (34)
\]

The subscript 1\(-i\) refers to either of the two scCO\(_2\)-polymer binary mixtures, and \(\phi_{1-i}\) is the volume fraction of scCO\(_2\) in the binary mixture. The chemical potential of scCO\(_2\), \(\mu_{1-i}\), in these binary mixtures is given by:

\[
\frac{\Delta \mu_{1-i}}{RT} = \chi_{1i} (1 - \phi_{1-i})^2 + \frac{v_0}{v_1} \ln(\phi_{1-i}) + (1 - \phi_{1-i}) \left( \frac{v_0}{v_1} \cdot \frac{v_0}{v_i N_i} \right) \quad (35)
\]

\(\Delta \mu_{1-i}\) is defined as the difference between \(\mu_{1-i}(T, P)\) and \(\mu_{1-i}^\circ(T, P)\), where \(\mu_{1-i}^\circ(T, P)\) is the chemical potential of the pure CO\(_2\) at the \(T\) and \(P\) of interest, and \(R\) is the ideal gas constant.

In the limit \(\phi_3 \to 0\), equations 21 – 27 reduce to the standard RPA expression for binary polymer blends:

\[
I(q) = I_{bon}(q) = \left( \frac{b_2}{v_2} - \frac{b_3}{v_3} \right)^2 \left( \frac{1}{S_{22}^0(q)} + \frac{1}{S_{33}^0(q)} - \frac{2 \chi_{23}}{v_0} \right) \quad (36)
\]

This expression was used to analyze scattering from the scCO\(_2\)-free blends to determine the temperature dependence of \(\chi_{23}\).
3.4 Small-angle Neutron Scattering of scCO₂-free Blends

Small-angle neutron scattering profiles obtained from a blend of SAN74(26) and dPMMA185 with φ₃ = 0.461 at atmospheric P (in the absence of scCO₂) are shown in Figure 3.1, where I(q) vs. q is presented as a function of T. Over the entire T range studied, the scattering profiles have the shape expected for homogeneous polymer blends, with a plateau at low q. The T = 60 °C data were acquired using the high-P configuration with a narrower q window. The low q intensity increases with increasing T. This indicates that the miscibility decreases with increasing T. The solid lines in Figure 3.1 are fits of binary polymer blend RPA (equation (36). It is evident that the SANS profiles are in quantitative agreement with binary RPA. The data at T = 140 °C (i.e., T_ref) were fit with χ₂₃ and l₂ as adjustable parameters as we were unable to find the statistical segment length of any SAN copolymer in the literature. The value of l₂ thus obtained was 0.83 nm. The T = 100 °C and T = 120 °C data were fit with χ₂₃ and α as fitting parameters. The fitted value of α at these T was found to be 0.997 ± 0.005. This implies that chain configurations are not affected by T in this regime.

The values of χ₂₃ obtained in the range 100 ≤ T ≤ 140 °C are shown by filled symbols in Figure 3.2. We use the usual empirical function to describe the T-dependence of χ₂₃:

\[
\chi = C + \frac{D}{T}
\]

where C and D are fitting parameters. A least-squares fit gives the line in Figure 3.2, χ₂₃ = 0.0920 – 39.622 / T. The dashed line in Figure 3.2 is an extrapolation of equation 37 to T = 60 °C. The empty circle in Figure 3.2 shows χ₂₃ obtained from the SANS fit at this value of T. Note that T_g of the blend (113 °C) is substantially higher than 60 °C. We thus expect that this sample was not well-equilibrated. In spite of this, we find that extrapolations of χ₂₃ based on data obtained at higher T are not too different from the explicit measurement at 60 °C. The value of α obtained at T = 60 °C was 1.27. It thus appears that the main effect of the departure from equilibrium is coil expansion, where the chains are kinetically trapped in a swollen state during sample preparation. Our analysis of the binary data ignores the possibility that the data at T = 100 °C may be affected by non-equilibrium effects as T_g of the blend is slightly higher. It is important to note that the plasticization of polymers by scCO₂ is a well-studied phenomenon, even in polymers for which scCO₂ is not a good solvent. [47] We assume that scCO₂ acts to reduce the T₉ of the polymers in our blends and validates the extrapolation of equation 37 into the T-range of interest.
Figure 3.1. Temperature-dependent SANS data for scCO$_2$-free SAN74(26)/dPMMA185 blend. Small-angle neutron scattering results from a blend of dPMMA185 and SAN74(26) studied as a function of $T$. The blend contained 46.1% dPMMA185 by volume. The scattering experiments were performed at $T = 60 \, ^\circ C$ (red circles), $100 \, ^\circ C$ (blue squares), $120 \, ^\circ C$ (green triangles), and $140 \, ^\circ C$ (orange inverted triangles). The solid lines are binary random phase approximation fits to the data with the Flory-Huggins interaction parameter, $\chi_{2,3}$, and $\alpha$, the average expansion factor, as adjustable parameters. The error on the SANS data points, in terms of one standard deviation in the measured intensity, are within the size of the data symbols.
Figure 3.2. Temperature-dependent $\chi_{23}$ between SAN74(26) and dPMMA185. Flory-Huggins interaction parameter between SAN74(26) and dPMMA185, $\chi_{23}$, as a function of $1 / T$ obtained from random phase approximation fits for a blend containing 46.1% dPMMA185 by volume. The data is fit by least-squared linear regression over the range of $100 \, ^\circ C \leq T \leq 140 \, ^\circ C$ to obtain the expression $\chi_{23} = 0.0920 - 39.622 / T$, shown as solid black line. The dashed line is the extrapolation of $\chi_{23}(T)$ to $60 \, ^\circ C$, to illustrate that the data collected at that $T$ is close to high $T$ extrapolation, despite being well below $T_g$.

The SANS data are presented in the form of a Zimm plot in Figure 3.3a, using the truncated range $0.133 \, \text{nm}^{-1} < q < 0.250 \, \text{nm}^{-1}$. It is evident that the data can be fit with reasonable success to linear expressions, as represented by solid lines in Figure 3.3a. Extrapolation of these fits to $q = 0 \, \text{nm}^{-1}$ yields values of $I_{0,Zimm}$ over the $T$ range studied. In addition, the RPA fits to the data were extrapolated to $q = 0$ to obtain $I(q = 0) = I_{0,RPA}$. In Figure 3.3b, we plot both $1 / I_{0,Zimm}$ and $1 / I_{0,RPA}$ versus $1 / T$. It is evident that both $1 / I_{0,Zimm}$ and $1 / I_{0,RPA}$ are linear functions of $1 / T$. (The $T = 60 \, ^\circ C$ data showed as unfilled symbols in Figure 3.3b were not included in the fit.) Estimates of the blend phase separation $T_s$ are obtained by extrapolating the lines in Figure 3.3b to meet the abscissa. The Zimm analysis predicts $T_s = 160 \pm 10 \, ^\circ C$ while the RPA analysis predicts $T_s = 160 \pm 30 \, ^\circ C$. These values are in reasonable agreement with each other, providing an estimated value of $T_s = 160 \pm 40 \, ^\circ C$. Concerns about polymer degradation prevented us from conducting experiments near $T_s$. 
Figure 3.3. (a) $1/I$ vs. $q^2$ for SAN74(26)/dPMMA185 SANS data and (b) determination of $T_s$.

(a) Reciprocal of the absolute scattering intensity, $1/I$, plotted against $q^2$, for a blend containing 46.1% dPMMA185 by volume as a function of $T$ at ambient $P$. The scattering experiments were performed at $T = 60 \, ^\circ C$ (red circles), $100 \, ^\circ C$ (blue squares), $120 \, ^\circ C$ (green triangles), and $140 \, ^\circ C$ (orange inverted triangles). Least-squared linear fits to the data are shown with solid lines. (b) Comparison of the plots of $1/I_0$ versus $1/T$, obtained from Zimm plots (red circles) and RPA (blue squares), where $I_0$ is the SANS intensity as $q$ approaches $0 \, \text{nm}^{-1}$. The data is fit with a least-squares linear regression to find $T$ at which $I_0$ diverges (i.e., $1/I_0 = 0$). This provides an estimate of the phase separation temperature, $T_s$; $T_s = 160 \, ^\circ C$ for the Zimm method and $T_s = 170 \, ^\circ C$ for the RPA method. Open symbols represent experiments performed at $T = 60 \, ^\circ C$ (not included in the fit).
3.5 Small-angle Neutron Scattering of scCO2/SAN74(26)/dPMMA185 Blends

Small-angle neutron scattering experiments of the multicomponent mixture containing scCO2, SAN74(26), and dPMMA185 were carried out according to the procedure outlined in Chapter 2. Figure 3.4 shows $I(q)$ obtained from a blend of scCO2/SAN74(26)/dPMMA185 with $\phi_{3,0} = 0.461$ (i.e., in the absence of scCO2) at $T = 40 \, ^\circ\text{C}$ as a function of $P$ in the range $9.7 \, \text{MPa} \leq P \leq 27.6 \, \text{MPa}$. The scattering profiles are qualitatively similar to the binary scattering profiles shown in Figure 3.1. It is evident that the low $q$ plateau obtained in the multicomponent blends increases with increasing $P$. This indicates approach toward macrophase separation with increasing $P$. SANS profiles obtained at $P = 31 \, \text{MPa}$ were strong functions of time, and qualitatively different from those shown in Figure 3.4.

![Figure 3.4. SANS data of scCO2/SAN74(26)/dPMMA185 as a function of $P$ at $T = 40 \, ^\circ\text{C}$.](image)

Small-angle neutron scattering results for the blend of scCO2/SAN74(26)/dPMMA185 ($\phi_{3,0} = 0.461$) at $T = 40 \, ^\circ\text{C}$ as a function of $P$. The scattering experiments were performed at $P = 9.7 \, \text{MPa}$ (red circles), 12.4 MPa (blue squares), 17.2 MPa (green triangles), 20.7 MPa (orange inverted triangles), 24.1 MPa (purple diamonds), and 27.6 MPa (brown rhombi). The solid lines are multicomponent random phase approximation fits to the data with $\chi_{13}$ and $\alpha$ as adjustable parameters. The error on the SANS data points, in terms of one standard deviation in the measured intensity, are within the size of the data symbols.

We used the multicomponent RPA to analyze the SANS data shown in Figure 3.4, combined with the scCO2-polymer solubility data in Figure 2.6. At a given $T$ and $P$, scCO2/SAN and scCO2/PMMA mixtures with $w_{1,2}$ and $w_{1,3}$, respectively, are in thermodynamic equilibrium with pure scCO2 filling the sample cell volume at the same $T$ and $P$. Thus the chemical potential of scCO2 in the two mixtures $\mu_{1,i}$ must be equal. We use the expression for $\mu_{1,i}$ from FHT (equation 35) to derive an expression that relates $\chi_{13}$ to $\chi_{12}$ based on this equality:
\[ \chi_{12} = \frac{1}{(1 - \phi_{1-2})^2} \cdot \left[ \chi_{13} \cdot (1 - \phi_{1-3})^2 + \frac{v_0}{v_1} \ln \frac{\phi_{1-3}}{\phi_{1-2}} + (1 - \phi_{1-3}) \cdot \left( \frac{v_0}{v_1} - \frac{v_0}{N_3v_3} \right) - (1 - \phi_{1-2}) \cdot \left( \frac{v_0}{v_1} - \frac{v_0}{N_2v_2} \right) \right] \]  

(38)

where \( \phi_{1-3} \) is calculated from \( w_{1-3} \) and \( v_1(T,P) \). The \( P \)-dependence of \( v_1 \), determined from the \( P-\rho-T \) data in Figure 1.3, is shown in Figure 3.5 for experimentally-relevant values of \( T \).

**Figure 3.5.** \( v_1 \) as a function of \( P \) at experimental \( T \).

Molecular volume of scCO\(_2\), \( v_1 \), determined from \( P-\rho-T \) data by the relation \( v = M_0 / \rho \). The dependence of \( v_1 \) on \( P \) and \( T \) is given in the experimentally-relevant range: \( 7.4 \text{ MPa} \leq P \leq 40 \text{ MPa} \) and \( 35^\circ\text{C} \leq T \leq 100^\circ\text{C} \).

It is evident from equation 38 that \( \chi_{12} \) at a given value of \( T \) and \( P \) is constrained to be a linear function of \( \chi_{13} \) (that is, \( \chi_{12} = A_1 \cdot \chi_{13} + A_2 \), where \( A_1 \) and \( A_2 \) are constants at each \( T \) and \( P \)), which can be calculated *a priori*. Figure 3.6 shows this function at \( T = 40^\circ\text{C} \) at the lowest and highest values of \( P \) considered at that value of \( T \). The \( A_1 \) and \( A_2 \) coefficients used to analyze that set of isothermal data are summarized in Table 3.1.
Figure 3.6. Relationship between $\chi_{12}$ and $\chi_{13}$ at $T = 40$ °C for $P = 9.7$ MPa and 27.6 MPa. Representative linear relationships between $\chi_{12}$ and $\chi_{13}$ obtained from equating chemical potential of scCO$_2$ in the binary scCO$_2$-polymer mixtures. The red line shows the relationship for the lowest $P$ studied in the isothermal P-scan at $T = 40$ °C, $P = 9.7$ MPa, while the orange line shows the relationship for the highest $P$ studied at this $T$ for which a homogeneous mixture was obtained ($P = 27.6$ MPa).

Table 3.1. Pressure-dependent Coefficients for Relationship Between $\chi_{12}$ and $\chi_{13}$ at $T = 40$ °C.  

<table>
<thead>
<tr>
<th>$P$ (MPa)</th>
<th>$A_1$</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.7</td>
<td>0.757</td>
<td>0.376</td>
</tr>
<tr>
<td>12.4</td>
<td>0.768</td>
<td>0.472</td>
</tr>
<tr>
<td>17.2</td>
<td>0.763</td>
<td>0.539</td>
</tr>
<tr>
<td>20.7</td>
<td>0.764</td>
<td>0.554</td>
</tr>
<tr>
<td>24.1</td>
<td>0.760</td>
<td>0.581</td>
</tr>
<tr>
<td>27.6</td>
<td>0.759</td>
<td>0.586</td>
</tr>
</tbody>
</table>

For the multicomponent mixture, there are three pair-wise interaction parameters, as seen in equation 27. $\chi_{23}$ is known as a function of $T$ (equation 37) and $P$ (assumed to have negligible dependence in the range of interest). It was shown above that $\chi_{12}$ is constrained to linear relationship with $\chi_{13}$. Thus, there is a single independent interaction parameter to be obtained from fitting SANS data with equations 21 – 27. The solid curves in Figure 3.4 represent multicomponent RPA fits using with two adjustable parameters: $\chi_{13}$ and $\alpha$. All other parameters required to calculate $I(q)$ were determined $a$ priori. $\phi_1$ was estimated using the solubility data shown in Figure 2.6. If we assume the volume change of mixing is negligible, then the total scCO$_2$ volume fraction can be calculated directly using the binary solubility data ($w_{1,i}$) along
with the pure component monomer and molecular volumes. The dependence of $\phi_1$ on $P$ thus obtained is shown in Figure 3.7. At low $P$, the change in $\phi_1$ is dominated by changes in the molar volume of scCO$_2$ in the vicinity of the critical point of CO$_2$. Increasing $P$ in this regime results in a sharp reduction of $\phi_1$. In contrast, a gradual increase in $\phi_1$ is seen at elevated $P$ due to the increased solubility of scCO$_2$ in both polymers.

![Figure 3.7. P- and T-dependence of $\phi_1$ in SAN74(26)/dPMMA185 ($\phi_{3,0} = 0.461$). Predicted volume fraction of scCO$_2$ ($\phi_1$) at experimentally-relevant $T$ in a blend of SAN77(26) and dPMMA125 containing $\phi_{3,0} = 0.461$ (scCO$_2$-free volume fraction) as a function of $P$ under the assumption of no volume change of mixing for scCO$_2$ between the binary and multicomponent blends.](image)

Having quantified all variables in the RPA expressions with the exception of the scCO$_2$-polymer interaction parameters, it is possible to calculate the theoretical scattering profiles as a function of the fit parameter $\chi_{13}$. In Figure 3.8 we plot $I_{0,RPA}$ calculated using equations 21 – 27 as a function of $\chi_{13}$ at $T = 40$ °C and $P = 9.7$ MPa. For each value of $\chi_{13}$, a corresponding value of $\chi_{12}$ was calculated according to equation (38. The range of $\chi_{13}$ is restricted to include positive $I_{0,RPA}$ values only. It is clear that $I_{0,RPA}$ is a non-monotonic function of $\chi_{13}$ and that $I_{0,RPA}$ diverges as $\chi_{13}$ approaches both -0.9 and 1.52. The horizontal line in Figure 3.8 represents the value of $I_0$ obtained from the experiments using the Zimm extrapolation, $I_{0,data}$. This line intersects the $I_{0,RPA}$ vs $\chi_{13}$ curve at two points: $\chi_{13} = 0.269$ and $\chi_{13} = 1.499$. Both of these values of $\chi_{13}$ produce RPA curves that are consistent with the SANS profiles. To determine the validity of these results, we consider the physics of the mixture. A good solvent for a polymer is identified by a value of $\chi \leq 0.5$. We know experimentally that scCO$_2$ is not a good solvent for dPMMA (or SAN): in all cases scCO$_2$ merely swells the polymer film, but shows no signature of dissolving the polymers in the conditions studied here. We can thus eliminate the value of $\chi_{13} = 0.269$ on these physical grounds. We conclude that $\chi_{13}$ is 1.499, and equation (38 gives $\chi_{12} = 1.512$. 

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Figure 3.8. Determination of $\chi_{13}$ from loci of $I_{0,RPA}(\chi_{13}) = I_{0,\text{data}}$.

Values of the SANS intensity extrapolated to $q = 0$ nm$^{-1}$, $I_0$, predicted by multicomponent RPA expressions ($I_{0,RPA}$) are shown as a function of the single independent interaction parameter, $\chi_{13}$, for $T = 40$ °C and $P = 9.7$ MPa. The experimentally-determined value of $I_0$ ($I_{0,\text{data}}$), obtained by Zimm-style ($1/I$ vs $q^2$) extrapolation of the data, is shown as a horizontal line. The values of $\chi_{13}$ which meet the condition of $I_{0,RPA} = I_{0,\text{data}}$ (i.e. $\chi_{13} = 0.269$ and $1.499$) are both consistent with the experimental results.

SANS data for the system of scCO$_2$/SAN74(26)/dPMMA185 blends with $\phi_{3,0} = 0.461$ was collected and analyzed for isothermal $P$-scans at $T = 35$, 60, 80, and 100 °C in an analogous manner to that described in Figure 3.4. The data, along with RPA fits, are presented in Figure 3.9. In all cases it is evident that the formalism described is able to successfully describe the data. This is somewhat surprising, since the range of conditions probed in this work varies over a large range of $T$ and $P$, and thus scCO$_2$ characteristics. In the low-$\rho_{\text{CO}_2}$ limit, data were collected quite close to the critical point of CO$_2$ (lowest $T_r = T / T_{c,\text{CO}_2} = 1.013$ and lowest $P_r = P / P_{c} = 1.027$), where the magnitude of density fluctuations are known to diverge. [48] It might be expected that the presence of these large fluctuations could anomalously increase the measured $I(q)$. However, null experiments performed with the sample cell containing only scCO$_2$ (i.e., in the absence of a polymer film) showed negligible scattering intensity compared to that measured from the multicomponent blend. Meanwhile, in the high-$\rho_{\text{CO}_2}$ limit, scCO$_2$ takes on liquid-like properties and the magnitude of density fluctuations is relatively small. In this regime, the scattering data clearly showed the transition from homogeneous mixtures to phase separated mixtures expected for phase separation of polymers, as evidence by low-$q$ scattering approaching divergence and time-dependent scattering profiles. Thus at all conditions probed where homogeneous mixtures were found, the RPA formalism developed satisfactorily describes the data.
Figure 3.9. SANS data for scCO$_2$/SAN74(26)/dPMMA185 blend ($\phi_{3,0} = 0.461$) in isothermal P-scans at $T = 35$, 60, 80, and 100 °C.

Small-angle neutron scattering results for the blend of scCO$_2$/SAN74(26)/dPMMA185 ($\phi_{3,0} = 0.461$) at $T = 35$ °C (a), 60 °C (b), 80 °C (c), and 100 °C (d) as a function of $P$. The values of $P$ for each scattering profile are indicated in the legends. The solid lines are multicomponent random phase approximation fits to the data with $\chi_{12}$ and $\alpha$ as adjustable parameters. Error bars on the SANS data represent one standard deviation in the measured intensity are within the size of the data symbols.

The results obtained from RPA fits to the scattering data shown in Figure 3.4 and Figure 3.9 are summarized in Figure 3.10, where $\chi_{12}$ and $\chi_{13}$ are shown as a function of $P$ for the temperatures studied in isothermal P-scans. The data fall into two regimes: a low-$T$ regime $T \leq 40$ °C in the vicinity of $T_{c,CO_2}$ and a second farther away from critical temperature, $T \geq 60$ °C. In
the low-\(T\) regime, \(\chi_{13}\) increases monotonically with \(P\), asymptotically approaching a plateau value of about 2.4. Conversely, in the high-\(T\) regime, \(\chi_{13}\) goes through a minimum (\(\chi_{12}\) and \(\chi_{13} \approx 0.3\) near \(P = 9\) MPa for \(60\) °C \(\leq T \leq 100\) °C) before increasing toward the plateau value. Data ranges in Figure 3.10 are limited by the location of the phase boundary, since \(\chi_{13}\) can only be determined for homogeneous mixtures where the RPA applies.

**Figure 3.10.** \(P\)-dependence of \(\chi_{12}\) and \(\chi_{13}\) obtained from RPA fits of SANS data. Pair-wise interaction parameter for scCO\(_2\) and SAN74(26), \(\chi_{12}\), and scCO\(_2\) and dPMMA185, \(\chi_{13}\), obtained from scattering profiles of the multicomponent mixture, as a function of \(P\), at all
experimentally-relevant $T$: 35 °C (red circles), 40 °C (blue squares), 60 °C (green up-triangles), 80 °C (yellow down-triangles), 100 °C (purple diamonds). 1 = scCO$_2$, 2 = SAN, and 3 = dPMMA. Solid lines are provided to guide the eye. The error bars for each value of $\chi_{13}$, representing one standard deviation in the measured value, are within the size of the data symbols in this figure.

It is evident from Figure 3.10 that $\chi_{12}$ and $\chi_{13}$ follow the same complex trends with $T$ and $P$. In Figure 3.11, the difference between scCO$_2$-polymer interaction parameters, $\chi_{13} - \chi_{12}$, is plotted as a function of $P$ for all experimental $T$. For nearly all $T$ and $P$ considered, $\chi_{13} - \chi_{12}$ is small and negative, indicating that dPMMA has slightly more favorable interactions with scCO$_2$ than SAN. The exception to this condition is found for $P < 8.96$ MPa, particularly in the range $40 \degree C \leq T \leq 60 \degree C$, where near $\chi_{13} - \chi_{12}$ is relatively large and positive. We do not have an explanation for this observation.

Figure 3.11. $P$-dependence of the difference $\chi_{13} - \chi_{12}$ obtained from SANS data. The difference in scCO$_2$-polymer interaction parameters, $\chi_{13} - \chi_{12}$, plotted as a function of $P$, at all experimental $T$: 35 °C (red circles), 40 °C (blue squares), 60 °C (green up-triangles), 80 °C (yellow down-triangles), and 100 °C (purple diamonds). 1 = scCO$_2$, 2 = SAN, and 3 = dPMMA.

Although the dependence of $\chi_{12}$ and $\chi_{13}$ on $P$ raises interesting questions into the nature of interactions, $P$ is really only a proxy for scCO$_2$ levels in the sample cell and a convenient experimental handle. For compression applied by a fluid, density is a more accurate measure of the condition of the system, especially in the case of supercritical fluids which experience significant variation in $\rho_{CO_2}$ in the near-critical regime. Figure 3.12 shows plots of $\chi_{12}$ and $\chi_{13}$ against $\rho_{CO_2}$ using the $P$-$\rho$-$T$ data of Span and Wagner. [12] The data appear to collapse onto a straight line. Least-squares fits to the data yields the following relationships:

$$\chi_{12} = 0.00279 \cdot \rho_{CO_2} - 0.0990 \quad (39)$$
\[ \chi_{13} = 0.00274 \cdot \rho_{\text{CO}_2} - 0.0753 \]  

While there is a strong correlation between \( \rho_{\text{CO}_2} \) and both \( \chi_{12} \) and \( \chi_{13} \), it is unlikely that density alone determines the thermodynamic interactions between sc\( \text{CO}_2 \) and the polymers of interest. Note that miscibility is greater (i.e. \( \chi_{13} \) is lower) when sc\( \text{CO}_2 \) has gas-like densities. This is somewhat counterintuitive, since solubility increases monotonically with \( P \) (and with \( \rho_{\text{CO}_2} \)). It is likely that the measured interactions account for interplay between molecular interactions as well as the unique features of \( \text{CO}_2 \) in the supercritical regime, including density fluctuations.
Figure 3.12. $\rho_{CO_2}$-dependence of $\chi_{12}$ and $\chi_{13}$ obtained from RPA fits of SANS data. scCO$_2$/dPMMA185 interaction parameter $\chi_{12}$ (a) and scCO$_2$/SAN74(26) interaction parameter $\chi_{13}$ (b) plotted as a function of $\rho_{CO_2}$, at all experimental $T$: 35 °C (red circles), 40 °C (blue squares), 60 °C (green up-triangles), 80 °C (yellow down-triangles), 100 °C (purple diamonds). The solid lines are least-squares linear fits to the full data sets, yielding the relationships $\chi_{13} = 0.00274 \cdot \rho_{CO_2} - 0.0753$ and $\chi_{12} = 0.00279 \cdot \rho_{CO_2} - 0.0990$.

In the literature, $\chi$ parameters are often plotted as a function of inverse $T$. In Figure 3.13a, we plot $\chi_{13}$ against $1000 / T$ over the range $9 \text{ MPa} \leq P \leq 22 \text{ MPa}$. At $P = 9 \text{ MPa}$, there
appear to be two regimes: $\chi_{13}$ is roughly independent of $T$ for $T \geq 60^\circ C$ but increases linearly with $1000 / T$ for $T > 60^\circ C$. The latter dependence is typically observed in polymer/polymer and polymer/solvent systems. As $P$ increases, the distinction between the two regimes becomes less pronounced. At high $P$, $\chi_{13}$ appears to be approximately a linear function of $1000 / T$. (Missing data in Figure 3.13 are due to phase separation.) $\chi_{13}$ vs. $1000 / T$ plots at $P$ below 9 MPa are much more complex and thus shown separately in Figure 3.13b. At $P$ very close to $P_{c,CO_2}$, there appear to be three separate regimes. The general trend of $\chi_{13}$ increasing with inverse $T$ is intriguing, since it suggests that miscibility is improved as $T$ increases. This contrasts with the trends in solubility, with show decreasing uptake of scCO$_2$ by each polymer at elevated $T$. 
Figure 3.13. $T$-dependence of $\chi_{13}$ at constant $P$ from RPA fits of SANS data. (a) scCO$_2$-PMMA185 interaction parameter $\chi_{13}$ plotted vs. $1000 / T$ at constant $P$, over the range $9 \text{ MPa} \leq P \leq 22 \text{ MPa}$. Solid lines are provided to guide the eye. Dashed lines cover the region where the mixture at $60$ °C has undergone macrophase separation ($P > 11.5 \text{ MPa}$). (b) scCO$_2$-PMMA185 interaction parameter $\chi_{13}$ plotted vs. $1000 / T$ at constant $P$, over the range $7.4 \text{ MPa} \leq P \leq 9 \text{ MPa}$. Solid lines are provided to guide the eye.
3.6 Effect of Density Fluctuations on scCO$_2$-Polymer Interactions

The reason for the behaviors seen in Figures 3.10 – 3.13 is not obvious. Although complex phase behavior in the presence of scCO$_2$ is reported widely in the literature, there have been relatively few attempts to explain observations in terms of underlying intermolecular interactions. In an important study, Koga et al. used neutron reflectivity to investigate the swelling of thin polymer films by scCO$_2$ and found a remarkably similar non-monotonic trend of $\chi_{CO_2-polymer}$ on $P_{CO_2}$ to that reported here in Figure 3.10, albeit at only a single $T$. [49, 50] Those authors attributed the unusual behavior to the dramatic density fluctuations which occur near the critical regime of scCO$_2$ as a result of the “density fluctuation ridge”. As $\rho_{CO_2}$ increases at a given $T$, the density fluctuations of neat scCO$_2$, given by $\langle (\Delta n)^2 \rangle / \langle n \rangle$ where $n$ is the number of molecules in a volume $V$, go through a maximum. The fluctuations of $n$ at a given time is

$$\Delta n = n - \langle n \rangle$$

(41)

where $\langle n \rangle$ is the average value. Taking the average of the squared fluctuations and dividing by the average, the result obtained quantifies the degree of inhomogeneity in molecular distribution. The value of $\langle (\Delta n)^2 \rangle / \langle n \rangle$ can be determined from the thermodynamic relation: [51]

$$\frac{\langle (\Delta n)^2 \rangle}{\langle n \rangle} = \frac{n}{V} \kappa_T k_B T$$

(42)

Here $\kappa_T$ is the isothermal compressibility and $n / V$ is the molecular density, related to $\rho_{CO_2}$. $\kappa_T$ can be determined from $P$-$\rho$-$T$ data by the following relation:

$$\kappa_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T$$

(43)

In Figure 3.14, we plot $\kappa_T$ as a function of $P$ at the experimental $T$ obtained from the data in Figure 1.3, from close to $P_{c, CO_2}$ up to $P = 40$ MPa. The $P$-$\rho$-$T$ data was differentiated numerically by finite differences to obtain the results displayed. There is a clear trend in the dependence of $\kappa_T$ on $P$ moving away from the critical point. As expected, close to the critical point the magnitude of $\kappa_T$ becomes anomalously large. This illustrates an important characteristic of supercritical fluids in general: in the vicinity of the critical point, the compressibility diverges as the free energy of compression reaches a minimum. While the data in Figure 3.14 is limited to experimentally-relevant isotherms for this work, the behavior is only further exacerbated in the limit of $T = T_{c, CO_2}$. As $T$ increases away from $T_{c, CO_2}$, there is a clear trend of damping out the critical phenomenon and the maximum value of $\kappa_T$ at subsequent isotherms drops off and is almost completely absent at $T = 100$ °C. It is also important to note that the location of the maximum in $\kappa_T$ with respect to $P$ is also shifting to higher values as $T$ increases. This provides a hint of the density fluctuation ridge, as it has been noted that many physical quantities related to the second derivative of $G$ go through an extremum along the ridge, including $\kappa_T$. [52] At high $P$, the values of $\kappa_T$ are small and less strongly dependent on $T$ (at $P = 40$ MPa, $\kappa_T = 0.004$ MPa$^{-1}$ at
35 °C, but increases to 0.010 MPa⁻¹ at 100 °C). This is indicative of the departure from the near-critical phenomenon to behavior more akin to that of subcritical fluids.

**Figure 3.14.** $P$-dependence of $\kappa_T$ of scCO$_2$ at experimental $T$.
Pressure-dependence of isothermal conductivity, $\kappa_T$, in the range $35 \leq T \leq 100$ °C. $\kappa_T$ was determined by differentiation of $P$-$\rho$-$T$ data according to equation (43). At each $T$ there is a maximum in $\kappa_T$ which decreases in magnitude and increases in $P$ value as $T$ increases away from $T_{c,CO_2}$.

Using equation (42) we calculate $\langle (\Delta n)^2 \rangle / \langle n \rangle$ as function of $T$ and $P$. These results are shown in Figure 3.15. It is clear that the trends in $\kappa_T$ are reproduced in the $T$- and $P$-dependence of $\langle (\Delta n)^2 \rangle / \langle n \rangle$. Across each isotherm, there is a maximum in $\langle (\Delta n)^2 \rangle / \langle n \rangle$ which decreases in magnitude and increases in $P$ as $T$ increases. It is interesting to note that at high $T$ the occurrence of a peak persists more evidently in $\langle (\Delta n)^2 \rangle / \langle n \rangle$ than in $\kappa_T$, suggesting that the critical phenomenon of density fluctuations persists well away from the critical point. The trends and magnitude of $\langle (\Delta n)^2 \rangle / \langle n \rangle$ are in good agreement with theoretical and experimental findings in the literature. [48, 53]
Figure 3.15. $P$-dependence of $\langle (\Delta n)^2 \rangle / \langle n \rangle$ of scCO$_2$ at experimental $T$.

Pressure-dependence of the density fluctuation magnitude, $\langle (\Delta n)^2 \rangle / \langle n \rangle$, in the range $35 \, ^\circ\text{C} \leq T \leq 100 \, ^\circ\text{C}$. $\langle (\Delta n)^2 \rangle / \langle n \rangle$ was determined according to equation (43). At each $T$ there is a maximum in $\langle (\Delta n)^2 \rangle / \langle n \rangle$ which decreases in magnitude and increases in $P$ value as $T$ increases away from $T_{c,CO_2}$. The locus of the maxima forms the density fluctuation ridge in the supercritical regime of the CO$_2$ phase diagram.

As described with respect to $\kappa_T$, the maximum in $\langle (\Delta n)^2 \rangle / \langle n \rangle$ form a region of unique properties. The locus of these maxima forms a smooth curve, and in the phase diagram of scCO$_2$ are represented by the density fluctuation ridge. [48] While the magnitude of $\langle (\Delta n)^2 \rangle / \langle n \rangle$ decreases along the ridge as $T$ increases, the generality of the feature could influence the observed behavior even at conditions well removed from the regime of critical density fluctuations. In Figure 3.16, we show a schematic phase diagram of CO$_2$ in the subcritical and supercritical regimes near the critical point. Below the critical point ($T_{c,CO_2} = 30.9 \, ^\circ\text{C}$ and $P_{c,CO_2} = 7.38 \, \text{MPa}$), CO$_2$ exists as a liquid at low $T$ and high $P$ and as a gas at high $T$ and low $P$. The vapor line separates these two phases. At $T$ and $P$ above the critical point, CO$_2$ becomes supercritical. At the critical point, the vapor line meets the density fluctuation ridge, which separates the supercritical regime into gas-like (below the ridge) and liquid-like (above the ridge) regions. It is evident from the discussion of $\langle (\Delta n)^2 \rangle / \langle n \rangle$ that the properties of scCO$_2$ are unique in the vicinity of the density fluctuation ridge, even well away from the critical point. This behavior could play an important role in the complex mixing observed between scCO$_2$ and SAN/dPMMA blends.
Figure 3.16. Schematic phase diagram of CO₂.
A schematic phase diagram of carbon dioxide is shown with respect to pressure and temperature in the near-critical region of the phase space. Below the critical point, CO₂ exists as a liquid or gas, and these phases are separated by the vapor line. Above the critical point CO₂ reaches the supercritical regime. At the critical point, the vapor line meets the density fluctuation ridge. Modified from ref [50].

To probe the effect of density fluctuations of scCO₂ on the observed mixture behavior, we can examine an alternative form of the CO₂ phase diagram. In Figure 3.17, we present the phase diagram of Nishikawa, et al. [48] They plot the reduced density $\rho_r = \rho / \rho_c$, where $\rho_c = 467.6 \text{ kg/m}^3$, against $T_r$ in the ranges $0 \leq \rho_r \leq 2.5$ and $0.75 \leq \rho_r \leq 1.3$. This covers the near-critical regime above and below the critical point with respect to $T$, and a large range of $\rho$ in the gas-like and liquid-like regions. In the supercritical regime, representative contour lines demonstrate the variation in the magnitude of density fluctuation in this region. As expected, $\langle (\Delta n)^2 \rangle / \langle n \rangle$ decreases with $T$ at constant $\rho$. In this region, along a given isotherm, there is a clear maximum in $\langle (\Delta n)^2 \rangle / \langle n \rangle$. Connecting these maxima produces the density fluctuation ridge. As $T$ increases, the ridge deviates by an increasing amount from the critical isochore at $\rho_r = 1$. In passing we note that the subcritical regime highlights the coexistence curve for gas and liquid phases, and the middle point of the coexistence curves forms the rectilinear diameter line, which is nearly along the same slope as the density fluctuation ridge, and the two lines meet at the critical point. A final noteworthy observation is that Nishikawa et al. found that these defining features of the phase diagram are in good agreement when comparing CO₂ and trifluoromethane (CF₃H) in spite of the significant differences in the properties of these two substances. Evidence suggests that these are truly general findings across many substances, speaking to the inherent importance of these density fluctuation properties.
Figure 3.17. Comparison of density fluctuation with isothermal experimental trajectories. Phase diagram of supercritical fluids (CO$_2$, solid lines; CF$_3$H, broken lines) in the vicinity of the critical point. Contour lines in the supercritical regime show representative density fluctuation magnitudes. Lines in supercritical regime represent the density fluctuation ridge, connecting the maxima of each contour line. Curve and line in subcritical regime represent the vapor-liquid coexistence and rectilinear diameter, respectively. Arrows represent the trajectories of isothermal $P$-scans used in SANS experiments of scCO$_2$/SAN74(26)/dPMMA185 at the indicated temperatures: 35 °C (red), 40 °C (blue), 60 °C (green), 80 °C (yellow), 100 °C (purple).

Comparing the trajectory of isothermal $P$-scans in Figure 3.17 and the relationship between $\chi_{13}$ and $P$ in Figure 3.10 provides insight into the relationship between $\chi_{13}$ and $\langle (\Delta n)^2 \rangle / \langle n \rangle$. At $T \leq 40$ °C the trajectory spans only the regime above the density fluctuation ridge. As $\rho$ (and $P$) increase, $\chi_{13}$ approaches a plateau, and $\langle (\Delta n)^2 \rangle / \langle n \rangle$ decreases and approaches zero (i.e., minimal fluctuations). At 60 °C, the trajectory begins at low $\langle (\Delta n)^2 \rangle / \langle n \rangle$ and crosses the density fluctuation ridge before phase separating as $\langle (\Delta n)^2 \rangle / \langle n \rangle$ begins to decrease. This is similar to the trend of $\chi_{13}$ which goes through a minimum at intermediate $P$ values in the range covered. Finally, at high $T \geq 80$ °C the trajectory spans the ridge from low $\langle (\Delta n)^2 \rangle / \langle n \rangle$ through a maximum and approaching the region of low $\langle (\Delta n)^2 \rangle / \langle n \rangle$. Again, this trend is in good agreement with that observed for $\chi_{13}$, which appears to go through a minimum before increasing towards the plateau values. While this analysis is qualitative, it is suggestive of a relationship between $\chi_{13}$ and $\langle (\Delta n)^2 \rangle / \langle n \rangle$.

3.7 Application of Lattice Fluid Theory to scCO$_2$/SAN/dPMMA Mixtures

In an attempt to represent the physics of multicomponent system more accurately, including the influence of attractive interactions between polymer chains [28] and the presence of compressible species, [54] we investigated the application of the lattice fluid theory to understand the pair-wise interactions. The lattice fluid theory, commonly called the Sanchez-Lacombe equation of state (SL), was derived to account for the mixture of fluids of arbitrary
geometry and size. [55, 56] Fortuitously, it was found that the SL theory was well-suited to overcome some of the shortcomings of FHT (including the prediction of LCST behavior and ability to account for changes in molecular volume. [57, 58] It accomplished this by account for the pure species equation of state parameters. It was also found to reduce to FHT under certain conditions, making it a successful generalization of the prevailing theory.

In comparison with the picture of a lattice completely filled with solvent molecules or polymer segments (as in Figure 1.1), the SL theory includes the presence of vacant lattice sites. This allows for the variation in size related to density changes of a compressible species. By minimizing the chemical potential to describe equilibrium, the resulting equation of state was found for a pure liquid:

\[
\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[ \ln(1 - \tilde{\rho}) + \left( 1 - \frac{1}{r} \right) \cdot \tilde{\rho} \right] = 0
\]  

(44)

For a given substance, the reduced variables in equation 44 are defined as follows:

\[
\tilde{T} = \frac{T}{T^*}; \quad T^* = \frac{\varepsilon^*}{R}
\]  

(45)

\[
\tilde{P} = \frac{P}{P^*}; \quad P^* = \frac{\varepsilon^*}{v^*}
\]  

(46)

\[
\tilde{\rho} = \frac{\rho}{\rho^*}; \quad \rho^* = \frac{M_w \cdot P^*}{R \cdot T^* \cdot r}
\]  

(47)

In equations 45 – 47, \(\varepsilon^*, v^*,\) and \(r\) are characteristic parameters which can be interpreted as interaction energy per mer, close-packed volume per mer, and the number of lattice sites occupied by a molecule with molecular weight \(M_w\), respectively.

The characteristic parameters are known for a variety of substances, primarily from \(P-T\) data, and are summarized in Table 3.2. A variety of sets of parameters exist for CO\(_2\). The particular choice made in this work was based on validity of \(T_c\) estimation made by the data set. [59] Parameters for SAN copolymers have been published as a function of composition in the range \(0.02 \leq w_{AN} \leq 0.70\), and that data is interpolated to obtain the values used here. [60] PMMA parameters in the literature are in good agreement and are used as reported. [57] This provides a good heuristic for determining SL characteristic parameters in general. The critical point based on the characteristic parameters is given by:
\[
\tilde{\rho}_c = \frac{1}{1 + r^{1/2}}
\]  
\[
\tilde{T}_c = 2\tilde{r}^2
\]  
\[
\tilde{P}_c = \tilde{T}_c \cdot \left[ \ln(1 + r^{-1/2}) + \left(\frac{1}{2} - r^{1/2}\right) / r \right]
\]  

For CO\textsubscript{2}, the critical point predicted using the parameters in Table 3.2 is: \(T_{c,\text{CO}_2} = 31.4\ ^\circ\text{C}; P_{c,\text{CO}_2} = 8.9\ \text{MPa};\) and \(\rho_{c,\text{CO}_2} = 431\ \text{kg} / \text{m}^3\). These estimates are in reasonably good agreement with the true values for the CO\textsubscript{2} critical point.

<table>
<thead>
<tr>
<th>Species</th>
<th>(T^*) (K)</th>
<th>(P^*) (MPa)</th>
<th>(\rho^*) (kg / m\textsuperscript{3})</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>CO\textsubscript{2}</td>
<td>283</td>
<td>660</td>
<td>1622</td>
<td>[59]</td>
</tr>
<tr>
<td>SAN74(26)</td>
<td>772</td>
<td>424</td>
<td>1140</td>
<td>[60]</td>
</tr>
<tr>
<td>dPMMA185</td>
<td>696</td>
<td>498</td>
<td>1269</td>
<td>[57]</td>
</tr>
</tbody>
</table>

In addition to the equation of state and characteristic parameters, the final aspect of the SL theory is the mixing rules. The focus of these rules is to quantify the non-trivial mixing effects in the system, and result in the determination of a binary interaction parameter, \(k_{1i}\), for each CO\textsubscript{2}-polymer binary (i = SAN or dPMMA). In the following equations, the quantities without subscripts refer to the mixture. In the formalism of the SL theory, \(k_{1i}\) is a \(T\)-dependent binary parameter that corrects for deviations in \(P^*\), as seen in equation 51. The characteristic values for each component of the mixture (i.e., \(T_i^*\), \(P_i^*\), and \(\rho_i^*\)) are defined identically to the pure component case in equations 45 – 47.

\[
P^* = \phi_1^2 P_1^* + \phi_i^2 P_i^* + 2\phi_1 \phi_i P_{1i}^*,\quad P_{1i}^* = \left(1 - k_{1i}\right)(P_1^* P_i^*)^{1/2}
\]  

The average close-packed mer volume \(v^*\) is used to describe the lattice size in the mixture:

\[
v^* = \phi_1^0 v_1^* + \phi_i^0 v_i^*
\]  

The average lattice sites per molecule, \(r\), describes the average molecular size:
\[
\frac{1}{r} = \frac{\phi_1^0}{r_1^0} + \frac{\phi_i^0}{r_i^0}
\]

(53)

And the size parameters in the mixture \( r_1 \) and \( r_i \) are related to the pure component values:

\[
r_j^0 = \frac{r_j \cdot \nu^*_j}{\nu^*_j}
\]

(54)

where \( j \) is scCO\(_2\), SAN, or dPMMA. In the above equations, \( \phi_j^0 \) are the close-packed volume fractions of the components, related to the regular volume fraction \( \phi_j \) by:

\[
\phi_1^0 = \frac{\phi_1}{\phi_1 + \frac{\nu_1^*}{\nu_2^*} \cdot \phi_2}
\]

(55)

Based on the equation of state and these mixing rules the chemical potential of CO\(_2\) \( \mu_1 \) in the neat CO\(_2\) (0) and CO\(_2\)-polymer (P) phases are derived:

\[
\frac{\mu_1^0}{RT} = \frac{r_1^0}{\frac{\nu_1^*}{\nu_2^*}} \left\{ -\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \cdot \tilde{\rho}_1} + \frac{1}{\tilde{\rho}_1} \left[ (1 - \tilde{\rho}_1) \cdot \ln(1 - \tilde{\rho}_1) + \frac{\tilde{\rho}_1}{r_1^0} \cdot \ln \tilde{\rho}_1 \right] \right\}
\]

(56)

\[
\frac{\mu_1^0}{RT} = \ln \phi_1 + \left(1 - \frac{r_1}{r_i} \right) \cdot \phi_i + r_i^0 \cdot \tilde{\rho} \cdot X_1 \cdot \left( \phi_i \right)^2 + \frac{1}{\tilde{T}_1} \left\{ -\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \cdot \tilde{\rho}} + \frac{1}{\tilde{\rho}} \left[ (1 - \tilde{\rho}) \cdot \ln(1 - \tilde{\rho}) + \frac{\tilde{\rho}}{r_1^0} \cdot \ln \tilde{\rho} \right] \right\}
\]

(57)

\[
X_1 = \left[ P_1^* + P_i^* - 2(P_1^* \cdot P_2^*)^{1/2} \left(1 - k_{ii} \right) \mathcal{v}_1^*/RT \right]
\]

(58)
In our case, the SL theory $\mu_1$ expressions were utilized as such: the pure component data was used to calculate $\mu_1^0$, and the pure component and solubility data of scCO$_2$ into each polymer ($w_{1-2}$ and $w_{1-3}$, Figure 2.6. scCO$_2$ solubility in SAN and PMMA.) for all $P$ at a single $T$ used as inputs to calculate $\mu_1^p$. The value of $k_{1i}$ at that value of $T$ was determined by minimizing the difference in $\mu_1$ for the full range of $P$. An example of this is shown in Figure 3.18 for $T = 35 \, ^\circ\text{C}$. At each $P$, $\mu_1$ is calculated in each phase. Since $\mu_1$ in each phase must be equal at equilibrium (which represents the condition of the solubility measurements), the value of $k_{1i}$ ($k_{13}$ in the case shown) is varied in order to minimize the difference. It is evident that the procedure does a reasonably good job of accomplishing this goal, with the two sets of data almost exactly overlapping (maximum difference of 0.8% at low $P$).

![Figure 3.18. $P$-dependence of $\mu_1$ used to calculate SL interaction parameter.](image)

Representative plot of $P$-dependence of $\mu_1$ at 35 °C is shown for pure scCO$_2$ (blue squares) and scCO$_2$-PMMA mixture (red circles), as determined by the SL theory. The difference at each $P$ is minimized by varying the SL interaction parameter $k_{13}$ in order to determine the equilibrium condition set by experimental solubility measurements. For scCO$_2$-PMMA at 35 °C, we find that the value of $k_{13}$ that minimizes the difference in $\mu_1$ was -0.0258.

The identical procedure to determine $k_{1i}$ can be carried out at each $T$ for which we have solubility data for SAN and PMMA. The results of this analysis are displayed in Figure 3.19. In the case of scCO$_2$-SAN ($k_{12}$) and scCO$_2$-PMMA ($k_{13}$), we see that each binary interaction parameter increases with inverse $T$, similar to the behavior of $\chi_{13}$. This again contrasts with our understanding of scCO$_2$ solubility in the polymers, which decreases monotonically with $T$. Linear fits to the data yield the following relationships:

$$k_{12} = \frac{67.736}{T} - 0.244$$

(59)
Compared with $\chi$, the values of $k$ are much smaller and negative. Also, at all conditions $k_{13}$ is smaller than $k_{12}$, the difference in the values is roughly constant. Conversely, the difference in $\chi$ decreases with $T$. Inherent in the definition of SL theory and the method used to find $k_{1i}$ is the lack of $P$-dependence, in contrast to $\chi_{1i}$.

$$k_{13} = \frac{53.274}{T} - 0.248$$  \hspace{1cm} (60)

Figure 3.19. $T$-dependence of SL interaction parameter for scCO$_2$-PMMA and scCO$_2$-SAN. SL interaction parameter for scCO$_2$-SAN, $k_{12}$, and scCO$_2$-PMMA, $k_{13}$, as a function of $T$. The parameters are found by comparing chemical potential of scCO$_2$ in the pure and polymer mixture phases, and are shown to vary linearly with inverse $T$, increasing as temperature decreases, indicating improved miscibility at elevated $T$.

Using the values of $k_{1i}$ obtained from solubility data, it is then possible to determine the corresponding $\chi_{1i}$ to facilitate comparison with the previously described results from SANS experiments. Sanchez and Lacombe consider $\chi$ as the "reduced residual chemical potential" defined equivalently to equation 35. [58] They then define the corresponding residual enthalpy and residual entropy of dilution:

$$\chi_H = -T \frac{\partial \chi}{\partial T}$$ \hspace{1cm} (61)

$$\chi_S = \frac{\partial (T\chi)}{\partial T}$$ \hspace{1cm} (62)
The enthalpic and entropic contributions to $\chi$ are then just additive:

$$\chi = \chi_H + \chi_S \tag{63}$$

Equation 63 accounts for the concentration effects on $\chi$, away from the limit of infinite dilution that would not be a good description of the mixtures of interest. The result is an expression for $\chi$ that depends on $T$ and $P$ explicitly, and $\rho_{\text{CO}_2}$ and $w_{1-i}$ implicitly.

$$\chi_H = \frac{r_i^0}{(\phi_i)^2} \cdot \left[ \left( \frac{\tilde{\rho}_i}{\tilde{\rho}^*} \right)^2 + \frac{\tilde{\rho}^*}{\phi_i} \cdot \frac{\langle \bar{v} - \bar{v}_i \rangle}{\tilde{T}^*} + \tilde{\rho}^* \cdot X_i \cdot \langle \phi_i \rangle^2 \right]$$

$$- \frac{r_i \cdot \tilde{\rho}^2 \cdot \psi \cdot P^* \cdot \beta}{\phi_i} \tag{64}$$

$$\chi_S = \frac{r_i^0}{(\phi_i)^2} \cdot \left[ \langle \bar{v} - 1 \rangle \cdot \ln(1 - \tilde{\rho}) - \langle \bar{v}_i - 1 \rangle \cdot \ln(1 - \tilde{\rho}_i) + \frac{1}{r_i^0} \cdot \ln \frac{\tilde{\rho}}{\tilde{\rho}_i} \right]$$

$$+ \frac{r_i \cdot \tilde{\rho}^2 \cdot \psi \cdot P^* \cdot \beta}{\phi_i} \tag{65}$$

In equations 64 and 65, two additional parameters appear: $\psi$, a dimensionless quantity, and $\beta$, the SL theory isothermal compressibility.

$$\psi = \tilde{\rho} \frac{d(1/\tilde{T})}{d\phi_i} - \frac{d(1/r)}{d\phi_i} + \bar{v} \cdot \frac{d(\tilde{P}/\tilde{T})}{d\phi_i} \tag{66}$$

$$\beta = \frac{\bar{v}}{\tilde{T} \cdot P^* \left[ 1/(\bar{v} - 1) + 1/r - 2/(\bar{v} \cdot \tilde{T}) \right]} \tag{67}$$

It is worth noting that $\beta$, as suggested by notation, is the isothermal compressibility of the scCO$_2$-polymer mixture specifically. These values predicted by the SL theory vary minimally, in the range approximately $1 \times 10^{-3}$ to $1.4 \times 10^{-3}$ MPa$^{-1}$ over the full range of $T$ and $P$ for PMMA and $6 \times 10^{-4}$ to $1.2 \times 10^{-3}$ MPa$^{-1}$ for SAN. This makes sense due to the very low values of $\kappa_T$ measured experimentally for polymers. Both neat polymers have $\kappa_T$ values in the vicinity of $1 \times 10^{-4}$ MPa$^{-1}$ above the $T_g$, which vary only slightly with respect to $T$ and hydrostatic $P$. [61, 62] Conversely, the SL $\beta$ for pure scCO$_2$ can be obtained using the corresponding pure component values to obtain the infinite dilution $\beta_i$. Values of $\beta_1$ obtained by this method compare reasonably
well with those determined in the preceding section (Figure 3.14), especially in the high-$T$ limit. Offsets in the near-critical regime could be expected due to the slight error in critical point location predicted by the set of scCO$_2$ characteristic parameters chosen, as discussed previously.

From the SL theory formalism outlined in this section, the $T$- and $P$-dependence of $\chi_{13}$ (and $\chi_{12}$) can be predicted. In Figure 3.20, the dependence of $\chi_{13}$ on $T$ and $P$ is shown for the experimentally-investigated isotherms. Somewhat surprisingly, the SL theory predictions are reasonably successful at predicting the complex behavior observed experimentally. For low $T$ near the critical point, the theory accurately captures the sharp dependence on $P$ at low $P$, as well as the trend of reaching plateau value of $\chi_{13}$ as $P$ increases. The theoretical prediction does show a slow decrease as $P$ increases further which seems reasonable due to the solubility increase at high $P$ and might be observed experimentally with further refined measurements in that regime. Even more impressive, at $T = 60$ and 80 °C, the SL theory predicts a minimum in $\chi_{13}$ at near-critical values of $P$. At $P$ increases further the prediction shows that a similar plateau is reached, as the trend in experimental $\chi_{13}$ (at 80 °C) suggests. The predictions at 100 °C are least successful, as the presence of a low-$P$ minimum is not clearly observed. However the slope change in $\chi_{13}$ in the vicinity of $P = 15$ MPa is suggestive of a continuation of the change in phenomenon that reflects the dampening of density fluctuations departing the near-critical regime. While not quantitative, the qualitative agreement between experiments and SL theory lends credence to the results found in this work, and could provide motivation for further investigation.
Figure 3.20. SL theory prediction of $T$- and $P$-dependence of $\chi_{13}$. Predicted dependence of $\chi_{13}$ on $T$ and $P$ from SL theory is shown as solid lines in the (a) low $T$ ($T \leq 40$ °C) and (b) high $T$ ($T \geq 60$ °C) regimes. Experimentally measured values of $\chi_{13}$ are shown as open symbols with dashed lines to guide the eye. Qualitative agreement with experimentally measured $\chi_{13}$ is observed, particularly at low and intermediate $T$.

3.8 Phase Behavior of scCO$_2$/SAN74(26)/dPMMA185 Mixtures

In addition to quantifying the interactions between components in the mixture, SANS data can be used to identify the location of phase boundaries from the signatures of phase
separation as discussed previously. Using this methodology, we map the phase behavior and gain additional insight into the balance of molecular interactions and pure component behavior.

As discussed in regards to Figure 3.4, qualitative determination of phase separation can be carried out from observance of scattering profile divergence and time-dependent profiles. For each isotherm studied in this work, similar observations were made, suggesting that spinodal-type phase separation is at play in this system independent of conditions. In Figure 3.21, the phase boundaries are shown as a function of $P$ and $T$, where a homogeneous, single phase mixture was found at low $P$ and phase separation was observed at high $P$. The mid-point of these two $P$ values we call the experimental phase separation pressure, $P_{s, \text{expt}}$. The magnitude of the scattering contrast between dPMMA and the two other components ($B_{13}$ and $B_{23}$) is much larger than that between SAN and scCO$_2$ ($B_{12}$); the dependence of the scattering length densities on $P$ and $T$ are given in Figure 2.7. This suggests that the observed phase separation reflects demixing of dPMMA and SAN. The distribution of scCO$_2$ between the polymers is not obvious, especially due to the kinetic limitations of macrophase separation of the polymers. Contrast matching experiments could be used to provide insight into the nature of scCO$_2$ partitioning between the nascent phases.

![Figure 3.21](image-url)

**Figure 3.21.** Experimentally-observed phase diagram of scCO$_2$/SAN74(26)/dPMMA185. The phase diagram of scCO$_2$/SAN74(26)/dPMMA185 with $\phi_{3,0} = 0.461$ is shown from the observation of scattering signatures of phase separation. Lines are provided to guide the eye.

In Figure 3.21, the phase separation pressure, $P_s$, is a non-monotonic function of $T$: it decreases with increasing $T$ in the low-$T$ limit (below 60 °C) but increases with increasing $T$ in the high-$T$ limit (above 60 °C). This non-monotonic phase boundary in is unusual, but can be qualitatively explained on the basis of the interactions between the three constituent species. At low $T$, SAN and PMMA are highly miscible ($\chi_{23} = -0.366$) and thus high $P$ is required to drive sufficient scCO$_2$ concentration to induce phase separation. As $T$ increases, the miscibility between SAN and PMMA decreases ($\chi_{23} = -0.142$ at 100 °C), and less scCO$_2$ is required to
induce phase separation. However, as $T$ increases the solubility of scCO$_2$ in the polymers also decreases (see Figure 2.6). Since the phase separation is induced by the uptake of scCO$_2$, a higher value of $P$ is needed to induce the phase transition at higher $T$.

We can also determine the location of a phase boundary through a Zimm-type analysis if the phase transition is second order. In Figure 3.22a, $1/I(q)$ vs $q^2$ for data in the low-$q$ regime is plotted as a function of $P$ at 35 °C. Linear fits to this data allows extrapolation to $q = 0$ nm$^{-1}$ to obtain estimates of $I(q = 0) = I_0$. These values $I_0$, when plotted as a function of $P$ as in Figure 3.22b, provide an additional method to determine the phase separation pressure, $P_{s,Zimm}$, of the multicomponent mixture. In the case of $T = 35$ °C, we find that $1/I_0 = 0$ at $P_{s,Zimm} = 35.6 \pm 0.8$ MPa. At this $P$, the low-$q$ scattering intensity is expected to diverge, thus prediction phase separation. $P_{s,Zimm}$ may be interpreted as the spinodal pressure. This agrees well with our observed phase separation at $P_{s,expt} = 33 \pm 2$ MPa.
Figure 3.22. Zimm analysis of SANS data to obtain the phase separation condition. (a) Zimm format plot ($1 / I$ vs. $q^2$) of SANS data in the low-$q$ regime for the multicomponent mixture at 35 °C. Solid are least-squares linear fits to the data sets. (b) Extrapolated reciprocal scattering intensity $1 / I(q = 0) = 1 / I_0$ plotted against $P$ at $T = 35$ °C. The solid line is a least-squares linear fit used to estimate $P_{s,Zimm}$, equal to 35.6 ± 0.8 MPa.

Carrying out the Zimm procedure for the remainder of the isothermal experiments, we determine a phase diagram in good agreement with the experimentally-observed behavior. The quantitative agreement between $P_{s,expt}$ and $P_{s,Zimm}$ at all values of $T$ indicates the absence of a metastable window, typically found between two stable thermodynamics states. This is a signature of second-order phase transitions. The values of $P_{s,expt}$ and $P_{s,Zimm}$ for each $T$ are listed in Table 3.3. Phase Separation Conditions for scCO$_2$/SAN74(26)/dPMMA185.
Figure 3.23. Phase diagram of scCO$_2$/SAN74(26)/dPMMA185 determined by Zimm analysis. Phase separation pressure $P_{s,Zimm}$ as a function of $T$ for the scCO$_2$/SAN74(26)/dPMMA185 blend as determined by Zimm analysis of SANS data. Lines are provided to guide the eye.

Table 3.3. Phase Separation Conditions for scCO$_2$/SAN74(26)/dPMMA185.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$P_{s,expt}$ (MPa)</th>
<th>$P_{s,Zimm}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>33 ± 2</td>
<td>35.6 ± 0.8</td>
</tr>
<tr>
<td>40</td>
<td>30 ± 2</td>
<td>29 ± 1</td>
</tr>
<tr>
<td>60</td>
<td>11.4 ± 0.3</td>
<td>11.2 ± 0.2</td>
</tr>
<tr>
<td>80</td>
<td>21.4 ± 0.7</td>
<td>22.3 ± 0.2</td>
</tr>
<tr>
<td>100</td>
<td>24 ± 3</td>
<td>25 ± 1</td>
</tr>
</tbody>
</table>

It is unlikely that hydrostatic pressure is an important variable in the study of phase boundaries in this regime. We were unable to find explicit studies of the effect of hydrostatic pressure on the thermodynamics of SAN/PMMA mixtures. In the well-studied case of mixtures of polymethylbutylene and polyethylbutylene, the phase separation temperature $T_s$ was observed to shift by 40 °C under the influence of applied $P$ greater than 300 MPa. [45, 46] In our case, $T_s$ changes by as much as 125 °C when equilibrated with a scCO$_2$ reservoir with $P = 33$ MPa ($T_s$ for this blend in the scCO$_2$-free state is 160 °C). It is thus appropriate to consider the effect of $\rho_{CO_2}$.
the density of the scCO$_2$ in the reservoir instead of $P$. Figure 3.24 shows the scCO$_2$/SAN/dPMMA blend phase behavior on a $\rho_{CO_2}$ vs. $T$ plot. The phase diagrams shown in Figure 3.23 and Figure 3.24 are qualitatively similar with non-monotonic dependences of the phase separation $P_s$ and $\rho_{CO_2}$ on $T$.

**Figure 3.24.** T-dependence of $\rho_{CO_2,s}$ for scCO$_2$/SAN74(26)/dPMMA185.

Phase separation density $\rho_{CO_2,s}$ as a function of $T$ for the multicomponent mixture, with $\rho_{CO_2,s}$ determined from $P_s,Zimm$ at each experimental $T$. The solid line is provided to guide the eye.

In order to elucidate the effect of $P$ and $\rho_{CO_2}$ on the phase boundaries further, we can return to the consideration of density fluctuations. It was clear from the previous discussion that $\langle (\Delta n)^2 \rangle / \langle n \rangle$ has a significant effect on the mixing of scCO$_2$ and polymers. When we focus specifically on the phase separation condition, an interesting correlation emerges. At each $P$ and $T$ of phase separation, as listed in Table 3.3, we can calculate the magnitude of density fluctuations and scCO$_2$-polymer interaction parameter. In a sense, $\langle (\Delta n)^2 \rangle / \langle n \rangle$ acts as a proxy for $P$ (or $\rho_{CO_2}$), while $\chi_{13}$ acts as a proxy for $T$. When $\langle (\Delta n)^2 \rangle / \langle n \rangle$ is plotted against $\chi_{13,s}$ (see Figure 3.25, a clear relationship is found which intuitively makes sense. When mixture components are highly miscibly (low $\chi_{13}$), significant density fluctuations are required to drive phase separation. Conversely, when miscibility decreases minimal density fluctuations result in phase separation. This corresponds to the observation from the isothermal trajectories in Figure 3.17, where phase separation occurs in the high $\rho_{CO_2}$ limit where $\langle (\Delta n)^2 \rangle / \langle n \rangle$ is approaches zero but the value of $\chi_{13}$ has reached a plateau. In Figure 3.25, it appears that the plateau limit of $\chi_{13}$ where no fluctuations are required for phase separation correspond to a value of approximately 2.66, which is quite close to plateau values we find. Conversely, the plot shows that even for of $\chi_{13}$ values corresponding to the good solvent condition ($\chi_{13} < 0.5$), density fluctuations could drive phase separation when the magnitude is greater than 2.81. This description of the impact of scCO$_2$ properties on the mixing behavior of this type of multicomponent mixture has not been
reported in the past, and points to the multi-faceted utility of supercritical fluids in the processing of polymeric systems.

**Figure 3.25.** Relationship between density fluctuation and interactions at phase separation.
4 Summary

Use of supercritical carbon dioxide (scCO$_2$) as a medium for the low-temperature, environmentally benign processing of polymers has gained interest as viable alternative to resource intensive and harmful methods use historically. In this dissertation, the effect of scCO$_2$ on the thermodynamics of miscible polymers blends was investigated to provide a broader understanding of the critical interactions and properties that govern mixing in systems of fundamental and practical interest.

Beginning with precise synthesis of model materials and careful characterization of material properties, a thorough thermodynamic analysis of the multicomponent system containing scCO$_2$, styrene-acrylonitrile random copolymer (SAN), and poly(methyl methacrylate) (PMMA) was presented. Molecular and chemical characterization allowed determination of the properties of the polymers which have significant impact on the miscibility in the scCO$_2$-free blend. Interactions and phase behavior in the scCO$_2$-free polymer blend were investigated by small-angle neutron scattering (SANS) to determine the miscibility of the macromolecular components and the proximity of the subsequent experiments to polymer phase separation. Solubility measurements of scCO$_2$ in each neat polymer were utilized to relate the chemical potential of scCO$_2$ in the multicomponent mixture to that in binary cases.

The multicomponent mixture was studied in a series of SANS experiments. Exposure of polymer blend films to reservoirs of scCO$_2$ permitted in situ study of the development of concentration fluctuations in the mixture as a function of system temperature and pressure. A new formalism of the multicomponent random phase approximation (RPA) was utilized to abstract information on thermodynamic interaction from SANS experiments. The analysis required a novel treatment of the data pairing SANS with solubility measurements. It was found that the analysis provided a unique physically-relevant solution to the RPA theory. The analysis method resulted in the identification of highly complex behavior of interaction parameters. This finding was qualitatively corroborated using the Sanchez-Lacombe equation of state, which predicts similar non-monotonic relationships between interaction parameters and pressure. When considering the effect of scCO$_2$ density, the unexpected result that interaction parameters collapse onto the straight line with positive dependence on density was observed, which suggests that scCO$_2$-polymer is improved at gas-like density conditions. To explore this unusual finding further, the influence of scCO$_2$ critical phenomenon was investigated through the use of density fluctuations. From comparison with the literature of scCO$_2$, it was discovered that the complex mixing behavior of scCO$_2$ and polymers could be correlated with density fluctuations, and especially with proximity to the density fluctuation ridge. This phenomenon has been attributed as the source for non-trivial behavior in scCO$_2$-polymer mixture before, but the persistence of the behavior has not been shown well away from the near-critical region previously.

Experiments showed that the mixture has a non-monotonic phase boundary that represents the spinodal condition. Analysis of the phase separation process suggests that the phase separation in this process has no metastable window as is frequently seen in polymer-containing mixtures. Consideration of the influence of scCO$_2$ density fluctuations at the phase separation points to the existence of an inverse relationship between density fluctuation magnitude and interaction strength between polymers and scCO$_2$. The absence of the metastable condition in these systems could potentially be attributed to the presence of density fluctuations to exacerbate the demixing process. These observations point to the balance of competing factors.
in understanding the thermodynamics of scCO₂-polymer-polymer systems: scCO₂-polymer interaction energy, polymer-polymer interaction energy, and critical phenomenon of scCO₂.
5 References


