Thermodynamics of model P_{α} MSAN/dPMMA blend: a combined study by SANS, ellipsometry and locally correlated lattice (LCL) theory

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ABSTRACT: We combine experiment and theory to elucidate how small, local, structural changes can impact miscibility in polymer blends. Small angle neutron scattering (SANS) experiments yield both the phase boundaries and the temperature dependence of the second derivative of the free energy of mixing. We demonstrate here, for the first time, that a fundamental characterization of pure component properties can be achieved through ellipsometry measurements on films of the pure polymers (thickness ~ 200 nm) to provide key data on the volume (or thickness)-temperature relationships; this development is significant given the scarcity of precise PVT data on pure polymers and blends. The experimental measurements allow us to undertake a detailed thermodynamic analysis of mixing using the locally correlated lattice (LCL) theory, which has been shown effective in rationalizing blend miscibility in terms of the pure component properties. We focus here on polymer blends of poly(α -methyl styrene-co-acrylonitrile) (P α MSAN) with deuterated poly(methyl methacrylate) (dPMMA) which differ in the degree of tacticity in the dPMMA component (atactic or syndiotactic), leading to an increase in miscibility for the latter. By combining LCL analysis of pure and mixed systems, we are able to connect tacticity changes to shifts in local non-bonded interactions, in free volume, and in thermal expansion coefficients, which in turn impact the thermodynamic compatibility of the blend components.

Introduction

Polymer mixtures and blends find numerous applications, including in materials with two-phase nano-structures (e.g., membranes, solar cells, composites) obtained by controlled demixing of components.¹⁻³ In order to exert this control and fulfill the potential that demixing has in material design, a detailed understanding of the thermodynamics of mixing and the kinetics of de-mixing in the blend is essential. The literature abounds in observations of blend phase boundaries often obtained by light scattering or transmission, for (usually) binary polymer mixtures.⁴ Phase behavior is then parameterized or fitted to various models. The simplest and best known of these is the Flory-Huggins (FH) lattice model,⁵⁻⁷ but there are many others. A key deficiency is that, while the overall behavior such as upper or lower critical solution temperatures can be fitted, it requires introducing one or more empirical parameters which are not related to molecular properties of the constituent polymers. For example, the widely used FH χ parameter is determined using only experimental results for the mixture of interest (no pure component behavior is captured) and has to include both temperature and concentration dependencies. Another weakness is that the result does not have any predictive power, being optimized to reproduce a known set of mixture data. Thus while there are large datasets on the blends⁸ and their phase boundaries, there has been little success in predicting the blend behavior using these methods.

The locally correlated lattice theory (LCL) of Lipson *et al.*⁹⁻¹² is a simple Equation of State (EOS) model which directly accounts for pure component properties, as well as mixture behavior. The theory is analytic, and derived from first principles such that volume changes on mixing (absent from FH and related models) and non-random mixing appear naturally. The LCL model is partially parameterized through characteristic parameters for the pure components, obtained by fitting pure component data, such as a pressure-volume-temperature (PVT) surface. The mixture is characterized through a single blend parameter which is a constant, independent of temperature, composition, and pressure. In the last two decades, some of the authors have investigated the capabilities of the LCL model to explore and understand data from binary blends and in particular neutron scattering data. One example is that the source of the effect of deuterium substitution on the phase boundary has

been identified, and we have been able to separate the effects of specific interactions on the entropy and enthalpy noting the very large contributions of non-ideal mixing to these.^{10,13}

Standard scattering theory, succinctly summarised by Konigsveld et al.⁴ (p. 277-278), relates the forward scattered intensity in a scattering experiment directly to the second derivative of the free energy of mixing Δg_{mix} with respect to composition ϕ ,

$$S(q \rightarrow 0)^{-1} = G'' \equiv \frac{\partial^2(\Delta g_{mix}/RT)}{\partial \phi^2} \quad (1)$$

where Δg_{mix} and G'' have units of energy per volume and mol per volume respectively. So long as the scattering data are accurately calibrated (to absolute units¹⁴) and an extrapolation of the structure factor $S(q)$ to zero angle (or wavenumber q) can be made, the measurement provides a direct thermodynamic determination, independent of any EOS model. As far as we are aware, no attempts have been made to quantify G'' within the one-phase region of a polymer blend from light scattering. The main problem is the very weak signal arising from the concentration fluctuations due to the small differences of refractive index in the component polymers. The advent of small angle neutron scattering (SANS) in the 70s and 80s effectively resolved this problem because contrast between the components can be gained (and tuned) by deuterium substitution.¹⁵ Another advantage is that SANS explores size scales comparable to molecular dimensions and concentration fluctuations, and avoids some of the artefacts appearing in the scattering data at very small angles due to non-equilibration of long wavelength fluctuations in either density or concentration.

The LCL theory requires pure component data, most frequently pressure-volume-temperature (PVT) measurements. However, rigorous PVT experiments on polymeric samples are challenging and require several grams of sample. There are tabulated and literature data for a number of polymers (e.g., Zoller and Walsh¹⁶) but very little indeed for deuterated or less common polymers, for instance with specific architectures or new chemistries. The absence of these data has proved a barrier to the widespread application of the LCL model to SANS results for blends. However, earlier work using LCL has shown that a full PVT analysis is not essential; indeed, if conditions of interest involve only atmospheric pressure then knowing the thermal expansion coefficient will suffice.

Ellipsometry is well established as a method for measuring the thermal expansivity α of polymer films, with reports as early as 1993.¹⁷ Moreover, the experiments require only a small amount of sample, ideal when costly deuterated (or research grade) polymers are involved. In this paper, for the first time, we combine analysis of SANS and ellipsometry data with LCL theory in order to understand data recently published for the blend of poly(α -methyl styrene-co-acrylonitrile), or P α MSAN, with deuterated poly(methyl methacrylate), or dPMMA.¹⁸ This blend presents the interesting case of a very modest change in tacticity of the PMMA component giving rise to a sizeable shift of 16 K in the phase boundary. The monomer structures, phase diagram, calorimetry data, previously reported SANS measurements,^{18,19} and $G''(T)$ analysis are summarized in Figures 1 (a)-(h) of the current paper.

This paper is organized as follows: In the Experimental and Modeling Methods section, we describe the experimental sample preparation, including the SANS and ellipsometry procedures, and present background on the Locally Correlated Lattice (LCL) model, which will be used to analyze the results. The Results and Discussion section begins with a forward scattering analysis of recent SANS data^{18,19} to determine the main thermodynamic quantity of interest, G'' , defined by Eq. 1. Next, the route from ellipsometry data to thermal expansion coefficients is outlined, with the experimental results being used to determine the values for the three polymers of interest (P α MSAN, dPMMA, and syndiotactic dPMMA). Validation of this approach is also presented by comparison of ellipsometry and PVT data for hPMMA, along with relevant caveats. We then apply the LCL theory using the experimental data from SANS and ellipsometry. This begins with a description of how we determine an internally consistent set of α values, which are then applied to obtain characteristic parameters for each of the pure components. We employ the SANS results to characterize the blends, which involves applying the LCL to data for G'' as a function of temperature to determine the single, constant parameter that describes the mixed component interaction. We then provide a detailed thermodynamic analysis of the effect of PMMA tacticity on the polymer blend miscibility, and summarize our findings.

Figure 1: Monomer repeat unit of (a) P α MSAN, (b) hPMMA and (c) dPMMA employed in this study. (d) Phase diagram of P α MSAN/dPMMA99k (red lines, atactic) and 110k-s (purple lines, syndiotactic) obtained from SANS. Filled and open circles correspond to spinodal and binodal temperatures, respectively, and lines serve as a guide to the eye. (e) DSC thermograms for the pure blend components; vertical ticks indicate T_g . (f) Ornstein-Zernike fits to the coherent SANS scattering data for P α MSAN/dPMMA99k=29/71 and (g) for P α MSAN/dPMMA110k-s annealed isothermally; low- q deviations in the data are attributed to incomplete equilibration near T_g . (h) Experimentally measured $G'' \equiv 1/S(q \rightarrow 0)$ by extrapolation of the forward scattering intensity, and $G''' = \mathcal{A} + \mathcal{B}/T$ fits for P α MSAN/dPMMA99k = 29/71 (red, $\mathcal{B} = 1.60$), and two other compositions indicated in (d), and P α MSAN/dPMMA110k-s 30/70 (purple, $\mathcal{B} = 2.30$). Selected SANS data in (f,g,h) have been previously reported by Aoki *et al.*^{18,19}

Experimental and Modeling Methods

Sample preparation

Deuterated poly(methyl methacrylate)(dPMMA) with similar molecular mass, $M_w=99$ kg/mol and 110 kg/mol, and low polydispersity ($M_w/M_n = 1.1$), synthesized by living anionic poly-

merisation, were purchased from Polymer Source Inc. Sample dPMMA99k is predominantly atactic, with a degree of syndiotacticity of $63\pm 5\%$ estimated from its glass transition temperature T_g and correlation with tacticity; sample dPMMA110k-s is $78\pm 3\%$ syndiotactic and determined by ^1H NMR and T_g measurements, as detailed in Supporting Information Fig. S1. We therefore refer to dPMMA99k as ‘atactic’ and dPMMA110k-s as ‘syndiotactic’, employing the customary 70% rr fraction boundary classification.^{20,21} For comparison (and validation) with previously reported PVT measurements, we also investigate hydrogenous PMMA, with $M_w = 152$ kg/mol ($M_w/M_n = 1.8$), termed hPMMA152k, which was also purchased from Polymer Source Inc. Finally, we employ hydrogenous random copolymer poly(α -methyl styrene-*co*-acrylonitrile) (P α MSAN) with 30%AN and 70% α -MSt,²² which was donated by BASF (Luran KR2556).

Key characteristics of the polymers are summarized in Table 1 and the monomer chemical structures are shown in Fig. 1. Glass transition temperature, T_g , of each homopolymer is determined by differential scanning calorimetry (DSC) using a TA Instruments Q2000, at 10 $^\circ\text{C}/\text{min}$ heating rate, and computed with the mid-point method.

Table 1: Polymer sample characteristics. Values for T_g obtained by ellipsometry and DSC are also indicated (discussed in the text).

Sample	$\langle M \rangle_w$ [kg/mol]	$\langle M \rangle_w / \langle M \rangle_n$	syndiotacticity (%)	$T_{g,ellip}$ [$^\circ\text{C}$]	$T_{g,DSC}$ [$^\circ\text{C}$]
dPMMA99k	99.1	1.1	63 ± 5	122 ± 2	122 ± 1
dPMMA110k-s	110	1.1	78 ± 3	126 ± 3	127 ± 2
P α MSAN	122	2.6	—	118 ± 2	118 ± 1
hPMMA152k	152	1.8			

Blend compositions were prepared by mass and then converted into volume fraction of P α MSAN/PMMA using the pure component densities ($\rho_{P\alpha MSAN}=1.08$ g/cm³ and $\rho_{dPMMA}=1.28$ g/cm³). The preparation of samples for SANS was detailed previously.^{18,19} In short, blends of composition P α MSAN/dPMMA99k 28/72, 41/59, 78/22 and P α MSAN/dPMMA110k-s 30/70 were solvent cast into 100-150 μm films, vacuum dried, and hot pressed into 1 mm-thick disks. The samples were then vacuum annealed for 36 h at 125 $^\circ\text{C}$ for 36 hours, prior to isothermal SANS measurements, described below.

Ellipsometry samples were prepared as follows: the polymers were first dissolved in cyclohexanone (purity $\geq 99.0\%$ ACS reagent, Sigma-Aldrich) at a concentration of 6% w/vol and stirred at room temperature for 48 h; the solution was then spin-coated onto a silicon wafer (orientation $\langle 100 \rangle$, single-side polished, 525 μm thick, purchased from Siegert). Each wafer was cut into a size approximately 10 mm $\times$ 10 mm, washed with acetone, and treated in a UV-ozone atmosphere for 15 min to create a clean and hydrophilic surface. Solutions were then spin coated with 4000 rpm for 30 s, resulting in 150-200 nm thick films, which were placed under vacuum (20 mbar) at 90 $^{\circ}\text{C}$ for one week, and then at 130 $^{\circ}\text{C}$ (above T_g) for 72 h to ensure complete solvent removal and polymer film relaxation. The films were cooled to ambient temperature at a controlled rate of 2 $^{\circ}\text{C}/\text{min}$.

Small Angle Neutron Scattering

The SANS data included here have been reported in our previous publications,^{18,19} and a brief description of the measurements is included here for completeness. Experiments were performed at the Larmor diffractometer (ISIS, UK), employing an increased flux (and larger beam divergence) configuration, yielding a narrower wavevector $q = (4\pi/\lambda) \sin(\theta/2)$ range of $0.006 < q < 0.6 \text{ \AA}^{-1}$. A temperature jump cell,²³ consisting of two brass ovens with quartz windows and a motorized sample carrier, was employed; samples were loaded at 125 $^{\circ}\text{C}$ and the temperature was increased, in a step-wise fashion, in steps of 8 $^{\circ}\text{C}$ (near T_g) and then 2 $^{\circ}\text{C}$, approaching the phase boundary. Acquisition times varied from 120 min (near T_g) to 3 min for the polymer blends, and 30 min for backgrounds and empty cells. Sample thicknesses were determined self-consistently using a digital micrometer and the measured neutron transmission. Scattering data were reduced and calibrated, and the contribution from the empty cell subtracted; the coherent scattering function was then obtained after subtraction of the appropriate volume fraction of the mostly-incoherent spectrum of (hydrogenous) P α MSAN.

Ellipsometry measurements

Film thickness, h , as a function of temperature was determined using a rotating analyzer spectroscopic ellipsometer with an automated retarder (VASE, J. A. Woollam Co., Lincoln,

NE). Supported films were mounted vertically on an integrated heat stage (HTC-100) placed in the ellipsometer beam. The temperature was increased, in a step-wise fashion, in increments of 5 °C (or 3 °C near T_g), from 30 to 180 °C (303-453 K). At each step, the temperature was held constant, while a spectroscopic scan over the wavelength range from 300 to 800 nm was conducted at a fixed angle-of-incidence of 70 degrees. The heating rate between the isothermal holds was fixed at 2 °C/min to match the cooling rate used in the sample preparation. While only pure component (PαMSAN and PMMA) thin film data will be employed for LCL analysis, for completeness, we have also measured the respective blends.

Data were analyzed using commercial software WVASE with a slab model consisting of a Si substrate, a native layer of silicon dioxide (thickness measured independently), and the polymer film. Reference data were used for the refractive index of Si at each temperature. In the model, the dispersion of the refractive index, n , of the polymer was described by the Cauchy equation,^{24,25} written as: $n = n_A + n_B/\lambda^2 + n_C/\lambda^4$, where n_A , n_B and n_C are temperature-dependent materials parameters, and λ is the wavelength of the incident light. In most cases, only two terms were needed for the fitting such that $n_C = 0$. At each temperature step, the model was fit to the data using a Marquart-Levenberg algorithm.²⁶ The thickness, h , and the Cauchy parameters for the refractive index were fit from the spectroscopic data at each temperature. The atmosphere above the film on the heating stage was air. After the films were heated and cooled, ellipsometry analysis found that they returned to their original thickness and refractive index, which indicates there was no oxidation or degradation during the experiments.

Background on the Locally Correlated Lattice (LCL) Theory

The locally correlated lattice theory (LCL) is a thermodynamic model for pure liquids and mixtures of polymers and/or small solvent-sized molecules. The molecules comprise segments and are modeled on a lattice, where each molecular segment occupies a single lattice site. The lattice also contains a certain fraction of vacant sites which varies as the fluid system expands/contracts (the size of the lattice site is fixed.) For any given volume, V , and temperature, T , the theory quantifies the probabilities for near neighbor non-bonded segment-segment contacts, and this leads to fundamental expressions for the energy (U),

enthalpy ($H = U + PV$), entropy (S), Helmholtz free energy ($A = U - TS$), and Gibbs free energy ($G = A + PV$). These expressions, for both pure fluids and mixtures, as well as calculations related to excess properties, chemical potentials, mixture miscibility, phase boundaries, and property changes upon mixing have been described previously in detail.^{9,10} The SANS data employed in this work are obtained at constant, atmospheric pressure (as is often the case) and so the free energy we use to relate to the free energy of mixing in eq. (1) above is the Gibbs free energy. Next, we briefly describe the LCL equation of state and the relevant component molecular parameters.

Based on $A(N, V, T)$ for a one-component system, where N is the number of molecules, the LCL expression for pressure, $P = -(\partial A / \partial V)_{N, T}$, is given by

$$\begin{aligned} \frac{P}{k_B T} = & \left(\frac{1}{v}\right) \ln \left[\frac{(V/N)}{(V/N) - rv} \right] + \left(\frac{3}{v}\right) \ln \left[\frac{(V/N) - (v/3)(r-1)}{(V/N)} \right] \\ & - \left(\frac{3}{v}\right) \left(\frac{(2r+1)^2}{(V/Nv) - (1/3)(r-1)} \right) \times \left(\frac{\exp[-\epsilon/k_B T] - 1}{(1/3)(2r+1)\exp[-\epsilon/k_B T] + (V/Nv) - r} \right) \end{aligned} \quad (2)$$

where k_B is the Boltzmann constant, and a fixed value of 6 has been taken for the lattice coordination number. Taking other values (e.g. 8 or 10) would also be acceptable, as long the value is fixed throughout. The three molecular parameters for a pure fluid are: r , the number of segments (occupied lattice sites) per molecule, v , the volume per lattice site, and ϵ , the segment-segment nonbonded interaction energy (ϵ is negative in value).

For the case of a mixture of components, “ i ” and “ j ”, there will be six molecular parameters: r_i , r_j , ϵ_{ii} , ϵ_{jj} , ϵ_{ij} , and v . In the mixture, the single value of the lattice site volume (v) will be a compromise value (an average) for the two pure components. ϵ_{ii} and ϵ_{jj} are the nonbonded interaction energies for $i-i$ and $j-j$ contacts respectively, and these are determined from fitting pure component data before modeling the mixture. ϵ_{ij} is the (temperature independent) interaction energy for the mixed $i-j$ contact. For convenience, we will quote this mixed interaction in terms of the parameter, g , defined by $\epsilon_{ij} = g(\epsilon_{ii}\epsilon_{jj})^{1/2}$ (rather than quoting ϵ_{ij} directly); a value of $g > 1$ corresponds to a favorable mixed interaction (relative to the geometric mean) and $g < 1$ is unfavorable. g is the only parameter that is fitted to data on the mixture. This means that just a single mixture datum (at

one value of T and composition) will suffice; this single datum can be either a single point on a miscibility (phase) boundary, or one G'' measurement, or a single measurement of the volume, or enthalpy, change of mixing. With this minimal input information, the model can then predict phase boundaries, mixing curves, and other mixture properties as they vary as a function of temperature, composition, and molecular weight.

We obtain the remaining model mixture parameters, r_i , r_j , ϵ_{ii} , ϵ_{jj} , and v , by fitting to corresponding pure component data. Most commonly we use pressure-volume-temperature (PVT) data, or related data, such as the (volumetric) coefficient of thermal expansion (at constant N, P), $\alpha_V = (1/V)(\partial V/\partial T)_{N,P}$. Full PVT data sets are not available for any of the polymers in the blends studied here, and we will thus seek to estimate α_V . We will explore the use of ellipsometry which directly probes thin film (α_N) expansion coefficients, whose relationship with the linear (α_L) and volumetric (α_V) coefficients will be discussed below.

We consider first the v parameter because only a single v value will be used for the mixture. Here a single reasonable compromise value must be ‘imposed’ on each pure component (although this restriction will not limit the ability to accurately fit the pure component’s experimental ambient pressure $V(T)$ behavior). Given the present blend components of P α MSAN and dPMMA (or s-dPMMA), we consult our previous results²⁷ from fitting full PVT data sets of similar polymers, SAN and hPMMA for which v parameter values of 6.9214 and 6.9576 mL/mol were obtained, respectively. As a compromise, we will take the average of those values (which are close/essentially the same already), and apply this as the v parameter (6.9395 mL/mol) in all pure component and mixture modeling for P α MSAN, dPMMA, and s-dPMMA here in this work.

With the v value set, only two parameters (r and ϵ) remain to be determined for each pure component, which can be done by fitting to the experimental value for α_V together with a single value of the specific volume at a given temperature. We have shown²⁸ that for polymers (where r will be large), the ϵ parameter will depend almost solely on the value of α . The specific volume will then dictate the value of the corresponding r parameter. We can approximate the specific volume at a given reference temperature and ambient pressure for each polymer. This approximation only needs to be reasonable; if it is correct within ~ 1 -2%, then the corresponding r parameter value will be correct within ~ 1 -2%, and that is

sufficient for our purposes here.

We choose a reference temperature of 425 K. We take the specific volume of hPMMA from our previous analysis,²⁷ and scale it by the ratio of the mass per polymeric repeat unit to account for deuteration in dPMMA (assuming hydrogenous and deuterated polymers have approximately the same volume per repeat unit); this leads to a dPMMA specific volume of 0.8212 mL/g at 425 K, 1 atm; we also assume this same value for s-dPMMA. For P α MSAN at 425K and 1 atm, we obtain an approximate specific volume of 0.9740 mL/g. This follows by using its specific volume in the glassy state at room temperature (0.9302 mL/g,²⁹ corroborated by gas pycnometry) together with the specific volume of the corresponding glassy dPMMA (0.7844 mL/g, accounting for deuteration), and then multiplying the ratio of these glassy values by the above specific volume value for the dPMMA melt at 425 K, 1 atm (an independent test verifying this approximation for the P α MSAN specific volume is described in the SI).

The fitted r and ϵ parameters are calculated using the LCL equation for P as a function of T and specific volume (eq. 2, given the molecular weight), together with the LCL equation for α_V as a function of T and specific volume. Given $v = 6.9395$ mL/mol, $T = 425$ K, $P = 1$ atm, and values for the polymer's corresponding specific volume and α_V , the two equations (for P and α_V) can thus be written to solve for the two unknowns (r and ϵ). The results for α_V obtained via ellipsometry measurements and the corresponding fitted LCL pure component parameters will be discussed next, followed by the analysis from modeling the blend.

Results and discussion

Small Angle Neutron Scattering: determination of $G''(T)$

The structure factor of a polymer blend $S(q)$ in the one phase region can be obtained from the SANS scattering intensity $I(q)$ following

$$I(q) = KS(q) + B \quad (3)$$

where K is a contrast factor

$$K = N_A \left(\frac{b_1}{v_1} - \frac{b_2}{v_2} \right)^2 \quad (4)$$

and N_A is the Avogadro number, b_1 and b_2 are the coherent scattering lengths of the two monomer units (1,2) and v_1 , v_2 are the respective monomer molar volumes. B is a q -independent background, mostly due to the incoherent scattering from the hydrogenous component. 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, $v_2=84.79$ cm³/mol, yielding $K=5.19 \times 10^{-3}$ cm⁻⁴ mol. In this formalism, $S(q)$ has units of [cm³/mol].

SANS data from polymer blends are frequently analysed using the Random Phase Approximation (RPA) and we have previously reported^{18,19} an extensive analysis of these blends employing this approach. In the current work, we explore the thermodynamic behavior of the blend and are thus principally interested in determining G'' . We therefore follow a simpler, robust analysis based on the q -extrapolation of the data to estimate the zero angle scattering intensity, $S(0)$, at constant temperature, to obtain $G''(T)$ as given by eq. (1). In the low- q range ($qR_g \lesssim 1$), the Ornstein Zernike (OZ) equation provides a good description of the scattering from the blends capturing the spectrum of concentration fluctuations with a Lorentzian profile

$$S^{-1}(q) = S^{-1}(0)(1 + \xi^2 q^2) \quad (5)$$

where ξ is the correlation length of the concentration fluctuations at a given temperature. A linear extrapolation of $S^{-1}(q)$ against q^2 leads directly to values of $S(0)$ (from the intercept) and the correlation length ξ (from the slope). In the data shown in Fig. 1, deviations from OZ behavior are observed at low q and attributed to the incomplete thermal equilibration of long wavelength concentration fluctuations^{23,30} in the vicinity of the glass transition temperature T_g (illustrated in Supporting Information Fig. S2). The low- q extrapolation can be nevertheless carried out in a robust manner. Values of G'' obtained in this way for the blends discussed here are shown in Figure 1h. Given that the temperature dependence of G'' can be well described by $G'' = \mathcal{A} + \mathcal{B}/T$, values of the spinodal temperature T_s can be obtained by extrapolation to $G'' = 0$. We obtain $G'' = -0.00383 + 1.60/T[K]$ [cm³/mol]

for P α MSAN/dPMMA99k at $\phi=28/72$ and $T_s=144.8$ °C, and $G'' = -0.00529 + 2.30/T[K]$ [cm³/mol] for P α MSAN/dPMMA110k-s at $\phi=30/70$ and $T_s=161.4$ °C.

Ellipsometry: determination of thermal expansion coefficients in thin films

An important question underlying our work is how the thermal expansivity of a polymer in a thin film is precisely related to its expansivity in the bulk state. To address this question, we first review the relevant literature. Then, as a means to validate our measurements of expansivity, we compare experimental values obtained by ellipsometry from hPMMA thin films with previously reported PVT values (for the bulk).

In bulk systems (not influenced by confinement effects), the coefficient of thermal expansion, α , is the measure of the fractional change in volume, V or length, L with temperature, T , respectively defined as

$$\alpha_V = \frac{1}{V} \frac{dV}{dT} \quad (6)$$

and

$$\alpha_L = \frac{1}{L} \frac{dL}{dT} \quad (7)$$

When analyzing experimental data, these equations are applicable to relatively narrow temperature ranges, as the expansivity varies with temperature. The temperature range employed for the measurement of α should be thus reported with its value. For a thin film of thickness, h , the expansivity in the direction normal to the substrate, α_N , is of the same form as α_L , but with h used in the place of L .

A simple geometric argument shows that for an isotropic solid, $\alpha_V \sim 3\alpha_L$.^{31,32} If the expansivity of a thin film is much greater than the expansivity of its substrate, as is the case for a polymer melt on a silicon substrate, then the expansion in the plane of the film is essentially prevented when it is attached to the substrate. Using the theory of elasticity applied to this situation, Wallace *et al.*³³ wrote that α_N is then related to α_L as:

$$\alpha_N = \frac{1 + \nu}{1 - \nu} \alpha_L \quad (8)$$

where ν is Poisson's ratio. For a liquid, such as a polymer melt, ν is 0.5. Then it follows that $\alpha_N = 3\alpha_L \simeq \alpha_V$. This analysis neglects any effects of confinement or adsorption at the interface on the measured expansivity.

The results of Wallace *et al.*³³ using a two-layer model, assuming a melt layer and an underlying glassy layer, indicated a glassy layer that is 40 nm thick, which is far below the thickness of the films used in our experiments; their results for α_N in the melt were somewhat lower than the bulk value. Miyazaki *et al.*³⁴ reported that α_N for polystyrene (measured via X-ray reflectivity) in both the melt and the glass regions increased with increasing film thickness. In the melt region, the dependence of the expansivity on film thickness was very weak. In the glass region, the expansivity increased strongly with increasing thickness values ranging between 10 and 30 nm, but much less above that thickness. On the contrary, Kawana and Jones,³⁵ using ellipsometry, found that α_N of glassy PS films decreased with increasing thicknesses between 10 and 100 nm. As in the work by Miyasaki *et al.*,³⁴ they found essentially no dependence of the expansivity of polystyrene melts on film thickness. More recently, Napolitano *et al.*³⁶ found in capacitive dilatometry experiments an increased expansivity (in both the glass and the melt) with increasing film thickness up to 50 nm, above which the values became constant. In summary, the literature indicates that thin film interfacial effects are largely lost for thicknesses above $\simeq 100$ nm. In the experiments reported here, we thus employ greater film thicknesses (i.e. not ultra-thin films), such that interfacial effects on α_N will be minimal.

The glass transition temperature, T_g , of polymer thin films can be defined as the temperature at which there is a change in the thermal expansivity. As the ellipsometry parameters, ψ (relating to the change in light's amplitude upon reflection) and Δ (relating to the change in the phase of polarization upon reflection), are linearly proportional to thickness over a narrow range, it is possible to determine T_g directly from measurements of ψ (or Δ) as a function of temperature, without analysing the data to determine the thickness.^{37,38} Ellipsometric estimations of T_g are thus comparatively straightforward, from the intersection of

slopes of h , ψ or Δ with temperature from the glass and melt states. However, a rigorous determination of α_N in polymer films is needed for LCL theory, and this requires precise measurements of both thickness and temperature. In turn, reliable thickness (and refractive index) measurements of thin films require the fitting of ψ and Δ pairs at multiple wavelengths and angles of incidence. There are examples in the literature at which the ellipsometry spectra are obtained quickly as the sample is cooled (or heated) at a constant rate,³⁹ but this method provides only a time-average thickness for a temperature range. For the most precise measurements of (h, T) pairs, spectroscopic scans over a range of wavelengths should be performed at a constant temperature.⁴⁰ This type of isothermal spectroscopic scan was performed in our experiments.

Examples of the ellipsometry spectra (Ψ and Δ) obtained from homopolymer thin films of P α MSAN, dPMMA99k, as well as hPMMA152k, thin films at two selected temperatures in the glassy and melt regions are presented in Fig. 2 (a-c). The spectra for the polymer melt films are red-shifted with respect to the glassy films. Although the shifts appear minor in the figure, shifts of only a few degrees are significant when considering that the ψ was measured typically with uncertainty of only 0.02 degrees, and Δ with uncertainty of 0.1 degrees. Spectra for dPMMA110k-s are provided in Supporting Information Fig. S3. Measurements of film thickness, h , as a function of temperature for the various homopolymers are shown in Fig. 2 (d-f). As described in the Experimental section, the films were equilibrated by cooling from the melt state at a rate of 2 °C/min. This same heating rate was used to increment the temperature between the ellipsometry scans. The straight-line dependence of h on T shows that there is no structural relaxation during reheating of the glass.

Figure 2: Ellipsometry spectra (Ψ and Δ) for homopolymer thin films in the glassy state ($T=40^\circ\text{C}$ or 313 K, shown with the square symbol) and the melt state ($T=180^\circ\text{C}$ or 453 K, shown with the triangle symbol) for (a) P α MSAN, (b) dPMMA99k and (c) hPMMA152k. Filled symbols correspond to Ψ (left axis) and open symbols correspond to Δ (right axis). The temperature dependence of the film thickness obtained by the ellipsometric heating scan for (d) P α MSAN, (e) dPMMA99k and dPMMA110k-s, and (f) hPMMA152k. Lines serve as guide to the eye and the intersection of two lines corresponds to $T_{g,ell}$.

In order to ensure consistency of our measurements, T_g values obtained by DSC ($T_{g,DSC}$) were compared to those measured in thin films by ellipsometry ($T_{g,ell}$). The solid lines in Fig. 2 (d-f) are best fits to the glassy and melt regions and the T_g is determined by the intersection of two lines. While the T_g of ultra-thin films is thickness-dependent, all films investigated here have thicknesses above 150 nm, for which the measured T_g is thickness-independent and agrees well with bulk data (cf. ellipsometry data for PMMA, regardless of tacticity^{41,42}). The glass transition temperatures obtained by ellipsometry and DSC (summarized in Table 1) agree well, despite the different methodologies (and slightly different heating rates).

The thin film expansivity, α_N was determined by the analysis of the data in Fig. 2, and the

results for the melt expansivity are summarized in Table 2. A detailed uncertainty estimation for α_N values in both the glassy and melt states is provided in Supporting Information Table S1. In order to confirm the validity of taking $\alpha_V \simeq \alpha_N$ we have carried out a series of ellipsometry experiments, under the same conditions as the other measurements, on a sample of hPMMA152k (Fig. 2c and f) for which PVT data ($M_w = 100$ kg/mol) are available in the literature.¹⁶ As expected, an excellent overlap is found between the bulk (3D) PVT measurement and the ellipsometry data (1D), as demonstrated in Supporting Information Fig. S4-S6.

Figure 3: Temperature dependence of the film thickness obtained by ellipsometry for (a) P α MSAN/dPMMA99k=29/71 and (b) P α MSAN/dPMMA110k-s=38/62 blends. Lines show linear fits in the glassy and melt states, whose intersection yields $T_{g,ell}$. Downward arrows indicate T_s , as measured by SANS, beyond which films are no longer planar. (c) AFM topography image of a P α MSAN/dPMMA99k=29/71 blend at the end of thermal annealing, at a scale $20 \mu\text{m} \times 20 \mu\text{m}$, and (d) of $1 \mu\text{m} \times 1 \mu\text{m}$; (e) AFM image of P α MSAN/dPMMA110k-s=38/62 after annealing, at scale $20 \mu\text{m} \times 20 \mu\text{m}$, and (f) $1 \mu\text{m} \times 1 \mu\text{m}$. (g) AFM line scan for P α MSAN/dPMMA99k=29/71 and (h) P α MSAN/dPMMA110k-s=38/62 corresponding to the lines indicated in panels (c) and (e).

Although not employed in LCL analysis, for completeness, we have also considered selected blend measurements by ellipsometry and AFM, shown in Fig. 3. The film thickness dependence on temperature for P α MSAN/dPMMA99k=29/71 is shown in Fig 3(a), and its glass transition temperature is estimated as $T_{g,ellip}=117 \pm 1 \text{ } ^\circ\text{C}$ (390 K), slightly lower than the value (394 K) obtained by DSC. The downward arrow indicates the spinodal temper-

ature $T_s=144.8\text{ }^\circ\text{C}$ (417.9 K) as found by SANS. Fig 3(b) shows ellipsometry results for a blend of P α MSAN/dPMMA110k-s=38/62, whose $T_{g,ellip}=114\pm3$ (387 K). The melt h data ($T > T_g$) for both blends increase linearly with temperature, as expected; however, the P α MSAN/dPMMA110k-s film shows a distinguishable change in slope upon heating near 430 K, which corresponds well to its spinodal temperature $T_s \simeq 433.9$ K (160.8 $^\circ\text{C}$) previously determined by SANS,¹⁸ also indicated by a downward arrow. AFM measurements at the end of each ellipsometry scan are shown in Fig 3(c-f), with line scans corresponding to Fig. 3(c,e) shown in Fig. 3(g,h). These indicate a profile roughness of ± 1 nm, greater than the initial blend and pure component film roughness of ± 0.5 nm. Deviations from linearity in the ellipsometry data in melt state above T_s are thus likely caused by demixing, and we therefore restrict the temperature range employed to determine α_N to $T_g < T < T_s$. Given the potential surface or substrate enrichment of blend components, as well as a possible coupling with demixing, precise depth profiling (e.g., by neutron reflectivity or secondary ion mass spectroscopy) would be required to elucidate the composition profile normal to the surface. This is outside the scope of the current work, but must be examined when interpreting ellipsometry data of polymer blends.

Overall, these are the first measurements of the thermal expansivity of the P α MSAN and dPMMA system by ellipsometry. To the best of our knowledge, data for α_V obtained from PVT measurements are not available in the literature for this system. The success of this analysis is significant for application of the LCL theory because it means that the required pure component data for a wide range of systems can be readily determined using this experimental approach when bulk *PVT* data are not available. Not only is ellipsometry more widely-available but it requires minute sample amounts compared to *PVT*.

LCL Characterization of Pure Components

With the ellipsometry data for the pure components, the LCL characterization can be completed. We will follow the implementation outlined above, and solve for the LCL r and ϵ parameters based on a value for the specific volume and the value of the volumetric coefficient of thermal expansion, α_V , for each pure component melt. As also noted above, we assume that $\alpha_V = (1/V)dV/dT = \alpha_N = (1/h)dh/dT$, and thus determine α_V from the best-fit slope

of the plot of $\ln[h]$ vs. T where h is the measured film thickness.

In modeling blends, we have stressed the importance of consistently fitting each pure component melt over the same temperature range.^{10,11} Ellipsometry data for all pure components range up to a temperature of about 450 K (448 K for dPMMA, and 453 K for s-dPMMA and P α MSAN); we will take this as the upper T limit of the data fitting range, and take a lower T limit of 403 K for all; the center of this data range is thus $\simeq 425$ K. The ellipsometry data from this fitting range were plotted in the form of $\ln[h]$ vs. T to obtain the resulting α_V values (the slopes), which we then use in the LCL fit for each pure component. These α_V values, along with the specific volume values at $T = 425$ K, $P = 1$ atm, are tabulated in Table 2. These values allow us to solve for the LCL model r and ϵ parameters which are also tabulated for each pure component.

Table 2: Pure component properties^a and LCL model parameters^b.

Component	V (mL/g) 425 K, 1 atm	α (/K) 425 K, 1 atm	V_{free}/V 425 K, 1 atm	$-\epsilon$ (J/mol)	r
P α MSAN	0.974	4.9×10^{-4}	0.1135	2384	15180
dPMMA	0.821	6.3×10^{-4}	0.1372	2127	10120
dPMMA-s	0.821	6.0×10^{-4}	0.1331	2166	11286
P α MSAN/dPMMA blend $g = 1.0018302$; P α MSAN/s-dPMMA blend $g = 1.0013188$					

^a The α values shown here (within the measurement uncertainty of Table S1) were best fits to the ellipsometry data for each melt in the 403-450 K range (slope of $\ln h$ vs. T); in the LCL modeling, these were then taken as the α_V values at the midpoint $T = 425$ K. The volume values corresponding to the ellipsometry data in the plots of Fig. 3 are based on the specific volume values tabulated here and the film height at $T = 425$ K; the corresponding film mass per area values applied in the height to volume conversions are 1.73×10^5 , 2.37×10^5 , and 2.30×10^5 g/cm² for P α MSAN, dPMMA, and s-dPMMA respectively, where the film height at $T = 425$ K, was taken from a linear fit of the $h(T)$ ellipsometry data. These conversions have followed from the assumption that the film mass per area remains fixed as the film expands with temperature.

^b The LCL v parameter is set at $v = 6.940$ mL/mol for all pure components. This same v value is also applied in all blend modeling together with the tabulated r and ϵ values, the latter of which apply in the mixture as r_i and ϵ_{ii} for any component i . The r_i values depend on the component molecular weights which are 99.1, 110, and 122 kg/mol for dPMMA, dPMMA-s, and P α MSAN respectively (see Table 1). We list the LCL parameters out to a large number of digits for completeness in reproducing model curves and results; this detail is of course much finer than the experimental uncertainties.

With all three of the pure component parameters (r , v , ϵ) characterized, we show plots

of the LCL model $V(T)$ curves at ambient pressure in Fig. 4. Together with this, we also include the corresponding ellipsometry $V(T)$ ‘data’ which are inferred from the expectation of holding a constant sample mass per area (the film mass per area values are based on matching the film height data at $T = 425$ K to the corresponding specific volumes; values for each polymer and additional information are provided in Table 2). The figure shows the results for all three of the pure components, dPMMA, dPMMA-s and P α MSAN. As expected, the T dependence of the volume is in good agreement for model and data.

Figure 4: LCL model applied to ellipsometry data: specific volume (ml/g) as a function of temperature (K) at ambient pressure for the pure component melts: dPMMA-s (syndiotactic), dPMMA (atactic), and P α MSAN. Model results are shown as curves, and corresponding values from ellipsometry data are shown as points. LCL model parameters and the molecular weights for each sample are available in Table 2. See text and Table 2 for details on converting film heights from ellipsometry data into specific volume.

LCL Characterization of Blends

With α results leading to a full characterization for each of the pure components, we next determine the g -values for the blends. Fig. 5 shows a plot of G'' versus T^{-1} for (a) P α MSAN with atactic dPMMA and (b) with syndiotactic dPMMA at fixed concentration of P α MSAN

segment (volume) fraction of (a) $\phi = 0.408$ and (b) 0.301. In each case, a single experimental data point in the one phase region, identified amongst the experimental data as the open symbol, fixes the value of g . The solid line then represents the LCL T -dependence of G'' and, in both cases, the theory captures experimental behavior rather well (i.e. the slope is not adjusted). Here we fit just a single point rather than minimizing the deviation over the full set of points. (Any single datum could have been chosen of course; we chose the point closest to the spinodal.) As noted above, an advantage of LCL is that it has only a single constant mixture parameter (g), so fixing its value requires only a single mixture datum (one measurement of G'' , one phase boundary point, etc.), and with this, predictions for mixture properties can be made over varied temperature, composition, and molecular weight. This efficiency is possible because LCL incorporates the properties of the pure components, and the result is enhanced predictive power. By contrast, implementation of the Flory-Huggins approach involves fitting two or more adjustable parameters to the mixture. For example, the Flory-Huggins model requires measurement of the temperature dependence of G'' , while LCL does not.

Both blends are now fully parameterized (Table 2). The g -values for the two blends are both > 1 , meaning that the mixed interaction in each case is favourable. However, the value for the dPMMA-s (syndiotactic) blend is closer to unity than for the atactic dPMMA blend, which shows that the strength of the favourable mixed segment interaction diminishes in the blend with the greater syndiotactic contribution.

Figure 5: Temperature dependence of G'' for the $\text{P}\alpha\text{MSAN/dPMMA99k}$ blend at composition, $\phi_{\text{P}\alpha\text{MSAN}} = 0.408$, and the $\text{P}\alpha\text{MSAN/dPMMA110k-s}$ blend at composition, $\phi_{\text{P}\alpha\text{MSAN}} = 0.301$. LCL model shown as curve; experimental SANS data as points (Fig. 1). The single LCL mixture parameter (g) was fit to the one hollow datum.

The LCL theory predictions for the coexistence and spinodal curves of both blends are shown in Fig. 6, and found to agree well with experimental data (symbols). In contrast with LCL, typical application of Flory-Huggins theory demands a χ -function, with two or more parameters required to specify its temperature and/or composition dependence. An additional advantage is tied to another aspect of the characterization: the theory captures pure component behavior, which leads to a deeper understanding of what is driving im/miscibility,

and also means that the theoretical results are transportable to other mixtures.

Figure 6: Phase diagrams for the P α MSAN/dPMMA99k (a) and P α MSAN/dPMMA110k-s (b) blends. LCL model spinodal boundary shown as solid curve and the binodal shown as dashed curve; experimental spinodal data shown as points

We note the α of syndiotactic dPMMA is closer than that of atactic dPMMA to the α of P α MSAN. In earlier work²⁸ it was shown that α values correlate directly to LCL predictions for the free volume (V_{free}) in a fluid. In the LCL theory $V_{\text{free}} = V - V_{\text{hc}}$, where V is the total volume at a given (T, P) , and V_{hc} is the constant hard-core volume of that material

($=rv$ for each molecule). There is a closer match between the V_{free} values of syndio-dPMMA and P α MSAN (see Table 2 for V_{free}/V values) and for LCST mixtures this correlates with increased miscibility, as observed experimentally. The closer match in V_{free} is also consistent with the LCL prediction for a smaller volume change on mixing for the P α MSAN/dPMMA-s blend than for the P α MSAN/dPMMA, which is illustrated in Fig 7.

Figure 7: LCL model predictions for the volume change on mixing as a function of composition at $T = 415$ K for the P α MSAN/dPMMA99k and P α MSAN/dPMMA110k-s blends.

Thermodynamic Analysis of the Effect of PMMA Tacticity on Miscibility with P α MSAN

With both blends fully parameterized within the LCL formalism, we can examine further their underpinning thermodynamics of mixing. In Fig 8 we plot ΔG_{mix} , ΔH_{mix} , and $T\Delta S_{mix}$ as a function of composition for each blend in the one phase region ($T = 425$ K, $P = 1$ atm). (For any property, X , ΔX_{mix} is defined^{9,10} as the value of X for the mixture at a specified composition, minus what would be the total X for the same amount of the two components in their pure (unmixed) state at the same T , P .) The thick lines show results for atactic dPMMA and the thin lines for syndiotactic dPMMA. Both blends show ΔG_{mix}

curves that dip only slightly below zero, with the syndiotactic dPMMA being somewhat more favourable. However, the contributions to the free energy differ considerably between the two. The syndiotactic blend has a significantly less unfavourable (i.e. more favourable) entropy change on mixing than the atactic blend. Prior analysis of pure fluids using LCL has shown that both α_V and V_{free} track closely with ϵ values — the parameter that characterizes the pure non-bonded nearest neighbor interaction strength. In addition, LCL studies on dozens of mixtures has revealed that the ϵ -difference between components controls the magnitude of the entropy of mixing;^{9–11} as this difference grows, so does $|\Delta S_{mix}|$. This is exactly the trend observed here, and it illuminates what is driving the change in miscibility. Going from the atactic to syndiotactic PMMA yields a closer match between blending components in ϵ values (as well as in V_{free} and α_V). $|\Delta S_{mix}|$ decreases, and since it is unfavourable for LCST blends, this promotes miscibility.

This analysis also leads to an explanation for why the g -parameter for the blend with syndiotactic dPMMA is smaller than that for the atactic blend. Recall that a smaller (positive) g means that the (favourable) mixed segment interaction is becoming weaker. Earlier work (on other blends^{9–11}) showed that as ΔS_{mix} becomes more favourable, a less favourable mixed interaction is required in order to maintain an LCST. With a delicate balance between ΔH_{mix} and $T\Delta S_{mix}$ near a critical point, shifting to more favourable ΔS_{mix} alone would lead to complete miscibility. Since both atactic and syndiotactic dPMMA exhibit LCST behavior with P α MSAN, the more favourable ΔS_{mix} for the syndiotactic dPMMA has to be countered by there being a slightly less favourable mixed segmental interaction energy, which is reflected in the ordering of the g values.

Figure 8: LCL model predictions for property changes upon mixing: ΔG_{mix} , ΔH_{mix} , and $T\Delta S_{mix}$ as a function of composition at $T = 415$ K. Results for the P α MSAN/dPMMA99k and P α MSAN/dPMMA110k-s blends.

We can also examine the contributions to $T\Delta S_{mix}$, since the LCL theory accounts for both the ‘ideal’ entropy change (reflecting solely an estimate of the numbers of molecular arrangements of non-interacting species) and the ‘excess’ term (reflecting how interactions between like and unlike species influence these arrangements, as well as the overall change in segmental density as a result of mixing); the overall (total) ΔS_{mix} is thus the sum of the ideal and excess contributions, and more detail on their calculation can be found in previous work.^{9,10} Fig 9 shows the total, ideal, and excess results for both blends; the results for $T\Delta S_{mix}$ (total) are reproduced from Fig. 8. Evidently, the ideal contribution will always be positive; as Fig. 9 shows it is very small, as expected in the case of a polymer blend, and essentially equal for the two blends. This makes sense, since it is primarily affected by M_w which was kept nearly identical for both atactic and syndiotactic blends. The dominant contribution is clearly the excess entropy of mixing. We conclude that a fairly modest increase in the syndiotactic content of the PMMA in this blend results in changes in local

packing that cause a significant shift in the excess entropy of mixing and lead to a measurable increase in blend miscibility.

Figure 9: LCL model predictions for the contributions to the entropy changes upon mixing ($T\Delta S_{mix}$) as a function of composition at $T = 415$ K: total change, excess contribution, and ideal contribution. Results for the P α MSAN/dPMMA99k and P α MSAN/dPMMA110k-s blends.

We elaborate further on the influence of molecular weight on ΔS_{mix} through the ideal entropy of mixing. LCL (and other mixing theories) predict that this ideal term will become more important as M_w decreases. In earlier work⁴³ it was shown that, having characterized a LCST blend (PS/PVME) of specified component M_w , LCL could correctly predict the LCST shift upon changing the M_w of one component (PS). We do so here for the case of another atactic blend whose M_w (dPMMA) is 40k,¹⁹ instead of the 99k sample used in all the work discussed so far ($G''(T)$ data provided in Supporting Information Table S2).

Fig. 10 shows that the LCL theory predicts an upward shift in the LCST by about 6 degrees, which is expected due to a slightly more favourable ideal entropy of mixing contribution (for completeness, Flory-Huggins predictions are included in Supporting Information

Fig. S7). In earlier studies on PS/PVME blends LCL predicted stronger shifts for comparable molecular weight changes of the PS component. This arises because the theory predicts that changing the molecular weight of the component with the lower coefficient of thermal expansion will have a more dramatic effect than a molecular weight change of the higher α_V component. In PS/PVME the lower α_V component is PS, and in P α MSAN/dPMMA it is P α MSAN. In this case the modest shift in the LCST is at least partially consistent with the experimental phase diagrams which are seen to be somewhat insensitive to the M_w change, although it is unclear why the experimental results do not show a modest increase in miscibility to reflect a slightly more favorable ideal entropy of mixing contribution. One explanation might point to a very small difference in the tacticity of the lower molecular weight dPMMA.

Figure 10: Comparison of phase diagrams for the P α MSAN/dPMMA40k and P α MSAN/dPMMA99k blends.¹⁹ LCL model spinodal boundary (curves) and corresponding experimental spinodal data (points). P α MSAN/dPMMA40k blend shown by the thick curve and larger points, and the P α MSAN/dPMMA99k blend by thin curve and smaller points.

Conclusions

The LCL theory has demonstrated^{9–11,13,43} ability in describing the behavior of polymer blends by accounting for pure component properties as well as blend behavior. However, its application has been restricted by a lack of pure component data in the form of PVT curves. In this paper, we have shown that pure component data in the form of volume expansion coefficients obtained from ellipsometry experiments can satisfactorily fill this gap. This observation opens the way to a much wider application of the LCL theory to understanding the behavior of polymer blends. Here we have employed the theory to understand the effect of tacticity changes on the mixing behavior of a blend of poly (α -methyl styrene-co-acrylonitrile) with deuterated PMMA of varying tacticity. Analysis of SANS data from the blends and ellipsometry data for the component polymers using the LCL theory shows that this blend has a large excess entropy of mixing. The different degree of syndiotacticity of PMMA sequences, from 63% (‘atactic’) to 78% (‘syndiotactic’), which gives rise to an increase in the blend LCST of 16 K, arises from a decrease in this unfavourable entropy change on mixing when going from atactic to more syndiotactic PMMA. Moreover, the theory also predicts the experimentally-observed relative insensitivity to changing the M_w of the PMMA component, since the ‘ideal’ contribution to the entropy of mixing, which is M_w -dependent, is very small beside the very large excess contribution.

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Associated Content

Tacticity determination for dPMMA specimens based on NMR and DSC; Evolution of SANS scattering intensity upon isothermal annealing near T_g ; Ellipsometry spectra (Ψ and Δ) for dPMMA110k-s film at selected temperatures; Glassy and melt expansivities for all thin film samples and uncertainty estimation; validation of ellipsometric melt expansivities with PVT data for hPMMA; Tabulated $G''(T)$ for P α MSAN/dPMMA blends of various compositions for dPMMA40k and dPMMA99k, obtained by SANS, and corresponding Flory-Huggins spinodal lines.

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