Thermodynamic Interactions in Blends of Poly(4-*tert*-butyl styrene) and Polyisoprene by Small-Angle Neutron Scattering

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ABSTRACT: The thermodynamic interactions between poly(4-*tert*-butyl styrene) [P(4tBS)] and 1,4-polyisoprene (PI; both hydrogenous) were obtained as functions of the temperature, PI molecular weight, and blend composition through the examination of miscible ternary blends of these two components with a common miscible labeled polymer [90% 1,2-deuterated polybutadiene (dPBD)] with small-angle neutron scattering. The thermodynamic interaction parameters between P(4tBS) and dPBD and between P(4tBS) and PI increased with increasing temperature and were consistent with lower critical solution temperature behavior. Although the binary blends of P(4tBS) and dPBD exhibited phase separation at elevated temperatures, the thermodynamic interaction parameters between P(4tBS) and PI remained large and negative and independent of the PI molecular weight. Finally, the thermodynamic interactions for PI and P(4tBS) depended strongly on the ratio of PI to P(4tBS) and were also sensitive to the amount of dPBD present in the ternary blend. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 3204–3217, 2004
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INTRODUCTION

Miscible homopolymer blends are of significant industrial value because they provide a convenient and economical way of producing new polymeric materials. Although extensive studies of isotopic blends,[1,2] polyolefin blends,[3–9] and polydiene blends[10–14] has furthered the understanding of the thermodynamics of mixing of polymers and provided data for testing theoretical approaches,[15,16] a number of outstanding issues still persist. One of these is the attempt to bridge between different families of polymers, that is, to understand the mixing of polyolefins with polydienes,[17] polyolefins with styrenics,[18] and polydienes with styrenics.[19]

In this article, we examine the thermodynamic interaction parameters for a new class of polymer blends, that is, blends of poly(4-*tert*-butyl styrene) [P(4tBS)] and 1,4-polyisoprene (PI). P(4tBS) and PI form mixtures that are optically clear and behave like miscible systems in linear viscoelastic and differential scanning calorimetry experiments. In fact, the unusual viscoelastic properties observed for binary blends of PI and P(4tBS) have largely motivated this study of the thermodynamic interactions in these blends. We have also determined that P(4tBS) is miscible with high-1,2-content polybutadiene (PBD) and established

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the thermodynamic interactions between P(4tBS) and 90% 1,2-deuterated polybutadiene (dPBD), and we have used the methodology of small-angle neutron scattering (SANS) of ternary blends to establish the interaction strength between P(4tBS) and PI. This method has allowed us to probe the interactions between unlabeled P(4tBS) and PI without resorting to deuterium substitution, which has been shown to significantly affect the phase behavior of polymer blends in a variety of systems, such as microstructurally mismatched polyolefins,[4] polystyrene (PS)/poly(vinyl methyl ether) (PVME),[20] and PS/polybutadiene.[21] Moreover, for mixtures of random copolymers of microstructurally different 1,4- and 1,2-polybutadienes and mixtures of mixed-microstructure polyisoprene and polybutadienes, the labeling of one of the components has led to the conversion of upper critical solution temperature phase behavior into lower critical solution temperature (LCST) phase behavior.[11,22] In particular, we examine (1) the temperature dependence of the thermodynamic interactions between unlabeled PI and P(4tBS), (2) the influence of the PI molecular weight on the thermodynamic interactions, and (3) the influence of the blend composition on the thermodynamic interactions.

In part, this study of the thermodynamic interactions of these blends complements our ongoing study of the viscoelastic properties of these blends. These polymer blends have very large differences in the glass-transition temperatures (T_g's) for the components, with the values of PI and P(4tBS) being −67 and 147 °C, respectively. A miscible polymer blend with such a significant dynamic asymmetry is expected to exhibit thermorheological complexity and failure of time–temperature superpositioning unless the blend exhibits strong attraction and, therefore, negates the dynamic heterogeneity. Detailed thermodynamic interactions, such as those presented in this article, make possible a quantitative comparison of the experimentally measured viscoelasticity and theoretical developments so that we can understand the dynamics of polymer blends.[23]

BACKGROUND

To probe the interactions between the hydrogenous polymers P(4tBS) and PI, we have used a method involving ternary and binary blends of these homopolymers with dPBD (~90% 1,2).[8] dPBD forms single-phase binary mixtures with P(4tBS) and PI, and the three polymers also form single-phase ternary mixtures.

For a binary blend of monodisperse polymers, the Gibbs free energy (ΔG_M) according to the Flory–Huggins–Staverman (FHS) theory is given by[24,25]

$$\Delta G_{\mathrm{M}} = k_{\mathrm{B}}T\left(\frac{\phi_1}{N_1\left(\frac{v_1}{v_0}\right)}\ln\phi_1 + \frac{\phi_2}{N_2\left(\frac{v_2}{v_0}\right)}\ln\phi_2 + \chi\phi_1\phi_2\right) \tag{1}$$

where k_B is Boltzmann's constant; T is the absolute temperature; v_i and N_i are the volume per repeat unit and the number of repeat units in a chain of component i, respectively; ϕ_i is the volume fraction of component i; and χ is the thermodynamic interaction parameter based on an arbitrary reference volume (v_0).

The scattering vector (q) dependence of the scattered coherent intensity (I_{coh}(q)) can be fit with the incompressible random-phase approximation (RPA) model to obtain χ between the two homopolymers.[25,26] In the RPA formulation, the coherent scattered intensity for a binary blend can be written as follows:[27]

$$I_{\mathrm{coh}}(q) = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \mathrm{S(q)} \tag{2}$$

where S(q) is the structure factor and b_i is the scattering length per repeat unit for species i. S(q) is given by

$$\frac{1}{\mathrm{S(q)}} = \left(\frac{1}{N_1 v_1 \phi_1 P_1(\mathrm{q})} + \frac{1}{N_2 v_2 \phi_2 P_2(\mathrm{q})} - 2\frac{\chi}{v_0}\right) \tag{3}$$

where P_i is the weight-average single-chain form factor for species i, which for a high-molecular-weight, flexible, monodisperse homopolymer component is simply the Debye function:

$$P_i = \frac{2}{x}[e^{-x} - 1 + x] \tag{4}$$

where x is equal to $N_i\ell^2\mathrm{q}^2/6$, ℓ is the statistical segment length, and q is equal to $(4\pi/\lambda)\sin(\theta/2)$. λ is the wavelength of the incident radiation, and θ is the scattering angle.

Equation 1 can be generalized for a ternary blend of monodisperse components to yield the

Gibbs free energy of mixing per unit of volume (ΔG_m):

$$\Delta G_m = k_B T \left[\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2} + \frac{\phi_3 \ln \phi_3}{V_3} \right] + X_{12}(T)\phi_1\phi_2 + X_{13}(T)\phi_1\phi_3 + X_{23}(T)\phi_2\phi_3 \quad (5)$$

where

$$X_{i,j}(T) = \frac{k_B T}{v_0} \chi_{i,j}(T) \quad (6)$$

V_i is equal to $N_i v_i$, N_i being the degree of polymerization and v_i being the monomer volume. $X_{i,j}(T)$ and $\chi_{i,j}(T)$ are the interaction strengths and the dimensionless thermodynamic interaction parameters between pairs of components. Similarly, the generalization of the RPA formulation to a single-phase ternary system results in the following expression for the observed coherent SANS intensity [$I_{coh}(q)$]:[8,27]

$$I_{coh}(q) = \mathbf{B}^T S(q) \mathbf{B} \quad (7)$$

In this expression, **B** is a 2 × 1 matrix containing the differences in the scattering length densities:

$$\mathbf{B} = \begin{bmatrix} \dfrac{b_1}{v_1} - \dfrac{b_3}{v_3} \\ \dfrac{b_2}{v_2} - \dfrac{b_3}{v_3} \end{bmatrix} \quad (8)$$

Finally, S(q) is the static structure factor matrix for the ternary blend and is related to the normalized form factors for the components [$P_i(q)$]:

$$\frac{1}{S(q)} = \begin{bmatrix} \dfrac{1}{\phi_1 V_1 P_1(q)} + \dfrac{1}{\phi_3 V_3 P_3(q)} - \dfrac{2X_{13}}{k_B T} & \dfrac{1}{\phi_3 V_3 P_3(q)} + \dfrac{X_{12} - X_{13} - X_{23}}{k_B T} \\ \dfrac{1}{\phi_3 V_3 P_3(q)} + \dfrac{X_{12} - X_{13} - X_{23}}{k_B T} & \dfrac{1}{\phi_2 V_2 P_2(q)} + \dfrac{1}{\phi_3 V_3 P_3(q)} - \dfrac{2X_{23}}{k_B T} \end{bmatrix} \quad (9)$$

Obtaining the dPBD/P(4tBS) and dPBD/PI interaction parameters from independent binary measurements, we can fit the ternary data with eqs 7–9, with the third interaction parameter ($\chi_{PI/P(4tBS)}$) being the only adjustable quantity. In this formulation, the χ parameter is a convenient measure of the excess Gibbs free energy. The combined effects in χ include contributions possibly from enthalpic interactions, equation-of-state effects such as volume changes upon mixing, conformational entropy effects such as local packing, and noncombinatorial entropic terms.[16,28] As a result, although the χ parameter provides a standardized, conveniently comparable measure of blend interactions, it needs to be considered in terms of the relative importance of the various effects that are implicit in the definition. Finally, the formulation of the Gibbs free energy and the fitting of the SANS data to the incompressible RPA implicitly ignore three-body effects.

EXPERIMENTAL

Sample Preparation

All the polymers used in this study were model polymers of low polydispersity prepared by living anionic polymerization.[29] The molecular weights and polydispersities for the polymers are given in Table 1. The blends were prepared by solution mixing as follows. The appropriate amounts of the blend components were codissolved in tetrahydrofuran to obtain the desired compositions. The resulting homogeneous solutions were slowly added to an excess mixture of approximately 80 vol % methanol and approximately 20 vol % acetone to precipitate the polymer blends. Finally, the samples were placed in a vacuum oven first for approximately 16 h at room temperature and then for approximately 6 h at 90 °C.

Table 1. Polymer Characteristics

	1,2-Content	M_w	M_w/M_n
DPBD (d6)	~90 mol %	77,700	1.06
		M_w	M_w/M_n
P(4tBS)		33,300	1.04
	1,4-Content	M_w	M_w/M_n
PI-a	93 mol % (79% cis)	40,000	1.03
PI-b	93 mol % (79% cis)	320,000	1.14

SANS

SANS samples were prepared in the following way to achieve uniform, bubble-free samples. A brass washer with an outer diameter of 25 mm, an inner diameter of 15 mm, and a thickness of 1 mm was placed on a quartz window. Appropriate quantities of the blend were placed in the annulus of the brass washer and heated in a vacuum oven above T_g of the blend. Once a bubble-free sample that filled the annulus completely was achieved, it was capped with a second quartz window. SANS measurements were performed on the 30-m SANS beam lines (NG3 and NG7) at the National Institute of Standards and Technology (Gaithersburg, MD).[30] Neutrons ($\lambda = 6$ Å and $\Delta\lambda/\lambda = 0.15$ or 0.22) were used with two different experimental arrangements with a sample-to-detector distance of 13.1 m. The resulting q ranges were approximately 0.0038–0.049 and 0.0038–0.042 $Å^{-1}$. The SANS data were reduced and corrected for parasitic background and empty-cell scattering. Absolute cross sections were obtained with the use of a silica secondary standard. Finally, a q-independent incoherent scattering correction, assumed to primarily originate from protons, was subtracted before data analysis.[25] The incoherent scattering calculations were based on the scattering from a purely protonated PI and the proton density of the studied samples.

RESULTS

Binary Blends

Temperature-dependent SANS data from binary blends of dPBD and PI were collected as a function of the blend composition for two molecular weights of PI [40,000 (PI-a) and 320,000 (PI-b)]. For both systems, the binary data were measured for three compositions: 25/75, 50/50, and 75/25.[31] As expected from literature sources, this blend exhibits LCST phase behavior[11,13,22,32,33] with the SANS intensity at low q increasing with increasing temperature. For a binary mixture, $I(q)$ at low q can be adequately described with the Ornstein–Zerneike equation:

$$I(\mathrm{q}) = \frac{I(0)}{1 + \xi^2 \mathrm{q}^2} \tag{10}$$

where ξ is the correlation length. Thus, as shown in Figure 1 for a 50/50 blend of dPBD and PI-a, the $1/I(\mathrm{q})$–q^2 data can be extrapolated to q = 0 to yield the scattering in the forward angle [$I(0)$] as a function of the temperature. Furthermore, the value of $I(0)$ for a single-phase binary blend is proportional to $(\chi_s - \chi)^{-1}$, where χ_s is the thermodynamic interaction parameter at the spinodal [the limit of stability, that is, $\chi_s = 1/2(1/\phi_1 N_1(v_1/v_0) + 1/\phi_2 N_2(v_2/v_0))$] and will approach infinity at the limit of stability. Because χ is approximately equal to $1/T$, the x intercept of a graph of $1/I(0)$ versus $1/T$ yields the spinodal temperature. Furthermore, the binodal temperature, if present, can also be qualitatively recognized from a plot of $1/I(0)$ versus $1/T$ as a discontinuous deviation from the roughly straight-line behavior in the single-phase region. The resulting $1/I(0)$–$1/T$ data for the two dPBD/PI systems are shown in the inset of Figure 1. Because of the low molecular weight of PI-a, the dPBD/PI-a blends are very far from their spinodal points. Additionally, the dPBD/PI-b blend limits of stability, while significantly closer to the experimental temperature window, are not close enough to determine the spinodal temperatures without degradation of the samples.

To obtain the thermodynamic interaction parameters for the dPBD/PI blends, we fit the scattering data to eqs 5–7. The data were fit with established ℓ values of PI[34] and with interpolation for dPBD based on literature values for PBDs of different microstructures.[1,2,33] Two unknowns, the thermodynamic interaction parameter ($\chi_{\mathrm{PI/dPBD}}$) and a chain expansion factor (α) accounting for possible changes in the radius of gyration (R_g) due to blending, were obtained from the fits of the data. The values of α lie between 0.98 and 1.03 (randomly distributed around 1) and indicate that the segment lengths used for the components from the pure component values are reasonably accurate. Values of $\chi_{\mathrm{PI/dPBD}}$ are shown in Figure 2 and are tabulated in Tables 2 and 3. All the data for χ reported in these tables and other tables and figures are based on a temperature-independent reference volume of 100 cm^3/mol.

Both systems are miscible in the temperature range examined, and the binary data for the two molecular weights show excellent agreement. As expected from a blend with LCST,[22] the values of χ increase with increasing temperature, indicating an increase in the concentration fluctuations in the system. Furthermore, the values of the interaction parameter, in light of the differences in the microstructure (i.e., the fractions of 1,2-

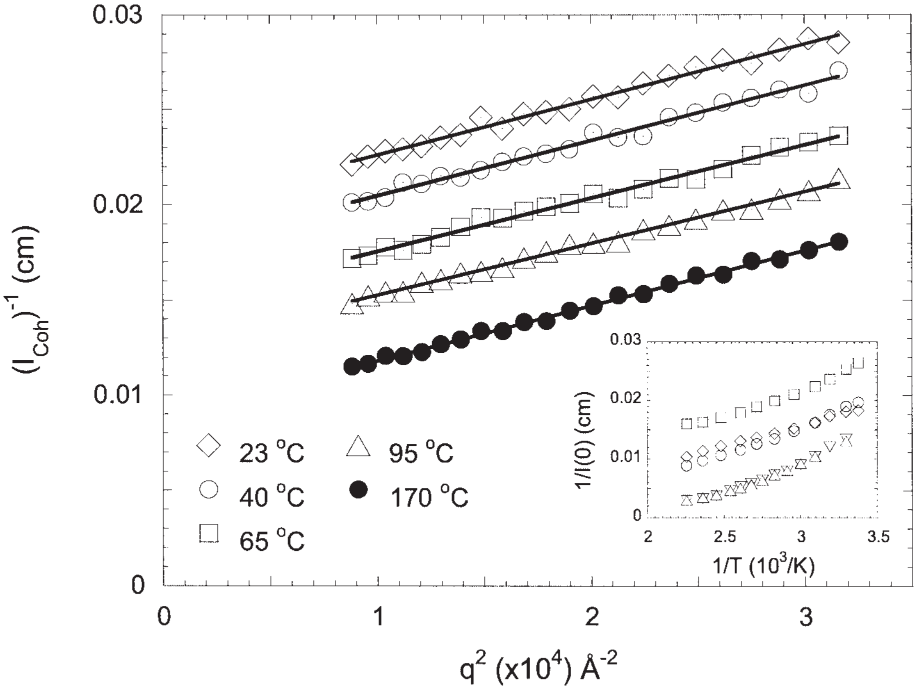


Figure 1. Zimm analysis of the SANS data for the 50/50 dPBD/PI-a blend as a function of temperature. The intercepts of the linear extrapolation of $1/I_{Coh}(q)$ (where I_{Coh} is the coherent SANS intensity) versus q^2 to q = 0 even at 170 °C indicate that the system is far from any limit of thermodynamic stability. The extrapolated values of $I(0)$ as a function of the temperature for all the dPBD/PI-a and dPBD/PI-b blends are shown in the inset: (□) 25/75 dPBD/PI-a, (○) 50/50 dPBD/PI-a, (◇) 75/25 dPBD/PI-a, (△) 75/25 dPBD/PI-b, and (▽) 50/50 dPBD/PI-b.

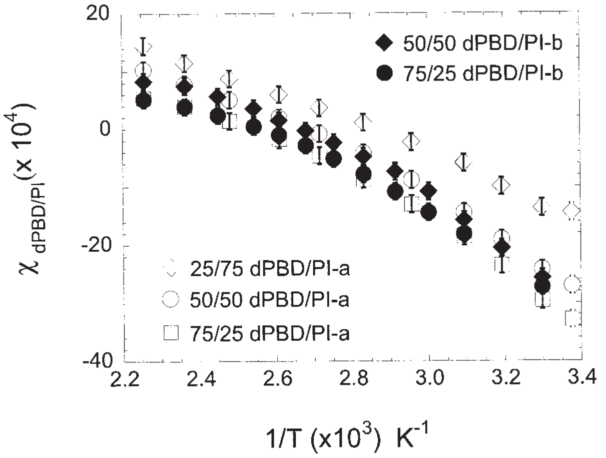


Figure 2. Temperature dependence of the thermodynamic interaction parameters for blends of dPBD/PI-a and dPBD/PI-b based on a reference volume of 100 cm^3/mol. The data indicate no dependence (within the error of the measurements) on the molecular weight of PI. Additionally, the data are consistent with LCST phase behavior for these blends.

and 1,4-addition units), are in reasonable agreement with those reported by Thudium and Han.[22] The final observation from Figure 2 is the presence of a small but significant composition depen-

Table 2. RPA Fitting Results for the dPBD/PI-a Blends[a]

Temperature (°C)	25/75 χ ($\times 10^4$)	50/50 χ ($\times 10^4$)	75/25 χ ($\times 10^4$)
23	−14.4	−27.0	−32.9
30	−13.6	−24.2	−29.6
40	−9.9	−19.0	−23.5
50	−5.9	−14.4	−18.5
65	−2.3	−8.8	−13.0
80	1.1	−4.2	−8.7
95	3.7	−0.8	−4.6
110	6.0	2.0	−1.8
130	8.8	5.1	1.4
150	11.5	7.8	3.9
170	14.5	10.3	5.4

[a] The χ values are given on the basis of a reference volume of 100 cm^3/mol.

Table 3. RPA Fitting Results for the dPBD/PI-b Blends[a]

Temperature (°C)	50/50 χ ($\times 10^4$)	75/25 χ ($\times 10^4$)
30	−25.7	−27.2
40	−20.5	
50	−15.7	−18.1
60	−10.8	−14.4
70	−7.4	−10.8
80	−4.8	−7.8
90	−2.4	−5.1
100	−0.3	−2.8
110	1.5	−1.0
120	3.6	0.5
135	5.7	2.4
150	7.5	3.9
170	8.3	5.2

[a] The χ values are given on the basis of a reference volume of 100 cm^3/mol.

dence for the interaction parameter. This composition dependence is roughly linear (and consistent with the findings of Thudium and Han) and is taken into account when these binary interaction parameters are used to fit the ternary data in the next section.

For the dPBD/P(4tBS) binary blend, the same three compositions were prepared. In these cases, the two fitted parameters were χ and ℓ for P(4tBS). Previously, dilute-solution-based intrinsic viscosity measurements have been used to investigate the unperturbed θ dimensions of P(4tBS), and no melt-state SANS-based segment length is available.[29,35] The resulting interaction parameters for the blends with compositions of 50/50 and 75/25 are shown in Figure 3. These χ data, as well as the P(4tBS) segment lengths, are also summarized as a function of the temperature in Table 4. The 25/75 dPBD/P(4tBS) blend data could not be collected because the sample was already phase-separated at the beginning of the experiment on account of the high temperatures required (because of the high T_g) to make it flow during the SANS sample preparation.

The segment length for P(4tBS) obtained from the fitting of the SANS data is significantly smaller than that anticipated from the dilute-solution intrinsic viscosity reported previously (ℓ = 8.4 Å).[29] This is not a surprising result because

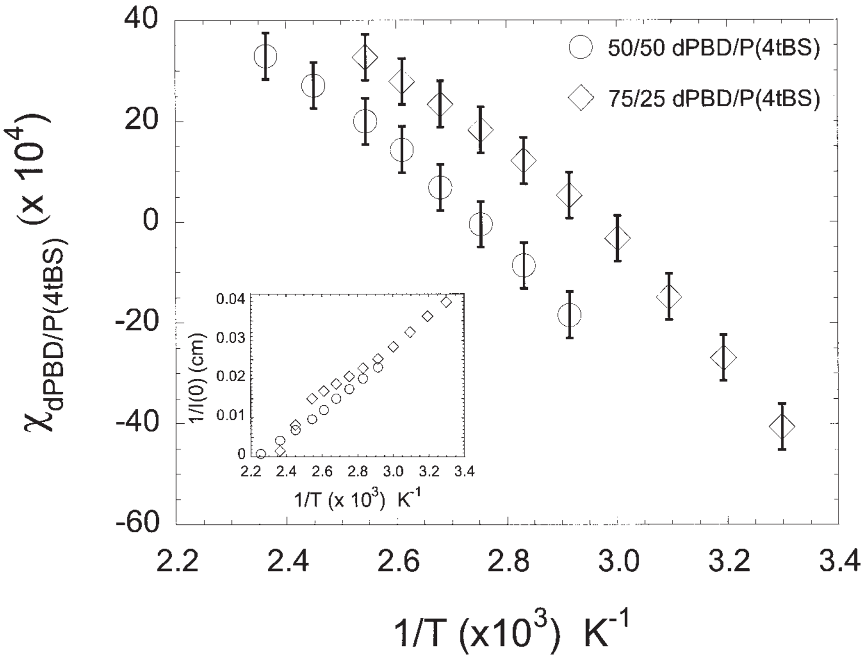


Figure 3. Temperature dependence of the thermodynamic interaction parameters for two blends of dPBD and P(4tBS). The inset shows the temperature dependence of the extrapolated values of $I(0)$. The 75/25 dPBD/P(4tBS) blend exhibits a binodal between 135 and 150 °C and can be seen in the discontinuous change in the values of $1/I(0)$. The χ values for these blends indicate LCST behavior and are significantly stronger than those observed for dPBD/PI.

Table 4. RPA Fitting Results for the dPBD/P(4tBS) Blends[a]

Temperature (°C)	50/50 dPBD/P(4tBS)		75/25 dPBD/P(4tBS)	
	χ ($\times 10^4$)	$\ell_{P(4tBS)}$ (Å)	χ ($\times 10^4$)	$\ell_{P(4tBS)}$ (Å)
30	—	—	−40.6	6.7_1
40	—	—	−26.9	6.5_6
50	—	—	−14.8	6.7_2
60	—	—	−3.2	6.5_9
70	−18.4	6.7_2	5.3	6.6_3
80	−8.6	6.4_7	12.2	6.5_8
90	−0.4	6.2_1	18.3	6.5_1
100	6.9	6.2_0	23.4	6.4_5
110	14.4	6.2_5	27.9	6.4_3
120	20.0	6.2_8	32.7	6.3_4
135	27.1	6.3_6	Phase separation	Phase separation
150	32.9	6.3_1	Phase separation	Phase separation
170	Phase separation	Phase separation	Phase separation	Phase separation

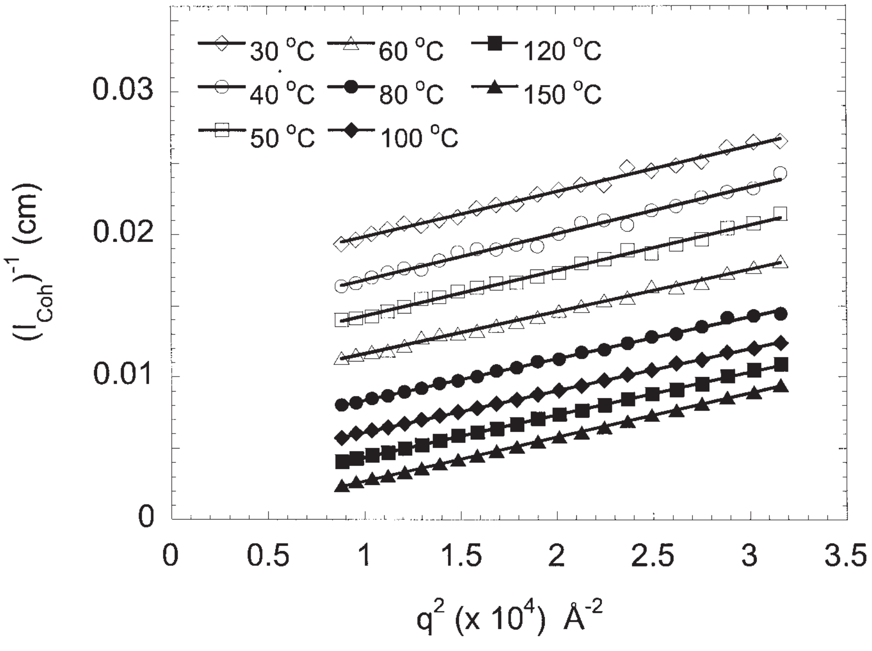
[a] The χ values are given on the basis of a reference volume of 100 cm^3/mol.

it has been previously reported that in many instances chain dimensions obtained from SANS experiments do not agree with those determined with intrinsic viscosities from θ solutions.[36] Additionally, there is a sufficient discrepancy in the temperature dependence of ℓ between the two blends to preclude any definite conclusions on the temperature dependence of the chain dimensions. It is conceivable that attempting to obtain chain dimensions from such chemically mismatched systems could lead to erroneous conclusions, but we are unaware of any reports that suggest that there are significant changes in the chain dimensions in such weakly interacting polymer blends.

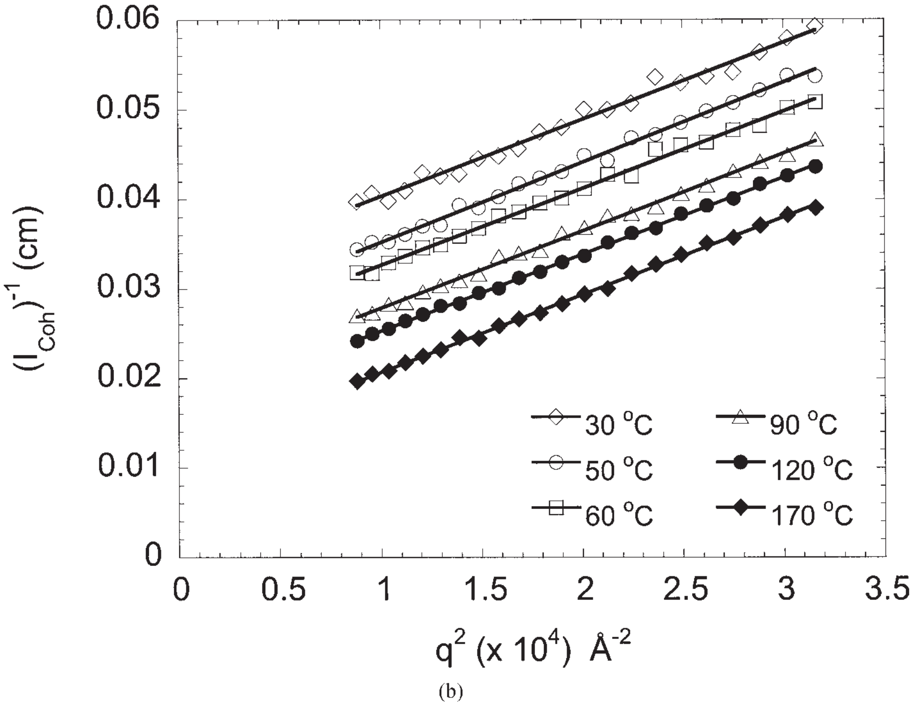
Like the dPBD/PI blends discussed previously, the data for $\chi_{P(4tBS)/dPBD}$ also reveal LCST behavior and a similar composition dependence. The presence of rather large negative χ values at low temperatures and the LCST phase behavior are somewhat surprising because an examination of the chemical structure of dPBD and P(4tBS) does not suggest any specific interactions between the two polymers. It is possible that, just as for blends of PI and PBD,[11,12,22,33,37,38] polyisobutylene (PIB) and random ethylene/butene-1 copolymers,[7] and polypropylene (PP) and other polyolefins,[9] the origin of the large negative χ values could be related to a slight deviation from Bertholet scaling.[4–7] It is possible that at high temperatures, equation-of-state effects, that is, differences in the thermal expansion coefficients of the two polymers, lead to the observed phase separation and the large positive interaction parameter values. The estimated spinodal points (see the inset in Fig. 3) support this argument with values of approximately 170 °C for both compositions studied.

Ternary Blends

The miscibility of the ternary blends is illustrated by the $1/I(0)$–temperature data shown in Figure 4(a–c). Unlike the binary blends, the extrapolation of the data to q = 0 does not provide a simple mechanism for estimating the spinodal temperature. However, the uniform temperature dependence and constant slopes of the linear fits of the data suggest that the samples are, at these temperatures, single-phase. Data from Figures 2 and 3 and the ternary blend scattering were used with eqs 7–9 to obtain the interaction parameters for the binary pairs of PI and P(4tBS). When no binary composition matched the ratio of the components in the ternary system [for dPBD/P(4tBS) and dPBD/PI blends], the binary data were interpolated or extrapolated to the required ratio. A representative ternary RPA fit for the dPBD/PI-a/P(4tBS) blend system is shown in the inset of Figure 5(a) for an equal-volume-fraction blend. The only parameters allowed to vary are $\chi_{PI/P(4tBS)}$ and a chain expansion parameter (α) to account for any changes in the coil dimensions in these blends. The R_g values for P(4tBS) are based on those obtained from the binary blends of P(4tBS) and dPBD. The values of α range from 0.97 to 1.03 [with the exception of the 10/45/45



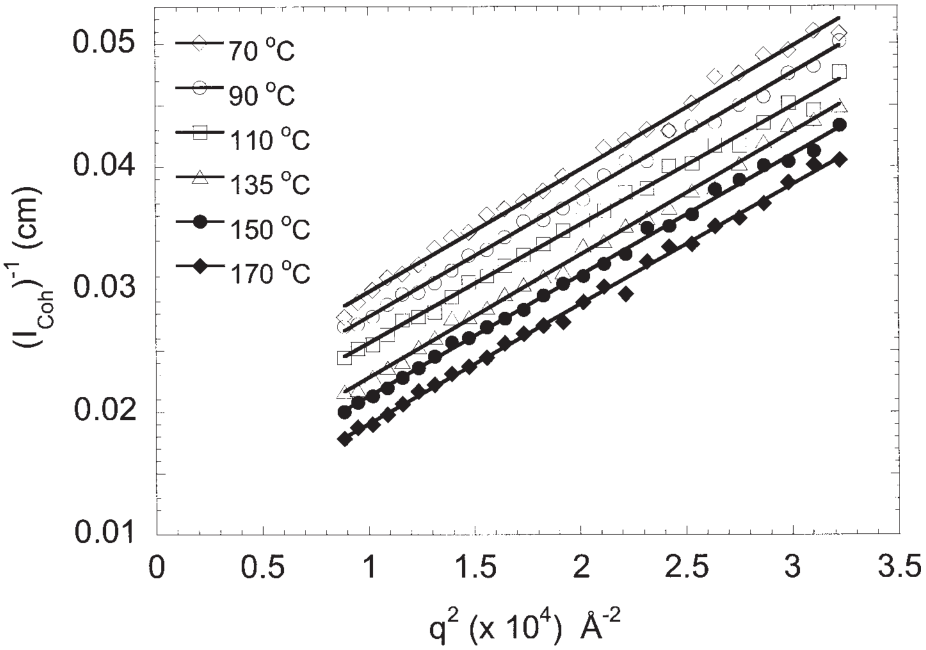
(a)



(b)

Figure 4. Temperature dependence of the Zimm analysis of ternary blends: (a) 33/33/33 dPBD/PI-a/P(4tBS), (b) 10/45/45 dPBD/PI-a/P(4tBS), and (c) 33/54/13 dPBD/PI-b/P(4tBS). The intercept values cannot be directly related to the thermodynamic interactions of the binary pairs, and the data are shown only to demonstrate their quality and the inference that single-phase blends are found in all ternary cases (I_{Coh} is the coherent SANS intensity).

dPBD/PI-b/P(4tBS) blend for the PI-b series, for which the values of α are as high as 1.08, with considerable uncertainty in those values because of the small amounts of dPBD] and suggest that the chain dimensions in these ternary blends are essentially unchanged from those of the pure



(c)

Figure 4. (*Continued from the previous page*)

components (for PBD and PI) and the binary blend [for P(4tBS)].

The values of $\chi_{PI/P(4tBS)}$ for the low-molecular-weight PI series (PI-a) from the ternary blends with dPBD/PI-a/P(4tBS) compositions (by weight) of 33/33/33, 20/40/40, 10/45/45, 33/27/40, 33/40/27, and 33/54/13 are shown in Figure 5(a) as a function of the temperature and are tabulated in Table 5. Figure 5(b) presents a similar graph for the temperature dependence of $\chi_{PI/P(4tBS)}$ in the high-molecular-weight PI (PI-b) system, with the numerical values tabulated in Table 6. The 33/33/33 composition blend for the PI-b system did not yield usable data, presumably because of complications during the sample preparation related to the high temperatures required for flow. The error bars for the interaction parameters obtained from ternary scattering experiments are somewhat larger than those of the binary data because of the added uncertainty from the substitution of the binary χ's. The hydrogenous pair of P(4tBS) and PI exhibit large negative values in the temperature range examined, indicating strong interactions, with the temperature dependence consistent with that of a system exhibiting an LCST, although even at the highest temperature examined (170 °C) the binary blend exhibits a large negative value for χ far from phase separation. As explained in the introduction, these strong interactions imply that no strong thermorheological complexity should be observed in the viscoelasticity of the P(4tBS)/PI blends. A detailed study of the viscoelasticity will be presented in a future article and compared with the predictions from the SANS experiments.

The values of $\chi_{PI/P(4tBS)}$ exhibit a rather strong dependence on the composition of the ternary blend but are nearly independent of the molecular weight of PI. The dependence on the blend composition has been examined in two ways, as demonstrated in Figure 6. First, at a constant volume fraction of dPBD (0.33), the impact on the ratio of PI to P(4tBS) has been examined [Fig. 6(a,c)]. The dependence is either linear or parabolic, with insufficient data available for P(4tBS)-rich blends because of the high processing temperatures and concomitant degradation of PI, and is similar at all temperatures examined. A similar slice of the compositional dependence is examined in Figure 6(b), in which, for equal-volume-fraction blends of PI (PI-a) and P(4tBS), the changes in $\chi_{PI/P(4tBS)}$ are examined versus the volume fraction of dPBD in the blends. In the fits for these blends, the effect of changing the ratio of dPBD to PI and of dPBD to P(4tBS) on $\chi_{dPBD/PI}$ and $\chi_{dPBD/P(4tBS)}$ is already factored into the calculations. Interestingly, the changes in $\chi_{PI/P(4tBS)}$ with the dPBD composition are comparable to the changes in the

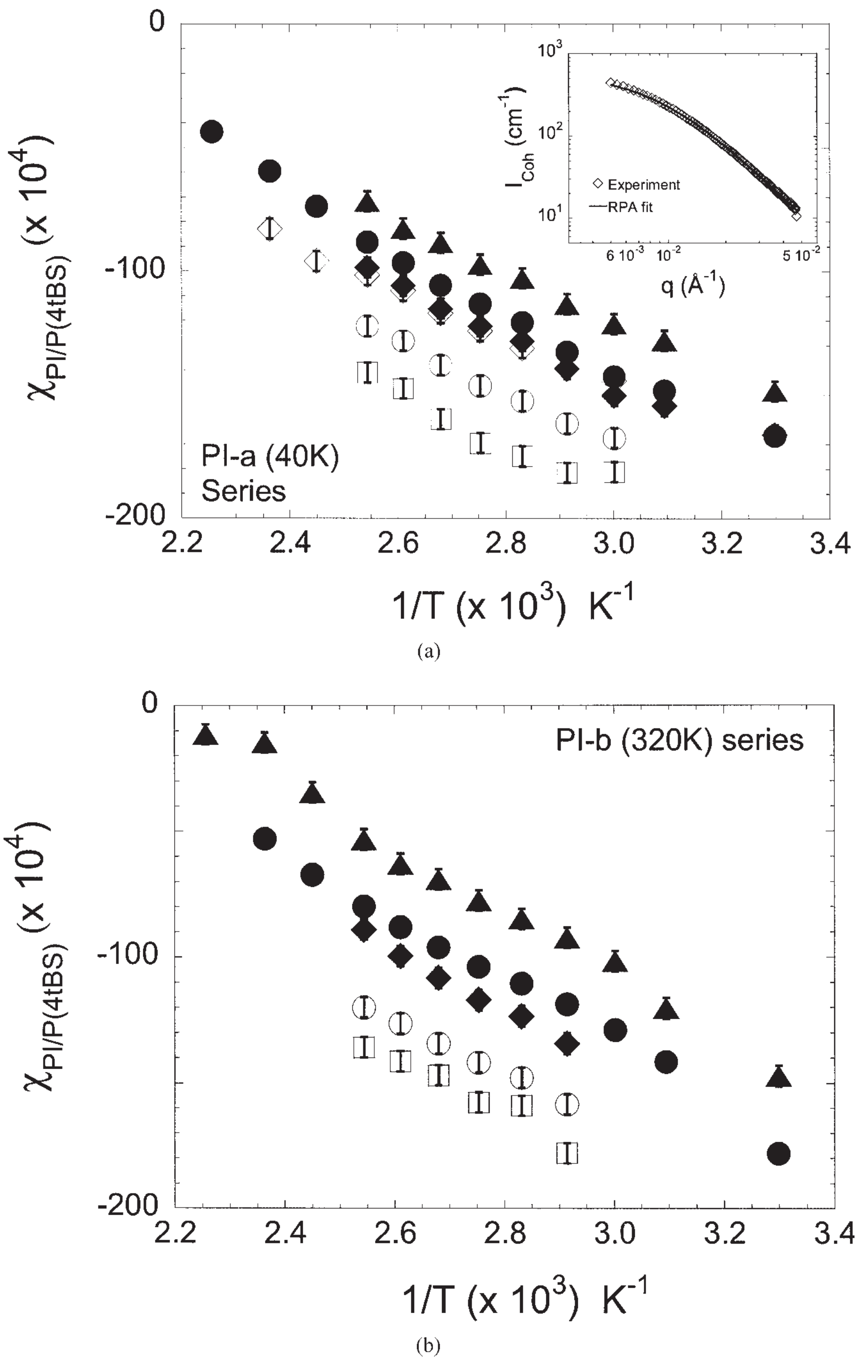


Figure 5. (a) Temperature dependence of the thermodynamic interaction parameters $\chi_{\mathrm{PI/P(4tBS)}}$ for the blend of PI-a/P(4tBS) at different compositions: (◇) 33/33/33, (○) 20/40/40, (□) 10/45/45, (♦) 33/27/40, (●) 33/27/40, and (▲) 33/54/13 dPBD/PI-a/P(4tBS). The inset is a representative fit of the ternary blend (33/33/33) at 100 °C (I_{Coh} is the coherent SANS intensity). (b) Temperature dependence of the thermodynamic interaction parameters $\chi_{\mathrm{PI/P(4tBS)}}$ for the blend of PI-b/P(4tBS) at different compositions: (○) 20/40/40, (□) 10/45/45, (♦) 33/27/40, (●) 33/27/40, and (▲) 33/54/13 dPBD/PI-a/P(4tBS).

PI [or P(4tBS)] composition in Figure 6(a,c). Such linear (or parabolic) compositional dependences for χ, with the values for compositions at the wings being considerably larger than those in the middle of the range, are similar to data for mixtures of isotopes,[2,39] mixtures of polybuta-

Table 5. P(4tBS)/PI-a Interaction Parameters from the RPA Fitting of dPBD/PI-a/P(4tBS) Ternary Blends[a]

Temperature (°C)	33/33/33 χ ($\times 10^4$)	20/40/40 χ ($\times 10^4$)	10/45/45 χ ($\times 10^4$)	33/27/40 χ ($\times 10^4$)	33/40/27 χ ($\times 10^4$)	33/54/13 χ ($\times 10^4$)
30	—	—	—	−166.1	−166.5	−148.4
50	—	—	—	−154.3	−148.4	−128.0
60	−144.3	−167.4	−181.1	−150.3	−142.6	−121.2
70	−139.2	−161.5	−181.4	−139.5	−132.6	−113.3
80	−131.0	−152.5	−174.8	−128.2	−120.6	−102.8
90	−124.1	−146.3	−169.5	−122.2	−113.1	−97.2
100	−116.9	−138.0	−159.8	−115.1	−105.7	−88.4
110	−107.9	−128.1	−147.4	−105.8	−96.5	−82.7
120	−101.6	−122.2	−141.0	−98.4	−88.2	−71.7
135	−95.9	—	—	—	−73.6	—
150	−82.8	—	—	—	−59.4	—
170	—	—	—	—	−43.5	—

[a] The χ values are given on the basis of a reference volume of 100 cm^3/mol.

dienes,[10] mixtures of polybutadiene and polyisoprene,[11,22,38] and many mixtures of polyolefins.[40] For the cases in which linear compositional dependences have been observed (i.e., mixtures of polybutadienes and mixtures of polybutadiene and polyisoprene[11,22,38,41]), the origins are thought to be equation-of-state effects (i.e., volume changes upon mixing). Given the large attractive interactions in the absence of specific interactions for PI and P(4tBS), we suggest that equation-of-state effects must dominate the thermodynamics of mixing. It would certainly be interesting to examine the pressure–volume–temperature properties of P(4tBS) and its mixtures with PI and PBD.[6,41]

Finally, as noted earlier, the incompressible FHS formulation and the incompressible RPA used to fit the SANS data implicitly neglect three-body effects. Although there is extensive literature on the effect of three-body interactions on measured binary interaction parameters for small molecules and even colloidal dispersions,[42] we are unable to ascertain the relative importance of three-body interactions on the reported values of $\chi_{\mathrm{PI/P(4tBS)}}$. We need to find at least two other pairs of polymeric cosolvents for PI and P(4tBS) to sort out the possibility of three-body effects affecting the measured χ values. Nevertheless, for the only other polymer blends for which such ternary systems have been studied (polyole-

Table 6. P(4tBS)/PI-b Interaction Parameters from the RPA Fitting of dPBD/PI-b/P(4tBS) Ternary Blends[a]

Temperature (°C)	20/40/40 χ ($\times 10^4$)	10/45/45 χ ($\times 10^4$)	33/27/40 χ ($\times 10^4$)	33/40/27 χ ($\times 10^4$)	33/54/13 χ ($\times 10^4$)
30	—	—	—	−178.1	−147.1
50	—	—	—	−141.5	−120.3
60	—	—	—	−128.9	−101.7
70	−158.5	−178.0	−134.3	−118.7	−92.4
80	−147.9	−159.0	−123.5	−110.5	−84.8
90	−141.8	−157.7	−117.1	−103.9	−77.6
100	−134.4	−146.9	−108.4	−96.2	−69.2
110	−126.4	−141.3	−99.7	−88.1	−63.0
120	−120.1	−135.8	−89.1	−80.0	−53.3
135	—	—	—	−67.3	−34.6
150	—	—	—	−52.9	−14.7
170	—	—	—	—	−11.5

[a] The χ values are given on the basis of a reference volume of 100 cm^3/mol.

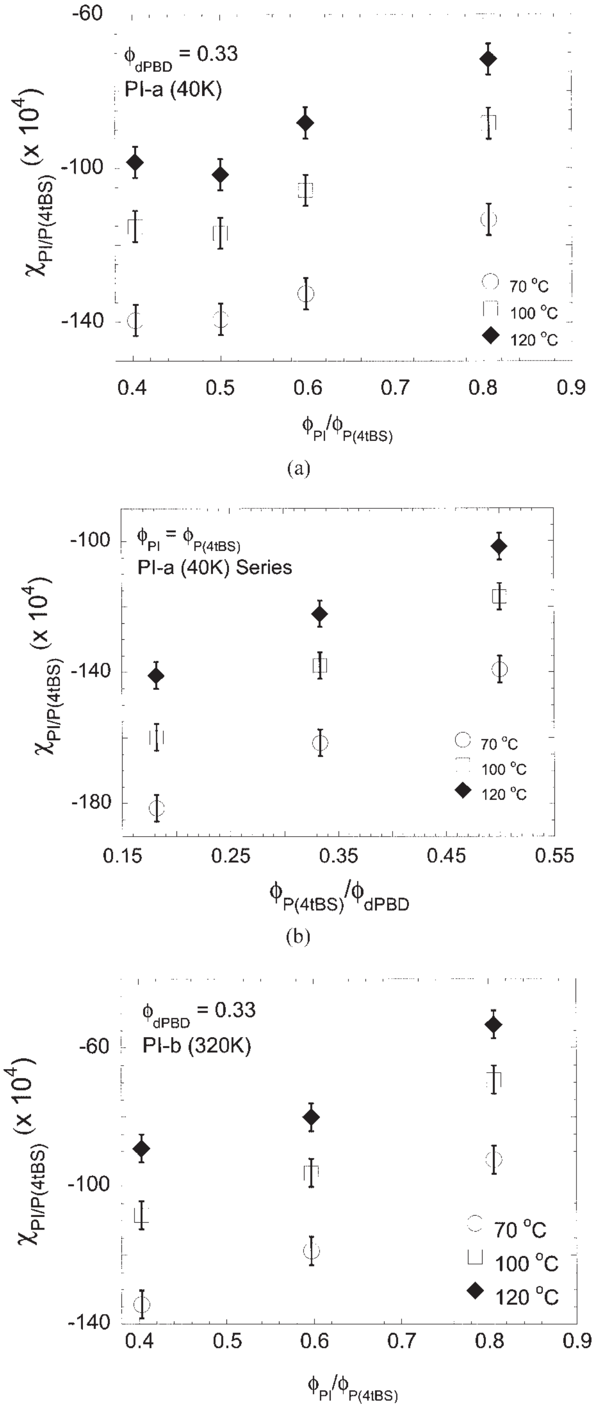


Figure 6. Composition dependence of $\chi_{PI/P(4tBS)}$ from (a,b) the PI-a series of blends and (c) the PI-b series. (a,c) The data were obtained at a constant level of dPBD (0.33) and specifically describe the variation of $\chi_{PI/P(4tBS)}$ with the PI/P(4tBS) ratio. (b) The data show the composition dependence of $\chi_{PI/P(4tBS)}$ with various levels of dPBD and a constant ratio of PI to P(4tBS). A significant composition dependence on the values of χ can be observed in all three cases.

fin blends and PS/deuterated PS/PVME blends), no discernible three-body effects have been implicated.[8,43]

CONCLUSIONS

We have characterized in this article miscible polymer blends of polyisoprene (and polybutadiene) with P(4tBS) over a wide range of compositions and have obtained thermodynamic interaction parameters for the hydrogenous versions of these polymers with ternary blends. Although it is surprising to find compatibility between a styrene derivative and polydienes, the large negative χ values and the presence of LCST come as additional surprises. These results naturally have a significant impact on the blending of styrene-based polymers with polydienes and polyolefins. Additionally, these results must also significantly affect the viscoelastic behavior of the blends, and this topic is currently being explored in our laboratory.

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