Effect of Deuterium Substitution on the Physical Properties of Polymer Melts and Blends

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Using our simple lattice-based equation of state we capture the effect of deuterium substitution in polystyrene (PS), predicting both the pure component melt properties as well as the remarkable shift in the coexistence curve when hPS is replaced by dPS in forming a blend with poly(vinyl methyl ether) (PVME). Taking advantage of a rare opportunity to compare with experimental pure component data, we demonstrate that by characterizing the deuterated component through analysis of neutron scattering data we are able to make predictions for the pure dPS *PVT* properties which are in superb agreement with experiment. Calculations and measurement show that the dPS volume (per repeat unit) is slightly larger than that for hPS at low pressure, an effect which can be correlated with a difference in the model energetic parameter, (ε). In addition, we find that the dPS coefficient of thermal expansion (α) is larger than that for hPS and thus closer to the value for PVME. We propose that the increased similarity of the α's for dPS and PVME is connected to the increased miscibility of the dPS/PVME blend, a linkage which may be helpful to experimentalists in anticipating the potential effect on phase stability of polymer blends when deuterium substitution is employed.

I. Introduction

In recent years valuable insight has been gained in the study of polymer solutions and blends using small angle neutron scattering (SANS).[1,2] Due to the unique properties of the neutron, this technique has a number of advantages over alternative approaches and has been used to study both dynamic and thermodynamic behaviour. Among the disadvantages when studying mixtures, however, is the fact that the hydrogen atoms on one of the components usually have to be replaced with deuterium in order to achieve enough scattering intensity. In most studies there is little or no discussion regarding the possible impact of deuterium substitution on the physical properties of the mixture. This is a logical consequence of decades of nuclear magnetic resonance (NMR) measurements on labeled molecules, large and small. However, as is well known, in the world of polymer mixtures there are systems in which the effects of H-D substitution can be strong enough to influence the experimental outcome.[3-7] We have become interested in determining whether deuterium labeling will influence polymer melt properties and, if so, what the effect should be on miscibility. This paper represents our first report on such studies.

The effect of replacing hydrogen by deuterium in molecules was discussed early on by Buckingham and Hentschel,[3] who were the first to consider isotopic mixtures of polymer molecules. While subtle, the direct microscopic consequence of replacing a carbon-hydrogen bond with a carbon-deuterium bond is that, due to the lowered zero-point energy, the carbon-deuterium bond length is shortened, which decreases the molecular hard-core volume. However, this shortened bond length also leads to a reduced electronic polarizability, weakening intermolecular interactions and potentially causing an increase in molar volumes, at least at low pressure. These trends oppose each other, and the quantitative impact on bulk properties is expected to be system dependent.

Deuterium substitution in polymer blends raises interesting questions because it appears to have an unpredictable effect. Simple isotopic blends have been shown to phase separate when high enough molecular weight is approached.[4] In blends of different chemical species (see for example, refs 7-9), deuterating one of the components may, or may not, lead to significant shifts in the miscibility behavior. As an example, in blends involving polystyrene (PS) and poly(vinyl methyl ether) (PVME), deuteration of the PS component leads to roughly a 40 degree increase in the lower critical solution temperature (LCST).[7] However, an analogous H-D switch in a blend of PS with tetramethyl polycarbonate (TMPC) has a much smaller effect on the LCST.[9] There appear to be no obvious trends associated with deuterium substitution, and the lack of predictability therefore represents a theoretical opportunity.

In recent years we have demonstrated the predictive power of a simple lattice-based theory (developed by one of us) to model the thermodynamic behavior of polymer solutions and blends.[10,11] The theory gives a closed-form equation of state that is relatively easy to apply, yielding analytic expressions for the free energy, chemical potential, and so on. As is the case with any statistical mechanical description, some experimental data are needed in order to secure values for the characteristic parameters of the system components; this is discussed in greater detail in the following section. In prior publications we have demonstrated that a relatively sparse amount of data may be exploited to characterize a system, an example being to use data from SANS experiments. However, in the course of analyzing SANS results we realized that the effect of deuterium substitution in one of the components amounted to an uncontrolled addition to the experimental protocol, and that the subsequent analysis of the data did not account for the effect of H-D substitution.[12] Given the potential for a dramatic shift in critical temperature, it would be useful to model the impact of deuteration. Indeed, an effective model should be able to serve as a valuable 'theoretical laboratory', providing the ability to test ideas about H-D differences and their impact on melt and mixture properties.

In this work we therefore apply our lattice theory to study PS/PVME blends, focusing in particular on modeling the effects of deuterating the PS component (i.e., "hPS" vs. "dPS") on the physical properties of both the PS melts and its mixtures. In fitting for values of the component characteristic parameters, the typical approach involves using pure component *PVT* data, however, such data are essentially unavailable for deuterated components. As mentioned above, an alternate route is to fit SANS data obtained for a mixture containing, for example, dPS, and then extract characteristic parameters for pure dPS from the overall fit. (The link between experiment and model thermodynamics is the direct connection between the zero angle scattering intensity and the second derivative of the Gibbs free energy.) After thus characterizing the dPS component, which allows us to calculate its pure melt properties, we take advantage of a rare opportunity to test this method, as we have recently been able to determine experimental *PVT* results for a sample of dPS.[13]

We note that there have been previous applications of other lattice-based theories where SANS data was studied and employed for model parameterization. Often the interest was not to resolve the effect of deuterium substitution on the deuterated component per se; examples of cases where this was an interest include the investigations in refs 14 and 15 where Lattice Fluid Theory (LF) and Lattice Cluster Theory (LC) were applied to model isotopic hPS/dPS blends. We note that a distinction of the present investigation is our strong focus on connecting the behavior of the deuterated component in the mixture with its corresponding pure component properties, e.g., *PVT* behavior. While this was not a focus in these previous studies, there is still the opportunity to make some comparisons, in terms of both the results, as well as the choices made for model implementation; these will be noted as they come up in the remainder of the text.

The remainder of the paper is organized as follows. In section II we give a brief theoretical background describing the equation of state and its associated microscopic parameters. We also outline some of the details related to mapping the SANS intensities to the modeled thermodynamic properties. In section III, the details of the model fitting are described and the results are presented, including predictions for dPS pure component behavior as well as a detailed comparison of blend phase diagrams. We then conclude in section IV.

II. Theoretical Background

In this work we model the polymeric melts and blends with a theoretical lattice-based equation of state designed for chain molecule fluids. The theory goes several steps beyond Flory-Huggins theory[16] in that it accounts for both the effects of compressibility and nonrandom mixing. The derivations, described in detail elsewhere,[10,11,17,18] follow an integral equation formalism in which site-site pair probabilities are calculated for all possible neighboring pairs of segments in the chain fluid. These temperature-dependent probabilities are used to calculate the system's internal energy, which can be integrated over temperature (starting from an athermal reference state) to give a closed-form expression for the Helmholtz free energy, thereby leading to all of the other thermodynamic quantities. The resulting equation of state is expressed in terms of a set of transferable and physically meaningful microscopic parameters which means that, after fitting the theory to (a limited set of) known physical properties, these same parameters can then be used to predict a broad range of behavior, i.e., other physical properties which may not be experimentally available.

To illustrate the general process we consider the equation of state, expressed below for the case of a pure chain fluid as the pressure as a function of the number of chain molecules (N), volume (V), and temperature (T),

$$\begin{aligned}\frac{P}{k_B T} &= \left(\frac{1}{v}\right)\ln\left(\frac{V}{V - rvN}\right) + \left(\frac{z}{2v}\right)\ln\left(\frac{V - (2vN/z)(r-1)}{V}\right) \\ &\quad - \left(\frac{z}{2v}\right)\left(\frac{r - (2/z)(r-1)}{(V/vN) - (2/z)(r-1)}\right) \\ &\quad \times \left\{\frac{[r - (2/z)(r-1)](\exp[-\varepsilon/k_{\mathrm{B}}T] - 1)}{[r - (2/z)(r-1)]\exp[-\varepsilon/k_{\mathrm{B}}T] + (V/vN) - r}\right\}\end{aligned} \quad . \tag{1}$$

In this equation the key microscopic parameters are v, the volume per lattice site, ε, the segment-segment interaction energy, and r, the number of segments per chain molecule; z is the lattice coordination number which is fixed at a value of 6.[19] The total volume, V, is comprised of filled and empty lattice sites, which means that the system is compressible, therefore $V > rvN$, where rv is the hard-core volume occupied by a single chain molecule. The equation of state has a similar form for the case of a mixture (e.g., a polymer solution or blend) where additional terms are incorporated to account for the presence of a second species. In this case, three additional parameters are required: r and ε for the second species, and the mixed interaction parameter, g, which scales the energetic interaction (ε_{ab}) between segments of species a and b according to $\varepsilon_{ab} = g(\varepsilon_{aa}\varepsilon_{bb})^{1/2}$. Both of the pure components and the mixture are modeled using a single value for the parameter, v; typically, we choose a value that is a compromise between the optimal v's for each component. Finally, it is important to note one further point regarding the use of the r parameter: Provided that the chain molecules are long enough (e.g. polymers), an r value ("r_{fit}") that was fit to one molecular weight ("M_{fit}") can later be scaled to predict the properties for a different molecular weight without additional fitting, and with no changes to the other parameters. Hence the r value for any predicted system ("r_{predict}") is scaled proportional to its molecular weight ("M_{predict}") according to $r_{\text{predict}} = M_{\text{predict}}(r_{\text{fit}}/M_{\text{fit}})$. Because this property is used frequently, we tabulate the r parameter as r/M.

In prior work we have followed a number of different approaches to characterizing systems of interest. The most widely-followed route to the pure component parameters r,

v, and ε is by fitting to the corresponding pure fluid pressure-volume-temperature (*PVT*) data, and this is the method we use here for hPS and PVME. The resulting sets of pure component parameters are then applied to model the mixture. Other options for obtaining r, v, and ε could involve far less data; for example, only a handful of values for the isothermal compressibility, or the coefficient of thermal expansion, would be necessary, as long as the experimental conditions were fairly representative of the modeling conditions of interest. A more recently developed option, of particular importance in the present work, is to fit to SANS data. This route, described in more detail below, will be used to obtain the pure component parameters for dPS.

One additional parameter, g, is required to model the mixture, which generally requires at least a datum point such as a critical solution temperature. We note one exception, involving mixtures of simple linear alkanes and/or their solutions with polyethylene. For these solutions we have found that applying our lattice theory with the geometric mean approximation ($g = 1$) leads to theoretical predictions in excellent agreement with experimental results.[18,20] We believe that this (limited) ability to predict mixture behavior without requiring a fit to any mixture data represents a particular strength of our lattice model, as other approaches do not appear to be similarly capable, even for these simple hydrocarbon mixtures.

As mentioned above, the typical scenario for determining g involves using one single experimental datum point such as a critical temperature e.g. an LCST or UCST. An alternative to using a critical temperature in fitting for g is to analyze experimental results for one or more thermodynamic mixing functions (e.g., ΔV_{mix} or ΔH_{mix}), although these data are often difficult to obtain for polymeric mixtures. As is the case for obtaining characteristic parameters of a deuterated component, our protocol also allows us to obtain *g* from SANS data, and that is the route we shall follow here. That is, we employ SANS results for the dPS/PVME blend to determine both the pure component parameters for dPS, as well as a value for *g*. Of course, extraction of Flory-Huggins χ-parameter values from SANS data is commonly done, however, as we discussed in an earlier work,[11] χ values tend to be somewhat opaque in terms of leading to substantive understanding of blend miscibility. The present approach keys on more unambiguous and transferable quantities.

In analyzing SANS blend data we exploit the relationship between the zero angle scattering intensity and the second derivative of the Gibbs free energy with respect to composition. The details of this mapping do require some care as ambiguity has arisen at times in the literature,[21-23] due in part to the fact that the data analysis has so often been performed in the context of an incompressible theory (Flory-Huggins theory). We use the following relationship which was detailed in ref 21 (eq 26),

$$\left(\frac{\partial^2 G}{\partial x_a^2}\right)_{T,P} \approx \frac{k_{\mathrm{B}}T}{I(0)}\rho^3 (v_a v_b)^2 \left(\frac{b_a}{v_a} - \frac{b_b}{v_b}\right)^2 . \tag{2}$$

In this equation G is the Gibbs free energy per total number of repeat units (type a and b), ρ is the total number of repeat units per volume, x_a is the mole fraction of repeat units of type a, v_a (v_b) is the pure fluid volume of a repeat unit of type a (b), b_a (b_b) is the scattering length of a repeat unit of type a (b), and $I(0)$ is the zero angle scattering intensity per unit volume (where $I(0)$ thus has units of inverse length). As discussed in ref 21 it is a reasonable approximation to use the pure fluid volumes per repeat unit (v_a and v_b) in place of the partial molar volumes (which appear in the more rigorous expressions), and further, to approximate ρ as $(x_a v_a + x_b v_b)^{-1}$. (Also ignored in eq (2) is the contribution to $I(0)$ due purely to density fluctuations which, because of the very small isothermal compressibilities of polymeric blends, are negligibly small compared to the scattering contribution from concentration fluctuations.)

In calculating our results for the dPS/PVME blend we used scattering lengths (b_a and b_b) of 1.07×10^{-11} cm [dPS][9] and 3.30×10^{-12} cm [PVME],[24] and temperature dependent volumes per repeat unit (v_a and v_b) which have values of 1.69×10^{-22} cm^3 [dPS][9] and 1.01×10^{-22} cm^3 [PVME][24] at T = 394K (and as mentioned above, ρ is thus calculated from v_a and v_b assuming zero volume change on mixing). It is noted however that it was not crucial to correct v_a and v_b for temperature dependence, i.e., simply using the values at 394 K at all temperatures does not strongly effect the overall results. Furthermore the choice of using a value for v_{hPS} to stand for v_{dPS} also does not strongly affect these particular calculations (due to the expected small difference in these values).

Combining a theoretical value for $(\partial^2 G/\partial x_{\mathrm{a}}^2)_{T,P}$, and the above values for b_a, b_b, v_a, v_b, and ρ, a "theoretical scattering intensity" ($I(0)$) can thus be evaluated from eq (2). The value of the theoretical $I(0)$ depends (through the theoretical $(\partial^2 G/\partial x_{\mathrm{a}}^2)_{T,P}$) on the model parameters (r, v, ε, g, etc.) which can thus be changed (fit) so that agreement is obtained with the actual experimental $I(0)$. In this work the theoretical $I(0)$ as a function of temperature at a single composition is fit to a corresponding set of experimental measurements. Further details and discussion of the fit will be given in the following section.

Finally, we wish to comment on the effect of polydispersity as it relates to the application of the model theory. While its effects on *PVT* properties are usually fairly minor, polydispersity can have a strong effect on the phase behavior.[25] The present theory, on the other hand, assumes the components to be monodisperse. This limitation is thus a potential concern when the polydispersity is high, as we noted in a recent paper[26] (with further discussion in the supporting information section). In general, we have found that our parameterizations are the most optimally transferable (i.e., for going from fitted to predicted systems) for cases in which the polydispersities of the components are roughly the same within all of the modeled systems considered. Regarding the present work, it is important to note that the polydispersity for the PVME is indeed high, however, for all of the experimental blend systems considered, its value is the same ($M_w/M_n = 2.13$), and thus we anticipate reasonable consistency in our predictions. Further comments will be made in section III when the phase diagrams are presented.

III. Results and Discussion

Before predictions can be made the system must be characterized. As noted above, the pure component parameters (*r*, *ε*, and *v*) for hPS and PVME were obtained by fitting to the corresponding pure fluid *PVT* data (refs 27 and 28). The parameter values are given in Table 1. In addition, Table 2 provides a summary of the data types, molecular weights, and *r* values for all systems of interest. The *PVT* fits covered roughly a 100 degree temperature range starting just above the glass temperature for PS (~365K) and were weighted for best agreement at low pressure. The results of these fits are illustrated in the upper (hPS) and middle (PVME) panels of Figure 1. In the fits, *v* was restricted to be the same for both hPS and PVME so that pure and mixed components could occupy the same lattice; the value of 7.667 mL/mol is seen to be a reasonable compromise. The value of *g* = 1.001317 was determined by fitting to the experimental LCST (394 K) in ref 29, with the pure component parameters fixed. It is worth noting here that all the significant figures reported are, indeed, significant. The sensitivity of mixture predictions to extremely small changes in *g* is not unique to this theory. Indeed, this feature, or its equivalent involving a mixture parameter serving an analogous function, is characteristic of mixing theories in general.

Table 1. Parameter Values for the Model Equation of State[a]

	r/M_w (g/mol)$^{-1}$	v (mL/mol)	ε (J/mol)
PVME	0.115343	7.667	- 1948.7
hPS	0.113767	7.667	- 2144.3
dPS	0.105605[b]	7.667	- 2106.0
g values for blends: 1.001317 (hPS/PVME), 1.000980 (dPS/PVME)			

[a] r is the number of lattice sites per chain molecule; v is the volume per lattice site, ε is the interaction energy between the sites; g scales the mixed interaction energy according to $\varepsilon_{ab} = g(\varepsilon_{aa}\varepsilon_{bb})^{1/2}$. ($M_w$ is the molecular weight.)

[b] This dPS r/M_w value corresponds to an r that is, per repeat unit, the same as the value for hPS (r/repeat unit = 11.849).

Table 2. Summary of Experimental Systems: Properties, Molecular Weights, and Modeled *r* Parameter Values

Fitted Systems			
	Reference	M_w (g/mol)	r
pure PVME - *PVT* data	28	99000	11419
pure hPS - *PVT* data	27	110000	12514
dPS/PVME blend - SANS data[a]	30	255000/99000	26929/11419
Predicted Systems			
	Reference	M_w (g/mol)	r
hPS/PVME blend - cloud point data[b]	29	120000/99000	13652/11419
dPS/PVME blend - cloud point data	7	119000/99000	12567/11419
pure dPS - *PVT* data	13	114000	12039

[a] The SANS data for this system was fitted (Figure 1), however its corresponding phase diagram (Figure 2) was a prediction.

[b] One experimental datum from this system, the LCST, was used to fit the g parameter; the remainder of the phase diagram does comprise a true prediction.

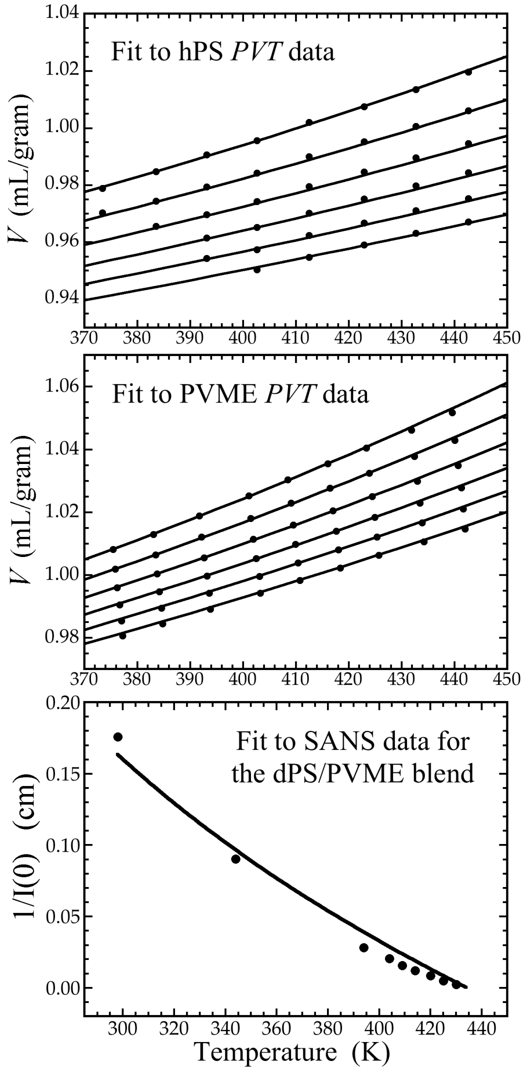

Figure 1. Fitting results for the model equation of state. The fit to the pure component *PVT* data for normal (hydrogenated) polystyrene (hPS) is given in the upper panel. The curves show the volume as a function of temperature at pressures of 0, 20, 40, 60, 80, and 100 MPa (top to bottom). The corresponding *PVT* fit for pure poly(vinyl methyl ether) (PVME) is given in the middle panel showing the volume as a function of temperature at 10, 20, 30, 40, 50, and 60 MPa. The experimental hPS and PVME *PVT* data are taken from refs 27 and 28 respectively. The deuterated polystyrene (dPS) parameters were obtained by fitting to SANS data for the dPS/PVME blend (ref 30); this is given in the lower panel which shows the inverse of the zero-angle scattering intensity as a function of temperature. The theoretical scattering intensity is calculated from $(\partial^2 G/\partial x^2)_{T,P}$ using eq 2.

As noted above, the pure component parameters for dPS were treated differently, by fitting to SANS data for the dPS/PVME mixture. Though the model for a binary blend requires a total of six parameters (r and ε for each component, v, and g), the SANS fit involved determination of only two, the pure component ε value for dPS, and the dPS/PVME blend g value. The route to the PVME parameters r and ε, as well as the mixture value for v (7.667 mL/mol), was described above. In addition, we assume that the dPS r value, per repeat unit, is the same as that for hPS. This same assumption, which equivalently amounts to the assignment of the same close packed volume per repeat unit, was also made in the hPS and dPS parameterizations in refs 14 and 15. Some implications of assuming this are discussed below.

The SANS analysis makes use of data from ref 30, which includes results for a series of measurements over a range of temperature (within the miscible regime) for a dPS/PVME blend of 50/50 weight percent. The bottom panel of Figure 1 shows the model fits for the zero angle scattering intensity as a function of temperature, along with the experimental points. The resulting pure component dPS parameters as well as g for the dPS/PVME mixture are given in Table 1.

Figure 2 focuses on predicted and experimental phase behavior for hPS/PVME and dPS/PVME blends. The hPS/PVME results are in gray, with the symbols representing experimental cloud point data[29] and the theoretical binodal (solid gray) and spinodal (dashed gray) given by the curves. While the value of g reflects a fit of the theoretical critical temperature to that of experiment, the remainder of the phase diagram is a true prediction, and it is clear that the theory does a very good job at characterizing the shape of the phase boundary. It is interesting to note that the experimental cloud points tend to fall between the theoretical binodal and spinodal, which is likely a reflection of the kinetics of phase separation in conjunction with the experimental time taken before ultimately measuring the scattered light from the phase separated domains. In other words, where there is a wide metastable gap the experimental cloud points are a consequence of nucleation and growth processes which is initiated once the binodal is crossed. It was noted in section II that the theory does not account for the effect of polydispersity. This should affect at least the binodal. Calculations in ref 31 for example (which assumed a concentration independent χ-parameter), showed a general broadening of the binodal upon increase in polydispersity, and further, skewing of the boundary was observed toward higher mass fractions of the more polydisperse component (which in the present case, would be the PVME).

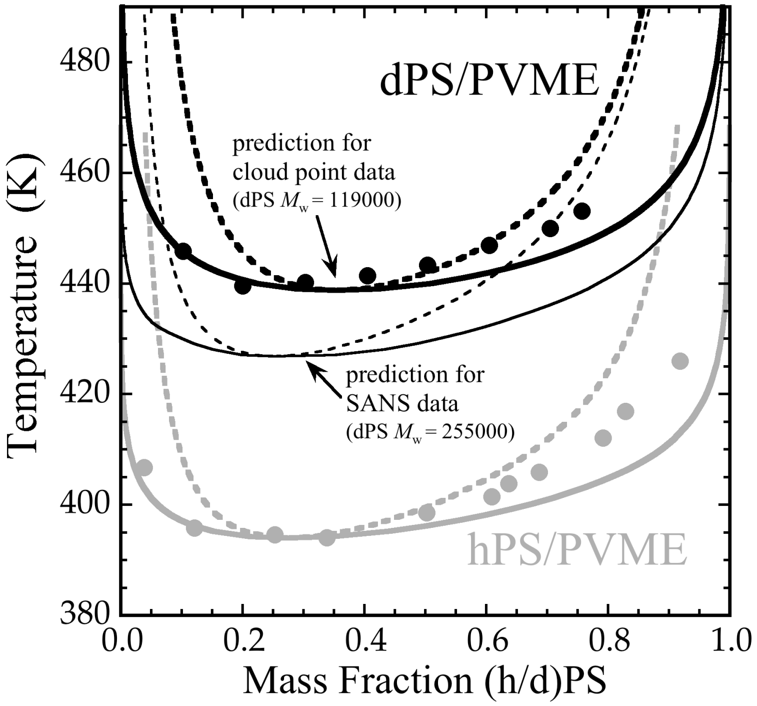

Figure 2. Predicted phase diagrams for two dPS/PVME blends and an hPS/PVME blend, and comparison with experimental results. In all three cases results for both the theoretical binodal (solid) and spinodal (dashed) curves are shown; experimental data are given by points. Note that *only one experimental datum point* from the data shown has been fit, viz. the LCST for the hydrogenated hPS/PVME blend. The phase diagram for the hPS/PVME blend is at the bottom (gray curves) and corresponds to a system with molecular weights of 120000/99000 g/mol; experimental data (gray points) are taken from ref 29. The diagram in the middle (thin black lines) is the prediction for the deuterated dPS/PVME blend from the SANS study in ref 30, the data from which were used to determine $\varepsilon_{\mathrm{dPS}}$ and g with the other parameters determined from pure component data, as described in the text. Note that the molecular weights for this blend are 255000/99000 g/mol, which means it is not directly comparable to the dPS/PVME cloud point data shown, which is for molecular weights 119,000/99,000 (black points, ref 7). Theoretical predictions for this (latter) dPS/PVME blend are shown in the set of thick black curves at the top, which result once the modeled dPS molecular weight has been scaled to match the experimental value.

Also shown in Figure 2 are the predicted phase diagrams (in black) for two different experimental dPS/PVME blends. Once again, the spinodal curves are dashed, the binodal curves are solid. The lower phase diagram, marked by the thin lines, is the prediction for the experimental system from which we fitted the SANS data; this blend had a dPS molecular weight of 255000 g/mol. The other phase diagram, marked by the heavy/thick lines, corresponds to an experimental system for which cloud point data are available[5] (also shown); this prediction follows from the same parameterization (Table 1), but with an r value that has been appropriately scaled for the significantly lower dPS molecular weight of 119000 g/mol. Recall that to account for changes in component molecular weight the r parameter is scaled keeping r/M_{w} and all other parameters constant. Given $r/M_{\mathrm{w}} = 0.105605$ (g/mol)$^{-1}$ in Table 1, the r value changes from 26929 to 12567 on going from $M_{\mathrm{w}} = 255000$ to 119000 g/mol (the PVME molecular weights are the same). This results in a significant enhancement of miscibility, with the modeled LCST value increasing by about 10 degrees. Note that our prediction for phase separation of this experimental blend (the cloud point data) is, in a sense, two steps removed from the original fitting of the parameters, first because the fits are derived from melt data and

SANS results in the one-phase region, and then by our ability to account for changing molecular weights. These solely theoretical predictions (the thick black curves) demonstrate outstanding agreement with experiment, not only in the location of the critical temperature, but also in the shape of the phase boundary.

It is one thing to capture, without fitting for it, a 40K shift in the LCST, and another thing to explain it. We have shown we can do the former for a particular blend of interest; we next show that we can make progress on the latter for this blend. An even more ambitious goal is to use our new understanding to make more general predictions regarding the effects deuteration on blend miscibility. Toward these ends we close this section by considering the differences between pure component melts of dPS and hPS.

Recall that we did not obtain our dPS parameters by fitting to any dPS pure component property (such as *PVT* data), but rather, the parameterization was obtained by fitting to SANS data for the dPS/PVME blend. Given that experimental data on deuterated polymeric melts are rare, blend fitting is likely to be the most available option in the majority of situations. If this route truly does capture the essential properties of pure dPS then our blend-fitted dPS parameters should allow us to predict the pure dPS *PVT* surface. In fact, we have a rare opportunity to test our theoretical description of dPS against pure component data which were collected from dPS samples generously donated by Professor Nigel Clarke.[13]

As a start, consider the parameters for hPS, obtained via pure component *PVT* fitting, compared with those for dPS from the SANS fit. As the results in Table 1 show, there is a small, but still significant, difference in the ε values: −2144 J/mol for hPS, vs. −2106 J/mol for dPS. This is in agreement with one of the expected microscopic effects of deuteration mentioned above, viz. weakened intermolecular interactions due to lowered polarizability of the C-D bond, relative to C-H.[3] The model calculations predict that the weaker $\varepsilon_{\mathrm{dPS}}$ leads to a small increase in the volume (per mole of repeat units) by about 0.5%. This is illustrated in Figure 3, which shows plots of the volume (per mole of repeat unit) as a function of temperature at atmospheric pressure. The lower curve is the calculated model $V(T)$ for hPS which traces fairly closely through the corresponding experimental data (to which the model was fit); for all the data points shown in this figure the associated error bars are no larger than the size of the symbols. The upper curve is *not a fit*, but our theoretically *predicted* $V(T)$ for dPS, predicted using the parameters extracted from the SANS fit on dPS/PVME blend, rescaled to match the experimental molecular weight. The theory, compared against the actual experimental dPS data we obtained on a sample of 114,000 g/mol[13] accurately predicts the slight increase in molar volume and compares almost quantitatively with experiment, even capturing the slight increase in difference between the hPS and dPS volumes as temperature is raised.

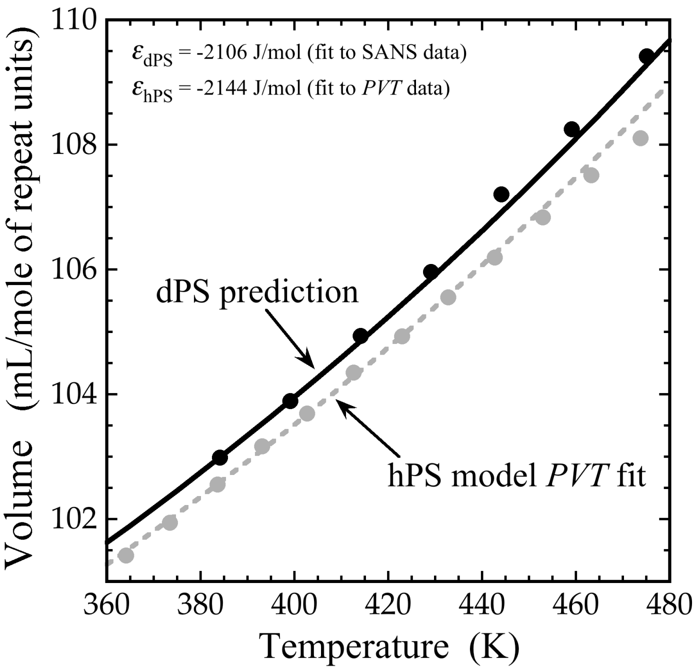

Figure 3. Predicted deuterated polystyrene (dPS) pure component *PVT* behavior. Shown is the volume as a function of temperature at atmospheric pressure. The prediction for dPS is given by the black curve; corresponding experimental data[13] are given by black points. (This prediction is based on a parameterization determined by fitting to SANS data for the dPS/PVME blend and not by fitting to the dPS data in this figure.) Shown for comparison are the fitted results for hydrogenated polystyrene (hPS), given by the dashed gray curve, along with the corresponding experimental data[27] given by gray points. The volume reported is the "volume per repeat unit" (mL per mole of repeat units) so as to allow comparison of the deuterated and hydrogenated systems.

In the discussion above we have connected the effect of change in molar volume (increasing upon deuteration) with the underlying differences in the hPS and dPS ε parameters. In fitting to just a limited amount of dPS/PVME SANS data we chose to restrict this blend fit to just two parameters (ε_{dPS} and g), and thus we assumed the r parameter for dPS to be the same (on a per repeat unit basis) as that determined for hPS. This is certainly a reasonable first approximation, as one should expect similarities in, for example, the effective number of configurations that would be available to similar dPS and hPS chains. A consequence, however, is that using the same r values for dPS and hPS means that they are also modeled with the same hard-core volume, since we are using a constant value for v. This choice, which obviates the addition of r as a fit parameter for dPS; means that ε, alone among the characteristic parameters, reflects the effect of deuteration. Even so, it is clear that enough of the bulk physical behavior has been captured such that the present $V(T)$ shows close to optimal agreement as it stands.[32]

As mentioned above, the assumption of assigning the same hard core volume to hPS and dPS repeat units was also used in the isotopic blend investigations in refs 14 and 15, and therefore the differences in their pure component ε values for hPS and dPS also carry the weight of the deuteration effect. It is interesting to compare the different sets of results. In the LC investigation,[15] fits were performed to hPS/dPS SANS data to obtain two of the three energetic parameters. The $\varepsilon_{\mathrm{dPS}}$ value was taken from a previous study[33] where its value was determined from SANS fits corresponding to a dPS/PVME blend. Therefore in ref 15, they fit only for $\varepsilon_{\mathrm{hPS}}$ and the mixed interaction, $\varepsilon_{\mathrm{hPS\text{-}dPS}}$. Two sets of resulting fitted parameters were reported; in one set $\varepsilon_{\mathrm{hPS}}/\varepsilon_{\mathrm{dPS}} = 1.002$ and in the other $\varepsilon_{\mathrm{hPS}}/\varepsilon_{\mathrm{dPS}} = 1.003$. (In both sets the $\varepsilon_{\mathrm{hPS\text{-}dPS}}$ values were somewhat less than what one would obtain from the respective geometric mean.) It is noted that they obtained $|\varepsilon_{\mathrm{hPS}}| > |\varepsilon_{\mathrm{dPS}}|$, which is agreement with our findings (and as mentioned, is the expected trend), on the other hand, the relative difference in the two ε's is larger in our case (where we have $\varepsilon_{\mathrm{hPS}}/\varepsilon_{\mathrm{dPS}} = 1.018$). The authors in ref 15 also note that the polarizability model gives a much larger difference between the ε's, $\varepsilon_{\mathrm{hPS}}/\varepsilon_{\mathrm{dPS}} = \alpha_{\mathrm{hPS}}^2/\alpha_{\mathrm{dPS}}^2 = 1.029$; thus our value is evidently intermediate. In the LF investigation,[14,34] they used $\varepsilon_{\mathrm{hPS}}$ obtained from pure component PVT fitting, and defined $\varepsilon_{\mathrm{hPS\text{-}dPS}}$ using the geometric mean approximation; thus they fit only $\varepsilon_{\mathrm{dPS}}$ to the SANS hPS/dPS blend data. In their case they obtained equivalent fits with two values for $\varepsilon_{\mathrm{dPS}}$. They then chose the larger magnitude value on the grounds, as noted above, that the cohesive energy density for the deuterated polymer should be smaller than that for the hydrogenated. They obtained a ratio in ε values, $\varepsilon_{\mathrm{hPS}}/\varepsilon_{\mathrm{dPS}}$, equal to 1.006, intermediate between the present results and those in ref 15.

Volumetric properties such as those studied above are clearly very important when it comes to understanding critical behavior in LCST-type polymer blends, which is correlated with fluid compressibility. Derivatives of $V(T)$, such as the isothermal compressibility, $\kappa = -(\partial \ln V/\partial P)_T$, and the coefficient of thermal expansion, $\alpha = (\partial \ln V/\partial T)_P$, are known to play a particularly important role in driving such phase behavior. The theoretical prediction is that α_{dPS} is larger than α_{hPS}, however, the key question is whether deuteration results in a better or worse match with the blending partner PVME. In Figure 4, the relative differences, $(\alpha_{\mathrm{PVME}} - \alpha_{\mathrm{dPS}})/\alpha_{\mathrm{hPS(400K)}}$ and $(\alpha_{\mathrm{PVME}} - \alpha_{\mathrm{hPS}})/\alpha_{\mathrm{hPS(400K)}}$, are plotted over the relevant range of temperature. Because α_{dPS} is greater than α_{hPS} , and thereby closer to α_{PVME}, it is seen that the difference in pure component α's is lower for the dPS/PVME blend than it is for the hPS/PVME blend. For dPS, the response to temperature changes is closer to that of PVME, and this better match in the so-called "equation-of-state" properties helps to explain the increased miscibility of the dPS/PVME system.

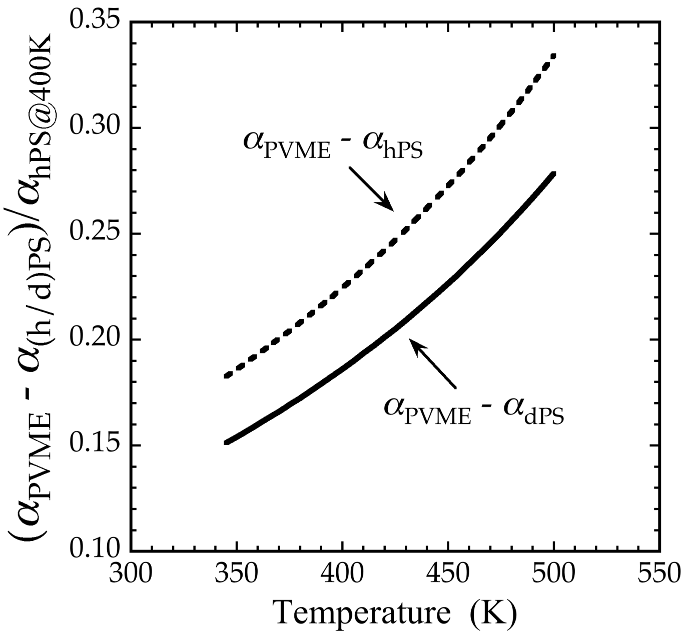

Figure 4. Comparison of the predicted pure component coefficient of thermal expansion (α) values for hydrogenated and deuterated polystyrene (hPS and dPS). Shown are α_{PVME} - α_{hPS} (upper/dashed curve) and α_{PVME} - α_{dPS} (lower/solid curve) as a function of temperature; these are the differences in α of hPS and dPS compared to that of PVME. All values are divided by (i.e. are relative to) the model value of α_{hPS} at 400K.

IV. Summary and Conclusions

The application of SANS in characterizing polymer mixtures requires labeling one of the components with deuterium. It has been convenient to consider the H-D replacement as innocuous, however, that is not always the case. For example, the dramatic shift in lower critical solution temperature (LCST) for dPS/PVME, relative to hPS/PVME has long been known. On the other hand, changing from hPS to dPS does not always have an effect on blend miscibility, the mixture PS/TMPC being a case in which there is little shift in the LCST. For large enough molecular weight the H-D switch certainly has a clearly visible effect, since the isotopic hPS/dPS blend shows phase separation when the molecular weights grow into the millions. This collection of observations raises questions which form the focus of this paper: Given experimental characterization data for a sample of deuterated polymer is there any observable effect of deuteration on the melt physical properties ? In the absence of such data on pure components, how can characteristic parameters for the deuterated polymer be obtained ? Once such a component has been characterized, how can the impact of deuteration on blend behaviour be predicted ? Or conversely, recognizing the popularity of SANS, how can one predict the adjustment of properties back to the case of a fully hydrogenated system ?

In this paper we have focused on dPS and on hPS, alone and blended with PVME. We have demonstrated that SANS data on a labeled blend may be used to characterize the labeled component, testing this route by comparing resulting predictions for pure component dPS *V(T)* behaviour with our own experimental data for the dPS *PVT* surface.

Incidentally, these data are the only published results, to our knowledge, for a high molecular weight deuterated polymer sample in the literature. We find that the net impact of shortened bond length and reduced polarizability for dPS, relative to hPS, results in a volume per mole of repeat units which is increased by about 0.5% for the deuterated sample, an amount which is well above the experimental error in the measurements.

In addition to a shift in the values for *V(T)* we also find an effect on the thermal expansion coefficient, such that within the blend temperature range of interest α_{PVME} is closer in value to α_{dPS} than to α_{hPS}. We propose this improved match in thermal expansion coefficients to be a driving force - likely *the* driving force - behind the enhanced miscibility of the dPS/PVME blend.

This work suggests that the combination of our lattice theory and a modest amount of experimental data may yield predictive ability in terms of the effects on melt properties and blend miscibility of substituting a hydrogenous with a deuterium labeled polymer. We plan to test this hypothesis with further studies, and also plan to use this approach to clarify the mixture thermodynamics in isotopic blends.

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Table of Contents Graphic

Effect of Deuterium Substitution on the Physical Properties of Polymer Melts and Blends

Ronald P. White, Jane E.G. Lipson, and Julia S. Higgins