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Effective interaction parameter between topologically distinct polymers

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

The magnitude of the thermodynamic interaction in a bulk binary homopolymer blend due to regular branching alone has been estimated from small angle neutron scattering (SANS) measurements for the first time using blends of star and linear poly(styrene)s of well defined structure. The value of χ for a blend of deuterated four arm star ($M = 100\ 000$ g/mol) with hydrogenous linear polystyrene ($M = 132\ 000$ g/mol) of comparable molecular weight is $\chi = 0.1278/T - 0.0002$ over the temperature range of 120–225°C for a segment volume of 100 cm^3/mol. The contribution to χ ascribable to architecture effects is just distinguishable from that due to isotopic substitution alone and in surprisingly good agreement with an approximate prediction from a mean field theory. The precise value of χ varies depending on which component is labeled.

Keywords: Star polystyrene; Linear polystyrene; Small angle neutron scattering (SANS)

1. Introduction

In binary blends of linear polymers, the bulk thermodynamic behavior varies not only with molecular weight of the two components, but also with small differences in chemical microstructure [1–3], tacticity [4], and with the degree and type of deuterium labeling [5]. The magnitude of the effective interaction parameter, χ, describing interactions owing to differences in branching of the two chains alone has been the subject of recent experimental study [6–8]. Theoretical work has considered randomly branched systems [9–12], but of primary interest here is the effect of regular branching, which has been addressed by Fredrickson et al. [13]. There have been a few recent theoretical studies for both stars [13–15] and combs [13,15] as well as some experimental work on the thermodynamics of blends of linear and regularly star branched polymers [16–18]. These have suggested that the thermodynamic interactions due to architecture are present, but the matter of experimentally determining the magnitude of these effects and comparing them to theory [13] remains. Fredrickson et al. [13] suggest that the interaction should be small in the case of star branched polymers with linear analogs, with the size of the effective interaction increasing with increasing number of arms, p, and increasing disparity between the size of the linear chains and the size of the star arms. The effect for bulk miscibility is subtle and for a modest number of arms of polymeric length Fredrickson et al. [13] suggest that bulk phase segregation is unlikely. In this contribution small angle neutron scattering (SANS) measurements are used to quantify the value of the bulk effective χ parameter for pairs of polystyrene polymers which differ as nearly as possible only in their regular branching structure.

2. Experimental

Linear polymers obtained from Polymer Source, Dorval, Quebec, Canada were characterized by Polymer Source, as well as at The University of Akron and at The Goodyear Tire & Rubber Company. The four arm stars were synthesized at The University of Akron by linking living poly(styryl)lithium arms of targeted molecular weight. Polystyrene arm precursors with narrow molecular weight distribution were synthesized anionically in benzene with *sec*-BuLi initiator [19]. The poly(styryl)lithium arm

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Table 1
Molecular characterization of star and linear polymers

Polymer	Sample	M_n (g/mol)	N	M_w/M_n
Linear hPS	hPS	132 000	1269	1.03
Linear dPS	dPS	143 000	1277	1.05
4-arm hPS star	h4s	85 000	817	1.02
4-arm dPS star	d4s	100 000	893	1.02

precursors were then coupled with 1,2-bis(methyldichlorosilyl)ethane [20]. While the arms were initiated with *sec*-BuLi, and therefore carry *sec*-butyl fragments at their outer ends, no crossover to diene monomer was used before coupling, in order to keep the chemical nature of the star polymers as close to that of the linear chains as possible. Coupling was performed with an excess of arms to ensure well-defined functionality of 4.0. Therefore, the products were fractionated to eliminate uncoupled arms, and the stars characterized by gel permeation chromatography (GPC) and by light scattering to determine the number of arms. The stars had number average molecular weights of 100 000 g/mol for the deuterated star (d4s), and 85 000 g/mol for the hydrogenous star (h4s), corresponding to total number of statistical segments, N, of 893 and 817, respectively, for a segment volume of 100 cm^3/mol. Details of the polymer molecular characteristics are summarized in Table 1. While the linear chains were slightly larger in overall molecular weight, and therefore not rigorous analogs, these differences are small and are explicitly accounted for when analyzing the scattering data to estimate effective χ.

Sample blends containing 18 wt% star (either hydrogenous or perdeuterated) with 82 wt% of the contrasting linear analog were prepared for SANS by dissolving the two polymers in toluene, and then solution casting in Teflon® beakers. Linear/linear blends were also made at compositions of 18 and 82 wt% deuterated component. The films were then dried under a roughing vacuum at 70°C for seven days. To create transparent, bubble free films of uniform thickness, the dried films were pressed inside one mm thick brass rings at about 120°C under 2500 lbs_f.

Scattering experiments were carried out on the NG3 30-m SANS instrument at the National Institute for Standards and Technology using neutrons with wavelength 6 Å and $\Delta\lambda/\lambda = 0.150$ FWHM. Using a sample to detector distance of 13 m provided a range of scattering vector, $\mathbf{q}$ ($= 4\pi\sin\theta/\lambda$), of 0.005–0.5 $Å^{-1}$ with an approximate resolution of 0.005 ($Å^{-1}$) [21]. The samples were placed in an evacuable sample chamber with a multi-specimen sample holder and temperature control (± 0.5°C). Measurements at temperatures from 120 to 225°C were made in vacuum, allowing appropriate time (ca. 15 min) after each setpoint change for thermal equilibration.

3. Results and discussion

The scattering at 195°C from one blend (d4s/hPS) containing 18 wt% deuterated four arm star in a matrix of hydrogenous linear PS is shown in Fig. 1. The data are fit with a structure factor derived for a regular branched n-arm star in the incompressible random phase approximation for incompressible systems [22] and a single interaction parameter (a more rigorous approach must account for compressibility and multiple interaction parameters [12,23], but is difficult to implement). Assuming that the polymer components behave as ideal (Gaussian) coils, unperturbed by weak interactions between segments, the measured intensity is given as [24]:

$$\frac{\left(\frac{a_{star}}{V_{star}} - \frac{a_{linear}}{V_{linear}}\right)^2}{[I(\mathbf{q})]_{measured}} = \frac{1}{\phi_{star}(N_b n)V_{star}S_{star}} + \frac{1}{\phi_{linear}NV_{linear}S_{linear}} - \frac{2\chi}{V_0} \quad (1)$$

where V_{star} is the segment molar volume ($= V_{linear} = V_0 =$ 100 cm^3/mol), N_b is the number of arms in the star, ϕ_i is the

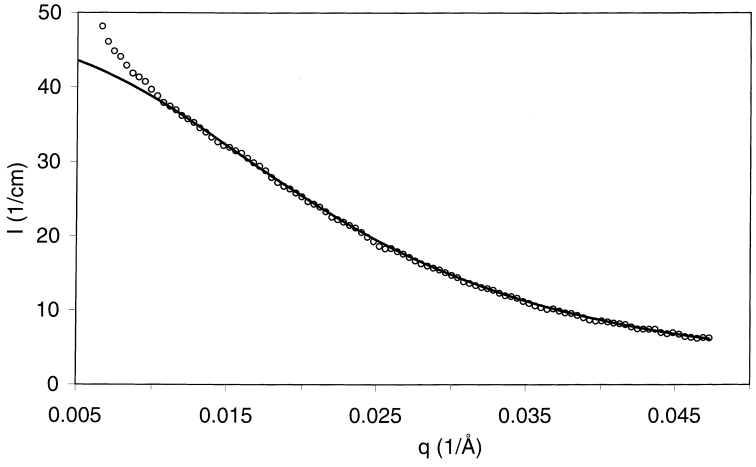

Fig. 1. SANS experimental data (○) with fit (-) to the RPA for a blend of 18% deuterated 4-arm star in a matrix of hydrogeneous linear PS (d4s/hPS), at 195°C.

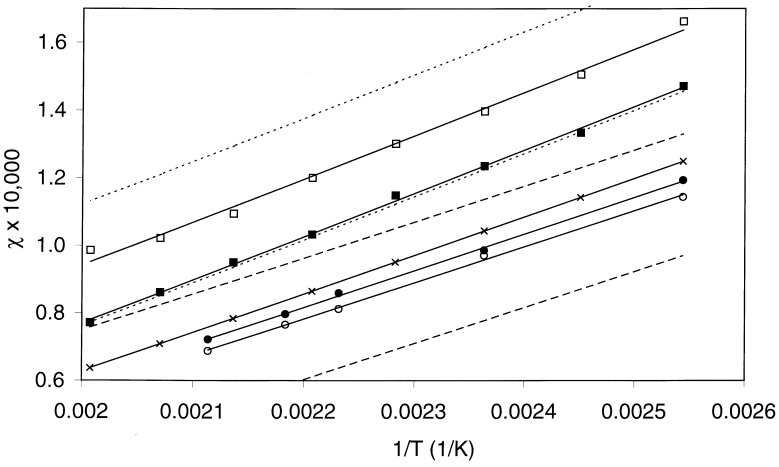

Fig. 2. Interaction parameter as a function of temperature for the linear/linear blends: 18 wt% hPS (●), 18 wt% dPS (○), 50 wt% dPS from Bates et al. [13] (×), and from star/linear blends: 18 wt% d4s (□), 18 wt% h4s (■). Uncertainty bands for the 18 wt% dPS linear/linear blend (long dashes) and 18 wt% d4s star/linear blend (short dashes) are also shown.

volume fraction of species i, and n is the number of segments per arm. N is the number of segments per linear chain, $(a/V)_i$ is the scattering length density for component i, $I(\mathbf{q})$ is the absolute intensity, and χ is the effective interaction parameter representing the strength of the interaction between molecules on a per segment basis. The structure factors for the star (S_{star}) and linear (S_{linear}) PS, which assume Gaussian statistics for each, were obtained through brief manipulation of the expression found in [24]:

$$S_{\text{star}} = \frac{1}{N_{\text{b}}} P_{11} + \frac{N_{\text{b}} - 1}{N_{\text{b}}} P_{12}, \tag{2}$$

$$S_{\text{linear}} = \frac{2(\mathrm{e}^{-xN} - 1 + xN)}{(xN)^2}, \tag{3}$$

where $P_{11} = \left(2(\mathrm{e}^{-xN} - 1 + xn)\right)/(xn)^2$ captures the intra-branch correlations, $P_{12} = ((1 - \mathrm{e}^{-x})/(xn))^2$describes the inter-branch correlations, and $x = (qb)^2/6$, where b is the statistical segment length. For linear polystyrene the value of b has been measured [25]. We take the value $b = 6.7$ Å and use the same statistical segment length for the star as well. The value of the statistical segment length manifests itself predominantly in the scattering at higher values of q. When this quantity is taken to have a known value, the curves can only be fit using a single parameter, χ, to match the shape of the curve. In the case of our data it was found necessary to allow a correction factor of order unity to provide for the degree of agreement seen in Fig. 1. This factor accounts for random and systematic errors in the determination of the absolute intensity, including loss of intensity due to the formation of bubbles in the cell at higher temperatures. The discrepancy between the fit and the data at small q has not yet been explained. The variations of χ with temperature determined for both star/linear blends, as well as for three linear/linear isotopic blends of PS are summarized in Fig. 2.

First we note that the magnitude of the χ values found for the linear/linear blends, with either labeling scheme, are very close to, but slightly below those found by Bates et al. [26] for linear/linear PS blends of a different composition (50 vol%) and chain lengths of 6.57×10^3 and of 4.97×10^3 for the deuterated and hydrogenous PS, respectively. Second, we see that the χ values for the star/linear blend are larger when the more highly branched component is deuterated, as has also been seen with randomly branched polyolefins [5,27] and isotopic polydiene blends as well [28].

The focus of this brief report, however, is the key finding that the values of effective χ for the blends containing the regularly branched polymers of well-defined architecture are consistent with the presence of a contribution to effective χ owing to architectural differences. At 220°C χ for the linear/linear blend is ca. 6×10^{-5}, whereas that for the star/linear blend is ca. 9×10^{-5} (averages between two labeling schemes), suggesting a contribution due to architecture alone of order 3×10^{-5}, which is half as large as the effective χ value due to isotopic substitution alone. This is consistent with the contention of Fredrickson et al. [13] that bulk phase separation is unlikely in a star/linear blend for low number of arms. We may compare this result to that of Alamo et al. [8] who measured χ for several compositions of monodisperse linear/linear and miscible polydisperse short-branched/linear blends of polyethylene in the melt (140–160°C, molecular weight 100–200 k). Their values of χ for the branched/linear blends were consistently lower than the values for the linear/linear blends, but the differences were within the experimental error reported.

Two potential limitations in the determination of the contribution of architecture effects to χ should be briefly addressed. Most importantly, the precision of the determination of such small values of χ depends sensitively on the precision of the molecular weight determinations. In our case the values of molecular weight (MW) were determined

independently in at least two labs using both light scattering and gel permeation chromatography. Uncertainties have been mitigated in one way by using the same linear polymers in both the linear/linear and star/linear blends. The estimated uncertainties in the χ values resulting from uncertainties in the molecular weights and absolute intensity calibrations are shown in Fig. 2 for the star/linear blend with 18% d4S and linear/linear blend with 18% dPS. The contribution to χ due to architectural effects is just large enough to be distinguished. Results already obtained with stars of somewhat higher number of arms [29] indicate a clear trend with increasing number of arms and this trend provides additional evidence that the contribution to χ due to branching is real. A less important issue is the difference in the detailed chemistry of the star/linear blend as compared to that of the linear/linear blend owing to the initiator fragments at the end of each arm. In the linear chains the ratio of volume of polystyrene repeat units to initiator fragments is ca. 1000:1 while that in the four arm stars is ca. 1000:4. We deem this difference to be negligible for consideration of bulk χ.

The magnitude of the effective χ due to architecture measured here should be compared to that predicted from the mean field approach described by Fredrickson et al. [13], though it must be kept in mind that that theory is intended only for stars of much larger arm number than considered. They estimate the magnitude of a contribution to an interaction density, α, associated with architectural asymmetry between components for an *athermal* blend of chemically identical linear and star homopolymers. The parameter, α, which is invariant to the choice of segment volume, is related to the more commonly used χ by $\chi = \alpha(v_1 v_2)^{1/2}$, where the v_i are the statistical segment volumes for the two blend components. In the case that p, the number of arms, is large and $(p-3)(R_{linear}/R_{arm})2 \gg 1$, with R_{linear} and R_{arm} being the radii of gyration of the linear chain and individual arm, respectively, the contribution to α due to the entropic corrections alone is given approximately as

$$\alpha_\varepsilon \approx \frac{1}{64\pi\sqrt{2}} \frac{(p-3)^{3/2}}{(1-\phi_{linear})^{1/2} R_{arm}^3},$$

where p is the number of arms and R_{arm} is the arm radius of gyration. For our system the theoretical contribution to χ due to architecture asymmetry is ca. 2×10^{-5}, which is in surprisingly good agreement with our experimental result considering that the theory is intended for large p.

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