Effect of Tacticity on the Phase Behaviour and Demixing of P_{α} MSAN/dPMMA Blends Investigated by SANS

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ABSTRACT: We investigate the effect of polymer tacticity on the phase behaviour and phase separation of polymer mixtures by small angle neutron scattering (SANS). Poly(α -methyl styrene-*co*-acrylonitrile) (P α MSAN) 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 blend's interaction parameter). One-phase (equilibrium) and time-resolved, spinodal demixing experiments, were analysed by the 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 χ 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 $a = 7.4\text{\AA}$, slightly larger than $6.9\text{\AA}$ reported for lower syndiotacticity dPMMA. Consideration of thermal fluctuations is required for the self-consistent analysis of the non-trivial 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 de mixing length scale of $\Lambda \approx 40\text{ nm}$ is obtained, in agreement with theory for deeper quenches, but deviates at shallower quenches, whose origin we discuss. CHC correctly describes demixing length and timescales, 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 behaviour across both sides of the phase boundary.

Keywords: polymer blends, small angle neutron scattering, Random Phase Approximation, Cahn-Hilliard-Cook theory, spinodal decomposition

Introduction

Polymer tacticity impacts thermal, mechanical, rheological and barrier properties of materials.^{1,2} Tacticity affects polymer chain dimensions in solution and melt, effectively modulating local conformation and rigidity of polymer segments,³⁻⁵ as well as the miscibility with other polymers.⁶⁻¹⁷ Small angle neutron scattering (SANS) can be employed to quantify polymer conformation and interactions of partially miscible polymer blends,¹⁸ generally in terms of the Random Phase Approximation (RPA), to yield the segment length of each component b and an effective interaction parameter χ , 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.⁶ The blend of iPVME/dPS showed steeper temperature dependence of interaction parameter compared to aPVME/dPS in the crystalline state of iPVME, while the amorphous state iPVME/dPS was less miscible than aPVME/dS. The more compact conformation of iPVME inferred from the statistical segment length obtained by SANS RPA analysis, yields stronger interaction with dPS per interactive group, which indicates the configuration affects the phase behaviour. However, iPVME undergoes crystallisation 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,¹⁹ glass transition temperature (T_g),^{20,21} chain dimensions^{3,4} to blend behaviour with various polymers.⁷⁻¹⁷ These include blends with poly(styrene-*co*-acrylonitrile) (SAN),¹⁶ polycarbonate (PC),¹³ Poly(vinyl chloride) (PVC),^{7,8,10,11,15} and poly(ethylene oxide) (PEO),^{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 favourable packing of chains.¹³ In terms of the difference in chemical conformation, isotactic PMMA is found in 10/1 helical conformation with the pitch of 2.11 nm, while syndiotactic

PMMA adapts an all-trans conformation, therefore, syndiotactic PMMA can more interact with other polymer species, resulting in the better miscibility.^{10,11}

Porous polymer materials can be fabricated via demixing induced by a range of methods, which include non-solvent induced phase separation, thermally induced phase separation, and reactive blending, with various capabilities and limitations.^{22,23} In order 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.^{24,25} In this context, ‘highly-interacting’ refers to a deep temperature dependence of blend interaction parameter χ , such that a large thermodynamic driving force for demixing can be imposed with a modest temperature variation across the phase boundary. Based on our recent overview of spinodal demixing²⁵ we select mixtures of poly(methyl methacrylate) (PMMA) with random copolymer poly(α -methyl styrene-*co*-acrylonitrile) (P α MSAN) as a model system, yielding a lower critical solution temperature (LCST) phase diagram above room temperature and above the glass transition temperature of both components. The thermodynamics of P α MSAN/dPMMA blends in both the one- and two-phase regions have been investigated by SANS by Higgins *et al.*,²⁶ whose demixing yields blends with a faint bluish appearance, associated with the small initial lengthscale of the spinodal structure (<100 nm), for the conditions investigated. Inspired by this study and the possibility of tuning component interactions with polymer tacticity, we investigate P α MSAN blends with dPMMA of similar molecular mass but varying syndiotacticity, from 63 $\pm$ 5% (termed ‘atactic’) to 78 $\pm$ 3% (‘syndiotactic’). We systematically investigate near-critical mixtures of these blends, across both sides of the phase boundary, employing isothermal and temperature-jump SANS measurements, which we analyse in terms of the RPA and Cahn-Hilliard-Cook (CHC) theories. Our findings demonstrate the significant consequences of modest tacticity changes in the thermodynamics and demixing of a fully amorphous, highly-interacting blend.

Experimental

Polymer mixtures

Deuterated poly(methyl methacrylate) (dPMMA) with two degrees of syndiotacticity ('atactic' and 'syndiotactic') and similar molecular mass (99 kg/mol and 110 kg/mol) and low polydispersity index ($PDI = 1.1$), synthesised by living anionic polymerisation, were purchased from Polymer Source Inc. Hydrogenous random copolymer poly(α -methyl styrene-*co*-acrylonitrile) (P α MSAN) with 30%AN and 70% α -MSt (Luran KR2556)²⁷ 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 heating rate of 10°C/min and computed by the mid-point method (Fig. S1). The syndiotacticity (the ratio of racemo-racemo triad) of dPMMA110k-s was determined to be 75% by ¹H NMR, and approximately 81% by DSC (Supporting information Fig. S2), and we thus obtain 78 $\pm$ 3%; we refer to this sample as 'syndiotactic', since the value is $\geq 70\%$. The dPMMA99k sample is estimated to have a degree of syndiotacticity of 63 $\pm$ 5% based on T_g measurement and its correlation with tacticity,^{19,20} detailed in Supporting Information Fig. S2 ; we refer to this sample as 'atactic'. Key characteristics of the polymer samples used are summarised in Table 1 and the monomer chemical structures are shown in Fig. 1.

Table 1: Polymer sample characteristics; Random copolymer P α MSAN comprises 30% AN and 70% α -MSt. The segment lengths a for P α MSAN was previously determined,²⁸ and that of dPMMA99k was fixed from literature data.^{29,30} 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, and polydispersity index $h \equiv (M_w / M_n - 1)^{-1}$. Parameter b is the coherent neutron scattering length and m is the mass of each repeat unit.

	$\langle M \rangle_w$ [kg/mol]	$\frac{\langle M \rangle_w}{\langle M \rangle_n}$	m [g/mol]	T_g [°C]	b [fm]	a [Å]	$\langle R_g \rangle_w$ [nm]	h
P α MSAN	122	2.6	98.66	118 $\pm$ 1	21.12	10.1 $\pm$ 0.4 ²⁸	14.5	0.63
dPMMA99k	99.1	1.1	108.1	122 $\pm$ 1	98.20	6.9 ^{29,30}	8.5	10.8
dPMMA110k-s	110	1.1	108.1	127 $\pm$ 2	98.20	7.4 $\pm$ 0.2	9.6	10.9

P α MSAN/dPMMA films were prepared by solution casting. Selected blend compositions were prepared by mass and then converted into volumetric ratio of P α MSAN using the pure component densities ($\rho_{P\alpha MSAN}$ =1.08 g/cm³ and ρ_{dPMMA} =1.28 g/cm³). The polymers were

first dissolved in tetrahydrofuran (THF, purity $\geq 99.7\%$ unstabilised HPLC grade, VWR) at a concentration of 8% w/vol and stirred at room temperature for 48h. The solution was drop cast onto glass coverslips (19 mm in diameter, VWR) and the solvent was allowed to evaporate at ambient conditions for one week. The resulting films (of approximately 100-150 μm thickness) were then carefully peeled off and placed under vacuum (20 mbar) for four weeks, while gradually increasing the temperature up to 110°C, which is just below the blend T_g , until no mass changes were observed. Approximately 6-10 films were then stacked together, and gently pressed (Specac hydraulic press, 4 ton) at room temperature with an aluminum mold to obtain approximately 1.0 mm thick films for one-phase, isothermal SANS experiments. Before the SANS experiments, samples were kept in an oven at 125°C for 36 hours and then gradually cooled down to room temperature under vacuum (20 mbar) to prevent absorption of moisture. Blends of composition P α MSAN/dPMMA99k 28/72, 41/59, 78/22 and P α MSAN/dPMMA110k-s 30/70 were investigated. The films were then wrapped in a thin aluminum foil (22 μm thick) to be mounted onto the 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 aluminum foil (minimising 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 P α MSAN/dPMMA99k 28/72 (atactic) and P α MSAN/dPMMA110k-s 30/70 (syndiotactic), which are effectively identical composition and polymer molecular masses, but vary in degree of syndiotacticity. This experimental protocol follows our previous work, examining the effect of composition and M_w on the phase behaviour of this system.²⁸

Small angle neutron scattering

SANS experiments were performed at ISIS (UK) using diffractometers SANS2D and Larmor and sample to detector distances $D_{s-d} = 12$ m and 4.1 m, respectively. These configurations yield a momentum transfer $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$, where θ is the scattering angle, ranging from $0.0015 < q < 0.5 \text{ \AA}^{-1}$ and $0.006 < q < 0.6 \text{ \AA}^{-1}$.

A custom-made brass experimental cell, consisting of two thermally controlled ovens and a mechanical actuator carrying the sample from one (pre-heating) oven to another (the ‘experimental oven’), with quartz windows and a 45° exit cone, was employed for both one-phase and demixing experiments.³¹ Neutron cloud point experiments were carried out at heating rate of $2^\circ\text{C}/\text{min}$ from 102°C (below T_g) to above the demixing temperature, in order to estimate the location of the phase boundaries, as illustrated in Fig. 2.

For one-phase (isothermal) experiments, only the ‘experimental’ oven was utilised. The film was loaded at 125°C (the final *ex situ* pre-heating 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_g to 2°C , near the phase boundary, were sampled. Acquisition times ranged from 120 min near T_g , 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 $q \geq 0.01 \text{ \AA}^{-1}$, and thus sufficient to accurately estimate G'' (or χ), although low- q deviations were observed (corresponding to long-wavelength fluctuations). Data acquisition for a neat P α MSAN 1 mm sample (used to estimate incoherent contribution) and the empty cell background (arising from aluminum foil and quartz windows) were 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 subtracted, using Mantid.³² 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 P α MSAN incoherent contribution.

Results and discussion

Phase Diagram of P α MSAN/dPMMA blends.

Figure 1: Monomer repeat units of P α MSAN and dPMMA and phase diagram of P α MSAN/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 guide to the eye. Black solid lines are T_g estimates obtained by the Flory-Fox equation and pure component data as given by Flory-Fox equation³³

The phase diagram for both P α MSAN/dPMMA99k and dPMMA110k-s blends, with varying syndiotacticity, is shown in Fig. 1, along with the glass transition temperatures. The spinodal temperatures (solid lines), T_s , were determined by extrapolation of $G'' \equiv \partial^2 \Delta G_m / \partial \phi^2$ 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 P α MSAN/dPMMA110k-s occur at higher temperature

($\simeq 16^\circ\text{C}$) above those of P α MSAN/dPMMA99k, indicating a 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 P α MSAN $\lesssim 0.3$ (v/v), 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 $1/T_{g,blend} = \phi_{P\alpha MSAN}/T_{g,P\alpha MSAN} + \phi_{dPMMA}/T_{g,dPMMA}$, 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 ($\simeq 20\text{-}30^\circ\text{C}$) 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 $2^\circ\text{C}/\text{min}$ from 102°C to 150°C , in order to estimate the location of T_b and T_s , as shown in Fig. 2 for a P α MSAN/dPMMA99k:28/72 blend. The total scattering intensity (ΣI) was plotted against temperature and various regimes could be identified: below T_g no intensity changes are observed, as expected; between T_g and T_b , the scattering intensity increases gradually, within the one-phase region; a change of slope is observed at both T_b and T_s . Based on the (isothermal) data analysis presented below, the temperature dependence of G'' (and χ) 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 $\approx 126^\circ\text{C}$ (above T_g) to $\approx 140^\circ\text{C}$ (near binodal for this mixture), within the one-phase region. Under isothermal conditions, samples did not reach equilibrium even after 36h annealing at 125°C due to the proximity of $T_{g,blend} = 120.9^\circ\text{C}$, and this out-of-equilibrium region is shown as a shaded area in Fig. 2. Above $T_b \approx 140.5^\circ\text{C}$, 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.

Figure 2: Total SANS scattering intensity during a cloud point measurement at heating rate 2°C/min for PαMSAN/dPMMA99k:28/72. The solid line is computed from RPA in one-phase region with $\tilde{\chi}_{12}/v_0 = 0.00201 - 0.83/T$.²⁸ The binodal T_b , spinodal T_s and glass transition T_g temperatures are indicated by vertical lines. The dashed line shows RPA deviations assigned to nucleation and growth in metastable region. Non-equilibrium behaviour near or below T_g is shown in grey. 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.

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

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

where N_A is the Avogadro number, $S(q)$ is the structure factor, b_i is coherent scattering length of monomer unit i and v_i is monomer molar volumes of the unit i . In the following discussion, we refer to component 1 as PαMSAN, and 2 as dPMMA, for which $b_1=21.12$ fm, $v_1=91.77$ cm³/mol, $b_2=98.20$ fm, $v_2=84.79$ cm³/mol, yielding a contrast prefactor $N_A(b_1/v_1 -$

$b_2/v_2)^2=5.19\times 10^{-3} \text{ cm}^{-4} \text{ mol}$. The structure factor $S(q)$ of blend of the blend is generally expressed by the mean-field, de Gennes' Random Phase Approximation (RPA),³⁴ as

$$\frac{1}{S(q)} = \frac{1}{S_1(q)} + \frac{1}{S_2(q)} - 2\frac{\tilde{\chi}_{12}}{v_0} \quad (2)$$

where $S_i(q)$ [cm^3/mol] is the structure factor of each component and $\tilde{\chi}_{12}$ is an effective specific interaction parameter. Taking component polydispersity into account, $S_i(q)$ reads³⁵

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

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 polymerisation of component i . The weight-average Debye form factor of the polymer chains is $\langle g_D(x) \rangle_w = \frac{2}{\langle x \rangle^2} \left[\left(\frac{h}{h+x} \right)^h - 1 + x \right]$, where $x \equiv q^2 \langle R_g^2 \rangle_n$ and $h = (M_w/M_n - 1)^{-1}$, and the n -average radius of gyration for a Gaussian coil $\langle R_g \rangle_n \equiv (\langle N \rangle_n a^2 / 6)^{0.5}$, where a is the segment length. In the forward scattering limit, $q \rightarrow 0$, Eq. 2 becomes

$$\frac{1}{S(0)} = \frac{1}{\phi_1 v_1 \langle N_1 \rangle_w} + \frac{1}{\phi_2 v_2 \langle N_2 \rangle_w} - 2\frac{\tilde{\chi}_{12}}{v_0} \equiv G'' \quad (4)$$

yielding a direct (and model-free) measurement of the second derivative of the free energy with respect to composition, $G'' \equiv \partial^2 \Delta G_m / \partial \phi^2$. In the habitual Flory-Huggins lattice framework, the interaction parameter χ at the spinodal is

$$\chi_s = \frac{v_0}{2} \left(\frac{1}{\phi_1 v_1 \langle N_1 \rangle_w} + \frac{1}{\phi_2 v_2 \langle N_2 \rangle_w} \right) \quad (5)$$

and therefore, from Eq. 4, follows that

$$(G'' \equiv) \frac{1}{S(0)} = \frac{2}{v_0} (\chi_s - \tilde{\chi}_{12}) \quad (6)$$

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

$$\tilde{\chi}_{12} = -\frac{1}{2} \frac{\partial^2 [\phi(1-\phi)\chi_{12}]}{\partial \phi^2} \quad (7)$$

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

$$S(q) = \frac{S(0)}{1 + \xi^2 q^2} \quad (8)$$

or equivalently

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

where the correlation length is given by $\xi = \sqrt{2kS(0)}$, and parameter k is defined below. The OZ formulation emphasises that the forward scattering intensity yields a susceptibility $S(0) \equiv 1/G''^{36,37}$ and thus requires no thermodynamic model assumption to obtain $G''(T)$ and thus characterise blend miscibility.

Figure 3: (a) Coherent SANS scattering data for P α MSAN/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_g , 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 highest and lowest temperature yielding $a_{dPMMA110k-s} = 7.4 \pm 0.2$ Å, and fixing $a_{P\alpha MSAN}$ to be 10.1 Å.²⁸ Open symbols correspond to the SANS data in two-phase region (which deviate from the RPA by more than a factor of 2), whose lowest temperature is taken as estimate for the binodal.

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

Filled symbols denote data in one-phase region, which can generally be described by RPA theory (eqs. 1,2,3), 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_g , and found to be out-of-equilibrium (for instance, by the differing slope in the OZ plot). A step-wise temperature profile (Fig. 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⁻¹), corresponding to long-wavelength fluctuations, which is attributed to the proximity to T_g (and shown by the temporal evolution of the total scattering intensity during an isothermal measurement, shown in Fig. S4). We therefore preferentially fit the higher q region to the RPA model, for

which thermal equilibration is achieved within measurement timescales, and take the low- q deviation into account to compute uncertainty in G'' and $\tilde{\chi}_{12}$. This approach is corroborated with the OZ analysis in Fig. 3(b), 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 Fig. 3(c), a peak emerges in the scattering data above 161°C, also visible in Fig. 3(a), 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 $T_b = 159 \pm 2^\circ\text{C}$. Polymer segment lengths a were estimated from Kratky analysis as ϕ and v are known, since the structure factor of one-phase blends at high wavenumber ($qR_g \gg 1$) can be written as $S(q)q^2 \approx 12 / \left(\frac{a_1^2}{\phi_1 v_1} + \frac{a_2^2}{\phi_2 v_2} \right)$. In order to increase the accuracy of the measurement of a of dPMMA110k-s, we fix the P α MSAN segment length to be $a(\text{P}\alpha\text{MSAN}) = 10.1 \text{ \AA}$, measured previously,²⁸ obtaining $a(\text{dPMMA110k-s}) = 7.4 \pm 0.2 \text{ \AA}$.

Figure 4: (a) Coherent SANS scattering data for P α MSAN/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_g 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, corroborating $a_{\text{P}\alpha\text{MSAN}} = 10.1 \text{ \AA}$ ²⁸ and $a_{\text{dPMMA99k}} = 6.9 \text{ \AA}$.^{29,30} Open symbols indicate SANS data in two-phase region (q power larger than 2), employed to estimate the binodal temperature.

The coherent scattering data for P α MSAN/dPMMA99k:28/72 (atactic) as a function of temperature are shown in Fig. 4(a). The coherent scattering data for P α MSAN/dPMMA99k

:41/59 and 78/22 are shown in Fig. 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 $\sim 10\text{-}15^\circ\text{C}$ lower than for the P α MSAN/dPMMA110k-s blend. The OZ analysis shown in Fig. 4(b) 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. Fig. 4(c) shows the corresponding Kratky plot, from which T_b is determined to be $140.5 \pm 1.5^\circ\text{C}$. Lines are computed from RPA with $a(\text{P}\alpha\text{MSAN}) = 10.1\text{\AA}$ ²⁸ and $a(\text{PMMA}) = 6.9\text{\AA}$, in agreement with previous literature,^{29,30} providing a good 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 P α MSAN, as the phase boundaries shift to higher temperature (despite the slightly higher M_w), and that its segment length also increases to $7.4 \pm 0.2\text{\AA}$. Next we examine the effect of tacticity on the component interactions, as measured by G'' or $\tilde{\chi}_{12}$.

Thermodynamics of P α MSAN/dPMMA blends in the one-phase region

Figure 5: (a) Second derivative of free energy of mixing with respect to composition $G'' \equiv \partial^2 \Delta G_m / \partial \phi^2$ as a function of inverse temperature $1/T$ for P α MSAN/dPMMA99k of three distinct compositions 78/22, 41/59, and 28/72 (corresponding to Fig. 4 and P α MSAN/dPMMA110k-s 30/70 (Fig. 3). Lines are fits to $G'' = \alpha + \beta/T$ with constant slope $\beta = 1.60$ for P α MSAN/dPMMA99k and with $\beta = 2.30$ for P α MSAN/dPMMA110k-s. (b) Corresponding plot for the effective interaction parameter $\tilde{\chi}_{12}/v_0$ (computed from Eq. 4), where the vertical ticks indicates the experimentally measured spinodal temperatures T_s . Lines are fits to $\tilde{\chi}_{12}/v_0 = A + B/T$ with constant slope $B = -0.83$ for P α MSAN/dPMMA99k and with $B = -1.55$ for P α MSAN/dPMMA110k-s.

Figure 5(a) provides a comparison of G'' as a function of $1/T$ and all data, at various compositions, which are to follow a linear relation with $G'' = \alpha + \beta/T$ and slope $\beta = 1.60$ [mol K/cm 3] and $\beta = 2.30$ [mol K/cm 3] for dPMMA99k and dPMMA110k-s, respectively. The steep temperature dependence of blend component interactions, and thus large β , indicates the ‘highly-interacting’ nature of this partially miscible blend.²⁵ The steeper slope of P α MSAN/dPMMA110k-s relative to that of P α MSAN/dPMMA99k demonstrates that increasing syndiotacticity further increases interaction ‘strength’, defined by this metric.

Fig. 5(b) plots the effective specific interaction parameter $\tilde{\chi}_{12}/v_0$ as a function of $1/T$, where we define $v_0 = \sqrt{v_{P\alpha MSAN} \times v_{dPMMA}} = 88.21$ cm 3 /mol. Lines are fits to the habitual

$\tilde{\chi}_{12}/v_0 = A + B/T$ with constant slope $B = -0.83$ [mol K/cm³] for P α MSAN/dPMMA99k and with $B = -1.18$ [mol K/cm³] for P α MSAN/dPMMA110k-s. When the reference volume is taken as $v_0 = 100\text{\AA}^3$,³⁸ $\tilde{\chi}_{12}/v_0 = A + B/T$ in unit of [mol/cm³] is converted to $\tilde{\chi}_{12} = A' + B'/T$ in unit of [$\text{\AA}^{-3}$], where A' and B' are computed by multiplying A and B by a factor 100/1.66. All G'' and χ parameters, for all compositions investigated, are tabulated in Table. 2.

Since M_w and composition ϕ are nearly identical in both blends, the combinatorial entropy in both cases is similar, viz. $\Delta S_{\text{combinatorial}} = \frac{1}{\phi_1 v_1 N_1} + \frac{1}{\phi_2 v_2 N_2}$, or $\Delta S_{\text{combinatorial}} = 4.9 \times 10^{-5}$ mol/cm³ and $\Delta S_{\text{combinatorial}} = 4.6 \times 10^{-5}$ mol/cm³ for P α MSAN/dPMMA99k and P α MSAN/dPMMA110k-s, respectively. The contribution to $\tilde{\chi}_{12}/v_0$ is very small, implying that the greater miscibility of P α MSAN/dPMMA110k-s must be associated to more favourable (enthalpic or non-combinatorial entropic) specific interactions upon increasing the dPMMA tacticity.

Table 2: Tabulated values G'' and $\tilde{\chi}_{12}/v_0$ of P α MSAN/dPMMA99k (atactic) and P α MSAN/dPMMA110k-s (syndiotactic) obtained by SANS in the one phase region, in the form $G'' = \alpha + \beta/T$, and $\tilde{\chi}_{12}/v_0 = A + B/T$, where $v_0 \equiv \sqrt{v_1 v_2} = 88.21$ cm³/mol. Typical confidence limits are ± 0.000004 and 0.003 for α and β , respectively. Conversion to reference volume $v_0=100$ $\text{\AA}^3$ (often employed to compare systems³⁸) is obtained by multiplication of factor 100/1.66 (corresponding to $100 \times N_A/(10^8)^3$ [from mol/cm³ to / $\text{\AA}^3$]).

	$G'' = \alpha + \beta/T$ [mol/cm ³]	$\tilde{\chi}_{12}/v_0 = A + B/T$ [mol/cm ³] [100 $\text{\AA}^3$]
P α MSAN/dPMMA99k 28/72	-0.003828+1.60/T	0.00201-0.83/T 0.121-50/T
P α MSAN/dPMMA99k 41/59	-0.003773+1.60/T	0.00198-0.83/T 0.119-50/T
P α MSAN/dPMMA99k 78/22	-0.003485+1.60/T	0.00184-0.83/T 0.111-50/T
P α MSAN/dPMMA110k-s 30/70	-0.005293+2.30/T	0.00274-1.18/T 0.165-71/T

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 Binder⁴² 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

$$S(q, t) = S_{T_f}(q) + [S_{T_i}(q) - S_{T_f}(q)] \exp(2R(q)t) \quad (10)$$

where $S_{T_i}(q)$ is the initial structure factor at the original one-phase temperature T_i , at a time set as $t = 0$. In practical terms, T_i is the temperature of the pre-heating 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), $S_T(q)$ becomes a “virtual” structure factor, changing sign (becoming negative) below a value q^* , and cannot thus be directly measured directly by experiment; t is time after the temperature jump, which is assumed to be instantaneous. The virtual structure factor, $S_{T_f}(q)$, is computed from Eq. 9, where $1/S(0) \equiv G''$ extrapolated to the corresponding T_f utilising the relation in Table 2. An illustrate $S_{T_f}(q)$ is shown in Supporting Information Fig. S8. The growth rate $R(q)$ of concentration fluctuations is given by

$$R(q) = -Mq^2(G'' + 2kq^2) \quad (11)$$

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

$$k = \frac{1}{6} \left(\frac{\langle R_{g1}^2 \rangle_z}{\phi_1 v_1 \langle N_1 \rangle_w} + \frac{\langle R_{g2}^2 \rangle_z}{\phi_2 v_2 \langle N_2 \rangle_w} \right) = \frac{1}{36} \left(\frac{(h_1 + 2)a_1^2}{(h_1 + 1)\phi_1 v_1} + \frac{(h_2 + 2)a_2^2}{(h_2 + 1)\phi_2 v_2} \right) \quad (12)$$

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

$$q^*(CH) \equiv \sqrt{-\frac{G''}{4k}} \quad (13)$$

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

$$\tau_c = \frac{1}{2R(q^*(CH))} = \frac{4k}{MG''^2} \quad (14)$$

Figure 6: Coherent scattering intensity following a time-resolved temperature jump experiment for P α MSAN/dPMMA99k 28/72 from an initial temperature $T_i=135^\circ\text{C}$ to various final temperatures T_f (a) 148°C , (b) 153°C , (c) 160°C and (d) 165°C . Open symbols ($\circ$) correspond to early stage spinodal decomposition data, and filled triangles ($\blacktriangle$) correspond to data outside the early stage. The lines are computed from the Cahn-Hilliard-Cook theory, Eq. (10), fitting G'' and M . The grey filled symbols ($\bullet$) correspond one-phase, isothermal data at $T_i=135^\circ\text{C}$, and $T=144^\circ\text{C}$, which is the highest temperature in one-phase region measured experimentally. The vertical green dashed line corresponds to $q^*(CH)$ computed by the maximum position at $R(q)$ for each jump, and the red solid line to $q_{exp}^*(t \rightarrow 0)$, which is the first experimentally measured peak q position after the jump. For clarity, representative uncertainties are included in panel (d) for the $t=85$ s dataset. As expected in time-of-flight SANS, error bars are larger at both ends of the q window.

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'' and M parameters as a function of temperature. Figure 6 shows scattering data at various times after jump for P α MSAN/dPMMA99k from common initial temperature $T_i = 135^\circ\text{C}$ to final T_f of (a) 148°C , (b) 153°C , (c) 160°C and (d) 165°C . The experimental realisation of temperature jump experiments involves displacing the blend film from the pre-heating cell (which is set at T_i) into the measurement cell (T_f), imposing a rapid heating profile (illustrated in Fig. S7), which can take $\sim 30\text{-}100$ 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 Eq. 10 and Eq. 11, by adjusting G'' and M , and ensuring self-consistency with the early stage assumptions, including that the data fall within the early stage τ_c estimation. Time points indicated in black (filled triangles) and in grey (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 $T_i = 135^\circ\text{C}$ (the initial temperature), as well as for $T = 144^\circ\text{C}$, the highest one-phase temperature measured experimentally for this blend.

The CHC model describes well scattering data for jumps to $T_f = 148^\circ\text{C}$ and 153°C , but not as well for the deeper quenches at $T_f = 160^\circ\text{C}$ and 165°C which we interpret as due to the short τ_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 $q_{exp}^*(t \rightarrow 0)$, and the green dashed lines correspond to $q^*(CH)$ computed from the maximum of $R(q)$ obtained for each temperature jump, effectively corresponding to Eq. 13. We find that $q^*(CH)$ appears systematically at lower values than $q_{exp}^*(t \rightarrow 0)$, and that the scattering peak moves (albeit slightly) towards 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 CH theory, for which the peak position q^* is *independent* of time during the early stages of spinodal

decomposition.^{39,40} However, both positive and negative q^* shifts during the initial stages of phase separation have been experimentally observed,^{43–45} 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: Temperature jump experiments for P α MSAN/dPMMA110k-s 30/70 from $T_i=150^\circ\text{C}$ to $T_f=$ (a) 168°C , (b) 175°C and from $T_i=140^\circ\text{C}$ to $T_f=$ (c) 170°C , and (d) 180°C . As above, open ($\circ$) and closed ($\blacktriangle$) symbols to early and intermediate stage spinodal decomposition data, and the lines are fitted to CHC theory, from Eq. (10). Grey ($\bullet$) symbols correspond to $T_i=150^\circ\text{C}$ or 140°C (with RPA fits), and $T=157^\circ\text{C}$, the highest temperature in one-phase region investigated. Note that $T_i=140^\circ\text{C}$ in panels (c,d) is just above $T_g \simeq 125^\circ\text{C}$, and deviations from CHC are interpreted as due to the initial out-of-equilibrium state of the sample.

Figure 7 shows time-resolved temperature jump scattering data for blend P α MSAN/dPMMA110k-s : 30/70 from initial temperature $T_i=150^\circ\text{C}$ to $T_f=$ (a) 168°C , (b) 175°C ,

and from $T_i = 140^\circ\text{C}$ to $T_f =$ (c) 170°C and (d) 180°C . The one-phase (isothermal) data for $T = 150^\circ\text{C}$ are shown in panels (a,b), as well as the RPA fit. Due to the proximity to T_g , even after 36h annealing at 150°C , the data 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 experimental data. Lines fit data well for the jumps from 150°C to 168°C , shown in Fig. 7(a), but less well to $T_f = 175^\circ\text{C}$, which we attribute to the commensurable timescales of thermal equilibration of the sample in the heating cell and τ_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 $T_i = 140^\circ\text{C}$ to both $T_f = 170, 180^\circ\text{C}$ 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 CHC predictions.

The dominant $q^*(t)$: experiment and CH(C) theory

Following the temperature jump into the spinodal region, the location of the scattering intensity maximum q_{exp}^* was determined as a function of time t , and shown by the data points in Fig. 8 for (a) P α MSAN/dPMMA110k-s for the two jumps from $T_i = 150^\circ\text{C}$ and (b) P α MSAN/dPMMA99k for all four jumps from $T_i = 135^\circ\text{C}$. A striking observation is that the experimentally observed $q^*(t)$ differs from the maximum wavenumber $q^*(CH)$ computed from linearised 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 compute numerically the peak positions of the scattering intensity based on CHC theory, considering the additional contribution of thermal fluctuations, as given by Eq. 10, and fixing the parameters obtained from the analysis shown in Figs. 6 and 7 (and thus ‘parameter-free’ in this sense). The solid lines in Fig. 8 correspond to those estimations and agree well with experimental data, within measurement uncertainty, during the early stage (i.e., up to

the respective τ_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 CH theory. While our data would also be compatible with a time-independent initial q^* , the experimentally observed $q_{exp}^*(t \rightarrow 0)$ would then differ from the corresponding $q^*(CH)$ calculated theoretically.

Figure 8: Experimentally measured peak position q^* as a function of time t after a temperature jump, for (a) P α MSAN/dPMMA110k-s with from $T_i=150^\circ\text{C}$ to $T_f=168^\circ\text{C}$ and 175°C and (b) for P α MSAN/dPMMA99k from $T_i=135^\circ\text{C}$ to $T_f=148^\circ\text{C}$, 153°C , 160°C and 165°C . The solid lines are computed numerically from CHC theory during the early stage of spinodal decomposition, whose upper time limit is indicated by the vertical lines at τ_c . The dashed lines are guides to the eye after τ , during the intermediate stage. The dominant $q^*(CH)$ (indicated on the right axis) and τ_c at each temperature are determined theoretically by the maximum $R(q^*)$ with using G'' and M obtained from Fig. 6 and Fig. 7. A power law corresponding to $q \propto t^{-1/3}$ is indicated for reference.

Here, τ_c is computed from Eq. 14 using the same G'' and M as in the data fits reported in Fig. 6 and Fig. 7. Table. 3 tabulates all values for q^* and τ . The experimental duration of early stage of spinodal decomposition τ_{exp} is separately determined by the duration for which q_{exp}^* follows the line predicted by CHC theory and is found to be in good agreement with τ_c . Beyond the early stage (as defined by τ_c), we observe $q^*(t) \propto t^{-1/3}$

for P α MSAN/dPMMA99k 135-165°C, indicating coarsening by evaporation-condensation or Brownian coalescence, characteristic of this common -1/3 scaling. The exponent α 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 CH theory alone lacks), with a single set of parameters, and thus that the role thermal fluctuations must be considered to obtain a comprehensive picture of thermally induced spinodal decomposition. The observed scattering intensity maximum $q_{exp}^*(t)$ must therefore be computed from numerical CHC calculations, which are trivial, to yield comprehensive data modelling. We further explore the implications of thermal fluctuations, and impact of T_i and T_f , in the next section.

Table 3: Tabulated values q^* , τ , $q(CH)$ and τ_c of all temperature jumps for P α MSAN/dPMMA110k-s 30/70 ($T_s=161.4$ °C) and P α MSAN/dPMMA99k 28/72 ($T_s=144.8$ °C). The uncertainty in temperature values is $\simeq 1^\circ\text{C}$; the error bars for q_{exp}^* are indicated in Fig. 8 and range between 10-20% for τ .

dPMMA	T_i (°C)	T_f (°C)	$\Delta T \equiv T_f - T_s$ (°C)	$q_{exp}^*(t=0)$ ($\text{\AA}^{-1}$)	τ_{exp} (s)	$q^*(CH)$ ($\text{\AA}^{-1}$)	τ_c (s)
110k-s	150	168	6.6	0.0134	170	0.0102	170
	150	175	13.6	0.0135	30	0.0114	45
99k	135	148	3.2	0.0135	450	0.0103	460
	135	153	8.2	0.0141	210	0.0121	210
	135	160	15.2	0.0144	90	0.0134	110
	135	165	20.2	0.0160	60	0.0143	45

Impact of thermal fluctuations on the observed $q^*(t)$

Figure 9(a) and (b) show the calculated evolution of scattering intensity $I(q, t)$ based on CHC theory for a shallower ($T_i=135$ to $T_f=148$ °C) and a deeper ($T_i=135$ to $T_f=165$ °C) quench, from the same initial one-phase temperature. We simulate the evolution of the scattering intensity from Eq. 10 and based on the experimentally measured parameters for P α MSAN/dPMMA99k, as a function of time (indicated on the graph). These calculations are similar to those reported by Strobl,⁴⁶ but here we have parameterised the results to the blend data and calibrated the curves to absolute units (of cm^{-1}) such that these can be di-

rectly compared to experimental scattering profiles. We first note that while the calculations refer to the early stages of spinodal decomposition, the intensity maximum of the scattering profile $q^*(t)$ is not constant in time, and the peak appears to shift to lower wavenumbers. A more detailed inspection of the evolution of $q^*(t)$ in time (indicated by markers) shows that it first increases and then decreases (in a trajectory reminiscent of a ‘boomerang’) in wavenumber over time, before eventually approaching a fixed value at long times. This value is indicated with a solid vertical line and corresponds to the $q^*(CH)$ as calculated by Eq. 13 for the parameters employed in the computation of scattering profiles. However, we note that this approach takes place at rather long times, exceeding the duration of the early stage τ_c (indicated by a red marker), beyond which the linearised treatment is no longer strictly valid as coarsening processes play an increasingly significant role (not included in the computation). Finally, we note that the deeper quench (shown in Fig. 9b) shows a smaller departure of q^* than the shallower quench (Fig. 9a), which is not surprising as the relative importance of initial concentration fluctuations expected to become smaller as the driving force for demixing increases. These observations are entirely consistent, quantitatively, with out experimental findings.

Figure 9(c) and (d) illustrate the dependence of $q^*(t)$ during the early stage on T_i and T_f , with panel (c) considering a fixed T_f and varying T_i , and panel (d) examining a fixed T_i and varying T_f (as generally adopted in experiments). The horizontal dashed lines correspond to $q^*(CH)$ and all profiles converge to its corresponding value, at sufficiently long times. In panel (c), we observe that the lower T_i , the larger the amplitude of the q^* digression, before approaching $q^*(CH)$, compatible with the expectation that the impact of thermal fluctuations diminishes for shorter temperature jumps (and the offset vanishes for T_i approaches the spinodal temperature T_s). Panel (d) however demonstrates that this effect *decreases* with increasing T_f (and thus quench depth) and that 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_i . These considerations agree well with the experimental observations reported in the previous section, namely in Fig. 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, $\Delta T \simeq 3 - 20^\circ\text{C}$, 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 τ_c . We emphasise that, while this behaviour could be suggestive of coarsening *during* the early stages of spinodal decomposition as proposed by Rappl and Balsara,⁴³ we find that the CHC framework can rationalise all data in terms of the well-known effect of thermal fluctuations originating the one-phase region.

Figure 9: Simulated coherent scattering intensity $I(q, t)$ following CHC theory and Eqs. (1, 10) using the G'' and M values fitted in (a) Fig. 6a and (b) Fig. 6d. Filled circles (●) indicate the maximum position in each profile and red marker corresponds to the maximum at $\tau_c = 1/2R(q^*)$. The dashed lines indicate times $t > \tau_c$ and thus outside the expected validity of CHC. (c,d) Computed q^* obtained numerically from CHC as a function of time for PaMSAN/dPMMA99k at (c) various initial temperatures from $T_i = 100^\circ\text{C}$ to $T_i = T_s$ and (d) various final temperatures from $T_f = 148^\circ\text{C}$ to $T_f = 165^\circ\text{C}$. G'' at each initial temperature is computed from $G'' = 0.00383 + 1.60/T$ and M at each jump given in Fig. 6. The horizontal dashed lines indicate $q^*(CH)$ as obtained from $q^* = \sqrt{(-G''/4k)}$, corresponding to the maximum in $R(q)$ at each temperature.

Correlation of G'' data across the phase boundary

The second derivative of Gibbs free energy of mixing G'' as a function of inverse temperature $1/T$, computed by several analysis methods, in both one- and two-phase regions, is shown in Fig. 10. As before, we find that dPMMA110k-s blends show a steeper slope than dPMMA99k blends and that, in both cases, the data obtained from RPA and CHC analysis agree rather well across the spinodal boundary. Such correlations were previously investigated by Han *et al.*,⁴⁷ Higgins *et al.*,²⁶ and Schwahn *et al.*,⁴⁸ broadly finding a reasonable agreement between G'' (or equivalent susceptibility) or χ parameter computed as described above. While the one-phase G'' (>0) data can be obtained to high precision from the RPA analysis and follow the expected linear dependence with $1/T$, the two-phase G'' (<0) data obtained by CHC analysis is considerably more scattered. For completeness, we compute G'' following four distinct methods, indicated in Fig. 10, specifically: from Eq. 13 and the experimentally observed $q^*(t \rightarrow 0)$; from fitting the highest (+) and lowest (-) values of G'' able to describe the temporal evolution of the scattering profiles with the CHC model, given by Eq. 10; and from fitting Eq. 11 to the experimentally measured $R(q)$ (shown in Fig. S10). We find that no method yields a particularly narrow measurement uncertainty, or clearer correlation with one-phase data, and 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) for $\Delta T \equiv T_f - T_s \lesssim 15.2^\circ\text{C}$. The CHC results from the shallower quenches might be impacted by the commensurable timescales of thermal equilibration in the cell and demixing, effectively resulting in a ‘slow’ (or at least slower, as shown in Fig. S11) quench, compared to those at larger ΔT .

Figure 10: Temperature dependence of G'' for P α MSAN/dPMMA110k-s and P α MSAN/dPMMA99k on both sides of the phase boundaries. Filled symbols correspond to data obtained from RPA analysis in one-phase region, yielding the solid lines $G'' = -0.00383 + 1.60/T$ for P α MSAN/dPMMA99k and $G'' = -0.00529 + 2.30/T$ for P α MSAN/dPMMA110k-s. In the two-phase region, $\circ$ are computed from $G'' = -4kq_{exp}^{*2}(t = 0)$ where $q_{exp}^*(t = 0)$ is determined experimentally from Fig. 8, $\triangle$ and ∇ indicate $G''+$ and $G''-$ estimated from fitting CHC theory (Eq. 11 and Eq. 10) to $I(q, t)$ data adjusting G'' and M , and $\square$ markers are obtained from fitting G'' and M to experimentally measured $R(q)$.

Deviations from mean-field behaviour 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 $\Delta T < 3^\circ\text{C}$ 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.

The 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

$$M = \phi_1 \phi_2 (\phi_1 v_1 D_1 + \phi_2 v_2 D_2) \quad (15)$$

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

$$D = \frac{k_B T d_T^2}{3 N^2 \zeta a^2} \quad (16)$$

where k_B is Boltzmann constant, d_T is the tube diameter of $\sim 6 \text{ nm}$ ²⁵ and ζ is the monomer friction coefficient and unit of D is $[\text{cm}^2/\text{s}]$. We fix the PMMA monomer friction coefficient to $\zeta_{dPMMA} = 0.04/T - 8.12 \times 10^{-5} [\text{dyn s/cm}]$,^{52,53} and fit the monomer friction for P α MSAN from the experimentally observed M yielding $\zeta_{P\alpha MSAN} = \frac{0.0007}{T} - 1.54 \times 10^{-6}$, 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 Fig. 11.

Figure 11: Experimentally measured mobility M as a function of inverse temperature $1/T$. $\triangle$ and ∇ indicate M estimated from CHC and the solid line corresponds to Eq. 15 and 16, fixing monomer friction coefficient ζ for dPMMA99k and 110k-s as $\zeta_{dPMMA} = \frac{0.04}{T} - 8.12 \times 10^{-5} [\text{dyns/cm}]^{52,53}$ and adjusting ζ for P α MSAN to be $\zeta_{P\alpha MSAN} = \frac{0.0007}{T} - 1.54 \times 10^{-6} [\text{dyn s/cm}]$. The two data points which deviate from the curve correspond to T-jumps from $T_i=140^\circ\text{C}$ near T_g , interpreted as jumps from an out-of-equilibrium state. The T_g of pure components is indicated by the vertical lines.

Initial spinodal lengthscale prediction $\Lambda \equiv 2\pi/q^*(\sim 0)$

We next consider the ability of CH(C) theory to predict the initial lengthscale 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 Λ and $G''(T)$ pairs. Specifically, G'' can be either computed from extrapolation from the one-phase data fitted to RPA, named $G''(1\phi)$, or from CHC fitting in the two-phase region; separately, the dominant lengthscale Λ can be calculated from the model $q^*(CH)$, of Eq. 13, or from the initial location of the intensity maximum, $q_{exp}^*(t \rightarrow 0)$. The solid lines

show the theoretical predictions for both systems (with only slightly different k) computed from $\Lambda = 2\pi/\sqrt{\frac{-G''}{4k}}$, and the data points are labelled according to the legend in Fig. 12, obtained from independent criteria. Overall, we find that the lengthscale prediction for dPMMA99k blends is in good agreement with the data for the two deeper quenches, but the shallower quenches yield smaller Λ from the experiment than the CH theory predictions. Data for dPMMA110k-s blends generally show broad agreement with CH theory. Lengthscale predictions Λ based on $G''(CHC)$ generally shows better agreement with 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 as predicting initial demixing lengthscales 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 (~ 10 °C) temperature quenches, and the difference in tacticity of both dPMMA specimens does not change this behaviour significantly.

Figure 12: Initial spinodal lengthscale $\Lambda \equiv 2\pi/q^*$ as a function of $-G''$ obtained for P α MSAN/dPMMA110k-s and P α MSAN/dPMMA99k. Four distinct estimates are made, indicated in the top right of the panel (detailed in the text). In short, $G''(1\phi)$ is computed from extrapolation from the one-phase data fitted to RPA, while $G''(CHC)$ is obtained from fitting two-phase kinetic data; wavenumber q^* is either determined directly from the data, as $q_{exp}^*(t \rightarrow 0)$ or computed from $G''(CHC)$. Lines are $\Lambda = 2\pi/\sqrt{\frac{-G''}{4k}}$ with the two corresponding k values for the atactic and syndiotactic blends.

Conclusions

We present a detailed SANS study of the thermodynamics and phase separation of P α MSAN/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 $78 \pm 3\%$ (syndiotactic), and dPMMA99k of $63 \pm 5\%$ (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 χ) 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 ‘non-instantaneous’⁵⁴ quenches unable to attain small phase sizes. From previous reports,^{25,26} this blend should yield spinodal structures of a few 10s of nm to be formed with ~ 10 °C thermal quenches, which can be readily implemented in practice. In a previous publication,²⁸ we investigated the role of M_w and blend composition ϕ on phase behaviour and demonstrated the formation of spinodal structures of initial phase size ~ 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 $\simeq 7\%$). Specifically, we obtain $G'' = -0.00383 + 1.60/T$ [mol/cm³] for atactic blend P α MSAN/dPMMA99k 28/72 and $G'' = -0.00529 + 2.30/T$ [mol/cm³] for syndiotactic blends (corresponding to $\tilde{\chi}_{12}/v_0 = 0.00201 - 0.83/T$ and $\tilde{\chi}_{12}/v_0 = 0.00274 - 1.18/T$ [mol/cm³], respectively). We find that the increase in syndiotacticity causes an upwards shift in the LCST phase boundary by $\approx 20^\circ\text{C}$ for P α MSAN/dPMMA110k-s, with respect to P α MSAN/dPMMA99k, and therefore an increase in the miscibility window. Given the dependence of the theoretically predicted spinodal (initial) lengthscale as $\Lambda \equiv 2\pi/q^* = 2\pi/\sqrt{-G''/4k}$, we could thus expect smaller phase sizes with the dPMMA blend of higher syndiotacticity.

A number of temperature jump experiments from one one-phase region into the spinodal, unstable, region were carried out by SANS and analysed 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 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 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 , 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 $\zeta_{P\alpha MSAN} = \frac{0.0007}{T} - 1.54 \times 10^{-6}$ [dyn s/cm], which describes data from both blends across the temperature range (except for quenches originating from near T_g).

Figure 13: (a) Simulated lengthscale, Λ , as a function of $\Delta T \equiv T - T_s$ for P α MSAN/dPMMA99k and P α MSAN/dPMMA110k-s blends with varying α or β in $G'' = \alpha + \beta/T$. The red and purple solid lines are computed from $G'' = -0.003828 + 1.60/T$ and $G'' = -0.005293 + 2.30/T$ corresponding to P α MSAN/dPMMA99k and P α MSAN/dPMMA110k-s, respectively. The dot-dashed lines correspond to $G'' = -0.003828 + 1.60/T$ (P α MSAN/dPMMA99k blends) with varying α . The dashed lines correspond to $G'' = -0.003828 + 1.60/T$ (P α MSAN/dPMMA99k blends) with varying β . (b,c) Spinodal temperature as a function of α and β . Filled symbols correspond to our obtained results, open symbols correspond to T_s with varying α and β . The shaded area indicates blends are in glassy state.

The initial spinodal lengthscale Λ could be well predicted, within measurement uncertainty from CHC theory and CH theory for both P α MSAN/dPMMA110k-s and P α MSAN/dPMMA99k blends. Agreement with theory becomes less good for shallow quenches within the spinodal, i.e. for $T_f \geq T_s$; this could be possibly due to (expected) deviation from mean-field behaviour, but equally from experimental technicalities related to the commensurability of timescales of the temperature change and demixing process, departing from an ‘instant-

taneous' quench. The minimum spinodal lengthscale attained in this study is ≈ 40 nm, amongst the smallest observed by thermally induced demixing.²⁵ In this particular case, the variation of syndiotacticity does not impact the lengthscale 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 ΔT . Figure 13 shows the dependence of Λ for dPMMA99k and dPMMA110k-s blends with quench depth $\Delta T \equiv T - T_s$, computed from the respective $G'' = \alpha + \beta/T$ relations obtained experimentally. At the quench depths ΔT of interest, the difference in resulting initial spinodal lengthscale is a modest $\simeq 4$ nm, within experimental uncertainty. The same figure includes simulated results obtained by modifying the α and β parameters for the P α MSAN/dPMMA99k blend, indicated by the dashed lines. Decreasing α decreases both Λ and T_s , while increasing β increases both Λ and T_s ; evidently the G'' parameters for P α MSAN/dPMMA110k-s lead to an increase in both α and β and these effects largely 'cancel out', resulting in the relatively small Λ 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 Flory-Huggins theory and merits a detailed thermodynamic investigation of the non-combinatorial 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

DSC for P α MSAN, 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 P α MSAN/ dPMMA99k and P α MSAN/dPMMA110k-s blends, growth

rate for each T-jump, quench depth dependence of G''/k and lengthscale, Onsager mobility term for P α MSAN/dPMMA99k and lengthscale prediction as a function of quench depth.

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