Nonuniversal Behavior of the Thermodynamic Interaction Parameter in Blends of Star and Linear Polybutadiene

T. D. Martter,[†] M. D. Foster,*,[†] T. Yoo,[†] S. Xu,[†] G. Lizzaraga,[†] R. P. Quirk,[†] and P. D. Butler[‡,§]

Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, and NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8562

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ABSTRACT: Values of the bulk thermodynamic interaction parameter, χ_{eff}, for blends of anionically polymerized star (number of arms = 4, 6, 8, 12) and linear polybutadienes (PB) of well-defined architecture and molecular weight were measured as a function of temperature using small-angle neutron scattering. Comparison of these measured values of χ_{eff} with results from comparable polystyrene (PS) blends suggests the existence of nonuniversal aspects in the thermodynamic interaction due to entropic contributions, χ_ϵ, arising from architectural differences in chains. While the value of χ_ϵ for PS star/linear blends increases monotonically with number of arms in the star, the value of χ_ϵ in the PB star/linear blends does not, a result which cannot be anticipated by the Gaussian field theory (GFT) of Fredrickson et al.[1] An important discrepancy between theory and experiment is also found for the variation of χ_ϵ with linear chain length. Theory anticipates the value of χ_ϵ should decrease with increasing linear chain size, but in fact it increases. Qualitative agreement with the GFT is found on two counts: χ_ϵ decreases with increasing concentration of star (when assuming χ_{isotopic} for linear/linear blends is constant with concentration), and χ_ϵ decreases with increasing length of the star arm. In general, the value of χ_ϵ for a PB blend of star and linear components is larger than the value of χ_ϵ for a comparable PS blend. Indeed, phase separation is observed in one particular PB blend of a six-arm star with a sufficiently large linear chain.

Introduction

The magnitude of bulk thermodynamic exchange interactions in binary blends of linear polymers can vary with several characteristics of the components including molecular weight, microstructure,[2−6] tacticity,[7] and isotopic labeling.[5,8,9] Typically, both the local and nonlocal interactions between chains are expressed in terms of a local segment−segment exchange interaction parameter,[10,11] which is therefore a function of these various component characteristics. Small-angle neutron scattering (SANS) has proven to be a sensitive and powerful tool for probing the effect of these molecular characteristics on bulk polymer blend thermodynamics.

Differences in component molecular architecture, particularly as represented by long-chain branching, could conceivably also contribute to the segment−segment interaction parameter. The effects of such branching on bulk thermodynamics have been studied theoretically for blends of linear polymers with star-branched,[1,12−14] comb-branched,[1,13] and randomly branched[15,16] polymers. The Gaussian field theory of Fredrickson et al.[1] proposes an entropic correction to the Flory−Huggins theory due to architecture effects for the case of athermal blends of regularly branched and linear polymers with identical repeat unit chemistry. They express their result in terms of an interaction parameter, α, which is invariant with the choice of segment volume, but α can be readily related to the more widely used parameter χ, which does depend on segment volume. While in general α has both enthalpic and entropic parts, only the entropic contribution, α_ϵ, is considered in that work. An expression is given for α_ϵ (eq 3.15 in ref 1) under the assumption that p, the number of arms, is much greater than one. This expression is complex and depends on p, the ratio R_1/R_2, where R_1 is the radius of gyration of the linear chain and R_2 is the radius of gyration for the star arm, and ϕ, the volume fraction of linear molecules in the blend. In the case that $(p - 3)(R_1/R_2)^2 \gg 1$; i.e., for large numbers of short arms or for large linear polymers, an integral in the expression may be simplified to a good approximation (except for ϕ very close to unity) to yield a *universal* form:

$$\alpha_\epsilon = \frac{1}{64\pi\sqrt{2}} \frac{(p-3)^{3/2}}{(1-\phi)^{1/2} {R_2}^3} \tag{1}$$

where the radius of gyration of the star arm is given by $R_2 = (N_2 a^2/6)^{0.5}$, with N_2 being the number of segments in an arm and a the segment length. The universal expression suggests that χ_ϵ, the entropic contribution to the interaction parameter χ, should increase with the number of arms in the star, decrease with an increase in the length of the arm, and decrease with an increase in the concentration of the star. The size of the linear chain plays no role in the universal expression. More recently, PRISM calculations for star/linear blends have been performed by Schweizer and co-workers.[14] These calculations suggest a weaker dependence of χ_ϵ on arm number than predicted by the field theory. They also suggest that for sufficiently long linear chains the dependence of χ_ϵ on number of arms nearly disappears or may be reversed.

The few published experimental studies[17−25] on the effect of branching on the thermodynamics of blends of branched and linear polymer chains offer a consensus

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[†] The University of Akron.
[‡] National Institute of Standards and Technology.
[§] Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37831.
* Corresponding author: e-mail mfoster@uakron.edu; phone (330) 972-5323; Fax (330) 972-5290.

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that architecture effects are measurable and can be large enough to lead to bulk phase separation in some circumstances. Studies have looked at three types of branching: random short-chain branching, comb branching, and star branching. For blends of linear and randomly branched polyethylenes, Alamo et al.[17] determined that phase separation occurs when the short chain branch content is higher than 8 branches per 100 backbone carbons. Bates et al.[18] reported entropy-driven phase separation for blends of highly branched comb and linear PEE [poly(ethylene-*r*-ethylethylene)]. They found that a 60 kg/mol linear PEE was miscible with a heavily branched 750 kg/mol PEE, but when the molecular weight of the linear component was increased to 220 kg/mol, phase separation resulted.

The effect of architecture on the bulk miscibility of blends of linear and *star* polymers has been studied some both for the case when the chemical structures of the two components differ and when they are the same. Faust et al.[19] and Russell et al.[20] studied blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME). Faust et al. found that the minimum in the cloud point curve did not change when the architecture of PS was changed from linear to 22-arm star. A change in the shape of the phase diagram did occur at high concentrations of PS. Russell et al. found a shift up in the cloud point curve of 10 °C when the architecture of the PS was changed from that of a linear chain to a 4-arm star. van Aert et al.[21] determined the effect of varying the number of arms on miscibility for blends of star-branched poly(2,6-dimethyl-1,4-phenylene ether) and linear PS. Phase separation occurred when the number of arms of the star was increased above 16. Tsukahara et al.[22] studied blends of very polydisperse highly branched bottle-brush-like PS and linear PS. Phase separation occurred for sufficiently high molecular weight of the linear polymer.

Research by Greenberg et al.[23-25] on blends of star and linear PS attempted to quantify changes in the interaction due to architecture with changes in the number of arms. They measured values of χ_{eff}, an overall interaction parameter, using SANS and from those values derived estimates of the interaction due to architectural effects alone, χ_ϵ, by measuring separately the interaction due to isotopic labeling in a linear/linear blend. χ_ϵ was found to increase with increasing the number of arms of the star. When the concentration of star was increased from 18% to 82% for a blend of 6-arm star hydrogenous polystyrene (hPS) with linear deuterated polystyrene (dPS), χ_{eff} decreased. The magnitude of the change with composition compared well quantitatively with the theoretical prediction from Fredrickson et al.[1] Changes with the number of arms showed the qualitative behavior expected from the theory, but the field theory overestimated the magnitude of the effect except for the case for a 4-arm star. A single experimental result[25] showed a much larger value of interaction parameter for a blend of a six-arm comb PS than for a blend with a comparable six-arm star PS. All of the results were consistent with the contention made by Fredrickson et al.[1] that bulk phase segregation due to architecture alone could be expected for star/linear blends only for very large numbers of arms but should be readily obtained in blends with a comb-branched component.

In this study the universality of the results found with PS blends is probed by comparison with measurements from star/linear blends of poly(butadiene) chains. The main objective is to determine the effect of the values of three parameters on the value of χ: the number of arms in the star, the concentration of the star, and the molecular weight of the star. The effect of the size of the linear component, which cannot be predicted using the universal expression above, is addressed as well. Comparison is made between the experimental results and values estimated from Fredrickson's theory.[1] PB was chosen due to the commercial importance of branched PB materials and the facility with which stars of well-defined arm number may be made. PB precursor arms are much more readily linked together than are PS arms. However, it must be noted that studies of PB blends are demanding in that small differences in microstructure of the components can lead to significant interactions on their own.[2-5] Where variations in microstructure may have played a role in these results their significance is discussed.

Experimental Section

Materials. The linear hydrogenous polybutadiene (hPB) and deuterated polybutadiene (dPB) polymers were purchased from Polymer Source (Dorval, Quebec, Canada).[26] Characterization of the molecular weight of the linear polymers was done at Polymer Source by gel permeation chromotography (GPC) and checked at The University of Akron (UA). The degree of 1,4-addition was determined for each polymer by ^{1}H NMR and FTIR at Polymer Source.

The star hPB and dPB with 4, 6, 8, and 12 arms were synthesized by living anionic polymerization at UA. The poly(butadienyllithium) arm precursors of known molecular weight were synthesized in cyclohexane with the initiator *sec*-butyllithium and then coupled together with the appropriate linking agent to form stars.[27] The coupling agents used to form the 4-, 6-, 8-, and 12-arm stars were silicon tetrachloride, 1,2-bis(trichlorosilyl)hexane, tetrakis[2-(dichloromethylsilyl)ethyl]silane, and tetrakis(trichlorosilylethane)silane, respectively. Coupling of the arms was performed with an excess of arm to drive the reaction to completion. This excess was later removed by fractionation from 0.5 wt % polymer solutions in toluene using methanol as the nonsolvent.

The molecular characteristics of all the polybutadienes are listed in Table 2. The number of arms in the star was determined by first characterizing the arm precursor and then the complete star by GPC with three in-line detectors: viscometer, refractometer, and light scattering. Molecular weights were confirmed using light scattering in a separate laboratory. Intrinsic viscosity measurements were performed for all star polymers in toluene at 35 °C, and the branching factor,[28] g', was calculated and compared with experimental results for stars in good solvent. The branching factor is defined as the ratio of intrinsic viscosities of the branched and linear species of equal overall molecular weight, $g' = [\eta]_b/[\eta]_l$. The experimental values of g', listed in Table 1, compared well with published experimental results,[28,29] indicating that the numbers of arms of the stars are very close to the intended values. Oxidation of the samples was slowed dramatically by the addition of <1% of the antioxidant BHT (2,6-di-*tert*-butyl-4-methylphenol) and by keeping the samples in the dark in a freezer or dry ice whenever they were not being measured. The degree of 1,4-addition in the polymers was kept as nearly constant as possible and was generally close to 94% as determined by ^{1}H NMR for the hydrogenous stars. The reaction conditions used are known to result typically in 91-93% 1,4-microstructure for hydrogenous polymers at the molecular weights used here.[27] Thus, we assume that 91-93% is a very good estimate for the degree of 1,4-microstructure in those samples labeled ">90%". The microstructure for the deuterated stars was checked using ^{1}H NMR (using the presence of residual ^{1}H atoms located randomly in the chains) and was found to vary slightly among the stars, but to

Table 1. Comparison of Experimentally Measured and Theoretical g' Values for the PB Stars

star polymer	$[\eta]_b$ (dL/g)	$[\eta]_l$ (dL/g)[a]	g' [b]	Zimm and Kilb g' [c]	good solvent exp g' [d]
4-arm star hPB (95K)	1.00	1.23	0.82	0.79	0.73
6-arm star hPB (52K)	0.47	0.79	0.59	0.67	0.58
6-arm star hPB (121K)	0.86	1.46	0.59	0.67	0.58
6-arm star hPB (181K)	1.12	1.98	0.56	0.67	0.58
8-arm star hPB (114K)	0.70	1.40	0.50	0.59	0.43
12-arm star hPB (107K)	0.47	1.33	0.35	0.49	0.34
4-arm star dPB (97K)	0.83	1.15	0.72	0.79	0.73
6-arm star dPB (57K)	0.40	0.78	0.51	0.67	0.58
6-arm star dPB (110K)	0.69	1.27	0.54	0.67	0.58
6-arm star dPB (205K)	1.04	1.96	0.53	0.67	0.58
8-arm star dPB (113K)	0.55	1.29	0.43	0.59	0.43
12-arm star dPB (116K)	0.41	1.31	0.31	0.49	0.34

[a] Calculated using the Mark−Houwink−Sakurada equation for PB in toluene at 35 °C:[30] $[\eta] = (0.285 \times 10^{-3})(N \times 54\ \text{g/mol})^{0.73}$. [b] $g' = [\eta]_b/[\eta]_l$. [c] $g = 3f - 2/f^2$ and then $g' = g^{0.5}$. [d] Experimental results for stars in good solvent.[29]

Table 2. Molecular Characteristics of Polybutadiene Polymers

polymer	name	M_n (g/mol)[a]	N[b]	M_w/M_n	% 1,4-addition
polybutadiene	hPB (17K)	17 500	330	1.03	>90
polybutadiene	hPB	84 000	1570	1.04	>90
polybutadiene	hPB	86 500	1620	1.04	94
polybutadiene	hPB	88 000	1650	1.07	>90
polybutadiene	hPB (336K)	336 000	6290	1.07	>90
deuterated PB	dPB (17K)	17 000	280	1.03	>90
deuterated PB	dPB	98 000	1640	1.06	~82
deuterated PB	dPB (325K)	325 000	5440	1.12	~82
4-arm star	h4s	95 000	1780	1.03	94
6-arm star	h6s (52K)	52 000	970	1.01	94
6-arm star	h6s	121 000	2270	1.01	94
6-arm star	h6s (184K)	184 000	3450	1.05	92
8-arm star	h8s	114 000	2140	1.06	93
12-arm star	h12s	107 000	2000	1.01	94
4-arm deuterated star	d4s	97 000	1620	1.04	86
6-arm deuterated star	d6s (57K)	57 000	950	1.04	88
6-arm deuterated star	d6s	110 000	1860	1.02	92
6-arm deuterated star	d6s (205K)	205 000	3430	1.00	86
8-arm deuterated star	d8s	113 000	1890	1.01	93
12-arm deuterated star	d12s	116 000	1950	1.02	86

[a] Determined by GPC with three in-line detectors: viscometer, refractometer, and light scattering. [b] Number of segments determined using a segment volume of 60 cm^3/mol.

consistently be slightly smaller than that of the hydrogenous stars, even though the same conditions were used for the synthesis of hydrogenous and deuterated stars.

SANS Sample Preparation. Binary blends of 18 wt % star and 82 wt % linear PB were dissolved in filtered toluene (filtered two times with a 0.02 μm filter) in a Teflon beaker. Since one blend component was always labeled, an "isotopic swap" analogue of each sample was prepared. That is, if in one sample the star was deuterated, in the "swap" sample the linear chain was deuterated. Samples for a concentration study for blends of 6-arm star hPB and linear dPB were also prepared. The majority of the solvent was removed by allowing evaporation at ambient conditions for 1 day. The samples were then further dried under roughing vacuum at room temperature for at least 3 days. Each dried sample was pressed into a brass ring spacer of inner diameter 10 mm and thickness 1.0 mm and then placed between quartz windows into a standard reusable brass sample holder. A list of the blends studied is given in Table 3.

Instrumentation. SANS measurements were performed on the NG3 30 m SANS instrument at the Cold Neutron Research Facility (CNRF) at the National Institute of Standards and Technology (NIST) (Gaithersburg, MD). The nominal wavelength of the neutron beam was 6 Å with a resolution ($\Delta\lambda/\lambda$) of 0.150 fwhm. A sample-to-detector distance of 13 m and detector offset of 20 cm were used with a 2 in. diameter beamstop, one neutron guide, and a sample aperture of 0.635 cm to yield an accessible range of scattering vector, q (= $4\pi \sin \theta/\lambda$) of 0.005 Å^{-1} < q < 0.05 Å^{-1}. The samples were placed inside a temperature-controlled, remotely controlled seven-position aluminum sample changer, which was located in a aluminum vacuum chamber. The chamber was evacuated (to 450 μm Hg) and then back-filled with nitrogen gas and a slight positive pressure maintained throughout the measurement. The temperature was varied stepwise, monotonically between

Table 3. Descriptions of SANS Samples

	polymer 1			polymer 2	
blend	name	ϕ	N[a]	name	N[a]
18hll	linear hpb	0.20	1620	linear dpb	1640
50hll	linear hpb	0.52	1620	linear dpb	1640
18dll	linear dpb	0.20	1640	linear hpb	1620
18h4s	4-arm hpb	0.20	1780	linear dpb	1640
18h6s	6-arm hpb	0.20	2270	linear dpb	1640
18h8s	8-arm hpb	0.20	2140	linear dpb	1640
18h12s	12-arm hpb	0.19	2000	linear dpb	1640
18d4s	4-arm dpb	0.17	1620	linear hpb	1620
18d6s	6-arm dpb	0.17	1860	linear hpb	1620
18d8s	8-arm dpb	0.16	1890	linear hpb	1620
18d12s	12-arm dpb	0.17	1950	linear hpb	1650
35h6s	6-arm hpb	0.38	2270	linear dpb	1640
50h6s	6-arm hpb	0.53	2270	linear dpb	1640
65h6s	6-arm hpb	0.67	2270	linear dpb	1640
82h6s	6-arm hpb	0.84	2270	linear dpb	1640
18h6l	6-arm hpb	0.20	2270	linear dpb	280
18h6h	6-arm hpb	0.20	2270	linear dpb	5440
18d6l	6-arm dpb	0.16	1860	linear hpb	330
18d6h	6-arm dpb	0.16	1860	linear hpb	6290
h6slmw	6-arm hpb	0.20	970	linear dpb	1640
h6shmw	6-arm hpb	0.20	3450	linear dpb	1640
d6slmw	6-arm dpb	0.16	950	linear hpb	1570
d6shmw	6-arm dpb	0.16	3430	linear hpb	1570

[a] Number of segments determined using a segment volume of 60 cm^3/mol.

40 and 160 °C in steps of 30 °C, with the temperature maintained to within ±0.1 °C at each temperature. A thermal equilibration time of 15 min was allowed at each temperature before collecting data. (The integral intensity of the scattered beam was seen to equilibrate in about 5 min.)

Other measurements were performed for purposes of data reduction and normalization. Data were collected with the beam blocked and with the instrument empty for estimating background contributions. Since the samples were mounted in cells with quartz windows, the scattering from an empty cell was also measured. To correct for incoherent scattering, a 100% hPB sample was measured. Transmission coefficients were measured for all samples at each temperature, both to optimize the normalization to absolute scattering and as a simple check for the development of bubbles. To convert the data to absolute intensities, an isotopic polymer blend standard sample was also measured. The raw data were azimuthally averaged and then converted to absolute coherent scattering intensity as a function of q.

Small-Angle Neutron Scattering Data Analysis. The scattering data were fit using the random phase approximation (RPA) approach with appropriate structure factors for the star and linear polymers. The measured absolute coherent scattering intensity, $I(q)$, is related to the structure factor, $S(q)$, by

$$I(q) = \frac{(b_a - b_b)^2}{V} S(q) \tag{2}$$

where b_i is the coherent scattering length of polymer i, V is the polymer segment volume, and q is the scattering vector. For the polybutadiene samples, a segment volume of 60 cm^3/mol was used at 40 °C. The coherent scattering lengths for hPB and dPB were calculated to be 4.13×10^{-13} and 6.66×10^{-12} cm. The structure factor for a binary blend of linear polymers is given by DeGennes in the RPA[31] as

$$S^{-1}(q) = \frac{1}{\phi_a N_a g_D(R_{g,a},q)} + \frac{1}{\phi_b N_b g_D(R_{g,2},q)} - 2\chi \tag{3}$$

where ϕ_i is the volume fraction of component i, N_i is the number of segments in the polymer chain, and χ is the effective thermodynamic interaction parameter, which we take here as a good estimate of the bare interaction parameter. The Debye function g_D captures the character of a Gaussian linear polymer chain:

$$g_D(R_{g,i},q) = \frac{2[R_{g,i}^2 q^2 + e^{-R_{g,i}^2 q^2} - 1]}{R_{g,i}^4 q^4} \tag{4}$$

where

$$R_{g,i} = a\left(\frac{N_i}{6}\right)^{0.5} \tag{5}$$

$R_{g,i}$ is the radius of gyration, and a is the segment length. The segment length for linear PB[7] has been previously measured to be 6.9 Å and found not to vary with temperature.[32] A value of 6.69×10^{-4} K^{-1} for thermal expansion coefficient[33] was used to adjust the molar volume with changing temperature.

For a star/linear blend, one of the Debye functions in eq 3 must be replaced by the form appropriate for a star polymer. Benoît extended the Debye function for the case of a star-branched polymer[34] in which the arms remain Gaussian:

$$P(q) = \frac{2}{p u_r^4}\left[u_r^2 - [1 - e^{-u_r^2}] + \frac{p-1}{2}[1 - e^{-u_r^2}]^2\right] \tag{6}$$

where

$$u_r^2 = \frac{N a^2 q^2}{6} = q^2 \langle R_g^2 \rangle_a \tag{7}$$

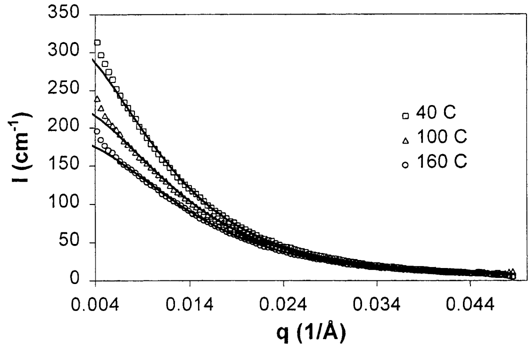

Figure 1. SANS experimental data with fits to the RPA (—) for a blend of 20 vol % 6-arm dPB in a matrix of 80 vol % linear dPB for three temperatures: 40 °C (□), 100 °C (△), and 160 °C (○).

and p is the number of arms, N is the number of segments in an arm of the star, and the subscript "a" denotes a quantity defined for one arm.

The appropriateness of the Gaussian approximation in the star structure factor has been addressed both theoretically[35] and experimentally.[36,37] It clearly cannot be rigorously correct, but further refining the structure factor is difficult. Alessandrini and Carignano[35] have presented a more complex structure factor based on renormalization group theory for the case of a star in good solvent, which is not the case here. Various studies[36,37] have inferred the existence of stretching of the arms away from the Gaussian state from experiments sensitive to the global dimensions of the stars. Horton et al.[36] specifically argued that the arms of star-branched polyethylenes are stretched in the case when there are more than 12 arms. Hutchings et al.[37] have attempted to measure directly the degree of arm stretching in PB stars using SANS of blends containing stars with a single labeled arm. They report that the arms in 3-, 4-, 8-, and 12-arm stars of a melt are all stretched, with the degree of stretching increasing with the number of arms. However, their analysis is complicated by the fact that they find it necessary to introduce two interaction parameters even to fit the data for a pure melt of partially labeled stars. In this work, at low numbers of arms the assumption of Gaussian statistics should lead to uncertainties commensurate in magnitude with uncertainties due to other factors.

If the Gaussian approximation is maintained, the only parameter that is unknown in these equations is χ_{eff}, and its value can then be determined by modeling of the scattering curves. Sample scattering curves for a blend of 20 vol % 6-arm hPB and 80 vol % linear dPB are shown with model fits for temperatures of 40, 100, and 160 °C in Figure 1. (From this point forward, all concentrations will be discussed as volume fractions or percentages.) To achieve the agreement seen here between the model and the experimental data, a prefactor of order unity was used to adjust the model. Slight deviations are seen at the lowest values of q considered. Such discrepancies are common in practice, generally attributed to the presence of some impurity in the sample, and avoided only with the cleanest samples.

Recent publications[38,39] have discussed the variation in χ_{eff} with concentration seen experimentally for isotopic blends of linear chains. While various reasons have been suggested for the existence of this behavior, the most recent reports appear to be coming to a consensus that this behavior is due to uncertainties in the experimental results. Difficulties in interpretation of χ_{eff} values should then be minimized by considering compositions near a volume fraction of 0.5, though substantial inaccuracies are not anticipated until the composition is shifted farther from 0.5 than is the case here. In the current study compositions away from 0.5 have been considered for two reasons. First, the dependence of the value of χ on composition of the star in the blend is an important prediction of the Gaussian field theory (GFT), which we wish

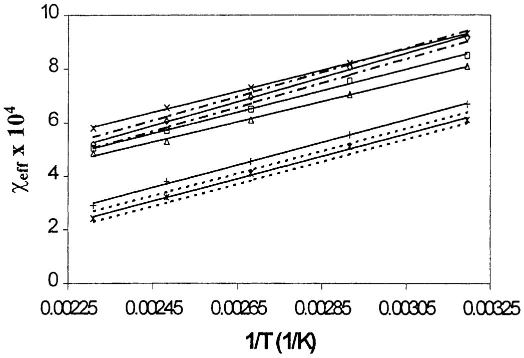

Figure 2. Effective thermodynamic interaction parameter as a function of temperature for several blends: blends of linear dPB with 20 vol % hPB (18hll) (*) and 52 vol % hPB (50hll) (+) and blends of 20 vol % star hPB with 80 vol % linear dPB with stars having four arms (18h4s) (◇), six arms (18h6s) (□), eight arms (18h8s) (△), and 12 arms (18h12s) (×).

to test. Second, use of a star volume fraction of 0.18 allows for a variety of measurements to be made with a small amount of deuterated star material. (The adoption of this particular composition is for ready comparison with our earlier work.[23–25])

Results and Discussion

The dependences of χ_{eff} on temperature for blends of 20 vol % hydrogenous stars with deuterated linear PB are shown in Figure 2. Data from isotopic blends of linear hPB with linear dPB at compositions of 20/80 and 52/48 (vol/vol) are shown for comparison and agree well with measurements by Bates et al.[9] and Schwahn and Willner.[5] The magnitude of χ_{eff} for the linear/linear blends is a measure of the contribution to χ due to isotopic labeling and the microstructure difference that is the same in the linear/linear blend and the four h-star/d-linear blends. A concentration effect for the linear/linear PB blends is seen experimentally, with the value of χ_{eff} for a volume fraction of the linear hPB at 0.20 being lower than that for a volume fraction of 0.52. The value of χ_{eff} derived from these data near the symmetric condition (50/50) should be free of composition artifacts. An estimate of the uncertainty in the value of χ_{eff} for the 20/80 linear hPB/linear dPB blend and the 4-arm star hPB blend based on uncertainties in the measurement of molecular weight and absolute intensities is shown by the dashed lines.

Upon branching of one of the components in the PB blend to form a four-arm star, while keeping the microstructures of the hydrogenous and deuterated components unchanged, χ_{eff} clearly increases over the value attributable to isotopic labeling and microstructure mismatch alone. The change in χ_{eff} is about 2.8×10^{-4} and constant with temperature, consistent with the contention that the architectural component is entropic in nature. (Though Graessley et al.[40] suggest that the temperature-independent portion of χ_{eff} is not necessarily due to just entropic contributions and could also be from enthalpic contributions.) The magnitude of the architectural effect is slightly larger than the contribution ($\sim 2.3 \times 10^{-4}$) due to isotopic labeling and microstructure mismatch at the highest temperature considered, 160 °C. However, since the isotopic effect in PB is strongly temperature dependent, the architectural effect at 40 °C is only about half as large as the isotope/microstructure effect. With further branching of the star to six arms the value of χ_{eff} decreases by an experimentally significant amount only at the lowest temperature of 40 °C. The temperature dependence for the blend with the six-arm star is somewhat different from that of the linear/linear blends and the four-arm star/linear blend. Increasing the branching in the star to eight arms results in a further slight decrease in χ_{eff}, but the temperature dependence remains the same as for the six-arm star/linear blend. Indeed, the data for the 12-arm star/linear blend show this same slope as well. This slope is indicative of the magnitude of the enthalpic contribution to χ_{eff} and the preponderence of our data suggests that this varies only within a narrow range. Changes in thermodynamic interactions with architecture are almost entirely entropic in nature.

The decrease in χ_{eff} with increasing p for $p = 4$, 6, and 8 is puzzling and contrary both to the prediction of the field theory[1] and expectations based on the behavior of the PS blends previously studied.[23–25] When the number of arms in the star is further increased to 12, the value of χ_{eff} increases to finally rise above that for the blend of 4-arm star hPB with linear dPB. However, the difference between the values of χ_{eff} for the 12-arm star/linear blend and 4-arm star/linear blend is experimentally significant only at the highest temperature. The nonmonotonic change in χ_{eff} with increase in number of arms is a central result of the present work. It suggests that the entropic effects of architecture upon thermodynamic interactions in the blend may not be universal with changes in chain chemistry. PRISM calculations[14] made available during the revision of this contribution suggest that for $N_{linear} = pN_{arm}$ (i.e., matching overall molecular weights of the linear and star) χ_{ϵ} attains a minimum, suggesting that the conditions chosen here may lead to a behavior particularly insensitive to the number of arms of the star. For sufficiently long linear chains (N_{linear} of order 2000), PRISM calculations suggest χ_{ϵ} may vary very little with number of arms or may even decrease with increasing number of arms. The precise behavior anticipated by the PRISM theory varies with details of the blend, and calculations for the parameters specifically pertinent to the PB blends here are not yet available. Nonetheless, one specific interpretation of the current results is that the data simply demonstrate the comparative insensitivity to branching found in a particular region of parameter space. This suggestion is consistent with the present authors' observations[41] that, for star/linear PB blends in which arm end-functionalization accentuates the change in χ_{eff} with number of arms, χ_{eff} consistently climbs with the number of arms.

To check whether the observed behavior is driven by labeling effects, blends in which the star was labeled with deuterium were also studied. Data for this series of blends, which contains an analogue for each star/linear blend of Figure 2, are shown in Figure 3. A linear/linear blend containing 20% linear dPB is shown for comparison. Here there is once again a slight microstructure mismatch between the star and linear component in each blend. The microstructure of the linear component is unchanging, and the 1,4-content of the stars varies from 86% to 93%, so the stars are more highly branched in regard to both long-chain and short-chain branching. The values of χ_{eff} are consistently lower for these blends in which the more highly branched component is labeled. This behavior differs from that found by Graessley et al.[8] for blends containing short-branched polyolefins but is qualitatively consistent with the predictions of a simplified lattice cluster theory

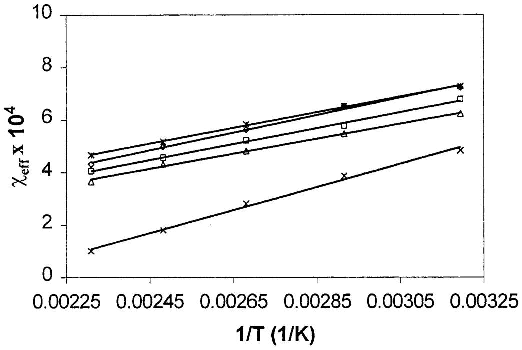

Figure 3. Variation in χ_{eff} with temperature for a series of blends analogous to those of Figure 2, but with the deuteration swapped to the star. The linear/linear blend (18dll) (×) has 20 vol % deuterated linear component. The star/linear blends of 17 vol % star dPB with 83 vol % linear hPB contain stars with four arms (18d4s) (◇), six arms (18d6s) (□), eight 18d8s (△), or 12 arms (18d12s) (*).

(LCT) of Dudowicz and Freed[42] as tested experimentally very recently by Schwahn and Willner.[5] (Reference 5 appeared during revision of this contribution.) The relative decrease in χ_{eff} (~25%) seen between the h-star series and the d-star series agrees well with that predicted from a calculation with the LCT expression (using parameter values suggested by Willner and Schwahn[5]) that accounts for microstructure differences and the labeling swap, but not for long-chain branching. However, the values of χ_{eff} estimated from the LCT expression exceed the observed values by factors ranging from 2.5 to 4. Estimations of χ_{eff} based on expected differences in the solubility parameters alone are unable to anticipate the observed behavior even qualitatively. The slope for the linear/linear blend data in Figure 3 is consistent with the slopes of most of the curves in Figure 2, while the slopes for the d-star blend data are somewhat lower than the slopes in Figure 2. Once again the temperature dependence of the four-arm star/linear blend appears distinct.

The trend in values of χ_{eff} with degree of branching is the same as that seen when the linear component was labeled. The value of χ_{eff} first increases in going from the linear/linear to four-arm star/linear blend and then decreases as p increases to 6 and 8. For $p = 12$ the value of χ_{eff} is equal to or just above the value for $p = 4$. The fact that the same ordering of the data with number of arms in the star is seen for both labeling schemes proves that labeling itself is not the source of the unexpected nonmonotonic behavior. Calculations using the LCT expression can replicate the relative ordering the curves for the different blends, based on considerations of microstructure alone. However, the fact that the same variation in χ_{eff} with arm number was observed in Figure 2 suggests to us that the results of Figure 3 should not be rationalized purely on the basis of microstructure variations.

A quantitative comparison between values of χ_ϵ derived from the measured values of χ_{eff} and those predicted by the theory of Fredrickson et al.[1] is provided in Table 4. The experimental value for χ_ϵ due to architectural effects was estimated by using the value of χ_{eff} from the linear/linear blend as an estimate of the contribution due to isotopic effects and microstructure mismatch. Subtracting the value of χ_{eff}(linear/linear) from the value of χ_{eff} for a particular star/linear blend yields the value of χ_ϵ ($\chi_\epsilon = \chi_{\mathrm{eff}}$(star/linear) − χ_{eff}(linear/linear)). The values from the theory were calculated using the "universal" form of the expression (eq 1), which is only rigorously appropriate for large numbers of arms. For the four-arm star blend the experimentally determined value of χ_ϵ is 2 orders of magnitude larger than that predicted by the theory, while for the 8- and 12-arm star blends the measured and calculated values of χ_ϵ are of the same order of magnitude. If the nonuniversal form of the equation for χ_ϵ from the theory is used (eq 3.15 in ref 1), the agreement is no better.

Table 4. Comparison of Theoretical and Experimental Values of χ_ϵ for Different Numbers of Arms of the Star

no. of arms p	$\chi_\epsilon \times 10^4$ (40 °C) exptl[a] h-star series	$\chi_\epsilon \times 10^4$ (40 °C) exptl[a] d-star series	$\chi_\epsilon \times 10^4$ (universal equation)[b]	$\chi_\epsilon \times 10^4$ (nonuniversal equation)
4	3.05	2.40	0.0421	
6	2.40	1.95	0.310	0.365
8	2.00	1.40	1.06	1.21
12	3.20	2.45	4.76	5.65

[a] Calculated by subtracting the value of χ_{eff} at 40 °C for the corresponding linear/linear blend from the value of χ_{eff} at 40 °C for the star/linear blend. [b] Determined using eq 1.

Table 5. Comparison of Measured and Theoretical Values of R_g

star	R_g (experimental),[a] Å	R_g (theory), Å
6-arm dPB	77 ± 1	81.0
12-arm dPB	63 ± 2	60.4

[a] Measured at a concentration of 1% star in linear matrix of matching overall chain length.

Values of χ_ϵ were estimated separately for the d-star series using the linear/linear blend data shown in Figure 3. These estimates are not as good because the microstructure of the stars varied slightly. They suggest a smaller magnitude for the long-chain branching effects, but the trend remains the same.

Perhaps the most obvious possible source of the discrepancy between the theory and the experimental data is the unknown degree of stretching present in the stars. Presumably the stretching grows more pronounced as the number of arms increases. As the importance of stretching changes, so too does the appropriateness of the current analysis, which assumes Gaussian arms. In particular, we note that Hutchings and Richards et al.[37] have contended that a dramatic increase in stretching of the arms of PB stars occurs when increasing p from 8 to 12. Therefore, we measured values of overall R_g for a 6-arm and a 12-arm deuterated PB star using Guinier analysis of data from blends having only 1% star in 99% linear hPB. The results are reported in Table 5. In fact, our experimental value of R_g for the six-arm star suggests no stretching, and the value for the 12-arm star suggests only a very modest stretching. After estimating the values of R_g for the arms from these experimental results, the values of χ_{eff} were derived from the data once again. The absolute values of χ_{eff} were changed by this refinement, but the variation in χ_{eff} with p was still not monotonic.

A second issue to consider is the degree to which the difference between χ_{eff}(star/linear) and χ_{eff}(linear/linear) may legitimately be ascribed solely to architectural differences. The change in architecture being considered really has two parts: the introduction of branch points and the simultaneous introduction of additional chain ends. The chemistry of the chain ends is not the same as that of the interior segments of the chains. Thus, changing the branching also changes, in a small way, the chemical makeup of the molecules, which can be thought of most generally as copolymers. All of the arm chain ends and one end of each linear chain are *sec*-butyl fragments remaining from the *sec*-butyllithium initiator used in the anionic polymerization. Koberstein and co-workers[43] have shown in a recent publication that for very short chains differences in chain end chemistry can manifest themselves in appreciable changes in the miscibility of blends of two linear components. We therefore make here three observations regarding the likelihood that chain ends alone could be responsible for the nonmonotonic behavior. First, for the chains studied here, which each contain approximately 2000 segments, the enthalpic effect one can estimate on the basis of simple solubility parameter arguments, and the density of chain ends in the system is orders of magnitude smaller than the effect observed for the four arm star. The solubility parameter, δ, for the *sec*-butyl chain end calculated using a group contribution approach is about 9.2 (cal/cm^3)$^{1/2}$ (assuming the same mass density as that for the bulk PB, 0.89 g/cm^3). For the PB segments one finds 8.04 (cal/cm^3)$^{1/2}$, so the value of χ_{AB} calculated for the interaction between a homopolymer of butyl units (A) and a homopolymer of butadiene units (B) would be 0.136. According to the copolymer theory,[44] one expects the interaction between two random copolymers with fractions y_1 and y_2 of butyl units to vary as $\chi(y_1,y_2) = (y_2 - y_1)^2\chi_{AB}$. Thus, the contribution to the interaction parameter due only to butyl ends is expected to be of order 3×10^{-7} for the case of the 4-arm star/linear blend and increase to only 4×10^{-6} for the 12-arm star/linear blend. First measurements of polybutadiene star/linear blends[41] in which the star ends have three other chemistries also suggest that butyl chain ends lead to the smallest end effect of the four possibilities studied so far.

Second, we note that the blends of PS stars studied previously[25] also had *sec*-butyl chain ends, and chain end effects were not apparent. If the chain ends were dominant in determining the behavior of the PB blends, one would anticipate that the effect of the ends would have been manifest in the PS blends as well.

Third, we expect that enthalpic contributions to χ_{eff} due to differences between the interior and end segments must affect the slope of χ_{eff} vs $1/T$ as well as the magnitude. With the PB star/linear blends there are some small variations in the temperature dependence among blends, suggesting that the changes in the blend thermodynamics with changes in the number of arms in the star may not be purely entropic in nature, but these differences are very small.

The final complication to consider is the effect of the small differences in microstructure among the samples used in the study. For reasons presented above we contend that the primary features of the behavior seen here cannot be ascribed simply to microstructure effects. Differences in the absolute values of χ_{eff} and χ_ϵ found for the two series of blends, those containing h-stars and those containing d-stars, are probably ascribable to microstructural effects, but the relative variations of χ_ϵ with number of arms cannot be rationalized with arguments concerning microstructure for the h-star blend series for which microstructure effects are rigorously excluded.

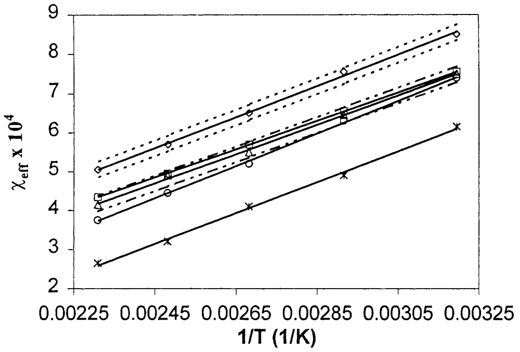

Figure 4. Variation in χ_{eff} with composition of star in blends of six-arm star hPB with linear dPB: $\phi_{star} = 0.20$ (◇), 0.38 (□), 0.53 (△), 0.67 (○), and 0.84 (*).

Table 6. Comparison of Theoretical and Experimental Values of χ_ϵ for Concentration Study

ϕ_{star}	$\chi_\epsilon \times 10^4$ (40 °C)[a]	$\chi_\epsilon \times 10^4$ (40 °C) using constant $\chi_{isotopic}$[b]	$\chi_\epsilon \times 10^4$ (universal equation)[c]
0.20	2.40	1.80	0.25
0.38	0.95	0.85	0.18
0.53	0.80	0.80	0.15
0.67	0.95	0.70	0.14
0.84	1.40	−0.55	0.12

[a] Calculated by subtracting the value of χ_{eff} at 40 °C for a linear/linear blend of the same concentration from the value of χ_{eff} at 40 °C for a star/linear blend. [b] Calculated by subtracting the value of χ_{eff} at 40 °C for the linear/linear blend 50hll from the value of χ_{eff} at 40 °C for a star/linear blend. [c] Determined using eq 1.

An attempt was also made to test the prediction of the theory that the magnitude of the entropic interaction in the star/linear blends should decrease with increasing concentration of star (with microstructure unchanging). The variation in χ_{eff} as a function of temperature for blends of 6-arm hPB with linear dPB at star concentrations of 20, 38, 53, 67, and 84 vol % is shown in Figure 4. The value of χ_{eff} decreases with increasing star concentration, and to that extent the data are consistent with expectations from theory. However, to make direct comparison with theory, values of χ_ϵ must be extracted from the measured values of χ_{eff}. For hydrogenous star volume fractions of 0.2, 0.53, and 0.84, data (in Figures 2 and 3) exist for the linear/linear isotopic blends at matching volume fractions of the hydrogenous component. For the other two star concentrations the value of χ_{eff} due to isotopic labeling alone was estimated by interpolation. Experimentally derived values of χ_ϵ are compared with theoretical values for a temperature of 40 °C in Table 6. While the value of χ_{eff} decreases monotonically with increasing star concentration, the value of χ_ϵ increases when ϕ_{star} increases from 0.67 to 0.84. This is due to a decrease in the experimentally determined value of $\chi_{linear/linear}$ when going from $\phi_h = 0.52$ to $\phi_h = 0.80$.

Recent theoretical discussions[38,39] of the experimentally observed concentration dependencies of χ_{eff} in linear/linear isotopic blends ($\chi_{isotopic}$) suggest that the curvature seen in χ_ϵ as a function of concentration is suspect. Both Kumar et al.[38] and Gujrati[39] argue that concentration variations in $\chi_{isotopic}$ such as reported here result from experimental uncertainties and that the value of $\chi_{isotopic}$ measured at $\phi_h = 0.5$ is the most reliable and provides the best estimate of the true effect. If this is true and values of χ_ϵ are estimated at all concentrations using a single value for $\chi_{isotopic}$, then the monotonic decrease in χ_ϵ with star concentration is recovered, as shown in the last column of Table 6. However, the question is then raised, "is the variation in χ_{eff} with star concentration itself an artifact of imperfect experimental procedure?" Experimental reports of concentration

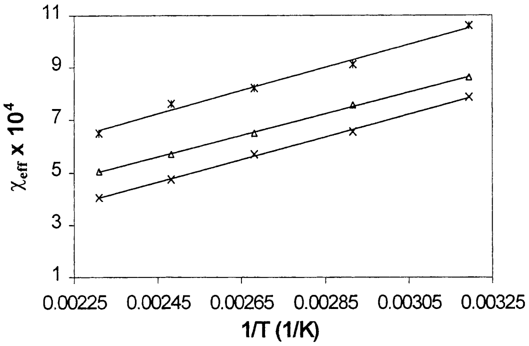

Figure 5. Demonstration of the effect of star arm size on χ_{eff} in blends of 20% 6-arm star hPB and 80% linear dPB (98K). Star arm length of 160 (h6slmw) (*), 380 (18h6s) (△), and 570 (h6shmw) (×).

dependences[44–47] for $\chi_{isotopic}$ have reported values for χ_{eff} which are either larger on both sides of $\phi_h = 0.5$ than at $\phi_h = 0.5$ or smaller on both sides, except for a study of high 1,2-addition PB blends by Sakurai et al.[2] which showed neither an upturn nor a downturn with concentration. In the present study $\chi_{isotopic}$ is found to be smaller away from the symmetric composition. In contrast, χ_{eff} for the star/linear PB blends decreases *monotonically* with star concentration, and this suggests that a concentration variation attributable to architectural effects really manifests itself here, though it is difficult to quantify. The experimentally determined absolute magnitudes of χ_ϵ for this series are an order of magnitude larger than the values predicted by the field theory. However, the relative changes in χ_ϵ with star composition are similar to those predicted by theory if correcting for isotopic (and microstructure) effects using the value of $\chi_{linear/linear}$ at $\phi_h = 0.52$.

A third parameter expected to impact the magnitude of thermodynamic interactions in star/linear blends is the size of the star arm. Gaussian field theory[1] predicts that the entropic interaction will decrease in magnitude with increasing arm size. As the fraction of segments in the star that are "far" from a junction point grows, the influence of the junction on segment–segment correlations in the star diminishes. PRISM calculations[14] suggest a more subtle variation. In Figure 5 data are shown for three blends in which the length of the deuterated linear component is 1640, but the length of arm in the hydrogenous star varies from 160 to 380 to 570 with the microstructure essentially constant. As the arm length increases, χ_{eff} decreases with the temperature dependence unchanged. The data for an analogous series (N_{arm} = 160, 310, 570) in which the stars are *deuterated*, shown in Figure 6, show the same trend. The microstructures of the d-stars vary slightly, but these variations do not alter the ordering of the curves or their relative slopes. However, the fact that the value of χ_{eff} is lower in each case for the blend in which the star is deuterated is consistent with the trend expected from an LCT calculation[5,42] intended to account for microstructure and labeling effects.

A quantitative comparison between experimentally derived values of χ_ϵ at 40 °C and those predicted by the theory of Fredrickson and co-workers[1] is made in Table 7. To obtain an experimental value for χ_ϵ, an estimate of $\chi_{linear/linear}$ (for sample 18hll) was subtracted from the value of χ_{eff} measured for the h-star/d-linear blend in the series for which the microstructures of the star and linear matched and were essentially unchanging. The rate of decrease in the value of χ_ϵ with increasing arm length is slower in the experimental data. The experimental values are also larger than the theoretical values by a factor of 5–10. Thus, once again the trend predicted by the Gaussian field theory is substantiated, but there is not quantitative agreement.

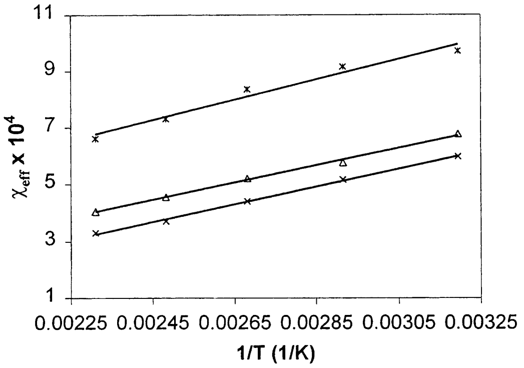

Figure 6. Effect of star arm size on χ_{eff} in blends for which the *star* is deuterated. Composition of the blend is 16% 6-arm star dPB and 84% linear hPB (86K). Star arm length is 160 (d6slmw) (*), 310 (18d6s) (△), and 570 (d6shmw) (×).

Table 7. Comparison of Theoretical and Experimental Values of χ_ϵ for Varying Length of Star Arm

length of arm N	$\chi_\epsilon \times 10^4$ (40 °C) experimental[a]	$\chi_\epsilon \times 10^4$ theoretical[b]
160	4.50	0.947
380	2.40	0.300
570	1.75	0.140

[a] Calculated by subtracting the value of χ_{eff} at 40 °C for the linear/linear blend from the value of χ_{eff} at 40 °C for the star/linear blend. [b] Calculated using universal expression in eq 1.

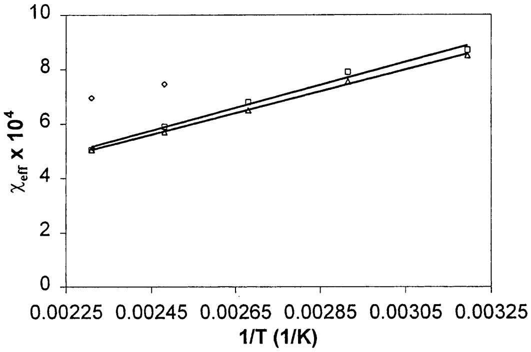

Figure 7. Variation in χ_{eff} of star/linear blends with increasing size of the linear component for blends of 20% 6-arm star hPB (121K) and 80% linear dPB. N_{linear} = 280 (18h6l) (□), 1640 (18h6s) (△), and 5440 (18h6h) (◇).

Experimental results clearly contradict theoretical expectations on a fourth point—the variation of χ_ϵ with linear chain size. The Gaussian field theory predicts that χ_ϵ should decrease as the size of the linear chain increases (as seen from the more complete expression for the interaction parameter, eq 3.15 in ref 1). PRISM calculations[14] suggest an even stronger trend in the same direction. Experiments show the opposite trend. To investigate the effect, the length of a deuterated linear chain was varied from 280 to 1640 to 5440 in blends with 20% hydrogenous six-arm star. As shown in Figure 7, when N of the linear chain increases from 280 to 1640 the variation in χ_{eff} is within the experimental uncertainty. We believe that this reflects the fact that while the d-linear chains of length 1640 and 5440

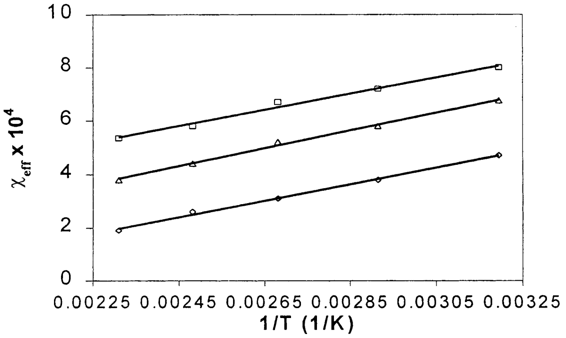

Figure 8. Variation in χ_{eff} of star/linear blends with increasing size of the linear component for a series nearly analogous to that of Figure 7, but with the star deuterated. Blends contain 16% 6-arm star dPB (110K) and 84% linear hPB with N_{linear} = 330 (18d6l) (◇), 1620 (18d6s) (△), and 6290 (18d6h) (□).

have matching microstructure (82% 1,4), the amount of 1,4-microstructure in the d-linear chain of length 280 is larger (ca. 94%). An LCT calculation[42] and comparison with other data[5] suggests that this difference, by itself, should lead to a smaller interaction parameter in $N = 280$ blend. However, the calculated effect far exceeds that which is observed. The change in χ_{eff} upon increasing the linear chain length from 1640 to 5440 is quite unambiguous, however. At temperatures of 40, 70, and 100 °C, the sample with linear dPB of $N = 5440$ is phase-separated, as evidenced by a divergence in the scattering intensity at small values of q (not shown). While the Gaussian field theory anticipates that phase separation should be unlikely for a blend with a six-arm star, it is important to keep in mind that the observed separation results from two driving forces: entropic effects (both short-chain and long-chain branching) and the enthalpic isotopic effect. The entropic effects alone are clearly insufficient to drive separation as is evidenced by the fact that the sample becomes miscible at higher temperatures. An attractive aspect of this observation of phase separation is that it locates a boundary of the thermodynamic behavior in these blends quite apart from any questions about the precision with which a value of χ_{eff} can be extracted from the data. Future work will further define the temperature of phase separation as a function of arm number. Even at 130 and 160 °C the values of χ_{eff} are seen to remain large, reflecting that the system is close to the spinodal condition. By way of comparison, a Flory–Huggins (FH) calculation of the critical value of χ expected for a blend of chemically distinct linear components with sizes the same as in the case of the star/linear blend predicts a critical value of the interaction parameter, χ_c, of 6.0×10^{-4}. The FH theory predicts a critical concentration, in terms of the smaller component, of $\phi_c = 0.61$, so the experimental system is probably far from the critical composition. The value of χ_{eff} at which phase separation is seen for the star/linear blend is certainly higher than the value of χ_c calculated for the corresponding linear/linear blend.

Data for a series of blends in which the linear chain length was once again varied, but the labeling was swapped to the star, are shown in Figure 8. The analogy is not precise, as the deuterated star has somewhat smaller arms ($N_{arm} = 310$) (and overall molecular volume) than its hydrogenous analogue ($N_{arm} = 380$) and should therefore be less prone to phase separation. The linear chain varies in length from 330 to 1620 to 6290 with the linear chain microstructure constant and the microstructure of the deuterated star essentially the same as that of the linear chains. Once again χ_{eff} increases with N_{linear}, but the magnitude of the effect is even larger. The value of χ_{eff} for the blend with the largest linear chain is nearly the same as that shown in Figure 7 for the blend with unlabeled star. Yet the blend with the deuterated star remains miscible at room temperature. This is the case despite the fact that the hydrogenous “high molecular weight” linear chain has $N = 6290$, while the deuterated “high molecular weight” linear chain has only $N = 5440$—a difference of about 14%. The value of χ_c for a corresponding linear/linear blend given by the Flory–Huggins theory is 6.4×10^{-4} ($\phi_c = 0.64$). Thus, the blend with the deuterated star ($\phi_{star} = 0.16$) is slightly farther off-critical in composition than is the blend with the hydrogenous star that phase separates ($\phi_{star} = 0.20$). It is possible that the small variations in actual composition and critical composition between the two blends are sufficient for the one blend to just be miscible while the other is not. More important, however, is probably the fact that in Figure 8 the microstructures of the two components are more closely matched, providing miscibility up to larger size of the linear component.

Our final observations regard the magnitude of the architecture effect in the PB blends in general as compared to the architecture effect in the PS blends. The values of χ_{eff} for the PB blends are always markedly higher than those for PS star/linear blends[25] with corresponding numbers of arms in the stars. This is due primarily to a larger contribution to χ_{eff} from the isotopic effect in the case of PB *and* to a larger architectural effect in PB. Microstructural differences contribute also to the interaction parameters but are not a controlling feature. Comparing data at 160 °C and using the same segment volume for both PS and PB, one finds that the interaction due to labeling and microstructure mismatch in the linear/linear isotopic PB blend is 4 times the interaction due to labeling in the PS blend. This finding is consistent with earlier observations on isotopic effects in PS and PB linear/linear blends by Bates and coworkers.[48] On the other hand, the magnitude of the architectural effect in the 8-arm star hPB/linear dPB blend is roughly 3.5 times the magnitude of the architectural effect seen in a PS blend with an 8-arm star at the same temperature.[25]

Conclusions

An experimental determination of χ_{eff} for blends of star-branched and linear PB shows two discrepancies between experiment and theory. First, the contribution to the thermodynamic interaction arising from architectural differences between the components, χ_ϵ, does not vary monotonically with number of arms in the star when compared at constant overall star chain size and matching star and linear chain lengths. This behavior was not predicted by a Gaussian field theory and is distinct from the behavior observed for PS blends, raising the possibility that there may be nonuniversal aspects in the thermodynamic interaction χ_ϵ arising from architectural differences in chains. Experimental results also contradict the Gaussian field theory expectation that χ_ϵ should decrease with increasing size of the linear chain. Qualitative agreement with the Gaussian field theory of Fredrickson et al.[1] is found on two counts: χ_ϵ decreases with increasing concentration of star (when assuming $\chi_{linear/linear}$ is constant with composition), and χ_ϵ decreases with increasing size of star arms. The boundary between the single and two-phase regions of the phase diagram has been located for one particular blend of 6-arm star hPB mixed with linear dPB having a molecular weight 3 times that of the star. In comparison to comparable PS star/linear blends the estimated values of χ_ϵ for a PB blend of an 8-arm star and linear chain are about 3.5 times as large.

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