Nacromolecules 2019, 52, 1112–1124

Article

Small Angle Neutron Scattering Study of the Thermodynamics of Highly Interacting $P\alpha$ MSAN/dPMMA Blends

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Supporting Information



ABSTRACT: Poly(methyl methacrylate) (PMMA) and poly(α -methylstyrene-co-acrylonitrile) (P α MSAN) form partially miscible blends with lower critical solution temperature (LCST) behavior. We revisit this system using small angle neutron scattering (SANS), examining the effect of molecular weight (M_w) of deuterated PMMA (dPMMA), blend composition (ϕ), and temperature (T) in the homogeneous region. All data are well-described by the Random Phase Approximation (RPA) theory, enabling us to determine thermodynamic and structural parameters, including the correlation length ξ , G" (the second derivative of the free energy of mixing with respect to composition), and the statistical segment length a of each component. Phase boundaries are computed by extrapolation of G'' with temperature, to yield the spinodal, and inspection of Kratky plots to yield the binodal. For PaMSAN, a is determined to be 10.1 \pm 0.4 Å. Unsurprisingly, this system deviates strongly from Flory– Huggins expectations, exhibiting a minimal $M_{\rm w}$ dependence of the phase boundaries and ϕ dependence of effective interaction parameter ($\tilde{\chi}$). Comparison of G" with values for other blend systems places P α MSAN/dPMMA in a class of highly interacting blends, expected from Cahn-Hilliard theory to yield small initial phase sizes upon spinodal demixing. This is confirmed experimentally, with an illustrative temperature jump resulting in an initial phase size of $\simeq 30$ nm.

INTRODUCTION

Demixing of polymer blends provides an attractive route to the fabrication of nano- and microporous materials, with applications ranging from membranes for separations,¹ biological scaffolds, to organic photovoltaics.² The characteristic length scale of the demixed structure is generally key to material performance and set by, often complex, phase separation pathways. These include rapid solvent evaporation or phase inversion and kinetic arrest, starting from polymerpolymer-solvent, ternary (or multicomponent) mixtures, or via the processing of immiscible blends. Thermal (or pressure) induced demixing of partially miscible binary systems yields a potentially simple and controlled approach to inducing welldefined polymeric structures. From an equilibrium state, in the homogeneous region of the phase diagram, a temperature jump (T-jump) into the two-phase, unstable, region can yield well-defined bicontinuous materials with prescribed dimensions. This method is in principle less costly and synthetically

demanding than block copolymer assembly, and provided that the structure of interest can be rapidly quenched (e.g., by cooling below glass transition temperature), it is exceptionally versatile.

Predictions of spinodal structures via polymer blend demixing strategy rely on the Cahn-Hilliard-Cook (C-H) theory,^{3–5} adapted to the context of polymer blends.⁶ In short, at early times, the dominant wavenumber of the isotropic, periodic structure can be analytically estimated to be $q^*=\sqrt{-G''/4k}$, where $G''\equiv rac{\partial^2\Delta G_{
m m}}{\partial \phi^2}$ is the second derivative of the free energy of mixing ΔG_{m} with respect to composition (ϕ) , and k is the so-called "square gradient term". The driving force for demixing is subsumed in G'' while the energetic

Received: November 14, 2018 Revised: January 9, 2019 Published: January 28, 2019

Table 1. Polymer	Sample	Characteristics:	PαMSAN	Comprises	30%	AN and	70% α-MSt
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	$\langle M \rangle_{\rm w} [\rm kg/mol]$	$\left< M \right>_w / \left< M \right>_n$	<i>m</i> [g/mol]	$T_{g} [^{\circ}C]$	<i>b</i> [fm]	a [Å]	$\langle R_{\rm g} \rangle_{\rm w} [{\rm nm}]$
$P\alpha MSAN$	122	2.6	98.66	118 ± 1	21.12	10.1 ± 0.4	14.5
dPMMA40k	39.5	1.1	108.1	115 ± 1	98.20	6.9	5.4
dPMMA99k	99.1	1.1	108.1	122 ± 1	98.20	6.9	8.5
dPMMA130k-P	131	2.0	108.1	117 ± 1	98.20	6.9	9.8
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^{*a*}Segment lengths *a* for P α MSAN were obtained from this work and for dPMMA from the previous literature.^{19,20} Chain dimensions R_g were computed according to $\langle R_g \rangle_w = (\langle N \rangle_w a^2/6)^{0.5}$ from the tabulated values. Parameter *b* is the coherent neutron scattering length, and *m* is the mass of each repeat unit.

penalty associated with composition gradients due to fluctuations is quantified by k.

The predictive ability of polymer blend thermodynamic theory to compute phase behavior and G'' is currently limited, given the well-known shortcomings of Flory-Huggins (FH) lattice theory, and the relative complexity of models such as polymer reference interaction site model (PRISM),⁷ lattice cluster theory (LCT),8 locally correlated lattice (LCL)9,10 theory, and others. These incorporate some structural information about the polymeric constituents, chain conformation statistics, and interaction potentials in some form. For instance, LCT explicitly considers monomer architecture, chain stiffness, energetic asymmetries, and nonrandom mixing, while LCL is an equation of state approach able to accommodate volume changes upon mixing as well as nonrandom mixing.^{9,10} Accurate blend data and rigorous theoretical comparisons with experimental data are still needed to advance this field.

Small angle neutron scattering (SANS) is a powerful means to investigate the thermodynamics of polymer blends and directly determine G'' and k in the one-phase region. The former can be simply related to forward scattering intensity S(q) \rightarrow 0), and both can be obtained from de Gennes Random Phase Approximation (RPA) theory.¹¹ Over the past four decades, various authors have experimentally investigated the early stages of spinodal decomposition (e.g., refs 12-14) with a combination of light, neutron, and X-ray scattering as well as various microscopies. A few studies have examined the validity of the C-H prediction of the initial length scale of polymer blend demixing, which we have recently reviewed and found to be remarkably accurate,¹⁵ despite neglecting hydrodynamic interactions, nonlinear terms to the diffusion equation, and limitations of the mean field assumption for blends (involved in estimating G'' and particularly k). Extrapolation of G''(T)with temperature from the one-phase region, which is positive, to the two-phase region, across the spinodal line, where it becomes negative, appears thus an effective approach to selecting G'' and, in turn, q* to predictively design bicontinuous structures.

In this paper, we investigate a model blend of poly(α -methylstyrene-*co*-acrylonitrile) (P α MSAN) with (deuterated) poly(methyl methacrylate) (dPMMA) by SANS. P α MSAN/ dPMMA forms a lower critical solution temperature (LCST) mixture, whose glass transition temperature ($T_g \approx 120$ °C) is near the critical temperature (≈ 140 °C), thus enabling precise time-resolved SANS experiments. This system has been previously reported by Higgins et al.¹⁶ and identified as a highly interacting blend,¹⁵ in terms of the magnitude of G'' for a modest, accessible quench depth ΔT within the spinodal line. In simple terms, refined below, this blend exhibits a large β (or slope) in the descriptive relation $G'' = \alpha + \beta/T$. We employ a M_w series of atactic dPMMA ($M_w = 40-130$ kg/mol) with

different polydispersity (PDI) and investigate an unprecedented composition window, encompassing critical and offcritical mixtures, and temperature range. We systematically map G'' (and effective $\tilde{\chi}$), correlation length ξ of concentration fluctuations, and segment lengths *a* across all conditions in the homogeneous region. We finally provide an illustration of a Tjump experiment into the unstable region to induce a bicontinuous nanoscale morphology of prescribed dimensions.

EXPERIMENTAL SECTION

Polymer Mixtures. Poly(α -methylstyrene-*co*-acrylonitrile) (P α M-SAN) was kindly donated by BASF (Luran KR2556) with 30% AN and 70% α -MSt.¹⁷ Deuterated poly(methyl methacrylate) was purchased from Polymer Source Inc. (40k and 99k) and synthesized in our laboratory (130k-P). The 40k and 99k were prepared by living group transfer polymerization and living anionic polymerization, respectively, while the 130k-P was obtained by radical polymerization, ¹⁸ and all specimens are largely atactic. Key characteristics of the polymers used are summarized in Table 1, and the monomer chemical structures are given in Figure 1. Glass transition temper-



Figure 1. Monomer repeat units of poly(α -methylstyrene-*co*-acrylonitrile) and (deuterated) poly(methyl methacrylate).

atures of the pure components were determined by differential scanning calorimetry (DSC) using a TA Instruments Q2000 instrument, at 10 $^\circ C/min$ heating rate, and computed with the midpoint method.

Blends of P α MSAN and dPMMA, at various M_w and compositions, were prepared by solution casting. All blend compositions were prepared by mass and then converted into volumetric ratio of P α MSAN using the pure component densities ($\rho_{P\alpha MSAN} = 1.07(5)$ g/cm³ and $\rho_{dPMMA} = 1.27(5)$ g/cm³). The polymers were first dissolved in tetrahydrofuran (THF, purity \geq 99.7% unstabilized HPLC grade, VWR) at a concentration of 8% w/v and stirred at room temperature for 48 h. The solution was drop cast onto glass coverslips (19 mm in diameter, VWR), and the solvent was allowed to evaporate at ambient conditions for 1 week. The resulting films (of approximately 100 μ m thickness) were then carefully peeled off, stacked together, and gently pressed (Specac hydraulic press, 4 ton) at room temperature with an aluminum mold to obtain approximately 1 mm thick films. The films were then placed under vacuum (20 mbar) for 4 weeks, while



Figure 2. Coherent SANS scattering data for P α MSAN/dPMMA40k blends of four different compositions: (a) 29/71, (b) 29/61, (c) 54/46, and (d) 82/18 v/v. Samples were heated in a stepwise manner for time intervals ranging from 120 min (near T_g) to 3 min, near the phase boundary. The filled symbols indicate data in the one-phase region of the phase diagram, while open symbols indicate demixed, out-of-equilibrium conditions. Data at 125 °C correspond to specimens annealed for 36 h prior to the experiment.

gradually increasing the temperature up to 110 $^\circ\text{C}$, which is just below the blend $T_{\rm g}$. Prior to the SANS experiment, the temperature was increased to 125 °C for 36 h and then cooled down to room temperature under (20 mbar) vacuum to prevent absorption of moisture. The 1 mm thick films were then wrapped in a thin aluminum foil (22 μ m) sachet to be mounted onto the temperaturecontrolled cell to acquire SANS data in the one-phase region. Selected thin (100 μ m) samples were also prepared for T-jump experiments into the two-phase region.

Cloud point curves of the various PaMSAN/dPMMA were measured using a temperature-controlled stage (Linkam Scientific THMS600) upon heating at 0.5 °C/min until the sample became cloudy and bluish. These optical cloud point measurements were consistently higher (by approximately 20-30 °C) that those determined by SANS, which is not unexpected given the smaller length scales probed by the latter.

Small Angle Neutron Scattering. SANS experiments were performed at ISIS (UK) Larmor, with a polychromatic $\lambda = 0.9-13.3$ Å unpolarized incident beam and $D_{s-d} = 4.1$ m, yielding a fixed momentum transfer range of approximately $0.003 < q < 0.7 \text{ Å}^{-1}$. For these measurements, a larger incident divergence was used to increase flux at the cost of a truncated momentum transfer range of 0.006 < q< 0.6 Å⁻¹. The elastic scattering vector is $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \approx \frac{2\pi}{\lambda}$, for

small scattering angles θ .

A custom-made T-jump cell was employed for both equilibrium, one-phase, and demixing experiments. The cell consists of two brass ovens with quartz windows and a motorized sample carrier, which rapidly (<1 s) transports the sample between the two ovens. The setup has been described elsewhere.^{21,22} For equilibrium, one-phase experiments, the sample was loaded at 125 °C (the final oven temperature) into the measurement oven, and the temperature was systematically increased, in a stepwise fashion, in steps of 8 °C (close to T_{o}) to 2 °C, near the phase boundary. Acquisition times varied

from 120 min (close to T_g) and 3 min, near demixing, for P α MSAN/ dPMMA blends, and 30 min for backgrounds and empty cells. All data were acquired in "event mode/list" enabling the measurement time-resolution to be selected a posteriori. This feature is particularly useful to ensure that data are at equilibrium (e.g., near T_g and phase boundaries), and data sets can be truncated accordingly. Sample thicknesses were determined using a digital micrometer, and selfconsistency with neutron transmission was confirmed.

Scattering data were reduced and calibrated, and the contribution from the empty cell was subtracted, using Mantid.²³ The coherent scattering function was then obtained after subtraction of the appropriate volume fraction of the calibrated spectra of the hydrogenous component P α MSAN (provided in the Supporting Information, Figure S1).

RESULTS AND DISCUSSION

Optical Cloud Point Boundaries. Prior to SANS measurements, the binary temperature-composition phase diagram of P α MSAN/dPMMA blends was estimated optically at a relatively low heating rate of 0.5 °C/min. For blends containing dPMMA40k, we obtained cloud points of 172, 170, 177, and 198 °C for compositions $P\alpha MSAN/dPMMA$ 29/71, 39/61, 54/46, and 82/18, respectively. Similar results were obtained for 99k and 130k-P, as shown in the Supporting Information, Figure S2. The optical cloud points thus indicate an asymmetric LCST phase diagram, with critical point (pprox30/ 70-40/60 v/v), in broad agreement with previous work.^{16,24} The faint, bluish, cloudy appearance of the specimens suggests demixed structures at a fine ($\leq 1 \mu m$) length scale. We take these as upper estimates of the phase boundaries of the system, given the relative proximity to $T_{\rm g}~(\approx 120~^{\circ}{\rm C})$, the limited spatial resolution of optical microscopy, and the finite heating

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rate employed in the measurement. Offsets of up to 30 °C between optical microscopy data upon demixing and onephase SANS were found, and these were consistent with the coarsening data obtained by time-resolved SANS following temperature jumps and ramps into the two-phase region. We have therefore relied on isothermal SANS in the one phase to establish the phase boundaries, as described below.

Inspection of SANS Coherent Scattering Data. The coherent scattering data for PaMSAN/dPMMA40k blends of various compositions, as a function of temperature, are shown in Figure 2. Filled symbols correspond to data identified in the one-phase region, with no structural peak, while open symbols indicate samples which have crossed into the two-phase region. Particular attention was given to lower temperature SANS measurements, as equilibration of concentration fluctuations is expected to be slow near Tg. The first measurements were carried out at 125 °C, following a 36 h annealing (ex situ); inspection of the data revealed that all samples, regardless of $M_{\rm w}$ and ϕ , had not reached equilibrium, as gauged by extrapolation from higher temperature measurements. These were therefore disregarded and are shown in brackets in Figure 2. Isothermal SANS measurements were carried out by increasing temperature in a stepwise manner, and waiting for the temperature of the experimental cell to be reached (within ± 0.2 °C, typically 300 s); we then ensured that the scattering intensity profile no longer evolved in time (made possible by the "event" mode operation of LARMOR). Typically, these additional "wait" time intervals (attributed to the equilibration of concentration fluctuations) ranged from 600 to 100 s, at approximately T_g + 20 °C to T_g + 50 °C. These data were then analyzed within the RPA and Ornstein-Zernike (OZ) formalisms, detailed below.

Upon increasing temperature further, a number of blend compositions ($P\alpha$ MSAN/dPMMA40k 29/71, 39/61, 54/46 v/v) exhibited a structural peak associated with demixing. From these observations, the phase boundaries can be estimated as approximately 144 °C at 29/71, 147 °C at 39/61, 162 °C at 54/46, and above 175 °C at 82/18. The highest temperature investigated was 175 °C to prevent sample degradation. Near the critical point, the experimentally available temperature window within the one-phase region is thus very narrow, $T_c - T_g \simeq 20-25$ °C.

RPA and OZ Analysis. The absolute coherent scattering intensity (in $[cm^{-1}]$ units) from a binary polymer blend in the one-phase region is given by

$$I(q) = N_{\rm A} \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 S(q)$$
(1)

where b_1 and b_2 are the coherent scattering lengths of monomer units 1 and 2, v_1 and v_2 are their monomer molar volumes of the units, and N_A is the Avogadro number. The forward scattering intensity (at a given temperature) has particular significance, as $G''(T) \equiv 1/S(q = 0, T)$ providing a direct estimation of the second derivative of the free energy of mixing. We refer to component 1 as P α MSAN, and 2 as dPMMA, for which $b_1 = 21.12$ fm, $v_1 = 91.77$ cm³/mol, $b_2 =$ 98.20 fm, and $v_1 = 84.79$ cm³/mol, yielding a contrast prefactor $N_A(b_1/v_1 - b_2/v_2)^2 = 5.19 \times 10^{-3}$ cm⁻⁴ mol. The structure factor of the homogeneous binary blend is written according to de Gennes' Random Phase Approximation (RPA),¹¹ as

$$\frac{1}{S(q)} = \frac{1}{S_1(q)} + \frac{1}{S_2(q)} - 2\frac{\ddot{\chi}_{12}}{\nu_0}$$
(2)

where $S_i(q)$ [cm³/mol] is the structure factor of each component, and χ_{12} is monomer-monomer interaction parameter. Considering component polydispersity, $S_i(q)$ can be written as²⁵

$$S_i(q) = \phi_i v_i \langle N_i \rangle_n \langle g_D(R_{gi}^2 q^2) \rangle_w$$
(3)

where ϕ_i is volume fraction, v_0 is a reference molar volume taken as $v_0 \equiv \sqrt{v_1 v_2}$, and $\langle N_i \rangle_n$ is the number-average degree of polymerization of component *i*. Term $\langle g_D(R_{gi}^2 q^2) \rangle_w$ is the weight-average form factor of a Gaussian chain, computed from the Debye function, assuming a Schultz–Zimm polydispersity distribution:^{22,25–28}

$$\langle g_{\rm D}(x) \rangle_{\rm w} = \frac{2}{\langle x \rangle^2} \left[\left(\frac{h}{h+x} \right)^h - 1 + x \right]$$
 (4)

where $x \equiv q^2 \langle R_g^2 \rangle_n$, $h = (M_w/M_n - 1)^{-1}$, and the n-average radius of gyration for a Gaussian coil $\langle R_g^2 \rangle_n^{1/2} \equiv \langle N \rangle_n a^2/6$, where *a* is the statistical segment length. For polydisperse components, care is needed in the estimation of *a* from SANS, which directly measures *z*-average dimensions and w-average masses (or *N*). From eq 4, in the limit $q \to 0$, then $\langle g_D(x \to 0) \rangle_w \to 1$, and eq 2 becomes

$$\frac{1}{S(0)} = \frac{1}{\phi_1 \nu_1 \langle N_1 \rangle_{\rm w}} + \frac{1}{\phi_2 \nu_2 \langle N_2 \rangle_{\rm w}} - 2\frac{\chi_{12}}{\nu_0}$$
(5)

recalling the Flory–Huggins χ value at the spinodal

$$\chi_{\rm s} = \frac{\nu_0}{2} \left(\frac{1}{\phi_1 \nu_1 \langle N_1 \rangle_{\rm w}} + \frac{1}{\phi_2 \nu_2 \langle N_2 \rangle_{\rm w}} \right) \tag{6}$$

yields from eq 5 that

$$(G'' \equiv) \frac{1}{S(0)} = \frac{2}{\nu_0} (\chi_s - \tilde{\chi}_{12})$$
(7)

where $\tilde{\chi}_{12}$ is an *effective* interaction parameter, measured by SANS, which can be related to the common Flory–Huggins parameter χ_{12} by

$$\tilde{\chi}_{12} = -\frac{1}{2} \frac{\partial^2 [\phi(1-\phi)\chi_{12}]}{\partial \phi^2}$$
(8)

where $\tilde{\chi}_{12} \equiv \chi_{12}$ for composition-independent interactions. At low angle scattering angles ($qR_g < 1$) the simpler OZ provides a good approximation to the data, where

$$S(q) = \frac{S(0)}{1 + \xi^2 q^2}$$
(9)

and thus

$$\frac{1}{S(q)} = \frac{1}{S(0)} + Aq^2 \tag{10}$$

with

$$A = \frac{1}{3} \left(\frac{\langle R_{g1}^2 \rangle_z}{\phi_1 v_1 \langle N_1 \rangle_w} + \frac{\langle R_{g2}^2 \rangle_z}{\phi_2 v_2 \langle N_2 \rangle_w} \right) = \frac{1}{18} \left(\frac{(h_1 + 2)a_1^2}{(h_1 + 1)\phi_1 v_1} + \frac{(h_2 + 2)a_2^2}{(h_2 + 1)\phi_2 v_2} \right)$$
(11)



Figure 3. Ornstein–Zernike fits to the low q coherent SANS scattering data, in the one-phase region, for $P\alpha$ MSAN/dPMMA40k at the v/v compositions indicated. The specimens annealed at 125 °C for 36 h have not reached equilibrium, as seen by the curved 1/I vs q^2 , and by an offset of the expected trend of 1/I(0) with temperature (Supporting Information, Figure S3). From these OZ fits, the forward scattering intensity S(0)and the correlation lengths ξ are extracted as a function of temperature and composition.

where the last equality is obtained by noting that $\langle R_{g}^{2} \rangle_{z} = \frac{h+2}{h+1} \langle R_{g}^{2} \rangle_{w}$ for finite (Schultz–Zimm) polydispersity. The correlation length is thus obtained as $\xi \equiv \sqrt{AS(0)}$ where, as previously noted, $1/S(0) \equiv G''$. An important selfconsistency test for the RPA involves the link between the correlation length ξ^2 and the forward scattering intensity, S(0)expressed by $\xi^2 = AS(0)$ which was ensured for all data (provided in the Supporting Information, Figure S3).

All SANS profiles of homogeneous blends, at temperatures above T_{σ} , were analyzed with RPA and OZ formalisms, and the latter is illustrated for the P α MSAN/dPMMA40k blend series in Figure 3. As expected, the inverse scattering intensity varies linearly with q^2 , and the slope of the curves yields thus A in eq 10, from which chain dimensions and segment lengths can be computed according to eq 11. The intercept of this plot is directly proportional to G'' allowing a direct estimation of the spinodal temperature by extrapolation to zero, as described below. Slope A is expected to be constant with temperature, according to eq 11. At 125 °C we observe this slope deviates from those measured at higher temperatures, away from T_{a} and that the dependence with (inverse) temperature departs from the linearity expected from $G'' = \alpha + T/\beta$. These measurements in near proximity to T_g are thus taken to be out of equilibrium and not analyzed further. Further, data at the lowest q values $(q^2 < 0.0001 \text{ Å}^2)$ in Figure 3a,b somewhat deviate from linearity, interpreted as due to the slow equilibration of long wavelength concentration fluctuations near T_g . While extrapolation of G'' to zero provides robust estimates

of the spinodal line, locating the binodal is generally more

involved. We therefore use deviations from RPA and the emergence of a shoulder or peak at temperatures sufficiently above T_g as evidence of demixing. Kratky plots $(Iq^2 \text{ vs } q)$ provide a useful means of identifying small departures from q^{-2} scaling. We therefore estimate spinodal lines from G''(T) and the binodal lines from Kratky deviations, ensuring selfconsistency with the spinodal.

Kratky Asymptote. The structure factor of one-phase blends at high wavenumber $(qR_g \gg 1)$ is given by

$$S(q)q^2 \approx 12 / \left(\frac{a_1^2}{\phi_1 v_1} + \frac{a_2^2}{\phi_2 v_2} \right)$$
 (12)

reaching therefore a constant value at high q in a so-called "Kratkty plot" (Iq^2 vs q). Illustrative plots for P α MSAN/ dPMMA40k blends are shown in Figure 4. We observe a peak emerging at 142 °C for PαMSAN/dPMMA40k:29/71, 147 °C for PaMSAN/dPMMA40k:39/61, and 164 °C for PaMSAN/ dPMMA40k:54/46, while no peak is observed for P α MSAN/ dPMMA40k:82/18. Scattering profiles deviating for the lines computed from RPA theory are thus concluded to be in the two-phase region, shown by open symbols in the graph. Demixing temperatures determined using Kratky plots are lower than those estimated from the coherent scattering shown in Figure 2 for P α MSAN/dPMMA40k:29/71 and 39/61, and are therefore taken as more accurate, given the higher sensitivity of this method.

The high q asymptote of Iq^2 depends thus only on the polymer component volume fraction ϕ_{i} the monomer molar volume v_i , and the segment length a_i of each polymer. Significantly, it does not depend on the polymer molecular



Figure 4. Kratky plots of P α MSAN/dPMMA40k at the four different compositions indicated. The filled symbols indicate one-phase region of the phase diagram. The lines correspond to RPA theory at the temperatures of lowest and highest of equilibrium with adjusting segment length of P α MSAN and fixing well-known segment length of dPMMA. The specimens annealed at 125 °C for 36 h have not reached equilibrium. The Kratky plateau depends on composition ratio and the segment length of each component. The open symbols indicate the two-phase region of the phase diagram, the lowest temperature of which gives our best indication of the binodal temperature.

weight distribution, nor temperature, unlike the preceding equations for lower angle scattering, since it measures the *local* polymer conformation. Since ϕ_i and v_i are known, a_i can be determined directly from the Kratky asymptote. To increase the accuracy of the measurement of *a* of P α MSAN, we fix the well-known PMMA segment length to a(PMMA) = 6.9 Å.^{19,20,29} Further, we collectively fit a(P α MSAN) as a function of composition ϕ_i for the various M_w (dPMMA) in Figure 5, where the lines represent confidence intervals. The upper and lower lines indicate a(P α MSAN) = 10.5 and 9.7 Å, respectively. We therefore obtain a(P α MSAN) = 10.1 \pm 0.4 Å which is, to our knowledge, the first determination of the segment length for this polymer.

Correlation Length and Second Derivative of Free Energy. RPA is found to fit well all one-phase scattering data as shown in Figure 6. During data analysis, the higher q region is preferentially fitted, given the lower angle deviations discussed above and related to slow thermal equilibration of long wavelength concentration fluctuations near T_g , which is evidently faster at higher q, as described by C–H theory in the homogeneous region.^{30,31}

Figure 7 provides RPA parameters $G'', \tilde{\chi}/v_0$, as well as OZ correlation length squared ξ^{-2} , as a function of temperature. Since $\xi^{-2} = (AS(0))^{-1} = G''/A$, both G'' and ξ^{-2} show an inverse temperature dependence (1/T), whose extrapolation to zero yields the spinodal temperature (for a given ϕ and M_w). The effective interaction parameter $\tilde{\chi}_{12}/v_0$ is then computed from eq 7 assuming a χ_s/v_0 calculated from Flory–Huggins theory, eq 6, indicated as a horizontal line in the figure. (RPA



Figure 5. Kratky asymptote as a function of composition of P α MSAN for blends with three dPMMA $M_w = 40k$, 99k, and 130k-P, where P indicates a polydisperse sample ($M_w/M_n \approx 2.0$). The symbols correspond to the experimentally measured Kratky asymptote values and associated uncertainty. The lines correspond to data fits to eq 12 for the segment length of P α MSAN, encompassing the largest and smallest values compatible with the data, yielding $a_{\text{P}\alpha\text{MSAN}} = 10.1 \pm 0.4$ Å (while fixing $a_{\text{PMMA}} = 6.9$ Å).

parameters for other $M_{\rm w}$'s are provided in the Supporting Information, Figures S4 and S5.)

The second derivative of the free energy G'' as a function of inverse temperature 1/T for all compositions ϕ and dPMMA

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Figure 6. Coherent scattering intensity and RPA fits for one-phase data of blends of P α MSAN/dPMMA of different M_w : (a) P α MSAN/dPMMA40k:82/18, (b) P α MSAN/dPMMA99k:78/22, and (c) P α MSAN/dPMMA130k-P:29/71, measured as a function of temperature.



Figure 7. Correlation length ξ^{-2} , second derivative of free energy of mixing *G*", and effective interaction parameter $\tilde{\chi}_{12}/\nu_0$ as a function of inverse temperature 1/T for P α MSAN/dPMMA40k with four compositions. Vertical dash lines indicates the experimentally measured spinodal temperature.

 $M_{\rm w}$ is given in Figure 8. All data fit linearly, following $G'' = \alpha + \beta/T$ with the same slope $\alpha = 1.60$ remarkably well. The intercept α is tabulated in Table 2. The large α (and thus steep temperature dependence of blend component interactions) established this as a "highly interacting" blend, as detailed below. (A comparison with the previous measurement of G'' as a function of 1/T is provided in the Supporting Information, Figure S6).¹⁶

The phase diagram for all blends investigated is shown in Figure 9, in broad agreement with that reported by Higgins et al.¹⁶ The solid lines indicate the spinodal, while the dashed line estimates the binodal. We find that both the shape and location of the phase diagram vary little with M_{w} , and the critical point for this blend is estimated at \leq 30% v/v P α MSAN. The phase

boundaries remain asymmetrical regardless of varying M_w . The spinodal curve of P α MSAN/dPMMA40k is above that of P α MSAN/dPMMA99k, which is consistent with the M_w dependence expected for LCST polymer blends. However, boundaries for P α MSAN/dPMMA130k-P appear above the lower M_w data. We note that the polydispersity of dPMMA130k-P is 2.0, while those of dPMMA40k and dPMMA99k are 1.1 and 1.1, respectively, which should affect the coexistence curve but not the spinodal, as this is expected to be determined by M_w and not the full size distribution. Although we do not have a complete SANS phase diagram for this blend (and optical microscopy data shown to be inaccurate, Figure S2), this might be due to an increased asymmetry of the phase boundaries upon increasing M_w , or an

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Figure 8. Second derivative of the free energy G'' as a function of inverse temperature (1/T) for (a) P α MSAN/dPMMA40k, (b) P α MSAN/dPMMA99k, and (c) P α MSAN/dPMMA130k-P:29/71, at the compositions indicated in the one-phase region. The lines are simultaneous data fits to $G'' = \alpha + \beta/T$ with constant slope β .

Table 2. Tabulated Values^{*a*} G'' and $\tilde{\chi}_{12}/\nu_0$ of P α MSAN/dPMMA Obtained by SANS in the One-Phase Region

dPMMA	$\phi_{ extsf{P}lpha extsf{MSAN}}$	$G'' = \alpha + 1.60/T, \alpha \text{ (mol/cm}^3\text{)}$	$ \tilde{\chi}_{12}/\nu_0 = A - 0.83/T, $ $A \; (mol/cm^3)$
40k	29/71	-0.003 84	0.002 03
	39/61	-0.003 76	0.001 99
	54/46	-0.003 63	0.001 93
	82/18	-0.003 43	0.001 87
99k	28/72	-0.003 83	0.002 01
	41/59	-0.003 77	0.001 98
	78/22	-0.003 49	0.001 84
130k-P	29/71	-0.003 73	0.001 95

^{*a*}In the form $G'' = \alpha + \beta/T$, where $\beta = 1.60 \text{ mol K/cm}^3$; and $\tilde{\chi}_{12}/\nu_0 = A + B/T$, where $= -0.83 \text{ mol K/cm}^3$, respectively.



Figure 9. Phase diagram of P α MSAN/dPMMA40k, 99k, and 130k-P computed from SANS data. The filled symbols correspond to the spinodal temperature estimated by extrapolation of $G'' \rightarrow 0$ vs 1/T. The open symbols indicate the estimated binodal temperatures from deviation of the one-phase Kratky plots. Lines serve as guide to the eye. We note that all blends, despite the varying M_{w} , exhibit nearly identical, asymmetric, phase boundaries. Blend T_g 's were estimated from pure component data by the Fox equation:³² $\frac{1}{T_{g,blend}} = \frac{\phi_{P\alpha MSAN}}{T_{g,p} \alpha_{MSAN}} + \frac{\phi_{dPMMA}}{T_{g,dPMMA}}$, and indicated by the gray area.

apparent upward shift caused by slow equilibration of concentration fluctuations during SANS measurement. Our

main observation, however, is that all blends of different $M_{\rm w}$ studied exhibit remarkably similar phase boundaries. This is rather typical of systems where the contribution of combinatorial entropy is small compared to that of specific interaction. Evidently, these results deviate from Flory–Huggins predictions, which is unsurprising, in particular for highly interacting blends.

Effective Specific Interaction Parameter $\tilde{\chi}_{12}$. In the context of Flory–Huggins lattice theory,^{33–35} the free energy of mixing is written as

$$\frac{\Delta G_{\rm m}}{k_{\rm B}T} = \frac{\phi \ln \phi}{\nu_{\rm I}N_{\rm I}} + \frac{(1-\phi)\ln(1-\phi)}{\nu_{\rm 2}N_{\rm 2}} + \frac{\phi(1-\phi)}{\nu_{\rm 0}}\tilde{\chi}_{12}$$
(13)

which, in turn, implies that

$$G'' \equiv \frac{\partial^2 \left(\frac{\Delta G_m}{k_B T}\right)}{\partial \phi^2} = \frac{1}{\phi_1 v_1 N_1} + \frac{1}{\phi_2 v_2 N_2} - 2\frac{\tilde{\chi}_{12}}{v_0}$$
(14)

which, combined with eq 7, allows for $\tilde{\chi}_{12}$ to be readily computed from experimental SANS data of $1/S(0) \equiv G''$. The temperature dependences of $\tilde{\chi}_{12}/v_0$ for P α MSAN/dPMMA40k blends of various compositions are shown in Figure 10a, and for various dPMMA $M_{\rm w}$ at a fixed composition $\approx 29/71$ in Figure 10b. Following from Figure 8, all are well-described by a linear dependence $\tilde{\chi}/\nu_0 = A - 0.83/T$, whose intercept A varies with composition ϕ , and marginally with M_w as tabulated in Table 2. The composition dependence of $\tilde{\chi}/v_0$ is apparent given the different intercepts in Figure 10a. In Figure 10b, $\tilde{\chi}_{12}/$ v_0 are found to differ slightly with M_{w} at the same composition and temperature. We therefore parametrize $\tilde{\chi}_{12}/v_0$ in terms of composition ϕ as well as molecular weight M_{w} , as previously done by several authors.^{36,37} We therefore write $\tilde{\chi}/\nu_0 = A' + B/$ $T + C(\phi, M_w)$, where $A = A' + C(\phi, M_w)$. In the limit of $\phi \rightarrow \phi$ 0, A' can be estimated as A' = 0.0021. Figure 11 shows the composition dependence of $C(\phi, M_w)$ obtained as $C(\phi, M_w) \equiv$ A - A'. Therefore, $\tilde{\chi}/v_0$ can be summarized as $\tilde{\chi}/v_0 = 0.0021 - 0.0021$ $0.83/T - 0.000\ 280\phi_{P\alpha MSAN/dPMMA40k} \tilde{\chi}/\nu_0 = 0.0021 - 0.83/T$ $-0.000 315 \phi_{P\alpha MSAN/dPMMA99k}$ and $\tilde{\chi}/\nu_0 = 0.0021 - 0.83/T - 0.0021$ $0.000 483\phi_{PaMSAN/dPMMA130k-P}$. Previously, Madbouly et al.²⁸ found $\chi = (0.525 - 22.5/T)/(1 - 0.4\phi_{PMMA})$ for blend of $P\alpha MSAN$ 97k (with 31% AN content) and PMMA 14k, by fitting phase boundaries obtained by light scattering to Flory-Huggins theory. This result is not in agreement with our SANS scattering data (as shown in the Supporting Information, Figure S7), likely due to the slow demixing kinetics and low



Figure 10. Effective $\tilde{\chi}_{12}/\nu_0$ as a function of 1/T for (a) P α MSAN/dPMMA40k with four compositions and (b) at constant composition, but three different $M_w = 40$ k, 99k, and 130k-P. The filled symbols correspond to experimental data obtained from SANS and RPA analysis, and the lines are fits $\tilde{\chi}_{12}/\nu_0 = A + B/T$ in the one-phase region, with constant slope *B*. The vertical ticks mark the experimentally measured spinodal temperature, while the open circles show the χ_s calculated by Flory–Huggins theory.



Figure 11. Parameter $C(\phi, M_w)$, subsuming the composition ϕ and M_w dependence of $\tilde{\chi}_{12}/\nu_0 = A + B/T + C(\phi, M_w)$ for all P α MSAN/ dPMMA blends investigated, with $M_w = 40$ k, 99k, and 130k-P, with common A = 0.0021 mol/cm³ and B = -0.83 mol K/cm³. The temperature was fixed at 139 °C (composition dependences of $\tilde{\chi}_{12}$ for various temperatures are provided in the Supporting Information, Figure S8).

refractive contrast for this blend, as also found in the context of our optical microscopy estimates. The significance and role of noncombinatorial entropy in the thermodynamics of this system will be discussed in a separate publication.

Magnitude of G'' **and Spinodal Structure Design.** A key prediction of the C–H theory of spinodal decomposition is that the initial length scale of the resulting bicontinuous structure has a dominant wavenumber given by

$$q^* (t=0) \simeq \sqrt{\frac{-G''}{4k}}$$
 (15)

yielding a length scale of $\Lambda \approx 2\pi/q^{*.^{30}}$ The generation of nanoscale spinodal structures by demixing induced by a T-jump thus requires a large G'' driving force for a relatively modest temperature quench depth. Large ΔT quenches are generally expected to lead to noninstantaneous processes, via a cascade of demixing steps.³⁸ To search for "highly interacting"

blends,¹⁵ we focus on $G'' = \alpha + \beta/T$ noting that not only the magnitude of β is relevant but specifically the *value* of G'' at a given $\Delta T \equiv T - T_s$. For instance, manipulating α by tuning M_w (following Flory–Huggins expectations, eq 14) can also displace $T_s \equiv -\beta/\alpha$ and thus increase ΔT . However, the operational range for a temperature quench is bound by T_g and a ceiling (or depolymerization) temperature (for an LCST system), and is thus relatively small (symptomatic of the few partially miscible polymer pairs known). Further, in the framework of RPA and FH theories, the "square gradient" parameter k [Å² mol/cm³] becomes

$$k = \frac{1}{6} \left(\frac{\langle R_{g1}^2 \rangle_z}{\phi_1 \nu_1 \langle N_1 \rangle_w} + \frac{\langle R_{g2}^2 \rangle_z}{\phi_2 \nu_2 \langle N_2 \rangle_w} \right)$$
(16)

and thus $k \equiv A/2$ by comparison with eq 11. Parameter k thus relates to $\sim b_i^2/v_i$ as well as composition, typically varying from 0.05 to 0.2 Å² mol/cm³ across typical systems.¹⁵ We therefore compile previously reported data for G''/k as a function of ΔT for a range of representative systems, including the extensive measurements presented in the current work, in Figure 12. On the right axis, we show the corresponding Λ [nm] computed using the C-H prediction discussed above. The lines and shaded areas in red correspond to our current work with the $P\alpha MSAN/dPMMA$ system, establishing this as one of the most highly interacting systems reported in the literature. While these (~ 10 nm) length scales are commonly accessible via microphase separation of block copolymers (albeit requiring rather exacting synthesis and monodispersity), nanoscale demixing of polymer blends (whose component synthesis is generally larger scale, lower cost, and with lenient polydispersity) is perceived as challenging. Blends of solution chlorinated polyethylene (SCPE) with dPMMA might have even steeper G''/k slopes, ^{15,39,40} albeit within a narrow miscibility window, highly sensitive to the regularity and extent of chlorination of PE.³⁹ From a practical standpoint, the proximity of T_g and T_s in P α MSAN/dPMMA blends makes Tjump experiments feasible with the expectation of relatively slow structural coarsening. This contrasts with, for instance, the TMPC/dPS system also shown in Figure 12,²² for which $T_{\rm s} - T_{\rm g} \ge 100$ °C, or polycarbonate/dPMMA for which $T_{\rm s}$ is likely below T_g (and thus preventing measurement of G'' in the one-phase region).41



Figure 12. Second derivative of the free energy divided by square gradient term, G''/k, and initial spinodal length scale $\Lambda \equiv 2\pi/\sqrt{-G''/(4k)}$ as a function of quench depth ΔT . A range of LCST blends are included for comparison, alongside our current work on P α MSAN/dPMMA: previous P α MSAN 85k/dPMMA 112k:24/76 by Higgins et al.,¹⁶ k = 0.086 Å² mol/cm³; poly-(tetramethyl bisphenol A polycarbonate) 54k/deuterated polystyrene 225k (TMSC/dPS),²² k = 0.091-0.096 Å² mol/cm³; PVME 64.3-159k/dPS 195-783k,^{42,43} k = 0.073 Å² mol/cm³; polyisoprene 85k/ 1,4-polybutadiene 374k (PI/dPB),⁴⁴ k = 0.071 Å² mol/cm³; as well as UCST systems of isotopic polybutadiene (hPB, N = 3180/dPB, N = 3550),¹³ k = 0.077 Å² mol/cm³; hPS/dPS, k = 0.050 Å² mol/cm³; and PMMA/dPS, k = 0.048 Å² mol/cm³; data computed by assuming N = 1000 for hPS/dPS, and N = 50 for PMMA/dPS.⁴⁵

The asterisk in Figure 12 corresponds the expected outcome of a T-jump with $\Delta T \approx 30$ K, which we would thus expect to yield a structure with $\Lambda \simeq 30$ nm according to C–H theory. Such an experiment was carried out by time-resolved SANS for a blend of P α MSAN/dPMMA99k:41/59, quenched from 140 to 180 °C, corresponding to $\Delta T \equiv T - T_s = 30$ K, since $T_s \approx 150$ °C for this system, as shown in Figure 13. At this

composition, k = 0.151 Å ² mol/cm³ taking into account component polydispersity, following eq 16.

The data shown in Figure 13a do not exhibit a time-invariant "early stage" regime as strictly expected for C-H theory (although unsurprising for such deep quench). The intensity peak is indicated by the black markers, and its location is plotted in Figure 13b as a function of time. The shift toward low q is expected for structural coarsening. The solid line is a guide to the eye facilitating the extrapolation to an initial q^* (t \approx 0), bounded by the uncertainty shown by the horizontal dashed lines (at $0.018 \le q^* \le 0.024$). The initial length scale is thus $\Lambda \equiv 2\pi/q^* \approx 30$ nm, in good agreement with our expectations above. Equivalently, analysis of q^* ($t \approx 0$) following a quench in the two-phase region data with C-H theory enables G'' to be *independently* estimated by rearranging eq 15 into $G'' = -4kq^{*2}$. We obtain $G'' \approx -2.7 \times 10^{-4} \text{ mol}/$ cm³, and plot this measurement (open symbol) alongside the one-phase, equilibrium data (closed symbols) in Figure 13c. The G'' results across the two sides of the stability boundary are in remarkable agreement and corroborate the validity of predictive structural design of spinodal structures based on this approach, and in particular approaching dimensions nearing R_{g} by employing deep quenches and highly interacting blend pairs.

CONCLUSIONS

We investigated the thermodynamics of P α MSAN/dPMMA blends by small angle neutron scattering (SANS) as a function of temperature, composition, and molecular mass (of dPMMA). In total, 8 distinct blends and up to 15 temperatures (each) were measured. In the one-phase region, the forward scattering intensity $S(q \rightarrow 0)$ was measured to yield G'', the second derivative of the free energy of mixing with respect to composition, employing an Ornstein–Zernike analysis of 1/S(q) vs q^2 . All S(q) profiles in the one phase were well-described by RPA theory (eq 2), from which the polymer segment lengths *a* and effective $\tilde{\chi}/v_0$ interaction parameters (as well as G'') were computed. Combined with an ensemble



Figure 13. T-jump experiment from 140 to 180 °C for a blend of P α MSAN/dPMMA99k:41/59. (a) The open symbols correspond to coherent SANS scattering data at various times after the jump, and the black filled symbols indicate the peak position q^* of the profile. The lines show the calculated RPA S(q) at 140 °C, at the start of the T-jump, and that near the spinodal at 150 °C. (b) Time dependence of q^* during (rapid) coarsening with line as guide to the eye. Dashed lines show the range of q^* at $t \approx 0$ as guide to the eye. (c) Second derivative of the free energy G'' as a function of inverse temperature 1/T: filled symbols correspond to one-phase data, and the open symbol shows G'' estimated from the T-jump data with $G'' = -4kq^{*2}$. The line has the same slope and intercept as that obtained in Figure 8b.

Kratky asymptote analysis of all data, the segment length for P α MSAN was determined, for the first time, to be 10.1 ± 0.4 Å. The phase diagram for all blends was estimated by systematic analysis of S(q) data as a function of temperature: the spinodal line was obtained by extrapolation of G'' vs 1/T to zero, corresponding to the thermodynamic stability limit. The metastable zone was instead estimated from analysis of S(q)and deviation for RPA approaching the phase boundaries. A structural peak in S(q) clearly corresponded to temperatures above demixing; however detection approaching the binodal line was more complex due to the associated slow demixing kinetics, in particular close to T_{g} . In this instance, the emergence of a peak in the Kratky analysis Iq^2 vs q provided a useful indicator for deviations from the q^{-2} scaling law for miscible blends. Further, given the proximity between T_g and the binodal line, great care was taken to ensure that the samples were thermally equilibrated by analyzing time-resolved S(q) data between temperature changes. Namely, the $T_{\sigma}(P\alpha MSAN) = 118 \ ^{\circ}C \text{ and } T_{\sigma}(dPMMA) = 115-122 \ ^{\circ}C$ (with varying M_w), while the critical point ~ 140 °C, which meant that measurements at the lower temperatures (up to 135 °C) could not reach equilibrium within experimental time scales and were thus not considered for analysis. All equilibrated one-phase measurements yielded self-consistent trends for G'' and correlation length ξ , following expectations from RPA.

The phase diagram obtained clearly does not follow Flory– Huggins expectations, in that the critical point and location of spinodal and binodal lines are broadly independent of M_w . The critical temperature is approximately 140 °C at a very asymmetric composition of $\simeq 20\%$ P α MSAN (v/v), even though the M_w of the polymer pairs is commensurate. We find that (model-free) G'' estimates follow $G'' = \alpha + \beta/T$ for all blend compositions, with a $\beta = 1.60$ mol K/cm³, meaning that the temperature dependence of G'' was the same for all blends. The intercept α evidently differed, from which the T_s was calculated, and found to deviate from Flory–Huggins expectations, which is unsurprising.

The effective Flory-Huggins parameter $\tilde{\chi}_{12}/v_0$ was then computed (eq 14) for all temperatures, composition ϕ , and $M_{\rm w}$. Often, this parameter is expressed as $\tilde{\chi}_{12}/\nu_0 = A + B/T$. However, as found in several other polymer blends, $^{45}\chi$ for this system is not only a function of T, but also ϕ - and M_{w} dependent, and an expression $\tilde{\chi}_{12}/\nu_0 = A' + B/T + C(\phi, M_w)$ was thus adopted. A common reference volume $v_0 \equiv \sqrt{v_{P\alpha MSAN} v_{dPMMA}} \equiv 88.21 \text{ cm}^3/\text{mol}$ was employed. Isolating the T-independent terms A' and $C(\phi, M_w)$ enabled a relatively simple parametrization, namely $A' = 0.0021 \text{ mol/cm}^3$ and $B = -0.83 \text{ mol K/cm}^3$. Parameter $C(\phi, M_w) = -3.15 \times$ $10^{-4}\phi$ [mol/cm³] for $M_{\rm w}$ = 99k and varies relatively little with $M_{\rm w}$, viz. -2.8 to 4.8 \times 10⁻⁴ ϕ across the $M_{\rm w}$ range. These (common) deviations from Flory-Huggins theory are generally attributed to additional noncombinatorial constraints to the free energy caused by monomer architecture, specific interactions, connectivity, compressibility, etc. These are generally subsumed into such complex parametrizations of $\tilde{\chi}_{12}$ for reasons of practicality. Physical insight can be gained by the detailed data interpretation with more comprehensive theories such as polymer reference interaction site model (PRISM),⁷ or lattice cluster theory $(LCT)^8$ that explicitly incorporated structural information, chain conformation statistics, and interaction potentials in some form, or with equations of state, such as those of locally correlated lattice

(LCL) theory which are for volume changes and nonrandom mixing. 9,10

A survey of the magnitude of the interaction G'' and its temperature dependence indicates that $P\alpha MSAN/dPMMA$ is one of the most highly interacting blends known.^{15,45} Interaction "strength" is defined here in terms of, not only the value of β in $G'' = A + \beta/T$, but actually the value of G'' at a specific $\Delta T \equiv |T - T_{c}|$. With these ideas in mind, we test the hypothesis that correspondingly small spinodal phase sizes can be achieved with rather modest T-jumps into the unstable region. We have recently reviewed the celebrated prediction of linearized C–H theory that the initial $q^* = \sqrt{-G''/4k}$ which we find to generally apply across a large range of systems. Selecting a representative blend and a rather deep quench (\approx 30 °C), specifically with a T-jump experiment from 140 to 180 °C and a blend of PαMSAN/dPMMA99k:41/59, we obtain the initial spinodal length scale $\Lambda \approx 30$ nm, in good agreement with linearized C-H theory.3,4,6 The temperature dependence of G'' thus seems to continue across the two-phase region, at least away from the immediacy of the stability lines where deviations from mean-field theory are expected. Our Tjump experimental data fit well with G'' extracted from our single-phase region data, which is promising for further T-jump experiments. By analysis with linearized C-H theory or C-H-C theory, we would work to establish the limitation of these theories in prediction of the characteristic length scales. Overall, our results comprehensively map the thermodynamics of a highly interacting polymer blend, benchmarked against a range of other systems, and demonstrate the possibility of generating nanoscale bicontinuous structures by extrapolation from one-phase thermodynamic data uniquely accessible by SANS. These length scales are commensurate with those obtained by block copolymer microphase separation, albeit requiring kinetic arrest during demixing for their practical utilization, for instance, in photovoltaics, catalysis, membranes, or scaffolds. Further improvements in the predictive ability of blend thermodynamic and dynamic theory remain a significant requirement to the full exploitation of such otherwise facile approaches to generating nano- and microscale demixed polymeric materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b02431.

Incoherent SANS background for P α MSAN, phase diagrams estimated by optical microscopy, RPA self-consistency test (ξ^2 vs I(0)), RPA data and parameters for dPMMA 99k and 130k-P blends, comparison with previous measurements of G''(T), and composition dependence of $\tilde{\chi}_{12}/\nu_0$ (PDF)

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Notes

The authors declare no competing financial interest.

Data presented in this paper are available on the Zenodo repository at 10.5281/zenodo.2537068.

ACKNOWLEDGMENTS

We thank ISIS neutron source (UK) for beamtime and Engineering and Physical Sciences Research Council (EPSRC, UK) for funding.

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