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Effective Interaction Parameter between Branched and Linear Polystyrene

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ABSTRACT: Values of the effective interaction parameter (χ) between regular, long-branched polystyrene chains and their linear analogues were measured with small-angle neutron scattering for several star-branched chains and one comb-type polymer. The contribution to this interaction due to architecture alone increases monotonically with star functionality for the set of polymers studied here. The interaction appears to be less sensitive to variations in arm size than would be expected from fluctuation theory predictions by G. H. Fredrickson, A. Liu, and F. S. Bates (Macromolecules 1994, 27, 2503) for a purely entropic interaction due to architecture. The change in χ with the volume fraction of the star in the blend is in agreement with the theory, however. The magnitudes of the interaction in the star/linear blends are small enough that bulk phase separation is unlikely, whereas that in the comb/linear blend is about 20 times higher for the same number of arms. Thus, bulk phase separation can be readily expected for comb/linear blends at commercially relevant values of molecular weights. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part B: Polym Phys* 39: 2549–2561, 2001

Keywords: star polymers; long-chain branching; phase behavior; small-angle neutron scattering (SANS); thermodynamics

INTRODUCTION

The bulk thermodynamic behavior of binary polymer blends is sensitive to a number of subtle differences between the components, including

the chemical microstructure,^{1–3} tacticity,⁴ and degree and type of isotopic labeling.⁵ Small-angle neutron scattering (SANS) measurements have played an important role in studies of these effects; therefore, isotopically labeled blends have been the focus of study. Differences in branching between the two components can also lead to thermodynamic interactions in the bulk,⁶ and this effect is the focus of the work presented here. Comparatively recent theoretical work has been done for blends containing regular stars^{7,8} or regular combs^{6,8} and for blends of linear and randomly branched homopolymers.^{9–11}

Only a few experimental studies^{12–18} have been done on the thermodynamics of blends of branched and linear chains. One grouping of

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these studies comprises those dealing with short-chain branching,^{12,13} whereas another has considered blends with long-chain-branched components.^{14–18} Both Faust et al.¹⁴ and Russell et al.¹⁵ considered the change in the behavior of miscible blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) when the PS architecture was changed from being linear to star-shaped. Faust et al. argued that during the change from a linear PS to a 22-arm star, the temperature of the minimum in the cloud-point curve did not shift (once corrections for sluggish kinetics were considered), but the shape of the cloud-point curve changed subtly. Russell et al.¹⁵ found that the minimum in the cloud-point curve moved up by about 10 °C when linear PS in a PS/PVME blend was replaced by a well-defined 4-arm PS star. Furthermore, replacing the PS star with a deuterated star led to an additional increase of about 10 °C. The primary focus of the work by Russell et al. was a consideration of the impact of changing the architecture on concentration fluctuations in PS/PVME blends. However, Russell et al. reported having measured the SANS blends of normal star and deuterated star PS for a range of compositions, showing a single scattering curve for the 50/50 blend. Their objective was to clarify the appropriate single-chain scattering function for the star polymers. The scattering was not reported in absolute units, and no value of the interaction parameter χ for the star/star blend was reported.

To properly understand the bulk interaction attributable purely to architectural effects, we initiated a systematic study of the value of χ in blends of well-defined star and linear homopolymers that were as similar in chemistry as possible. Such measurements are essential for a comparison with existing theory and to aid in the subsequent refinement of the theory. In a brief report of initial experimental results for the interaction found in blends of 4-arm stars and linear PS analogues,¹⁸ we noted that the magnitude of the interaction, although small, was measurable and was close in magnitude to that anticipated by the theory of Fredrickson et al.⁶

Fredrickson et al.⁶ considered athermal binary blends in which the components were identical in chemistry but had various architectures, that is, star-branched or comb-branched homopolymers mixed with linear chains compared with linear/linear homopolymer blends. The conventional interaction parameter, χ , is expressed in terms of an invariant, α , which is independent of how the

statistical segments of the blend components are defined:^{19,20}

$$\chi = \alpha(\nu_1\nu_2)^{1/2}, \quad (1)$$

where ν_1 and ν_2 represent the volumes of the statistical segments of the blend components. These authors assumed that α may be thought to contain two contributions, an enthalpic contribution, $A(\phi)$, and an entropic contribution, $B(\phi)$, with

$$\alpha = A(\phi)/T + B(\phi). \quad (2)$$

For blends of star/linear homopolymers, the entropic contribution to α , denoted α_e , may be expressed in terms of the number of arms, p , and the arm radius of gyration, R_2 (radius of gyration $R_2^2 = N_2b^2/6$, where N_2 is the number of segments in one arm and b is the segment length). For stars with a large number of short arms or for large homopolymers for which the condition $(p-3)(R_1/R_2)^2 \gg 1$ is met, where R_1 is the radius of gyration of the linear chain, the universal form of α_e is given by

$$\alpha_e \approx \frac{1}{64\pi\sqrt{2}} \frac{(p-3)^{3/2}}{(1-\phi_1)^{1/2}R_2^3} \quad (3)$$

where ϕ_1 is the volume fraction of the linear component in the binary blend. Fredrickson et al.⁶ concluded that χ should be small for star branched polymers with linear analogues, with the size of the effective interaction increasing with an increasing number of arms and an increasing disparity between the size of the linear chains and the size of the star arms. The effect for bulk miscibility is subtle, and bulk phase segregation is predicted to be unlikely for modest numbers of arms of polymeric length.

For comb/linear homopolymer binary blends,⁶ the restriction that only large numbers of arms be considered is removed from the theory. The authors considered combs with regularly spaced branches of M statistical segments, spaced along the backbone every L statistical segments. The value of α_e may be much larger because there are more branched points per molecule than for the star homopolymers. Bulk phase separation is favored for combs with closely spaced short branches. For overall molecular volumes of the linear and comb polymers that are comparable and for L comparable to M , phase segregation is

predicted to occur when M is about $N_1^{2/3}$, where N_1 is the number of segments in the linear chain. Fredrickson et al.⁶ concluded that for linear/comb homopolymer blends, phase separation should be easily accomplished in practice. Experimental studies on blends of linear and short-branched polyethylenes^{12,13} have shown that for low branch contents [<4 branches/100 backbone carbon atoms for weight-average molecular weight (M_w) $\sim 10^5$], the mixtures are homogeneous, whereas for higher numbers of branches (>8 branches/100 backbone carbon atoms), the blends are found to phase-separate. Very recently, Chen et al.²¹ showed that phase separation may be observed in blends of highly branched comb poly(ethylene-*r*-ethylethylene) with a linear analogue.

For model polyolefins, theoretical and experimental studies^{5,22–25} suggest that the interactions between saturated hydrocarbons of differing molecular architectures may often be satisfactorily rationalized with simple enthalpic arguments. For isotopic blends of saturated hydrocarbons, χ has been found to increase when the polymer with more short-chain branching is deuterated.⁵ These findings are consistent with a simple theory expressing χ in terms of the solubility parameters of a blend's components. Deuteration reduces the solubility parameter of a component slightly.⁵ Changes in molecular architecture leading to changes in contact density also alter solubility parameters. Further support for this view is provided by simulations performed by Maranas et al.^{24,25} These authors suggested a link between the thermodynamic interactions, which are found to be primarily enthalpic in nature, and differences in local packing. A correlation among regular mixing, thermodynamic interaction parameter, χ , and solubility parameters is found.

In the study at hand, the thermodynamic interactions between regular, long-branched PS and linear analogues with similar overall molecular weights are quantified for a series of blends with SANS. The primary objective is to provide experimental results on well-defined blends that can serve as a basis for comparison in the development of theoretical treatments. Key to this study are the preparation of the requisite polymers of well-defined architectures and molecular weights and the use of isotopic blends. Although the primary focus is on the change in interaction with the number of arms and type of branching (star vs comb), changes in χ with labeling schemes and blend compositions are addressed as well.

EXPERIMENTAL

Materials

Linear hydrogenous and deuterated polystyrenes (hPS and dPS, respectively), as well as an 8-arm star-branched polymer, were purchased from Polymer Source (Dorval, Quebec).²⁶ Characterization of the linear homopolystyrenes was performed independently by Polymer Source and at the University of Akron and Goodyear Tire & Rubber Co. Star PSs of various numbers of arms were synthesized at the University of Akron by living anionic polymerization with the so-called arm-first method. Star macromolecules with functionalities of up to six were obtained by the reaction of stoichiometrically monofunctional living poly(styryl)lithium with multifunctional electrophilic deactivators with chlorosilane linkages. Star polymers with higher functionalities (up to 21) were obtained by the polymerization of a small amount of divinylbenzene (DVB) isomers initiated by living poly(styryl)lithium chains. The linking reaction with DVB can be thought of as a block copolymerization of DVB followed by linking reactions of carbanionic chain ends with the pendant vinyl groups in the DVB block. Hydrogenous and deuterated stars were synthesized with both types of linking agents.

The star-branched polymers were obtained first by the synthesis of poly(styryl)lithium arm precursors of known, narrow molecular weight distributions with anionic polymerization in benzene initiated with *sec*-butyllithium.²⁷ The poly(styryl)lithium arms were then linked with the linking agent to form stars. We kept the chemical nature of the silane-linked stars as close to that of the linear PS chains as possible by not performing crossover to diene monomers before coupling. The arms did carry *sec*-butyl fragments at their outer ends. Coupling reactions with 1,2-*bis*(methyl-dichlorosilyl)ethane, 1,2-*bis*(trichlorosilyl)ethane, and *tris*(ethyltrichlorosilyl) methane were intended to produce stars with functionalities of four, six, and nine, respectively. Linking was performed with an excess of arm precursor to drive the coupling reactions toward completion. Because a crossover to diene was not used to promote coupling, coupling did not always go to completion with the last two silane coupling agents, even in the presence of excess arm precursor. The products were fractionated (by selective precipitation) at least two times to eliminate uncoupled arms. To determine the number of arms, we char-

Table I. Molecular Characterization of Star and Linear Polymers

Polymer	Sample	Arms	M_n (g/mol) ^a	R_g (Å)	N^b	M_w/M_n	
Linear hPS and dPS							
Hydrogenous PS	hPS	—	50,000	60	484	1.03	
Hydrogenous PS	hPS	—	132,000	97	1270	1.03	
Hydrogenous PS	hPS	—	212,000	123	2040	1.04	
Hydrogenous PS	hPS	—	231,000	129	2220	1.04	
Deuterated PS	dPS	—	143,000	98	1280	1.05	
Deuterated PS	dPS	—	252,000	130	2250	1.08	
Deuterated PS	dPS	—	391,000	161	3490	1.05	
Deuterated PS	dPS	—	674,000	212	6010	1.08	
Silane-linked PS star							
Deuterated 4-arm star	d4s	4	100,000	65	893	223/arm	1.02
Hydrogenous 4-arm star	h4s	4	85,000	62	817	204/arm	1.02
Deuterated 5-arm star	d5s	5	164,000	76	1460	293/arm	1.11
Hydrogenous 5-arm star	h5s	5	131,000	70	1260	252/arm	1.19
Deuterated 6-arm star	d6s	6	157,000	68	1410	234/arm	1.10
Hydrogenous 6-arm star	h6s	6	192,000	75	1710	286/arm	1.08
Hydrogenous 8-arm star	h8s	8	390,000	98	3750	469/arm	1.07
DVB-linked PS star							
Hydrogenous 12-arm	hDVB12	12	140,000	49	1350	112/arm	1.04
Hydrogenous 14-arm	hDVB14	14	290,000	65	2790	200/arm	1.09
Hydrogenous 17-arm	hDVB17	17	190,000	48	1830	107/arm	1.06
Hydrogenous 21-arm	hDVB21	21	650,000	81	6250	289/arm	1.17
Deuterated 15-arm	dDVB15	15	200,000	50	1790	119/arm	1.04
Deuterated 16-arm	dDVB16	16	200,000	49	1790	112/arm	1.05
Comb PS polymer							
Hydrogenous 6-branch	h6c	6	69,000	46	663	63/arm	1.35

^a Averages of GPC results from at least two laboratories with an uncertainty of $\pm 3\%$. The average molecular weights were derived from GPC by simultaneous comparison with inline LS measurements and calibration with linear standards corrected for the functionality reported here.

^b Number of segments in the overall chain or arm, as designated.

acterized the molecular weight and polydispersity of the final products, the stars, by gel permeation chromatography (GPC) and light scattering (LS). The 8-arm star that was purchased also had initiator fragments at the ends of the arms and had short sequences of diene (isoprene) repeat units on the core end of each arm. The purchased star was characterized in the same manner as the other star polymers. In the DVB-linked stars, the variation in star functionality is somewhat larger than for the silane-linked stars. The functionalities given in Table I, therefore, represent average values.

A 6-branch comb PS was synthesized at IBM Laboratories²⁸ with living free-radical polymerization. The comb polymer had a larger polydispersity index than did the star polymers, and the number of arms per molecule varied more than for the stars. The branches were attached to the backbone with a benzyl group ($C_6H_5-O-CH_2$ PS arms), which allowed us to cleave off the branches

to check their molecular weight and polydispersity. An alkoxyamine functionality was present at the outer end of each branch.

Details of the polymer molecular characteristics for all the polymers used are summarized in Table I. GPC was measured independently in three laboratories. In two laboratories, GPC was coupled directly with a laser light scattering detector. The reported molecular weights are number-average molecular weights (M_n 's) obtained by the averaging of the GPC results from at least two laboratories. The GPC measurements actually provided values of the relative hydrodynamic volumes. They were cross-checked by LS in the following way. Relative hydrodynamic volumes were converted to actual hydrodynamic volumes by calibration of the GPC with linear standards. To obtain a molecular weight, we had to assume an architecture (functionality) for each molecule. For each polymer, when we assumed the functionality reported in Table I, there was good agreement

Table II. Blend Nomenclature and Composition and Molecular Weight of the Components

Sample	Component 1	Weight Percentage of 1	N_1^a	Component 2	N_2^b
dPS100k	dPS143k	18	1280	hPS132k	1270
hPS100k	hPS123k	18	1270	dPS143k	1280
d4s100k	d4s	18	893	hPS132k	1270
h4s100k	h4s	18	817	dPS143k	1280
h5s200k	h5s	18	1260	dPS252k	2250
d5s200k	d5s	18	1460	hPS231k	2220
50d6s200k	d6s	50	1410	hPS231k	2220
d6s200k	d6s	18	1410	hPS231k	2220
h6s200k	h6s	18	1710	dPS252k	2250
h6s100k	h6s	18	1710	dPS143k	1280
h8s400k	h8s	18	3750	dPS391k	3490
hDVB12	hDVB12	18	1350	dPS143k	1280
hDVB14	hDVB14	18	2790	dPS252k	2250
hDVB17	hDVB17	18	1830	dPS252k	2250
hDVB21	hDVB21	18	6250	dPS674k	6010
dDVB15	dDVB15	18	1790	hPS212k	2040
dDVB16	dDVB16	18	1790	hPS212k	2040
h6c	h6c	18	663	dPS50k	484

^a Chain length of component 1.^b Chain length of component 2.

between the value of M_w implied by the GPC and the M_w measured directly by inline LS. There were always small discrepancies between the LS values and GPC values, and observations on the magnitudes of these discrepancies were used to determine the uncertainties stated for the molecular weights.

The chain lengths in terms of the numbers of segments in a chain, N , are given for a segment volume of 100 cm³/mol. For the stars, N_{arm} is given as well. Radii of gyration, R_g , for the linear chains were calculated with

$$R_g^2 = \frac{a^2 N}{6},$$

where a is the length of the statistical segment taken as $a = 6.7 \text{ \AA}^{29}$ for both the star and linear chains. Radii of gyration for the stars were estimated by correction of the calculated R_g for the corresponding linear chain by the g factor for the appropriate number of arms with the theory of Zimm and Stockmayer.³⁰

Sample Preparation

Blends containing 18 wt % star (either hydrogenous or deuterated) with 82 wt % of the contrast-

ing linear analogue were prepared by dissolution of the polymers in toluene. One sample blend of the composition 50 wt % was also prepared. The solutions were filtered three times with 0.45- μm -pore nylon filters and then cast into films in Teflon[®] beakers, with 7 days allowed in a fume hood for evaporation of the solvent. The films were then dried under roughing vacuum (0.1 Pa) at 70 °C for 7 days to ensure removal of excess toluene. The dried polymer blend films were pressed inside brass rings 1 mm thick. To obtain transparent, bubble free films, we pressed the samples at 120 °C under 1130 kg between pieces of Mylar[®] foil.²⁶ A summary of the samples investigated and the nomenclature used is shown in Table II.

Measurements

SANS measurements were performed on the NG3 30-m SANS instrument at the Cold Neutron Research Facility of the National Institute for Standards and Technology (Gaithersburg, MD). A neutron beam with a wavelength λ of 6 Å with a resolution of $\Delta\lambda/\lambda$ of about 0.150 full width at half-maximum was used. The chosen instrumental setup used a sample-to-detector distance of 13 m, which provided a range of values of the scattering vector q ($4\pi\sin\theta/\lambda$) of 0.005–0.05 Å^{−1} with a resolution³¹ of approximately 0.005 Å^{−1}.

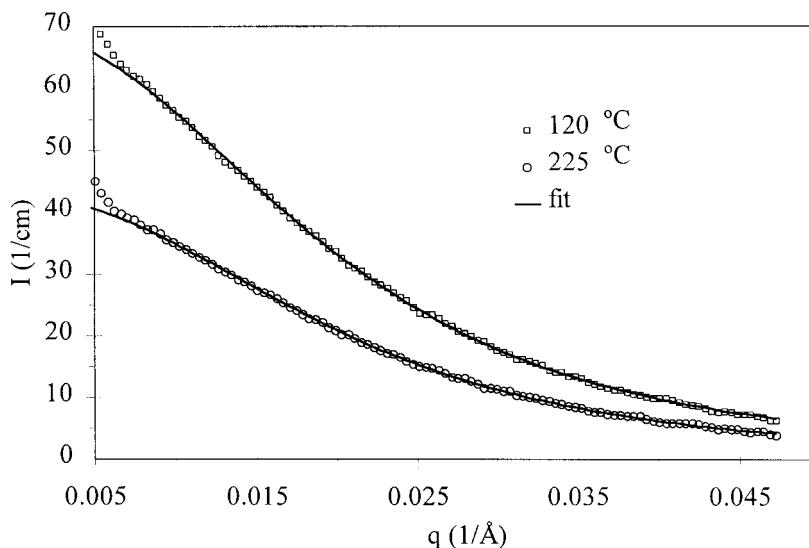


Figure 1. SANS experimental data with fits to the RPA (—) for a blend of 18 wt % deuterated 6-arm star in a matrix of linear hPS of symmetric molecular weight (sample d6s200k) for two temperatures: (\square) 120 and (\circ) 225 °C. Error bars are smaller than the symbols.

The samples, sandwiched between quartz windows, were placed in sample holders provided by the National Institute of Standards and Technology laboratory. The sample holders were then placed inside a seven-slot computer-controlled aluminum sample changer, the temperature of which could be controlled between room temperature and 225 °C (± 0.5 °C). This sample changer sat inside a stainless steel vacuum chamber that was evacuated to a dynamic vacuum of about 1 Pa. Equilibration times of about 15 min were allowed after each set-point change to ensure thermal equilibrium.

In addition to measurements of the samples, other measurements were performed for reduction and normalization of the data. These included measurements of the empty cell (quartz windows only), the blocked beam and empty beam (for background estimation), standard samples, sample transmission, and standard and empty cell transmissions. All measurements were performed under the same conditions and with the same instrument configuration.

RESULTS AND DISCUSSION

Examples of scattering curves obtained for an 18 wt % star/linear blend at 120 and 225 °C are given in Figure 1. The absolute coherent scattering in-

tensity, $I(q)$, obtained from a single-phase binary isotopic polymer mixture is related to the structure factor $S(q)$ by

$$[I(q)]_{\text{measured}} = \frac{(b_1 - b_2)^2}{(V_1 V_2)^{1/2}} S(q) \quad (4)$$

where b_i and V_i are the segment scattering length and segment molar volume of the blend component i , respectively, and q is the scattering vector. For isotopic PS, V_D and V_H are nearly equal,³² and so corrections in b or $S(q)$ are not necessary. As shown previously,¹⁸ scattering curves obtained for blends of star and linear PS of similar molecular weights can be fit well with structure factors derived for linear chains and regularly branched n -arm stars in the incompressible random phase approximation (RPA)³³ and with a single interaction parameter. If we assume Gaussian statistics for the polymer coils in both cases, branched and linear, the measured intensity is given by

$$\frac{\left[\left(\frac{b}{\bar{V}} \right)_1 - \left(\frac{b}{\bar{V}} \right)_2 \right]^2}{[I(q)]_{\text{measured}}} = \frac{1}{\phi_1 N_1 S_1(R_{g,1}, q)} + \frac{1}{\phi_2 N_2 S_2(R_{g,2}, q)} - \frac{2\chi}{V_0}, \quad (5)$$

where V_1 is the segment molar volume ($= V_2 = V_0 = 100 \text{ cm}^3/\text{mol}$), ϕ_i is the volume fraction of species i , N_i is the number of segments per chain, $(b/V)_i$ is the scattering length density for component i , and χ is the effective interaction parameter representing the strength of interaction between molecules on a per segment basis.

For branched molecules, N can be expressed in terms of the number of branches, N_b ($N_b = p$), and the number of segments per arm, n , as $N = N_b n$. The assumption of Gaussian statistics for the arms of the stars is incorrect but should not be a major difficulty for low numbers of arms. Stretching of the arms away from this limiting behavior increases as p increases. The structure factors for the star (S_{star}) and linear (S_{linear}) PS were obtained through brief manipulation of an expression given by Hammouda:³⁴

$$S_{\text{star}} = \frac{1}{N_b} P_{11} + \frac{N_b - 1}{N_b} P_{12} \quad (6)$$

$$S_{\text{linear}} = \frac{2(e^{-xN} - 1 + xN)}{(xN)^2} \quad (7)$$

where

$$P_{11} = \frac{2(e^{-xn} - 1 + xn)}{(xn)^2} \quad (8)$$

captures the intrabranch correlations,

$$P_{12} = \left(\frac{1 - e^{xn}}{xn} \right)^2 \quad (9)$$

describes the interbranch correlations, and $x = (qa)^2/6$, where a is the statistical segment length previously measured²⁹ for linear PS as $a = 6.7 \text{ \AA}$. Various temperature dependencies have been reported for the segment size. We followed Boothroyd et al.,³⁵ who reported a temperature coefficient of $0.0 \pm 0.1 \times 10^{-3} \text{ K}^{-1}$. [The temperature coefficient is defined as $d \ln(\langle S^2 \rangle_0)/dT$, where $\langle S^2 \rangle_0$ is the unperturbed mean square radius of gyration.] We use the same statistical segment length for the star as well. When the value of the statistical segment length, which manifests itself predominantly in the scattering at higher values of q , is taken to have a known value, the scattering curves can be fit with the single interaction parameter χ . Scattering was obtained for a number of star/linear PS blends and for two linear/

linear isotopic blends of PS and a comb/linear blend of PS. In general, it was found to be necessary to allow for a multiplicative shift factor of order unity for all the data to provide for the degree of agreement seen in Figure 1. This correction factor accounts for random and systematic errors during measurement, including loss of intensity due to the formation of bubbles in the samples at high temperatures. Values of the interaction parameter varied linearly with inverse temperature for all samples.

The variations of χ with temperature for blends of hydrogenous silane-linked stars in matrices of linear dPS of similar molecular weights are summarized in Figure 2 for functionalities of four¹⁸ to eight. Results obtained for a blend of 18 wt % linear hPS in a matrix of linear dPS are also included for comparison. For all cases shown in Figure 2, the interaction parameters are positive, and of the order of 10^{-4} , with the χ values increasing as the arm functionality of the stars increases. The results obtained for the isotopic linear/linear blend compare well with results obtained by Bates and Wignall³² for an isotopic linear/linear PS blend of a composition (50 vol %) and chain lengths ($N = 6.57 \times 10^3$ for the deuterated component and $N = 4.97 \times 10^3$ for the hydrogenous component) differing from ours. The estimated uncertainty of $\pm 0.2 \times 10^{-4}$ in the χ values resulting from uncertainties in the molecular weights and absolute intensity calibration is shown also. The difference between a curve for the 4-arm star/linear blend and the curve for the linear/linear isotopic blend represents the contribution to χ due to architecture alone. An average value for the architecture contribution is found by a consideration of the results for both possible labeling schemes in the star/linear blend. The contribution to χ due to architectural effects for the 4-arm star/linear blend is just large enough to be distinguished. However, for larger numbers of arms, the contribution to the interaction parameter due to architecture with respect to linear/linear blends is clear. It is apparent that there is an enthalpic contribution to χ in each case, as the curves have non-zero slope. The slope increases slightly as functionality increases in this plot, but when all the data are considered (discussed later), it appears that the temperature dependence (slope) is nearly invariant with the architectures of the blend components. Thus, the enthalpic contribution must be nearly entirely due to isotopic labeling. For this reason, the contribution to χ due

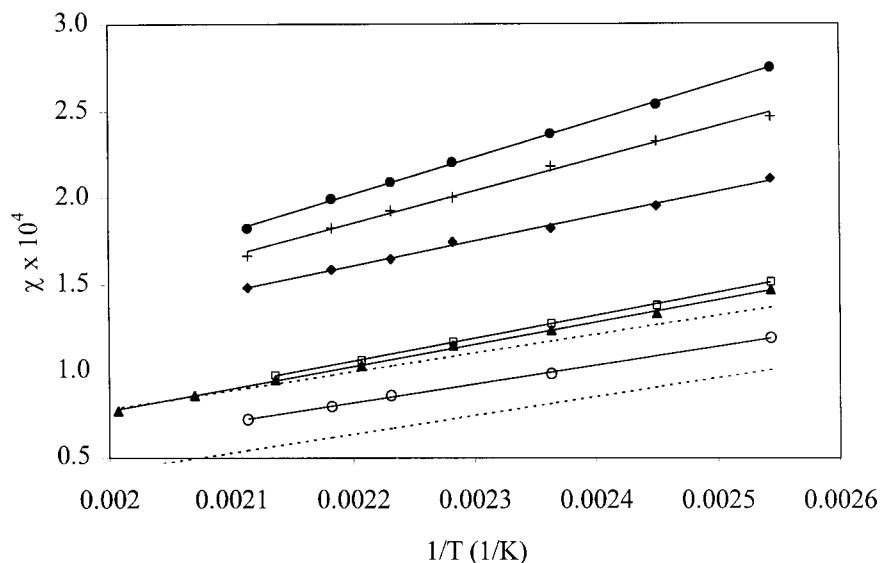


Figure 2. χ as a function of temperature for blends containing 18 wt % of the hPS component, linear or star-shaped: (○) hPS100k, (▲) h4s100k, (□) h5s200k, (◆) h6s200k, (+) h6s100k, and (●) h8s400k. Uncertainty bands (---) for the linear/linear hPS/dPS blend (—) corresponding to $\pm 0.2 \times 10^{-4}$ are also shown.

to isotopic labeling alone was taken to be the same for all blends.

Limitations in the determination of χ and the contribution of architecture effects to χ arise from the precision of the molecular weight measurements and the differences in the detailed chemistry of stars versus the linear chains. The first issue is an important one because the precision of the determination of such small values of χ depends sensitively on the precision of the molecular weight determinations. However, in this study M_n 's were determined independently in at least two labs with both LS and GPC. Uncertainty in the molecular weight determinations ($\pm 3\%$) was included in the calculation of uncertainty in χ . Uncertainties in χ due to imprecision in molecular weight measurements have been mitigated in one way by using the same linear polymer in both the linear/linear blends and star/linear blends whenever possible. The second issue, a less important one, is the presence of initiator fragments at the end of each arm and the presence of a core that is chemically different from the linear chains. When structure factors incorporating these contributions were calculated for the star components, fits of the data to the RPA gave rise to identical values of the interaction parameter as for the cases in which the core and chain ends were ignored. Moreover, even for the case of the largest functionality of the silane-linked stars,

the ratio of volumes of PS repeat units to initiator fragments was about 1000:1, whereas that in the 8-arm star was about 4000:8. We consider this difference to be negligible in determining the value of the effective interaction parameter.

The data in Figure 2 also reveal information on the changes wrought in α_e by variations in the molecular weight of the linear chain in the star/linear blend. For the 6-arm stars, two different blends with two linear chain molecular weights were made. One blend contains linear chains with $M_n = 143,000$ g/mol, and the other blend (h6s200k) contains linear chains with $M_n = 252,000$ g/mol. The interaction parameter decreases as the linear chain molecular weight increases. The effect is also evident for the 5-arm star blend, but in a less obvious way. The 5-arm star blend was composed with a linear polymer with a molecular weight nearly twice that of the star. We believe that this is the reason the value of χ for the hydrogenous 5-arm star blend is so similar to that of the 4-arm star blend. If the molecular weights of the star and linear chains had been matched, the value of χ for the 5-arm star blend would have been markedly higher. This will be checked in future measurements.

A similar trend in χ is obtained for blends of 18 wt % deuterated silane-linked star with linear PS, as seen in Figure 3. The interaction parameter increases with the number of arms in the star.

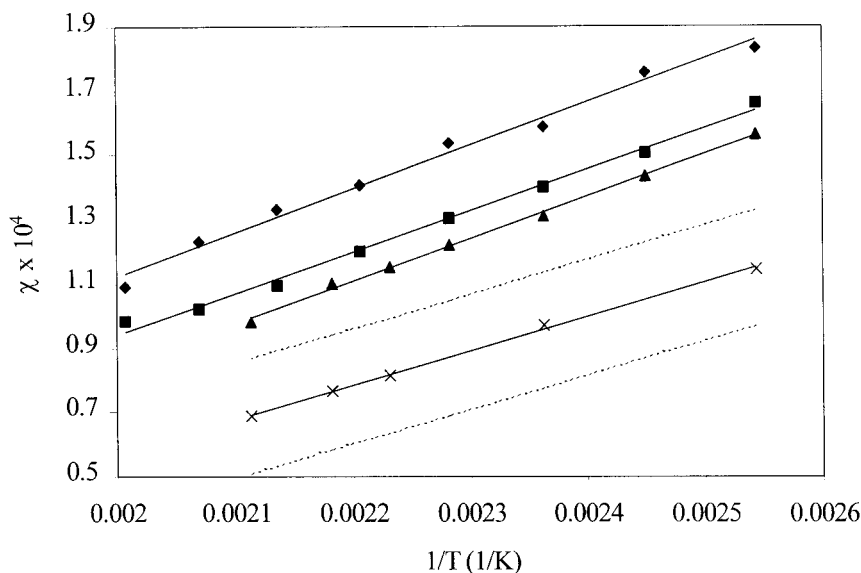


Figure 3. χ as a function of temperature for blends containing 18 wt % of the dPS component, linear or star-shaped: (x) dPS100k, (▲) d4s100k, (■) d5s200k, and (◆) d6s200k. Uncertainty bands are shown illustratively for the linear/linear dPS/hPS blend (short dashes).

A comparison of the data for the deuterated star blends with that for the hydrogenous star blends reveals one additional interesting feature. Although χ values for the blends with deuterated 4-arm and 5-arm stars were higher than those for the corresponding blends with hydrogenous stars, the same is not true for the 6-arm star blends.

The impact of blend composition on the apparent value of χ was studied with the 6-arm star blends. An additional measurement was made on a blend with a 50/50 composition. A plot of χ as a function of $1/T$ for the two blends containing 18 wt % 6-arm star (hydrogenous or deuterated) and for the third blend containing 50 wt % star is shown in Figure 4. When the composition of deuterated star increases from 18 to 50%, the value of χ drops about 25%.

This drop in χ is in good agreement with the behavior anticipated from the theory of Fredrickson et al.⁶ In their treatment, which ignores labeling effects, changing the composition of star from 18 to 50% is predicted to cause a drop in χ of about 40%. The drop in our data is smaller, but the difference can be accounted for simply by a consideration of the effect of labeling. Londono et al.³⁶ showed that in linear/linear isotopic blends of PS, increasing the composition of one component from 18 to 50% leads to an increase in χ of about 15%. If one imagines that the architecture

effect and labeling effect are approximately additive, a net decrease of 25% would be expected during a change in the composition of the star/linear blend from 18 to 50%. This is in very good agreement with the experimental result.³⁶ Also, these limited data on the composition dependence of χ in the star/linear blend suggest that the effect of architecture on the interaction parameter is stronger than the effect of labeling. Certainly, additional star/linear blend compositions need to be measured to further clarify the phenomenon.

To investigate the effect that further increases in functionality have on χ , we studied blends of stars linked with DVB. Properly comparing the results obtained for the two types of star/linear blends requires that two distinctions be made. First, the DVB-linked stars are characterized not only by larger numbers of arms but also by cores that are chemically different from the cores of the silane-linked stars. The DVB cores are chemically more similar to the PS arms than are the silane cores. However, the DVB cores are larger and less well-defined than are the silane-based cores. Second, the functionality is not as narrowly defined for the DVB-linked stars. Despite these differences, the results obtained for the interaction parameters follow the same general trend as seen for the silane-linked stars. That is, χ increases with star functionality, as shown in Figure 5. The interaction parameters for

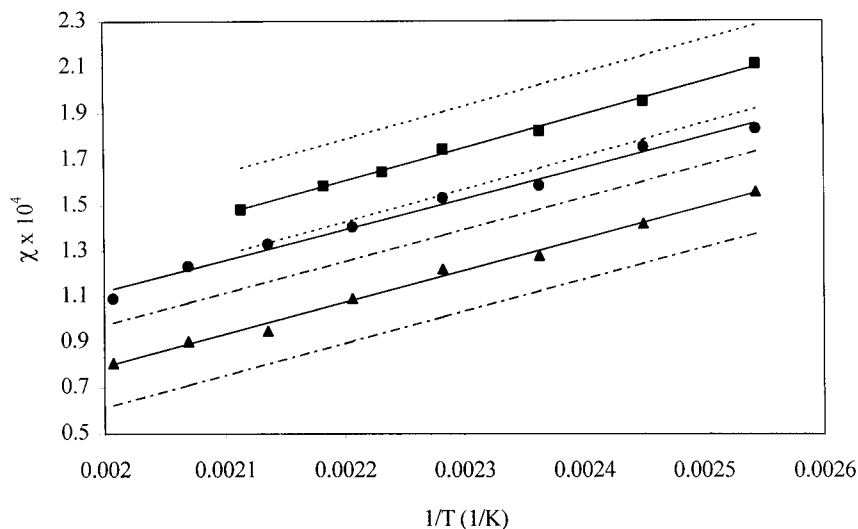


Figure 4. χ as a function of temperature for three blends of 6-arm star PS. Two blends contain 18 wt % of the dPS component [(●) d6s200k] or hPS component [(■) h6s200k2], and the third blend [(▲) 50d6s200k] contains 50 wt % of the deuterated star. Uncertainty bands are shown for the h6s200k2 blend (—) and 50d6s200k blend (---).

the blends with DVB-linked stars are higher than those for the blends with silane-linked stars. The blend containing the hydrogenous 12-arm DVB-linked star is characterized by an interaction parameter twice that obtained for the blend containing the hydrogenous 8-arm star. In contrast to the behavior seen for the silane-linked stars, here the

effect of swapping the labeling is unmistakable. When the branched chain is deuterated, the value of χ is much larger. The effect is in the same direction as that seen for short-branched polyolefin blends^{5,37} and isotopic polydiene blends.³⁸ The magnitude of the difference is much larger, however, for our blends of DVB-linked stars.

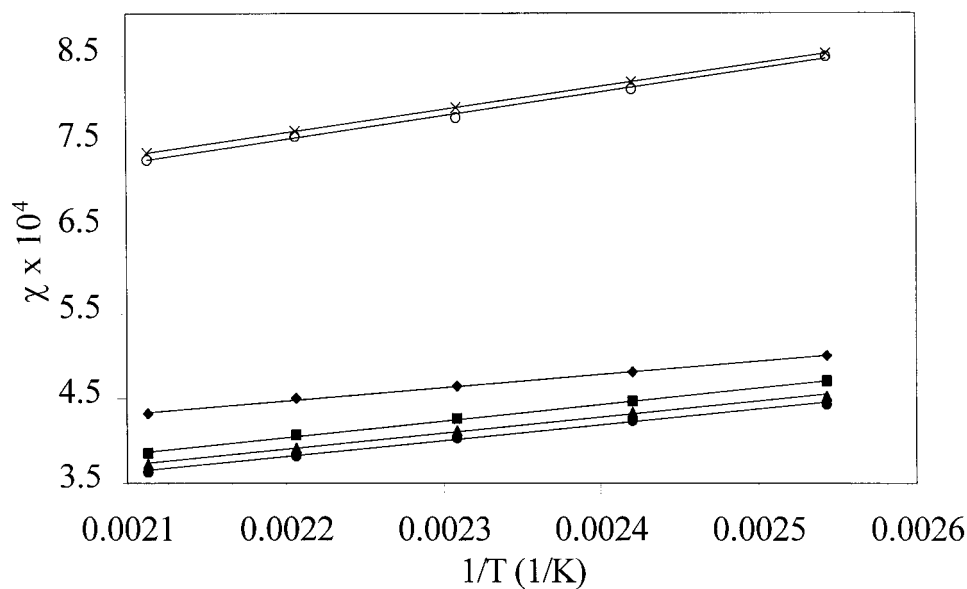


Figure 5. χ as a function of temperature for blends of DVB-linked star/linear PS blends for both labeling schemes (18 wt % hPS and 18 wt % dPS) and various functionalities: (●) hDVB12, (▲) hDVB14, (■) hDVB17, (◆) hDVB21, (○) dDVB15, and (×) dDVB16.

Table III. Interaction Parameter Values Measured at 220 °C for a Series of PS Isotopic Blends

Blend	χ at 220 °C ($\times 10^{-5}$)	$\Delta\chi$ ($\times 10^{-5}$) ^b	Theoretical Architecture Contribution ($\times 10^{-5}$)
Linear/linear	6	0	
4-arm star/linear	9 ^a	3	2
5-arm star/linear	9 ^a	3	5
6-arm star/linear	13 ^a	7	8
Hydrogenous 8-arm star/linear	17	11	8
Hydrogenous 12-arm star/linear	35	29	16
Hydrogenous 14-arm star/linear	36	30	9
Deuterated 15-arm star/linear	71	65	22
Deuterated 16-arm star/linear	71	65	30
Hydrogenous 17-arm star/linear	37	31	31
Hydrogenous 21-arm star/linear	42	36	9

^a Averages of χ between labeling schemes (defined in the text).

^b Difference between the experimental value of χ for a given blend and the value measured for the linear/linear isotopic blend (defined in the text).

For purposes of quantitative comparison among the different blends and with the theory of Fredrickson et al.,⁶ Table III summarizes the experimentally determined values of χ at 220 °C for all blends. For the 4-arm, 5-arm, and 6-arm stars, for which we have hydrogenous and deuterated analogues that are reasonably well matched, one may calculate a value of χ averaged between the two labeling schemes, and this is the value that is given. A comparison between this average and the theory seems most prudent because the theory has no means by which to account for labeling differences. For the DVB-linked stars, no two blends are similar enough in both functionality and arm size to perform such an average reasonably. Included in the table as well are theoretical values for the entropic contribution to χ predicted with the universal approximate expression (eq 3) given by Fredrickson et al.⁶ This theoretical value accounts not only for the differences in functionality among the various blends but also for variations in sizes of the arms from blend to blend. A closer comparison may be attempted with a more detailed expression (see eq 3.15 in ref. 6) given by those authors. That expression accounts additionally for the effect of changing the size of the linear chain but requires computing a cutoff length, for which no exact expression is given in ref. 6. The third quantity tabulated is $\Delta\chi$, the difference between the experimental value of χ for a given star/linear blend and the value measured for the linear/linear isotopic blend. $\Delta\chi$ is an estimate of the architectural contribution to χ for that blend. Thus, we should make a comparison between $\Delta\chi$

and the theoretical predictions, keeping in mind that the theoretical values are for an athermal blend and we have taken liberties in appropriating the theory for comparison with blends containing stars with small numbers of arms. To our knowledge, there is no published theory including enthalpic effects to which one could make a comparison.

For the silane-linked stars, which have smaller numbers of arms, the experimentally estimated contributions to χ due to architectural effects are similar in magnitude to the predicted values. For the DVB-linked stars, the experimental value is markedly higher in all but one case. One also sees that although the experimentally determined χ values simply increase monotonically with star functionality (with only h-DVB or d-DVB stars for comparison), the theoretical values do not. This is due to the fact that arm size varies through the series of polymers. If the effect of arm size were to have the relative importance predicted by the theory, one would have expected very similar experimental χ values for the blends of the 6-arm and 8-arm silane-linked stars because of the much larger arms on the 8-arm star. Also, the experimentally observed χ values for the blends with DVB-linked stars should have fallen in a different order, for example, with the χ value for the blend containing the 14-arm star lying substantially below that for the blend with the 12-arm star. Further study with appropriately chosen star materials can address the relative importance of the variation in arm size. It is important to note that even in the face of these discrepancies between

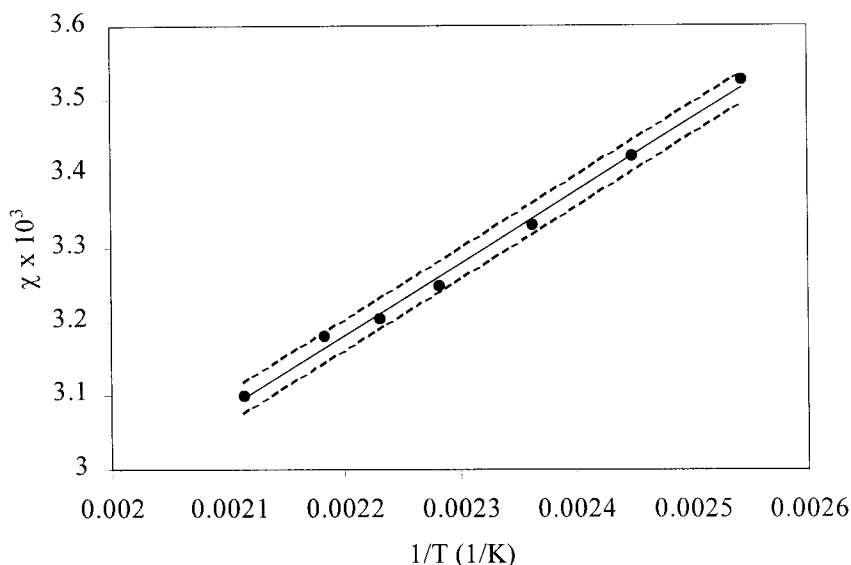


Figure 6. χ as a function of temperature for the comb/linear PS blend containing 18 wt % h6-branch PS comb in a matrix of linear dPS of symmetric molecular weight. An estimate of the uncertainty is shown with short dashes.

the theory and experimental results, an important prediction of the study by Fredrickson et al.⁶ is confirmed. The general magnitude of the effect predicted for stars is correct. Thus, interactions due to architecture alone are insufficient to lead to bulk phase separation for star/linear blends over a wide range of molecular weights and numbers of arms.

Consideration of the data from the comb/linear blend suggests that another prediction of the theory⁶ is correct. The effect of architecture on χ is much larger when the branched polymer is a comb. The values of effective χ for the 6-arm comb/linear blend (Fig. 6) are more than 20 times higher than the values seen for the 6-arm star/linear blends. This comparison is not as rigorous as that among the various star/linear blends because the comb is less well-defined and differs chemically from the star. Further work is underway to provide a more precise comparison. We note that the size of interaction seen in the comb/linear blend is approaching that for which one would expect a 50/50 blend to bulk phase separate at the temperatures studied here. A naive estimate of the critical value of χ for this blend, with the Flory approximation for a symmetric linear blend ($\chi_c = 2/N$), is 0.003. This suggests that if the composition of comb were increased up to 50%, phase separation would be seen.

CONCLUSIONS

The thermodynamic interactions between long-branched and linear analogues in well-defined blends have been quantified with SANS. For each blend, the contribution due to architectural effects alone can be estimated by comparison with the interaction due to isotopic labeling alone seen in a linear/linear isotopic blend. This contribution due to architectural differences can be quantified as such without any assertions being made as to whether it is entropic or enthalpic in origin. However, it is striking to find that it is similar in magnitude to the entropic contribution predicted by the theory of Fredrickson et al.⁶ for an athermal blend. Thus, the theory's assertion that bulk phase segregation is unlikely for blends of linear chains with stars is substantiated.⁶

A clear trend of χ increasing with star functionality is seen for this series of stars, even though theory would suggest that variations in arm size should lead to variations in χ that are not simply monotonic in the number of arms. Agreement with theoretical expectations is seen on two other points, however. First, the variation in χ with the composition of the star/linear blend predicted by the theory is seen experimentally, although more compositions should be measured to test this more fully. Second, the interaction between a comb-branched chain and its linear analogue is

much stronger than that between a linear analogue and a star with the same number of arms as the comb.

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