Effect of Tacticity on the Phase Behavior and Demixing of dPMMA Blends Investigated by SANS

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ABSTRACT: We investigate the effect of polymer tacticity on the phase behavior and phase separation of polymer mixtures by small-angle neutron scattering (SANS). Poly(α-methyl styrene-co-acrylonitrile) (PolMSAN) and deuterated poly-(methyl methacrylate) (dPMMA) with two degrees of syndiotacticity were selected as a model partially miscible blend, as one of the most highly interacting systems known (defined by the temperature dependence of the blend–interaction parameter). One-phase (equilibrium) and time-resolved, spinodal demixing experiments were analyzed by de Gennes’ random phase approximation (RPA) and Cahn–Hilliard–Cook (CHC) theory, respectively. The second derivative of the Gibbs free energy of mixing with respect to composition (\(G'' \equiv \partial^2 \Delta G_m/\partial \phi^2\)) and corresponding \(\chi\) parameter were obtained from both RPA and CHC analysis and found to correlate well across the phase boundary. We find that blends with higher PMMA syndiotacticity exhibit greater miscibility and a steeper \(G''\) temperature dependence by \(\sim 40\%\). The segment length of dPMMA with higher syndiotacticity was found to be \(a \approx 7.4\) Å, slightly larger than \(6.9\) Å reported for lower syndiotacticity dPMMA. Consideration of thermal fluctuations is required for the self-consistent analysis of the nontrivial evolution of the spinodal peak position \(q^*\) over time, corroborated by CHC model calculations. The temperature dependence of the mobility parameter, \(M\), can be described by a “fast-mode” average of the diffusion coefficients of the blend constituents, except for quenches originating near the glass transition. A minimum demixing length scale of \(\Lambda \approx 40\) nm is obtained, in agreement with the theory for deeper quenches, but deviates at shallower quenches, whose origin we discuss. CHC correctly describes demixing length and time scales, except for quenches into the vicinity of the spinodal boundary. Our data demonstrate the significant effect of relatively minor polymer microstructure variations on polymer blend behavior across both sides of the phase boundary.

INTRODUCTION

Polymer tacticity impacts thermal, mechanical, rheological, and barrier properties of materials. Tacticity affects polymer chain dimensions in solution and melt, effectively modulating local conformation and rigidity of polymer segments, as well as the miscibility with other polymers. Small-angle neutron scattering (SANS) can be employed to quantify polymer conformation and interactions of partially miscible polymer blends, generally in terms of the random phase approximation (RPA), to yield the segment length of each component \(b\) and an effective interaction parameter \(\chi\), usually interpreted within the framework of the Flory–Huggins theory.

SANS has been employed to examine the role of tacticity in blends of deuterated polystyrene (dPS), with isotactic and atactic poly(vinyl methyl ether) (iPVME and aPVME). The blend of iPVMEDPS showed steeper temperature dependence of interaction parameter compared to that of aPVME/dPS in the crystalline state of iPVMEDPS, while the amorphous state iPVMEDPS was less miscible than aPVME/dPS. The more compact conformation of iPVMEDPS inferred from the statistical segment length obtained by SANS RPA analysis yields stronger interaction with dPS per interactive group, which indicates that the configuration affects the phase behavior. However, iPVMEDPS undergoes crystallization in the melt state; therefore, the SANS data were treated with care for crystalline melting temperature and interpreted accordingly. To the best of our knowledge, no studies have reported a combined SANS investigation of the demixing and thermodynamic properties of the effect of tacticity in polymer blends, which is the main purpose of this paper.

The effect of PMMA tacticity has been studied from various perspectives, ranging from synthesis methods,\textsuperscript{16} glass-transition temperature (\(T_g\)),\textsuperscript{20,21} chain dimensions,\textsuperscript{3,4} to blend behavior with various polymers.\textsuperscript{7–17} These include blends with poly(styrene-co-acrylonitrile) (SAN),\textsuperscript{16} polycarbonate (PC),\textsuperscript{13} poly(vinyl chloride) (PVC),\textsuperscript{7,10,11,15} and poly(ethylene oxide) (PEO).\textsuperscript{9,17} Generally reporting that higher syndiotacticity PMMA blends show greater miscibility and attribute the shift of phase boundaries to higher temperatures to the more

Received: October 5, 2019
Revised: December 11, 2019
Published: January 3, 2020

DOI: 10.1021/acs.macromol.9b02115
Macromolecules 2020, 53, 445–457
Table 1. Polymer Sample Characteristics

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<tr>
<th>Sample</th>
<th>$M_w$ [kg/mol]</th>
<th>$M_a$ [kg/mol]</th>
<th>$m$</th>
<th>$T_g$ [°C]</th>
<th>$h$ [Å]</th>
<th>$a$ [Å]</th>
<th>$R_g$ [nm]</th>
<th>$\rho$ [g/cm³]</th>
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<tr>
<td>PzMSAN</td>
<td>122</td>
<td>2.6</td>
<td>98.66</td>
<td>118 ± 1</td>
<td>21.12</td>
<td>10.1 ± 0.4</td>
<td>14.5</td>
<td>0.63</td>
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<tr>
<td>dPMMA99k</td>
<td>99.1</td>
<td>1.1</td>
<td>108.1</td>
<td>122 ± 1</td>
<td>98.20</td>
<td>6.9 ± 2.0</td>
<td>8.5</td>
<td>10.8</td>
</tr>
<tr>
<td>dPMMA110k-s</td>
<td>110</td>
<td>1.1</td>
<td>108.1</td>
<td>127 ± 2</td>
<td>98.20</td>
<td>7.4 ± 0.2</td>
<td>9.6</td>
<td>10.9</td>
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</table>

"Random copolymer PzMSAN comprises 30% AN and 70% α-MSt. The segment length $a$ for PzMSAN was previously determined and that of dPMMA99k was fixed from literature data. To design bicontinuous structures via thermally induced phase separation, thermally induced phase separation, and reactive blending, with various capabilities and limitations. To design bicontinuous structures via thermally induced demixing, a precise understanding of blend thermodynamics is required and, specifically, highly interacting blend systems are needed to achieve nanoscale dimensions through this method. Syndiotacticity, from 63 nanometers random copolymer poly(α-methyl styrene-co-acrylonitrile) (PzMSAN) and similar molecular mass (99 and 110 kg/mol) and low polydispersity index (PDI = 1.1), synthesized by living anionic polymerization, was purchased from Polymer Source Inc. Hydrogenous random copolymer poly(α-methyl styrene-co-acrylonitrile) (PzMSAN) with 30% AN and 70% α-MSt (Luran K2556) was kindly donated by BASF. Glass-transition temperatures $T_g$ of the pure components were determined by differential scanning calorimetry (DSC) using a TA Instruments Q2000 with a heating rate of 10 °C/min and computed by the midpoint method (Figure S1). The syndiotacticity (the ratio of racemo–racemo triad) of dPMMA110k-s was determined to be 75% by $^1$H NMR and approximately 81% by DSC (Supporting Information Figure S2), and we thus obtain 78 ± 3%; we refer to this sample as syndiotactic, since the value is ≥70%. The dPMMA99k sample is estimated to have a degree of syndiotacticity of 63 ± 5% based on $T_g$ measurement and its correlation with tacticity, detailed in the Supporting Information Figure S2; we refer to this sample as atactic. Key characteristics of the polymer samples used are summarized in Table 1, and the monomer chemical structures are shown in Figure 1.

![Figure 1](image-url)

Figure 1. Monomer repeat units of PzMSAN and dPMMA and phase diagram of PzMSAN/dPMMA99k (atactic) and dPMMA110k-s (syndiotactic). Filled symbols indicate spinodal temperature from extrapolation of G" vs 1/T, and open symbols correspond to binodal temperature from Kratky plots, obtained by SANS. Lines serve as a guide to the eye. Black solid lines are $T_g$ estimates obtained by the Flory–Fox equation and pure component data as given by the Flory–Fox equation.13

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**EXPERIMENTAL SECTION**

**Polymer Mixtures.** Deuterated poly(methyl methacrylate) (dPMMA) with two degrees of syndiotacticity (atactic and syndiotactic) and similar molecular mass (99 and 110 kg/mol) and low polydispersity index (PDI = 1.1), synthesized by living anionic polymerization, was purchased from Polymer Source Inc. Hydrogenous random copolymer poly(α-methyl styrene-co-acrylonitrile) (PzMSAN) with 30% AN and 70% α-MSt (Luran K2556) was kindly donated by BASF. Glass-transition temperatures $T_g$ of the pure components were determined by differential scanning calorimetry (DSC) using a TA Instruments Q2000 with a heating rate of 10 °C/min and computed by the midpoint method (Figure S1). The syndiotacticity (the ratio of racemo–racemo triad) of dPMMA110k-s was determined to be 75% by $^1$H NMR and approximately 81% by DSC (Supporting Information Figure S2), and we thus obtain 78 ± 3%; we refer to this sample as syndiotactic, since the value is ≥70%. The dPMMA99k sample is estimated to have a degree of syndiotacticity of 63 ± 5% based on $T_g$ measurement and its correlation with tacticity, detailed in the Supporting Information Figure S2; we refer to this sample as atactic. Key characteristics of the polymer samples used are summarized in Table 1, and the monomer chemical structures are shown in Figure 1.

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dPMMA110k-s 30/70 were investigated. The films were then wrapped in a thin aluminum foil (22 μm thick) to be mounted onto a temperature-controlled cell to acquire SANS data in the one-phase region.

The sample preparation procedure was identical for demixing (temperature jump) experiments although, in this case, a single film of 100–150 μm thickness was wrapped in an aluminum foil (minimizing multiple scattering, given the much greater scattering intensity in the two-phase region). In all cases, sample thicknesses were determined using a digital micrometer. For these experiments, we compare PrMSAN/dPMMA99k 28/72 (atactic) and PrMSAN/dPMMA110k-s 30/70 (syndiotactic), which are effectively identical in composition and polymer molecular masses but vary in degree of syndiotacticity. This experimental protocol follows our previous work, examining the effect of composition and Mw on the phase behavior of this system.

Small-Angle Neutron Scattering. SANS experiments were performed at ISIS (U.K.) using diffractometers SANS2D and Larmor and sample to detector distances Dm/d = 12 m and 4.1 m, respectively. These configurations yield a momentum transfer \( q = \frac{2 \pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \), where \( \theta \) is the scattering angle, ranging from 0.0015 < \( q < 0.5 \) Å\(^{-1}\) and 0.006 < \( q < 0.6 \) Å\(^{-1}\).

A custom-made brass experimental cell, consisting of two thermally controlled ovens and a mechanical actuator carrying the sample from one (preheating) oven to another (the “experimental oven”), with quartz windows and a 45° exit cone, was employed for both one-phase and demixing experiments. Neutron cloud point experiments were carried out at a heating rate of 2 °C/min from 102 °C (below \( T_g \)) to above the demixing temperature, to estimate the location of the phase boundaries, as illustrated in Figure 2.

Figure 2. Total SANS scattering intensity during a cloud point measurement at heating rate 2 °C/min for PrMSAN/dPMMA99k:28/72. The solid line is computed from RPA in the one-phase region with \( \xi_G/\xi_M = 0.00201-0.83/T \). The binodal \( T_G \) and spinodal \( T_s \) temperatures are indicated by vertical lines. The dashed line shows RPA deviations assigned to nucleation and growth in the metastable region. Nonequilibrium behavior near or below \( T_s \) is shown in gray. The inset, which corresponds to cloud point data at every 4 °C from 102 °C, shows the \( I(q) \) cloud point data as a function of temperature.

For one-phase (isothermal) experiments, only the “experimental” oven was utilized. The film was loaded at 125 °C (the final ex situ preheating oven temperature) into the measurement cell, and the temperature was increased, in a stepwise fashion, to the desired temperature. Intervals of 8 °C near \( T_s \) to 2 °C near the phase boundary, were sampled. Acquisition times ranged from 120 min near \( T_s \) where sample equilibration is longer and the neutron scattering intensity is lower (\( I(0) \sim 20 \text{ cm}^{-1} \)) to 3 min near the phase boundary (for which \( I(0) \sim 60 \text{ cm}^{-1} \)). We found this time to be sufficient to equilibrate concentration fluctuations at \( q \geq 0.01 \) Å\(^{-1}\), and thus sufficient to accurately estimate \( G^* \) (or \( \chi \)), although low-\( q \) deviations were observed (corresponding to long-wavelength fluctuations). Data acquisition for a neat PrMSAN 1 mm sample (used to estimate incoherent contribution) and the empty cell background (arising from aluminum foil and quartz windows) was carried out for 30 min. All data were acquired in time-of-flight “event mode”, which enables the temporal slicing of data after the experiment, during data analysis. This feature is important to ascertain sample equilibration and to adapt time resolution to the magnitude of intensity changes and available data statistics.

Scattering data were reduced and calibrated, and the contribution from the empty cell was subtracted, using Mantid.26 The self-consistency of sample thickness, neutron transmission, and incoherent background intensity was verified to ensure accurate data calibration. The coherent scattering profile was then obtained by subtraction of the appropriate volume fraction of PrMSAN incoherent contribution.

RESULTS AND DISCUSSION

Phase Diagram of PrMSAN/dPMMA Blends. The phase diagram for both PrMSAN/dPMMA99k and dPMMA110k-s blends, with varying syndiotacticity, is shown in Figure 1, along with the glass-transition temperatures. The spinodal temperatures (solid lines), \( T_s \), were determined by extrapolation of \( G^* \equiv \partial^2 \Delta G_m/\partial q^2 \) with inverse temperature, obtained from the forward SANS scattering intensity as \( 1/S(0) \equiv G^* \) for all compositions, as detailed below. The binodal temperatures (dashed lines), \( T_b \), were estimated from deviations from RPA analysis in the Kratky representation. Our first observation is that the phase boundaries for PrMSAN/dPMMA110k-s occur at a higher temperature (≈16 °C) above those of PrMSAN/dPMMA99k, indicating greater component miscibility for syndiotactic dPMMA (and despite its slightly higher \( M_w \) of 110 kg/mol). The critical point for both blends is located at PrMSAN \( \leq 0.3 \) (\( \sqrt{\phi} \)), corroborated by optical microscopy data. For completion, the glass-transition temperature \( T_g \) of the blends is also shown, computed from the Flory–Fox expression \( 1/T_g^{blend} = \phi_{PrMSAN}/T_g^{PrMSAN} + \phi_{dPMMA}/T_g^{dPMMA} \) based on the pure component values, indicated in Table 1. The proximity between the phase boundary and \( T_g \) is expected to be beneficial in terms of resolving the kinetics of demixing; however, the narrow temperature window (≈20–30 °C) between the two transitions also poses challenges to ensure thermal equilibration of concentration fluctuations within the one-phase region.

SANS Cloud Point Measurements. Prior to all isothermal experiments, SANS cloud point measurements were carried out at a heating rate of 2 °C/min from 102 to 150 °C, to estimate the location of \( T_s \) and \( T_b \) as shown in Figure 2 for a PrMSAN/dPMMA99k:28/72 blend. The total scattering intensity (\( \sum I \)) was plotted against temperature, and various regimes could be identified: below \( T_s \) no intensity changes are observed, as expected; between \( T_s \) and \( T_b \), the scattering intensity increases gradually, within the one-phase region; a change of slope is observed at both \( T_s \) and \( T_b \). Based on the (isothermal) data analysis presented below, the temperature dependence of \( G^* \) (and \( \chi \)) and chain conformation was established, allowing the superposition of the RPA theory prediction alongside the cloud point data. There is good agreement between measurement and RPA prediction from \( \approx 126 °C \) (above \( T_s \)) to \( \approx 140 °C \) (near binodal for this mixture), within the one-phase region. Under isothermal conditions, the samples did not reach equilibrium even after 36 h of annealing at 125 °C due to the proximity of \( T_g^{blend} = 120.9 °C \), and this out-of-equilibrium region is shown as a shaded area in Figure 2. Above \( T_b \approx 140.5 °C \), scattering data also gradually deviates from RPA, as expected within the
metastable region, where demixing takes place by nucleation and growth. A clear peak emerges on the scattering profile between 142 and 146 °C, which agrees with \( T_s \) estimations obtained from SANS isothermal experiments, of 144.8 °C for this blend.

**RPA Analysis in the One-Phase (Equilibrium) Region.**

The coherent scattering intensity \( I(q) \) from a polymer blend in the one-phase region is written by

\[
I(q) = N_i \left( \frac{b_i}{v_i} - \frac{b_k}{v_k} \right)^2 S(q)
\]

where \( N_i \) is the Avogadro number, \( S(q) \) is the structure factor, \( b_i \) is the coherent scattering length of monomer unit \( i \), and \( v_i \) is the monomer molar volumes of unit \( i \). In the following discussion, we refer to component 1 as PMMA110k and 2 as dPMMA, for which \( b_1 = 21.12 \text{ fm} \), \( v_1 = 91.77 \text{ cm}^3/\text{mol} \), \( b_2 = 98.20 \text{ fm} \), \( v_2 = 84.79 \text{ cm}^3/\text{mol} \), yielding a contrast prefactor \( N_0 (b_1/v_1 - b_2/v_2) = 5.19 \times 10^{-3} \text{ cm}^{-4} \text{ mol} \). The structure factor \( S(q) \) of the blend is generally expressed by the mean-field, de Gennes’ random phase approximation (RPA), as

\[
\frac{1}{S(q)} = \frac{1}{S_1(q)} + \frac{1}{S_2(q)} - 2 \frac{\Delta S}{\pi v_0} q_{12}
\]

where \( S_i(q) \) [cm\(^3\)/mol] is the structure factor of each component, and \( \chi_{12} \) is an effective specificity interaction parameter. Taking component polydispersity into account, \( S(q) \) reads

\[
S(q) = S_1(q) \left( \frac{\phi_1 v_1 (N_1)_w}{g_0 (R_g^2)} \right)_w
\]

where \( \phi_i \) is the volume fraction, \( v_i \) is a reference molar volume taken as \( v_0 = \sqrt[6]{\phi_i (N_i)_w} \), and \( (N)_w \) is the number average degree of polymerization of component \( i \). The weight-average Debye form factor of the polymer chains is

\[
g_0(x) = 2^{\frac{1}{2}} \left( \frac{k}{h + x} \right)^{\frac{1}{2}} - 1 + x \right)^{-1},
\]

where \( x = q^2 (R_g^2) \) and \( h = (M_w/M_n - 1)^{-1} \), and the m-average radius of gyration for a Gaussian coil \( (R_g) \equiv \langle (N)_w a^2/6 \rangle^{1/2} \) where \( a \) is the segment length. In the forward scattering limit, \( q \to 0 \), eq 2 becomes

\[
\frac{1}{S(0)} = \frac{1}{\phi_1 v_1 (N_1)_w} + \frac{1}{\phi_2 v_2 (N_2)_w} - 2 \frac{\Delta S}{v_0} \equiv G^*
\]

yielding a direct (and model-free) measurement of the second derivative of the free energy with respect to composition, \( G^* = \partial^2 \delta G_{\Delta q}/\partial q^2 \). In the usual Flory–Huggins lattice framework, the interaction parameter \( \chi \) at the spinodal is

\[
\chi_s = \frac{v_0}{2} \left( \frac{1}{\phi_1 v_1 (N_1)_w} + \frac{1}{\phi_2 v_2 (N_2)_w} \right)
\]

and therefore, from eq 4, follows that

\[
(G^* = \frac{1}{S(0)} - \frac{2}{v_0} (\chi_s - \chi_{12}^*)
\]

where \( \chi_{12} \) is an effective interaction parameter, measured by SANS, which can be related to the common Flory–Huggins parameter \( \chi_{12} \) by

\[
\chi_{12} = \frac{1}{2} \frac{\partial^2 \delta G_{\Delta q}}{\partial q^2}
\]

and thus \( \chi_{12}^{**} = \chi_{12}^{*} \) for composition-independent interactions. At low scattering angles (\( q R_g < 1 \)), the simple Ornstein–Zernike (OZ) expression provides a good approximation to the data, where

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

or equivalently

\[
\frac{1}{S(0)} = \frac{1}{S(q)} + 2kq^2
\]

where the correlation length is given by \( \xi = \sqrt{2kS(0)} \), and parameter \( k \) is defined below. The OZ formulation emphasizes that the forward scattering intensity yields a susceptibility \( S(0) \equiv 1/G^* \) and thus requires no thermodynamic model assumption to obtain \( G^*(T) \) and thus characterize blend miscibility.

The coherent scattering data for PtMSAN/dPMMA110k-s:30/70 blends as a function of temperature are shown in Figure 3a, as well as in the Ornstein–Zernike (OZ) and Kratky representations (at selected temperatures) in Figure 3b,c, respectively.

Filled symbols denote data in the one-phase region, which can generally be described by the RPA theory (eqs 1–3),

Figure 3. (a) Coherent SANS scattering data for PtMSAN/dPMMA110k-s (syndiotactic) obtained by sequential isothermal measurements. Filled symbols correspond to the one-phase region, while open symbols indicate the two-phase region, estimated from the emergence of a peak and departure from RPA scaling. Due to the proximity to \( T_s \) data at 125 °C (despite annealing for 37 h) are not at equilibrium; RPA deviations are also found at low-\( q \) interpreted as due to (expected) slow equilibration of long-concentration fluctuations. (b) Ornstein–Zernike plots of the one-phase data shown in (a), which are all described by RPA, with deviations discussed above. (c) Kratky plot of the one-phase (filled symbols) and two-phase (open symbols) data, with lines computed using RPA at the highest and lowest temperatures yielding \( d_{dPMMA110k-s} = 7.4 \pm 0.2 \text{ Å} \) and fixing \( d_{PtMSAN} \) to be 10.1 Å. Open symbols correspond to the SANS data in the two-phase region (which deviate from the RPA by more than a factor of 2), whose lowest temperature is taken as the estimate for the binodal.
Figure 4. (a) Coherent SANS scattering data for PzMSAN/dPMMA99k (atactic), where filled and open symbols correspond to, respectively, the one- and two-phase regions. Low-q deviations from RPA indicate incomplete equilibration attributed to the proximity to \( T_C \) and finite annealing time during sequential isothermal measurements. (b) Corresponding Ornstein–Zernike plot for data in the one-phase region. (c) Kratky plot for selected data in the one- and two-phase regions, where lines show RPA estimates at the highest and lowest temperatures in the one-phase, region corroborating \( \alpha_{PzMSAN} = 10.1 \text{ Å}^{2} \) and \( \alpha_{dPMMA99k} = 6.9 \text{ Å}^{2} \). Open symbols indicate SANS data in the two-phase region (\( q \) power larger than 2), employed to estimate the binodal temperature.

Figure 5. (a) Second derivative of free energy of mixing with respect to composition \( G'' \equiv \partial^2 \Delta G_\alpha / \partial \phi^2 \) as a function of inverse temperature \( 1/T \) for PzMSAN/dPMMA99k of three distinct compositions 78/22, 41/59, and 28/72 (corresponding to Figure 4 and PzMSAN/dPMMA110k-s 30/70 (Figure 3)). Lines are fits to \( G'' = \alpha + \beta/T \) with constant slope \( \beta = 1.60 \) for PzMSAN/dPMMA99k and with \( \beta = 2.30 \) for PzMSAN/dPMMA110k-s. (b) Corresponding plot for the effective interaction parameter \( \chi_{12}/\nu_0 \) (computed from eq 4), where the vertical ticks indicate the experimentally measured spinodal temperatures \( T_C \). Lines are fits to \( \chi_{12}/\nu_0 = A + B/T \) with constant slope \( B = -0.83 \) for PzMSAN/dPMMA99k and with \( B = -1.55 \) for PzMSAN/dPMMA110k-s.

shown by the solid lines. The initial experimental measurements were conducted at 125 °C following a 37 h annealing (ex situ) in the near-vicinity of \( T_C \) and found to be out of equilibrium (for instance, by the differing slope in the OZ plot). A stepwise temperature profile (Figure S3) of isothermal measurements was adopted, with equilibration times between steps. At selected temperatures (above 146 °C), the scattering intensity does not fully reach equilibrium at low wavenumbers (\( q \lesssim 0.01 \) – 0.02 Å), corresponding to long-wavelength fluctuations, which is attributed to the proximity to \( T_C \) (and shown by the temporal evolution of the total scattering intensity during an isothermal measurement, shown in Figure S4). We therefore preferentially fit the higher \( q \) region to the RPA model, for which thermal equilibration is achieved within measurement time scales, and take the low-\( q \) deviation into account to compute the uncertainty in \( G'' \) and \( \chi_{12} \). This approach is corroborated with the OZ analysis in Figure 3b, showing the parallel linear slopes at all temperatures (bar low-\( q \) deviations) and thus intercepts proportional to \( G'' \), as described by eq 9. In the Kratky representation, \( Iq^2 \) vs \( q \), shown in Figure 3c, a peak emerges in the scattering data above 161 °C, also visible in Figure 3a, where open symbols identify data assigned to the two-phase region. The phase boundary is thus estimated to be between 157 and 161 °C, with binodal temperature \( T_b = 159 \pm 2 \) °C. Polymer segment lengths \( a \) were estimated from the Kratky analysis as \( \phi \) and \( v \) are known, since the structure factor of one-phase blends at high wavenumber (\( qR_g \gg 1 \)) can be written as

\[
S(q)q^2 \approx 12\left( \frac{\phi_1^2}{\phi_1^2 + \phi_2^2} + \frac{\phi_2^2}{\phi_1^2 + \phi_2^2} \right).
\]

To increase the accuracy of the measurement of \( a \) of dPMMA110k-s, we fix the PzMSAN segment length to be \( a(PzMSAN) = 10.1 \text{ Å} \), measured previously, obtaining \( a(dPMMA110k-s) = 7.4 \pm 0.2 \text{ Å} \).

The coherent scattering data for PzMSAN/dPMMA99k:28/72 (atactic) as a function of temperature are shown in Figure 4a. The coherent scattering data for PzMSAN/ dPMMA99k:41/59 and 78/22 are shown in Figures S5 and S6. As above, the initial 125 °C measurement (following a 36 h ex situ annealing) was found to be out of equilibrium, and data above 139 °C was also found to deviate from RPA at the lowest wavenumbers. A peak in the scattering profile emerges between 144 and 148 °C (beyond which data are shown with open symbols) and therefore ~10–15 °C lower than for the PzMSAN/dPMMA110k-s blend. The OZ analysis shown in Figure 4b in the one-phase region shows lines of common slope at various temperatures, except at the lowest \( q \) or initial temperature, as expected for RPA, despite incomplete thermal equilibration of long fluctuations. Figure 4c shows the corresponding Kratky plot, from which \( T_b \) is determined to be 140.5 ± 1.5 °C. Lines are computed from RPA with \( a(PzMSAN) = 10.1 \text{ Å}^{2} \) and \( a(PMMA) = 6.9 \text{ Å} \), in agreement...
Table 2. \(G^\circ\) and \(\tilde{\chi}_{12}/\nu_0\) of PzMSAN/dPMMA99k (Atactic) and PzMSAN/dPMMA110k-s (Syndiotactic) Obtained by SANS in the One-Phase Region, in the Form \(G^\circ = \alpha + \beta/T\), and \(\tilde{\chi}_{12}/\nu_0 = A + B/T^{a,b}\)

<table>
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<th>(G^\circ = \alpha + \beta/T)</th>
<th>(\tilde{\chi}_{12}/\nu_0 = A + B/T)</th>
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<td>0.00201 – 0.83/T, 0.121 – 50/T</td>
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<td>PzMSAN/dPMMA99k 41/59</td>
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<tr>
<td>PzMSAN/dPMMA99k 78/22</td>
<td>(-0.033485 + 1.60/T)</td>
<td>0.00184 – 0.83/T, 0.111 – 50/T</td>
</tr>
<tr>
<td>PzMSAN/dPMMA110k-s 30/70</td>
<td>0.005293 + 2.30/T</td>
<td>0.00274 – 1.18/T, 0.165 – 71/T</td>
</tr>
</tbody>
</table>

"Typical confidence limits are ±0.000004 and 0.003 for \(\alpha\) and \(\beta\), respectively. The reference volume is taken as \(\nu_0 = \sqrt{\chi T} = 88.21 \text{ cm}^3/\text{mol}. Conversion to reference volume \(\nu_0 = 100 \text{ Å}^3\) (often employed to compare systems) is obtained by multiplication of factor 100/1.66 (corresponding to 100 \times N_A/(10^5)^3 (from \text{mol/cm}^3 to \text{Å}^3))."

with the previous literature, \(^{29,30}\) providing a detailed description of all one-phase data within measurement uncertainty.

From the analysis so far, we ascertain that the blend syndiotactic dPMMA is more miscible with PzMSAN, as the phase boundaries shift to a higher temperature (despite the slightly higher \(M_c\)) and that its segment length also increases to 7.4 ± 0.2 Å. Next, we examine the effect of tacticity on the component interactions, as measured by \(G^\circ\) or \(\tilde{\chi}_{12}\).

**Thermodynamics of PzMSAN/dPMMA Blends in the One-Phase Region.** Figure 5a provides a comparison of \(G^\circ\) as a function of 1/T and all data, at various compositions, which are to follow a linear relation with \(G^\circ = \alpha + \beta/T\) and slope \(\beta = 1.60 \text{ [mol K/cm}^3\]\) and \(\beta = 2.30 \text{ [mol K/cm}^3\] for dPMMA99k and dPMMA110k-s, respectively. The steep temperature dependence of blend component interactions, and thus large \(\beta\), indicates the “highly interacting” nature of this partially miscible blend. \(^{25}\) The steeper slope of PzMSAN/ dPMMA110k-s relative to that of PzMSAN/dPMMA99k demonstrates that increasing syndiotacticy further increases interaction strength, defined by this metric.

Figure 5b plots the effective specific interaction parameter \(\tilde{\chi}_{12}/\nu_0\) as a function of 1/T, where we define \(\nu_0 = \sqrt{\chi \nu_{\text{PzMSAN}} \times \nu_{dPMMA} = 88.21 \text{ cm}^3/\text{mol}. Lines are fits to the habitual \(\tilde{\chi}_{12}/\nu_0 = A + B/T\) with constant slope \(B = -0.83 \text{ [mol K/cm}^3\]) for PzMSAN/dPMMA99k and with \(B = -1.18 \text{ [mol K/cm}^3\]) for PzMSAN/dPMMA110k-s. When the reference volume is taken as \(\nu_0 = 100 \text{ Å}^3\), \(\tilde{\chi}_{12}/\nu_0 = A + B/T\) in the unit of [mol/cm] is converted to \(\tilde{\chi}_{12} = A + B'T/T\) in the unit of [Å\(^3\)], where \(\nu_0 = \text{constant} \times B\). All \(G^\circ\) and \(\chi\) parameters, for all compositions investigated, are tabulated in Table 2.

Since \(M_c\) and composition \(\phi\) are nearly identical in both blends, the combinatorial entropy in both cases is similar, viz. \(\Delta S_{\text{combinatorial}} = -\frac{1}{\phi_\text{PzMSAN}} \frac{1}{\phi_\text{dPMMA}}\) for PzMSAN/dPMMA99k and PzMSAN/dPMMA110k-s, respectively. The contribution to \(\tilde{\chi}_{12}/\nu_0\) is very small, implying that the greater miscibility of PzMSAN/dPMMA110k-s must be associated with more favorable (enthalpic or non-combinatorial entropic) specific interactions upon increasing the dPMMA tacticity.

**Cahn–Hilliard–Cook Analysis in the Two-Phase (Spinodal) Region.** When a blend is quenched into the spinodal region, the (initial) evolution of the concentration fluctuation spectrum is generally described by the Cahn–Hilliard (CH) \(^{39,40}\) and Cahn–Hilliard–Cook (CHC) \(^{41}\) theories, as detailed by Binder \(^{42}\) in the context of polymer blends. Analysis of SANS data requires consideration of thermal fluctuations in the one-phase (equilibrium) region and thus CHC is employed, for which the scattering intensity \(S(q, t)\) is expected to evolve with time according to

\[
S(q, t) = S(q) + [S(q) - S'_M(q)] \exp(2RTq)t
\]

where \(S_q(q)\) is the initial structure factor at the original one-phase temperature \(T_o\) at a time set as \(t = 0\). In practical terms, \(T_o\) is the temperature of the preheating oven, and the (equilibrium) scattering intensity is generally well described by the RPA, as given in eq 2. At the final temperature \(T_f\) (corresponding to the experimental oven), \(S(q)\) becomes a “virtual” structure factor, changing sign (becoming negative) below a value \(q^*\), and cannot thus be directly measured by experiment; \(t\) is the time after the temperature jump, which is assumed to be instantaneous. The virtual structure factor, \(S'_M(q)\), is computed from eq 9, where \(1/S(0) \equiv G^\circ\) extrapolated to the corresponding \(T_o\) utilizing the relation in Table 2. An illustrate \(S'_M(q)\) is shown in the Supporting Information Figure S8. The growth rate \(R(q)\) of concentration fluctuations is given by

\[
R(q) = -Mq^2(G^\circ + 2q^2)
\]

where \(M\) is a “diffusional mobility” parameter, and \(k\) is the so-called “square gradient term”, capturing the energy penalty of creating an additional interface between demixed phases. In the context of the mean-field approximation of RPA, it can be expressed as

\[
k = \frac{1}{6} \left( \frac{\langle R^2_{x1} \rangle_x}{\phi_\text{PzMSAN} \langle N_x \rangle_x} + \frac{\langle R^2_{x2} \rangle_x}{\phi_\text{dPMMA} \langle N_x \rangle_x} \right) + \frac{1}{36} \left( \frac{(h_1 + 2) a_1^2}{\phi_\text{PzMSAN} \langle N_x \rangle_x} + \frac{(h_2 + 2) a_2^2}{\phi_\text{dPMMA} \langle N_x \rangle_x} \right)
\]

considering component polydispersity (required for PzMSAN), where the index \(h\) is given in Table 1 for all samples. The growth rate exhibits a maximum at

\[
q^*(CH) = \sqrt{\frac{G^\circ}{4k}}
\]

yielding a dominant initial length scale of \(\Lambda \approx 2\pi/q^*(t = 0)\) during the early stages of spinodal decomposition, whose duration can be estimated by

\[
\tau = \frac{4k}{2R(q^*(CH))} = \frac{4k}{MG^\circ}
\]
We have carried out systematic temperature jump experiments into the spinodal region, at near-critical composition, for both blends and employed CHC analysis to extract $G^\ast$ and $M$ parameters as a function of temperature. Figure 6 shows the scattering data at various times after jump for PaMSAN/dPMMA99k from common initial temperature $T_i = 135^\circ$C to final $T_i$ of (a) $148^\circ$C, (b) $153^\circ$C, (c) $160^\circ$C, and (d) $165^\circ$C. The experimental realization of temperature jump experiments involves displacing the blend film from the preheating cell (which is set at $T_i$) into the measurement cell ($T_f$), imposing a rapid heating profile (illustrated in Figure S7), which can take $\sim 30$–$100$ s, depending on $\Delta T \equiv T_f - T_i$. For consistency, we define the initial time $t = 0$ from the initial jump, although thermal equilibration will occur a few tens of seconds after $t = 0$, effectively limiting the shortest time resolution accessible in demixing kinetics. We fit all data with CHC, following eqs 10 and 11, by adjusting $G^\ast$ and $M$ and ensuring self-consistency with the early-stage assumptions, including that the data fall within the early-stage $\tau_c$ estimation. Time points indicated in black (filled triangles) and gray (filled circles) correspond to values inside and outside the early-stage time interval, respectively. In all panels, we include the equilibrium scattering data and RPA profile at $T_i = 135^\circ$C (the initial temperature), as well as for $T = 144^\circ$C, the highest one-phase temperature measured experimentally for this blend.

The CHC model well describes scattering data for jumps to $T_i = 148^\circ$C and $153^\circ$C, but not as well for the deeper quenches at $T_i = 160^\circ$C and $165^\circ$C, which we interpret as due to the short $\tau_c$ (commensurate with thermal equilibration time following the jump) and data scatter due to short integration times. The solid lines correspond to CHC fits within the early stages of spinodal decomposition. The vertical red lines mark the position in $q$, where the first peak in the scattering data is experimentally resolved, denoted by $q^\ast_{exp}(t \to 0)$, and the green dashed lines correspond to $q^\ast(CH)$ computed from the maximum of $R(q)$ obtained for each temperature jump, effectively corresponding to eq 13. We find that $q^\ast(CH)$ appears systematically at lower values than $q^\ast_{exp}(t \to 0)$ and that the scattering peak moves (albeit slightly) toward lower $q$, even during the early stages of spinodal decomposition. This effect is more significant for shallower quenches and becomes nearly imperceptible within measurement uncertainty for the deeper quenches. Evidently, this contrasts with the CH theory, for which the peak position $q^\ast$ is independent of time during the early stages of spinodal decomposition.39,40 However, both positive and negative $q^\ast$ shifts during the initial stages of phase separation have been experimentally observed41–43 and, in some cases, related to coarsening43 during the early stages. Below, we find our results to be consistent with the expected role of thermal fluctuations, captured by CHC predictions, as discussed below.

Figure 7 shows the time-resolved temperature jump scattering data for blend PaMSAN/dPMMA110k-s: 30/70 from initial temperature $T_i = 150^\circ$C to $T_f = (a) 168^\circ$C and (b) $175^\circ$C and from $T_i = 140^\circ$C to $T_f = (c) 170^\circ$C and (d) $180^\circ$C. As above, open (○) and closed (▲) symbols correspond to early- and intermediate-stage spinodal decomposition data, and the lines are fitted to the CHC theory, from eq (10). Gray (∗) symbols correspond to $T_i = 150^\circ$C or $140^\circ$C (with RPA fits), and $T_f = 157^\circ$C, the highest temperature in the one-phase region investigated. Note that $T_f = 140^\circ$C in panels (c, d) is just above $T_c \approx 125^\circ$C, and deviations from CHC are interpreted as due to the initial out-of-equilibrium state of the sample.

DOI: 10.1021/acs.macromol.9b02115
Macromolecules 2020, 53, 445–457
show lower scattering intensity at low-q than expected by RPA, which is associated with the incomplete thermal equilibration of long-wavelength concentration fluctuations. The solid lines are CHC fits, showing variable agreement with the experimental data. Lines fit data well for the jumps from 150 °C to 168 °C, shown in Figure 7a, but less well to $T_i = 175$ °C, which we attribute to the commensurable time scales of thermal equilibration of the sample in the heating cell and $\tau_c$. A more complex analysis involving a q-dependent Onsager mobility term $\Lambda(q)$ did not significantly improve the agreement with experimental observations. Further, temperature jumps from $T_i = 140$ °C to both $T_f = 170$ and 180 °C show significant deviations from CHC analysis, which we attribute to the proximity of $T_i$ to the glassy state and likely a more complex (time and q-dependent) mobility parameter $M$, discussed below. We next consider our experimental observations of the dominant wavenumber $q^*$ and corresponding peak positions of the scattering intensity based on the CHC theory, during the early stage (i.e., up to the respective $\tau_c$ for each condition). We note that the theoretical CHC prediction yields a variation of $q^*$ even during the early stages, and this curvature contrasts with the time-independent $q^*$ expected for the CH theory. While our data would also be compatible with a time-independent initial $q^*$, the experimentally observed $q^*_\text{exp}(t \to 0)$ would then differ from the corresponding $q^*(CH)$ calculated theoretically.

Here, $\tau_c$ is computed from eq 14 using the same $G^*$ and $M$ as in the data fits reported in Figures 6 and 7. Table 3 tabulates all values for $q^*$ and $\tau_c$. The experimental duration of the early stage of spinodal decomposition $\tau_{exp}$ is separately determined by the duration for which $q^*_\text{exp}$ follows the line predicted by the CHC theory and is found to be in good agreement with $\tau_c$. Beyond the early stage (as defined by $\tau_c$), we observe $q^*(t) \propto t^{-1/3}$ for $\tau_{exp}$, indicating coarsening by evaporation–condensation or Brownian coarsening, characteristic of this common $-1/3$ scaling. The exponent $\alpha$ in $q^*(t) \propto t^\alpha$ for other temperature jumps is found to be less than $-1/3$, suggesting that those data correspond to the crossover from the early to intermediate stages.

Overall, we conclude that CHC provides a fully self-consistent description of all demixing data (which the CH theory alone lacks), with a single set of parameters, and that the role of thermal fluctuations must be considered to obtain a comprehensive picture of thermally induced spinodal decomposition. The observed scattering intensity maximum $q^*_\text{exp}(t)$ must therefore be computed from numerical CHC calculations, which are trivial, to yield comprehensive data modeling. We further explore the implications of thermal fluctuations, and the impact of $T_i$ and $T_f$ in the next section.

**Dominant $q^*(t)$: Experiment and CH(C) Theory.** Following the temperature jump into the spinodal region, the location of the scattering intensity maximum $q^*_\text{exp}$ was determined as a function of time $t$ and shown by the data points in Figure 8 for (a) PzMSAN/dPMMA110k-s for the two jumps from $T_i = 150$ °C and (b) PzMSAN/dPMMA99k for all four jumps from $T_i = 135$ °C. A striking observation is that the experimentally observed $q^*(t)$ differs from the maximum wavenumber $q^*(CH)$ computed from the linearized CH theory alone, $39,40$ given by eq 13, with parameters $G^*$ and $k$ corresponding to that temperature and blend composition. Those are indicated by the horizontal dashed lines at the respective temperatures and are systematically lower than the $q^*(t)$ observed experimentally during the initial stages of spinodal decomposition. We therefore numerically compute the peak positions of the scattering intensity based on the CHC theory, considering the additional contribution of thermal fluctuations, as given by eq 10, and fixing the parameters obtained from the analysis shown in Figures 6 and 7 (and thus “parameter-free” in this sense). The solid lines in Figure 8 correspond to those estimations and agree well with the experimental data, within measurement uncertainty, during the early stage (i.e., up to the respective $\tau_c$ for each condition). We note that the theoretical CHC prediction yields a variation of $q^*$ even during the early stages, and this curvature contrasts with the time-independent $q^*$ expected for the CH theory. While our data would also be compatible with a time-independent initial $q^*$, the experimentally observed $q^*_\text{exp}(t \to 0)$ would then differ from the corresponding $q^*(CH)$ calculated theoretically.

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**Table 3. Tabulated Values of $q^*$, $\tau$, $q^*(CH)$, and $\tau_c$ of All Temperature Jumps for PzMSAN/dPMMA110k-s 30/70 ($T_i$ = 161.4 °C) and PzMSAN/dPMMA99k 28/72 ($T_i$ = 144.8 °C)**

<table>
<thead>
<tr>
<th>dPMMA</th>
<th>$T_i$</th>
<th>$T_f$</th>
<th>$\Delta T \equiv T_i - T_f$</th>
<th>$q^*_\text{exp}(t = 0)$</th>
<th>$\tau_{exp}$</th>
<th>$q^*(CH)$</th>
<th>$\tau_c$</th>
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<tr>
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*The uncertainty in temperature values is ±1 °C; the error bars for $q^*_\text{exp}$ are indicated in Figure 8 and range between 10 and 20% for $\tau_c.*
Impact of Thermal Fluctuations on the Observed $q^*(t)$. Figure 9a,b shows the calculated evolution of scattering

$\chi$ as a function of inverse temperature $1/T$, computed by several analysis methods, in both one- and two-phase regions, is shown in Figure 10. As before, we find that $q^*$ does not actually reach $q^*(CH)$ during the early stage, which is estimated by $T_c$. We emphasize that while this behavior could be suggestive of coarsening processes play an increasingly significant role (not included in the computation). Finally, we note that the deeper quenches approach $q^*$ faster, as the driving force for demixing is greater, and are less impacted by the initial thermal fluctuations, at constant $T_f$. These considerations agree well with the experimental observations reported in the previous section, namely, in Figures 6 and 7, impacting the observed offset between $q^*$ and $q(CH)$. Experimentally, we find that this effect can be considerable for the temperature jumps investigated here, $\Delta T \approx 3 - 20 \, ^\circ C$, and generally exceeds the wavenumber $q$ resolution of experimental measurements. Significantly, the measured $q^*$ does not actually reach $q^*(CH)$ during the early stage, which is estimated by $T_c$. We emphasize that while this behavior could be suggestive of coarsening processes play an increasingly significant role (not included in the computation). Finally, we note that the deeper quenches approach $q^*$ faster, as the driving force for demixing is greater, and are less impacted by the initial thermal fluctuations, at constant $T_f$. These considerations agree well with the experimental observations reported in the previous section, namely, in Figures 6 and 7, impacting the observed offset between $q^*$ and $q(CH)$. 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that the slopes of $G^*$ data with $1/T$ in the two-phase region appear generally lower than those observed in the one-phase region. We find that the measured $G^*$ for dPMMA99k blends in the two-phase region deviates from the RPA extrapolated line (from the one-phase region) for $\Delta T \equiv T_i - T_s \lesssim 15.2$ °C. The CHC results from the shallower quenches might be impacted by the commensurable time scales of thermal equilibration in the cell and demixing, effectively resulting in a "slow" (or at least slower, as shown in Figure S11) quench, compared to those at larger $\Delta T$.

Deviations from mean-field behavior could also potentially cause such offsets in the data and are expected near the critical point, on either side of the phase boundary, where concentration fluctuations dominate. The Ginzburg criterion estimates the temperature range associated with such deviations and, while several definitions are possible,48–51 we estimate $\Delta T < 3$ °C to be smaller than those observed experimentally. Overall, however, apart from near $T_s$, the correlation between $G^*$ data across the phase boundaries appears to be rather consistent.

**Mobility Parameter $M$.** We next consider the experimental results for the mobility parameter $M$ and compare these with theoretical models. We tentatively write $M$ as a combination of the individual diffusion coefficients $D$ of each component,25,48 expressed in terms of the fast mode as

\[ M = \phi_1 \phi_2 (\phi_1 \nu_{D_1} + \phi_2 \nu_{D_2}) \]

where $D$ for each polymer component is given by reptation in this $q$ range and thus

\[ D = \frac{k_b T d^2}{3a^2 \zeta_d} \]

where $k_b$ is the Boltzmann constant, $d$ is the tube diameter of $\sim 6$ nm,25 and $\zeta_d$ is the monomer friction coefficient and unit of $D$ is [cm/s]. We fix the PMMA monomer friction coefficient to $\zeta_{\text{PMMA}} = 0.04/T - 8.12 \times 10^{-5}$ [dyn s/cm]22,53 and fit the monomer friction for PtMSAN from the experimentally observed $M$ yielding $\zeta_{\text{PtMSAN}} = \frac{0.0007}{T} - 1.54 \times 10^{-6}$, which seems pertinent for this copolymer based on previous data.52 With these monomer friction coefficients, all data for both dPMMA110k-s and dPMMA99k blends can be rather well described by eq 15, as shown in Figure 11.

**Initial Spinodal Length Scale Prediction $\Lambda \equiv 2\pi/\sqrt{-\frac{\zeta}{4k}}$.** We next consider the ability of CH(C) theory to predict the initial length scale of the spinodal structure, based on eq 13 and $G^*$, against our experimental observations. Four distinct estimates are made, indicated in the top right of the panel, based on four schemes to compute $\Lambda$ and $G^*(T)$ pairs. Specifically, $G^*$ can be either computed from extrapolation from the one-phase data fitted to RPA, named $G^* (\text{RPA})$, or from CHC fitting in the two-phase region; separately, the dominant length scale $\Lambda$ can be calculated from the model $q^*(\text{CH})$, of eq 13, or from the initial location of the intensity maximum, $q^*_{\text{max}}(t \to 0)$. The solid lines show the theoretical predictions for both systems (with only slightly different $k$) computed from $\Lambda = 2\pi/\sqrt{-\frac{\zeta}{4k}}$, and the data points are labeled according to the legend in Figure 12, obtained from independent criteria. Overall, we find that the length scale prediction for dPMMA99k blends is in good agreement with the data for the two deeper quenches, but the shallower quenches yield smaller $\Lambda$ from the experiment than the CH theory predictions. Data for dPMMA110k-s blends generally show broad agreement with the CH theory. Length scale predictions $\Lambda$ based on $G^*(\text{CH})$ generally show better agreement with the experiment, likely due to the fact that this value is more robust since it is based on the entire dataset and not the peak position alone. Overall, we find that CHC is effective at predicting initial demixing length scales following spinodal decomposition, except for shallow quenches for which both measurement and the validity of theory remain somewhat unclear. This highly interacting blend enables phase sizes as small as $<40$ nm to be accessed with rather modest ($\sim 10$ °C)
temperature quenches, and the difference in tacticity of both dPMMA specimens does not change this behavior significantly.

## CONCLUSIONS

We present a detailed SANS study of the thermodynamics and phase separation of PzMSAN/dPMMA, on both sides of the phase boundary. We comparatively examine blends with two dPMMA samples of similar $M_w$ and differing in degree of syndiotacticity, termed atactic and syndiotactic according to the customary classification. The impact of the difference of syndiotacticity of dPMMA110k-s of 78 ± 3% (syndiotactic) and dPMMA99k of 63 ± 5% (atactic) on the blend thermodynamics is experimentally examined in detail. This partially miscible blend is one of the most highly interactive systems known, in terms of the steepness of the dependence of $G^*$ (or corresponding $\chi$) with $1/T$, which implies that a small temperature variation can cause a significant response in $G^*$. We are motivated by the potential of achieving nanoscale phase dimensions via thermally induced spinodal decomposition, which requires both rapid temperature quenches and a large variation of component interactions $G^*$ to avoid slow or “noninstantaneous” quenches unable to attain small phase sizes. From previous reports, this blend should yield spinodal structures of a few tens of nanometers to be formed with $\sim 10$ °C thermal quenches, which can be readily implemented in practice. In a previous publication, we investigated the role of $M_w$ and blend composition $\phi$ on phase behavior and demonstrated the formation of spinodal structures of initial phase size of $\sim 35$ nm. In this paper, we examine whether a modest change in polymer (dPMMA) tacticity can significantly alter blend thermodynamics. Based on SANS measurements across a range of temperatures in the one-phase, equilibrium region of the phase diagram, and employing RPA analysis, we demonstrate that blends with syndiotactic dPMMA exhibit steeper $G^*(1/T)$ dependence by approximately 40% and also a slightly larger polymer segment length (by $\approx 7\%$). Specifically, we obtain $G^* = -0.00383 + 1.60/T$ [mol/cm$^3$] for atactic blend PzMSAN/dPMMA99k 28/72 and $G^* = -0.00529 + 2.30/T$ [mol/cm$^3$] for syndiotactic blends (corresponding to $\tilde{X}_{12}/S_0 = 0.00201 - 0.83/T$ and $\tilde{X}_{12}/S_0 = 0.00274 - 1.18/T$ [mol/cm$^3$], respectively). We find that the increase in syndiotacticity causes an upward shift in the LCST phase boundary by $\approx 20$ °C for PzMSAN/dPMMA110k-s, with respect to PzMSAN/dPMMA99k, and therefore an increase in the miscibility window. Given the dependence of the theoretically predicted spinodal (initial) length scale as $\Delta \equiv 2\pi/q^* = 2\pi/\sqrt{G^*}$, we could thus expect smaller phase sizes with the dPMMA blend of higher syndiotacticity.

A number of temperature jump experiments from the one-phase region into the spinodal, unstable, region were carried out by SANS and analyzed by the Cahn–Hilliard–Cook (CHC) theory for both dPMMA110k-s and dPMMA99k blends. The influence of thermally driven concentration fluctuations is significant and captured by the CHC theory, including the initial $q^*$ time dependence during the early stages of spinodal decomposition. As concentration fluctuations are significant and well resolved by SANS, $q^*$ is not expected to be constant in time, even at early times. CHC analysis provides an independent measurement of $G^*$, which is negative within the spinodal region, and found to correlate reasonably well with one-phase $G^*$ measurements across the phase boundary. Deviations from the theory are observed when the initial jump temperature $T_i$ is near $T_g$ and possible explanations are discussed.

We find that the mobility term $M_s$ setting the kinetics of demixing alongside the driving force $G^*$, can be expressed in terms of the diffusion coefficient $D$ of each polymer component with a fast-mode mixing rule. We obtain a monomer friction coefficient $\zeta_{PM SAN} = 0.0007 - 1.54 \times 10^{-6}$ [dyn s/cm], which describes data from both blends across the temperature range (except for quenches originating from near $T_g$).

The initial spinodal length scale $\Lambda$ could be well predicted, within measurement uncertainty from the CHC theory and CH theory for both PzMSAN/dPMMA110k-s and PzMSAN/dPMMA99k blends. An agreement with the theory becomes less good for shallow quenches within the spinodal, i.e., for $T_i \geq T_j$; this could be possibly due to (expected) deviation from mean-field behavior, but equally from experimental technicalities related to the commensurability of time scales of the temperature change and demixing process, departing from an “instantaneous” quench. The minimum spinodal length scale attained in this study is $\sim 40$ nm, among the smallest observed by thermally induced demixing. In this particular case, the variation of syndiotacticity does not impact the length scale perceptively: despite the steeper $G^*$ temperature dependence, the upward shift in phase diagram with increasing dPMMA tacticity results in a commensurate $-G^*$ for a similar $\Delta T$. Figure 13 shows the dependence of $\Lambda$ for dPMMA99k and dPMMA110k-s blends with quench depth $\Delta T \equiv T - T_\nu$, computed from the respective $G^* = \alpha + \beta/T_\nu$ relations obtained experimentally. At the quench depths $\Delta T$ of interest, the difference in the resulting initial spinodal length scale is a modest $\approx 4$ nm, within experimental uncertainty. The same figure includes simulated results obtained by modifying the $\alpha$ and $\beta$ parameters for the PzMSAN/dPMMA99k blend, indicated by the dashed lines. Decreasing $\alpha$ decreases both $\Lambda$ and $T_\nu$ while increasing $\beta$ increases both $\Lambda$ and $T_\nu$; evidently, the $G^*$ parameters for PzMSAN/dPMMA110k-s
lead to an increase in both $\alpha$ and $\beta$, and these effects largely “cancel out”, resulting in the relatively small $\Lambda$ difference. Overall, it is clear that varying polymer tacticity offers a powerful means to modulating polymer blend component interactions. Evidently, this effect cannot be captured by the Flory–Huggins theory and merits a detailed thermodynamic investigation of the noncombinatorial entropic and enthalpic contributions to the free energy of mixing, which we suggest may arise from packing differences caused by the effect of tacticity on the chain conformation. Further work in this area is needed for the predictive design of spinodal structures.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02115.

DSC for PoMSAN, dPMMA110k-s, and dPMMA99k, tacticity dependence of $T_g$ for PMMA, temperature profiles of SANS isothermal experiments, comparison of SANS intensity and RPA expectation for dPMMA99k one-phase experiments, coherent scattering profiles and OZ plots for dPMMA99k, temperature profile of the measurement cell for the T-jump experiment, quality of T-jump experiments, virtual structure factor, Ginzburg criterion, mobility term for PoMSAN and dPMMA99k and PoMSAN and dPMMA110k-s blends, growth rate for each T-jump, quench depth dependence of $G''/k$ and length scale, Onsager mobility term for PoMSAN and dPMMA99k and length scale prediction as a function of quench depth (PDF).

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### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors thank the ISIS neutron source (U.K.) for beamtime and the Engineering and Physical Sciences Research Council (EPSRC, U.K.) for financial support. The authors are grateful to Zhen-Gang Wang (California Institute of Technology) and Jack F. Douglas (National Institute of Standards and Technology) for discussions regarding various forms of the Ginzburg criterion and Daniel Read (University of Leeds) for discussions on polymer diffusion and monomer friction coefficients.

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