Influence of Architecture on Arm Dimensions and Interaction Parameters in Polybutadiene Star Polymers

L. R. Hutchings and R. W. Richards*

Interdisciplinary Research Centre in Polymer Science, University of Durham, Durham DH1 3LE, United Kingdom

Received June 23, 1998; Revised Manuscript Received September 29, 1998

ABSTRACT: Star branched polymers of polybutadiene with 3, 4, 8, and 12 arms have been synthesized with one arm perdeuterated. Small-angle neutron scattering data have been collected for each of the star polymers and for the four-arm star polymer mixed with hydrogenous linear polybutadiene of the same molecular weight either as a single arm or of the whole star. The labeled four-arm star polymer has also been mixed with the equivalent hydrogenous star polybutadiene. For the pure labeled star polymer the scattering is dominated by a peak located at a scattering vector determined by the radius of gyration of the arm. As the labeled star polymer is diluted by adding hydrogenous polymer, the peak declines in amplitude and the maximum scattered intensity shifts to zero scattering vector. The scattered intensity for each sample has been fitted with expressions based on random phase approximation theory and the radius of gyration of the labeled arm was obtained. Two interaction parameters were needed to obtain acceptable fits of the theoretical expressions to the data. Indisputable evidence for increased stretching of the labeled arm as the number of arms in the star polymer increases has been obtained, and the stretching factor has been compared to predictions of a liquid state theory of star polymers. The interaction parameters obtained are considered to be reflections of the differential screening of core and corona segments of the star molecules, an integral aspect of the liquid state theory, rather than true Flory−Huggins-type interaction parameters.

Introduction

The study of star polymers is motivated by several factors: (a) they constitute models of junction points in networks; (b) star polymers have viscoelastic properties that differ considerably from their linear counterparts; and (c) the individual arms are examples of chains fixed at one end to a point and thus, depending on the number of arms in the star, may exhibit configurational properties akin to brushlike layers; in particular they may be stretched. This last aspect has relevance to steric stabilization and grafting of polymers to surfaces. Theoretical and experimental investigation of star polymers has been extensive and much of it has recently been reviewed.[1] A major aspect of the configurational properties of star polymers is the view that the arms of the star must be stretched to minimize repulsive interactions between segments on different arms, a view first advanced by Daoud and Cotton[2] for star polymers in dilute and semidilute solutions. Experimental data,[3−5] mainly small-angle neutron scattering (SANS), confirm that the arms are stretched in dilute solutions in a good solvent and from the exponents in the scattered intensity−scattering vector scaling relation, it was suggested that the section of polymer near the core was stretched to a greater extent than the corona region. Boothroyd et al.[3] also obtained evidence that even in the melt state the dimensions of star polyethylenes were larger than anticipated from a simple Gaussian configuration of the arms. A model wherein a repulsion of chains from the core region was proposed to account for the observed increase in the dimensions.[6] Subsequently, Richter et al.[7] observed the development of an interference function peak in semidilute solutions of star polymers, and it seems most likely that such scattering is contributing to that observed by Boothroyd et al. but was not allowed for in the analysis. Therefore we must accept the conclusions from Boothroyd et al. with caution. Similarly Macknight and co-workers[8] also concluded that the core region in star polymers was more stretched than the corona. This observation was based on small-angle neutron scattering from a star diblock copolymer where either the core region or the corona region was deuterium-labeled. However, the scattering law used was inappropriate for the architecture of the star polymer and hence again we cannot accept this conclusion with confidence. Finally, in this brief review of earlier work on star polymers we note that Richter et al.[9] claim to have SANS data on polystyrene stars with 12 arms where one of them was deuterated. However, it is clear that deficiencies in the synthesis procedure results in a mixture of stars containing a varying number of deuterated arms since they noted that the number of labeled arms in a star is distributed according to a binomial distribution. Moreover, they made no remark that a maximum was evident in their SANS data and from the plots presented it is impossible to ascertain whether such a maximum is present. Consequently, the claims made that the arms are very stretched in dilute solution are based on ambiguous evidence, and there is a conflict between the dimensions obtained for the single labeled arm and the global dimensions of the star that is not rationalized.

Despite these cautionary comments, the notion of the arms of a star polymer being stretched is entirely reasonable. Grayce and Schweizer[10,11] have developed a model for star polymers based on the Polymer Reference Interaction Site Model (PRISM) and establish that the arms are expanded compared to the equivalent linear polymer. Moreover, this expansion persists into the bulk melt state and the parts of the arms near the core of the star are stretched to a greater extent than

---

* To whom correspondence should be addressed.

10.1021/ma980980w CCC: $18.00

the corona. Summarizing, then, there is experimental evidence that the arms of star polymers in dilute solution are stretched to a greater extent than the linear equivalent molecules. These observations have been based on the *global* dimensions of the stars. As the concentrations of the stars are increased, interstar correlations become evident and the extraction of factors pertaining to the stretching of the arms becomes fraught with uncertainty. As a result the ability to examine the predictions regarding arm stretching in the bulk state by using dispersions of fully labeled stars in hydrogenous stars is moot. What is required to examine these aspects are star polymers where *only one arm* of the molecule is labeled. The use of such partially labeled star polymers brings other problems from the thermodynamic interactions between the labeled arm and the unlabeled arms and also with the surrounding polymer matrix.

The thermodynamics of polymer–polymer mixtures are most commonly discussed in terms of the Flory–Huggins expression for the free energy change on mixing. Although it is well-known that the Flory–Huggins theory is not a rigorous description of the thermodynamics (notably its failure to account for the volume changes on mixing), its ease of use and conceptual simplicity make it a popular choice. Furthermore, the theory is able to provide reasonable estimates of the location of binodal and spinodal boundaries. The success, or otherwise, of such predictions is very dependent on the accuracy of the values of χ, the interaction parameter between the two polymers in the mixture. Originally, χ was derived on the basis of enthalpic interactions but it is now accepted that χ has some entropic character and is best viewed as a free energy term. In principle: because χ is defined for interactions between segments of the polymer chains, there should be neither a molecular weight dependence nor a composition dependence for χ. Composition-dependent values of χ have been frequently observed and attempts have been made to describe the theoretical basis of such composition-dependent values of χ, but complete success is still elusive.

The observation of the variation in the values of χ and its dependence on such aspects as temperature, polymer microstructure; and composition has been facilitated by the application of small-angle neutron scattering to polymer mixtures. This method is nonperturbative and can be applied over a wide range of conditions (temperature, pressure, flow) and relies only on the existence of sufficient scattering contrast between species in the mixture to generate a scattered intensity of sufficient magnitude. In addition to the availability of the SANS technique, the evaluation of χ is reliant on the development of the random phase approximation (RPA)[12−15] and its application to the interpretation of the scattering from polymer mixtures and copolymers.

It was the application of the expression for the scattered intensity obtained by using RPA theory that first identified the existence of unfavorable interactions between polymers differing only in the replacement of protons by deuterons.[16,17] Notwithstanding the influence of deuteration, small-angle neutron scattering has been extensively used to determine values of χ for a range of polymer mixtures and block copolymers. Factors addressed include molecular structure,[18,19] the influence of compressibility,[20,21] the influence of the locus of deuteration,[22] and the temperature dependence of χ.[23−26] Rarely is a composition-independent value of χ observed. Although the switching of deuterium labeling from one component to another in the mixture resulting in an alteration of the value of χ can be accepted where there are specific interactions between the two polymers, the observation of such effects in their absence is surprising. Evidently the underlying fundamental aspects of χ are still an open question.

Much of the experimental work reported to date has been concerned with linear homopolymers and block copolymers, but since χ contains entropic as well as enthalpic factors, we anticipate that molecular architecture may have an influence on χ. There has been some theoretical discussion of the influence of this aspect on χ[27,28] but no significant body of experimental data exists as yet. The possibility that molecular architecture may play a role in determining χ becomes increasingly important for mikto star polymers (star polymers where the branches are chemically distinct) and star diblock copolymers mixed with linear homopolymers. This paper addresses two aspects of star polymers: first, an attempt to provide definitive evidence that arms of a star polymer are stretched in the bulk state, and second, the evaluation of χ for the partially labeled star polymer and its mixtures with linear and star polymer of the unlabeled linear and star polymers of the same chemical type. A key factor to obtaining unambiguous data is the use of the correct scattering law to interpret the SANS data. This aspect is given some attention in the next section, which also includes a précis of the Grayce and Schweizer[10] model of star polymers. The Experimental Section contains some details of the synthesis not covered elsewhere and describes the SANS experiments. The results obtained are discussed in relation to current theories.

Theoretical Background

Scattering Law. In the absence of any interaction between polymers A and B in a mixture and assuming incompressibility, the structure factor is given by[12]

$$S_{\mathrm{inc}}(Q) = \frac{{S_0}^{\mathrm{AA}}{S_0}^{\mathrm{BB}} - (S^{\mathrm{AB}})^2}{{S_0}^{\mathrm{AA}} + {S_0}^{\mathrm{BB}} + 2S^{\mathrm{AB}}} \qquad (1)$$

where the ${S_0}^{ij}$ are the Q-dependent partial structure factors and cross-partial structure factors (when $i \neq j$) for the components of the mixture where Q is the modulus of the scattering vector. $Q = |Q| = (4\pi/\lambda)\sin\theta$, for neutrons of wavelength λ, and scattering angle 2θ. Hence when $i = j$, the partial structure factor describes the self-correlation of the local order parameter of polymer species i in Fourier space as a function of Q. When $i \neq j$ the partial structure factor describes the correlation between the order parameter of the two species. The major challenge in interpreting the scattering from any polymer mixture is to obtain expressions for each of the partial structure factors because these will depend on the nature and architecture of the polymers forming the mixture. There have been a number of attempts to provide expressions for a variety of block copolymers and their mixtures with homopolymers.[13−15] Some of these set out the structure factor for star polymers, and where all arms or rays are identical, the original expression derived by Benoit[29] a number of years ago in the absence of RPA theory is obtained. What has not been available until recently is a general scheme where the structure factors for copolymers of arbitrary architecture can be written down. Balsara et al.[30] provide a method that approaches generality, but a particularly straightforward way has been proposed by Read.[31] This approach describes each of the S^{ij} parameters in eq 1 by using self-, co-, and propagator terms and the method is applicable if each molecular species has a Gaussian distribution of segments. Self-terms describe the correlations within the molecular species and the Q variation of a Gaussian distribution of segments in space is the well-known Debye equation scaled by the square of the degree of polymerization. Co-terms describe how like chains correlate with each other, and the co-terms may be multiplied by a propagator term if a different species intervenes between the two like species in some way but connects them to each other. As an example, consider the star molecules already mentioned above, i.e., $(n - 1)$ arms of type A and 1 arm of type B (which in our case is a deuterated version of A).

In this case we have one self-term for the single B arm. For the A arms there are $(n - 1)$ self-terms, each A arm is correlated with $(n - 2)$ other A arms, but since they meet at a point like center there are no propagator terms; thus

$$S^{\mathrm{AA}} = (n-1)A_{\mathrm{self}} + (n-1)(n-2){A_{\mathrm{co}}}^{2}$$

The B arm correlates with $(n - 1)$ A arms via co-terms and hence

$$S^{\mathrm{AB}} = (n-1)B_{\mathrm{co}}A_{\mathrm{co}}$$

The structure factor expressed by eq 1 is the bare structure factor in the absence of any thermodynamic interaction between the A and B arms. Such interactions are allowed for by incorporating the interaction parameter χ into the expression for the intensity of scattered radiation. For small-angle neutron scattering the intensity of scattering is expressed by the differential scattering cross section, $\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega$, and application of RPA theory gives

$$\frac{\mathrm{d}\sum(Q)}{\mathrm{d}\Omega} \propto \left(\frac{1}{S_{\mathrm{inc}}(Q)} - 2\chi\right)^{-1} \qquad (2)$$

where the constant of proportionality in eq 2 will be the contrast factor between A and B polymers. Figure 1 shows the form of this cross section for a partially labeled star polymer, only one arm deuterium labeled, as a function of the number of unlabeled arms for a fixed χ value (panel a) and as a function of χ for a fixed number of unlabeled arms (panel b). As one would anticipate we see the typical RPA or correlation hole peak, which remains at a constant value of Q defined by the radius of gyration of the arms, and $Q_{\max} = \sqrt{2}/R_{\mathrm{g}}$ for these partially labeled stars. As χ increases the amplitude of the maximum becomes larger and becomes infinite (≡ spinodal point) when $\chi N_{\mathrm{arm}} \sim 10$ where N arm is the number of monomer units in each arm of the star.

When such a polymer is mixed with a third component, C, we now have to consider all possible thermodynamic interactions between the species in the mixture. The most useful approach is that of Balsara et al.,[30] where the interactions in the mixture are symbolized by χ_{AC}, χ_{BC} and χ_{AB} and the component C is considered to be the matrix in which the AB copolymer is dispersed.

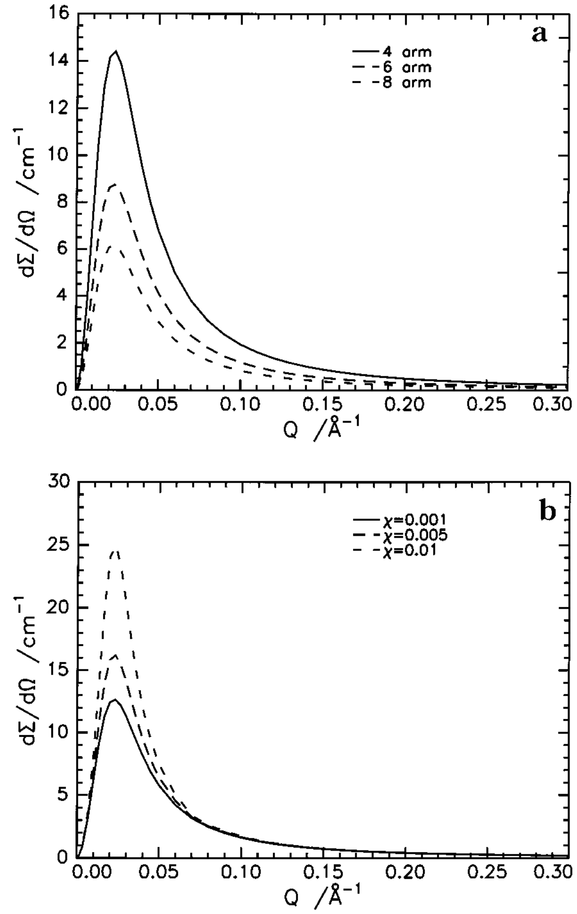

Figure 1. Scattering cross sections from RPA expressions for single-arm-labeled stars. (a) Influence of number of arms; the interaction parameter between labeled and unlabeled arms is zero. (b) Influence of the interaction parameter between labeled and unlabeled arms for a four-arm star. In both cases the molecular weight of the arms was 30 000 and the scattering length densities appropriate for deuterio and hydrogenous polybutadiene were used.

In addition to ensuring that all interactions are accounted for, accurate evaluation of the interaction parameters requires that the scattering be in absolute units [reciprocal centimeters for $\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega$]. Consequently the final expression for the cross section must properly account for all the contrast factors in the system. Balsara et al. achieved this by using the cross section defined by Akcasu and Tombakoglu[32] and written as

$$\frac{\mathrm{d}\sum(Q)}{\mathrm{d}\Omega} = K^{\mathrm{T}}S(Q)K \qquad (3)$$

where in an m-component mixture, K is an $(\mathrm{m} - 1)$ column vector of contrast factors between the selected component and that component chosen as matrix, i.e.,

$$K = \frac{b_i}{v_i} - \frac{b_{\mathrm{c}}}{v_{\mathrm{c}}} \qquad (4)$$

and K^{T} is its transpose, b_i is the scattering length of monomer unit of species i, and v_i is the volume occupied by the monomer unit. In eq 3, $S(Q)$ represents the full scattering law, i.e., the right-hand side of eq 2. The general form of the scattering cross section is given in more detail in the Appendix.

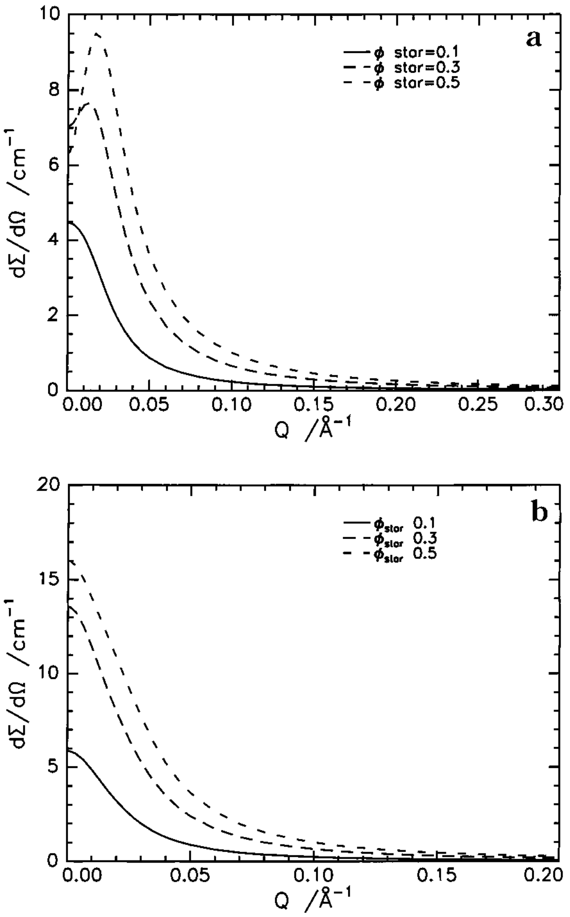

Figure 2. Influence of adding linear hydrogenous polybutadiene to a partially labeled four-arm star: (a) molecular weight of linear polymer is the same as that of the arms in the star; (b) molecular weight of linear polymer is equal to that of the whole star polymer.

Incorporating a third component influences the observed scattering quite markedly. We show in Figure 2 the effect of adding linear polymer A of the same molecular weight as the arm (panel a) and linear A of the same molecular weight as the star polymer (panel b); in each case the linear polymer is the matrix in which the partially labeled star polymer is dispersed. In both cases the previously well-resolved RPA peak becomes masked, the maximum shifts to lower *Q*, the intensity falls (dilution effect), and the intercept on the d$\Sigma(Q)$/dΩ axis becomes finite rather than zero. The value of this intercept is mainly influenced by the composition of the mixture and only very marginally by the values of the three interaction parameters.

PRISM Theory of Star Polymers. We do not give the details of the theory here since these are available elsewhere;[10,11] we present in précis form the underlying physical basis responsible for the stretching of the core units and the predictions that are made concerning the dimensions of an individual arm. A factor that is extremely relevant to the data presented here is that the theory is applicable to stars with a modest number of arms, whereas the Daoud−Cotton model[2] is valid in the limit of a large number of arms in the star. The star polymer is modeled as a number of pearl necklace chains attached to a rigid central branch point. Local bending potentials mimic the bending and twisting of the arms and each spherical unit making up an arm interacts with all others via a pairwise-additive, spherically symmetric potential. The structure of the fluid polymer system (PRISM theory is a liquid state theory) is determined by strong short-range repulsive interactions. Likewise, interactions between the spherical units and low molecular weight solvent are also via hard-sphere potentials mediated by the presence of solvent. In the presence of solvent, excluded volume interactions are principally between corona regions on different arms and between core and corona regions in the same star. As the polymer concentration increases, the core regions are shielded to some extent by the corona regions and thus complete screening of excluded volume interactions between core and corona does not take place and hence the core region remains stretched. Monomer density is thus transferred to the outer regions of the star and hence the star molecule swells relative to the dimensions of a star wherein there are no interactions between the arms. Grayce and Schweizer define a number of parameters that can be used as criteria of the stretching. For the present purposes the most pertinent factor is g_{arm}, the ratio of the mean square distance from the center of the star to the end of an arm to the mean square end-to-end distance of the untethered equivalent linear polymer. For a fixed degree of polymerization, g_{arm} increases as the number of arms increases. However, as the degree of polymerization of an arm increases, the value of g_{arm} decreases for fixed star functionality. This is due to the corona region becoming a greater component of the star polymer and the influence of the stretched core region becoming attenuated. The different strength of interactions sensed by the core and corona regions due to incomplete screening may result in more than one interaction parameter being needed to describe the thermodynamics of partially labeled stars. One interaction parameter may be attributable to intramolecular core−corona interactions, the second being due to intermolecular corona−corona interactions.

Experimental Section

Polymers. The general procedure for the synthesis of single-arm-labeled star polybutadienes is exemplified by the preparation of stars with a functionality (*f*) equal to 4. Deuteriopolybutadiene was synthesized at 313 K by anionic polymerization of the deuterio monomer dissolved in benzene with *s*-butyllithium as initiator. The polymerization was left overnight before a large excess of tetrachlorosilane was added and the reaction mixture was left for a further 2 h. This results in the addition of a single polymer molecule to the silane core. Solvent and unreacted chlorosilane were then removed by distillation and fresh benzene was added to dissolve the chlorosilane-capped polymer, followed by a solution of living hydrogenous polybutadiene in excess of that required to react with all chlorine sites remaining. The polymer was recovered from solution and the uncoupled linear polymer separated from the star polymer by fractionation. Figure 3 shows size-exclusion chromatograms of the partially labeled star polymer before and after fractionation. A more detailed description of this synthesis method has been given elsewhere.[33] Figure 4 shows schematic sketches of the silane cores of all the partially labeled star polybutadienes investigated. Synthesis of the 8- and 12-arm stars involved three extra steps. Addition of the silane core to the living deuteriopolybutadiene produced some material with more than one arm per core. This higher molecular weight material was removed from the single-arm-functionalized cores by a series of fractionations. Excess unreacted chlorosilane core was then removed by repeated precipitation and redissolution by addition of methanol to the benzene solution of the polymer, removal of the solvent, and redissolution in fresh benzene. This procedure was repeated

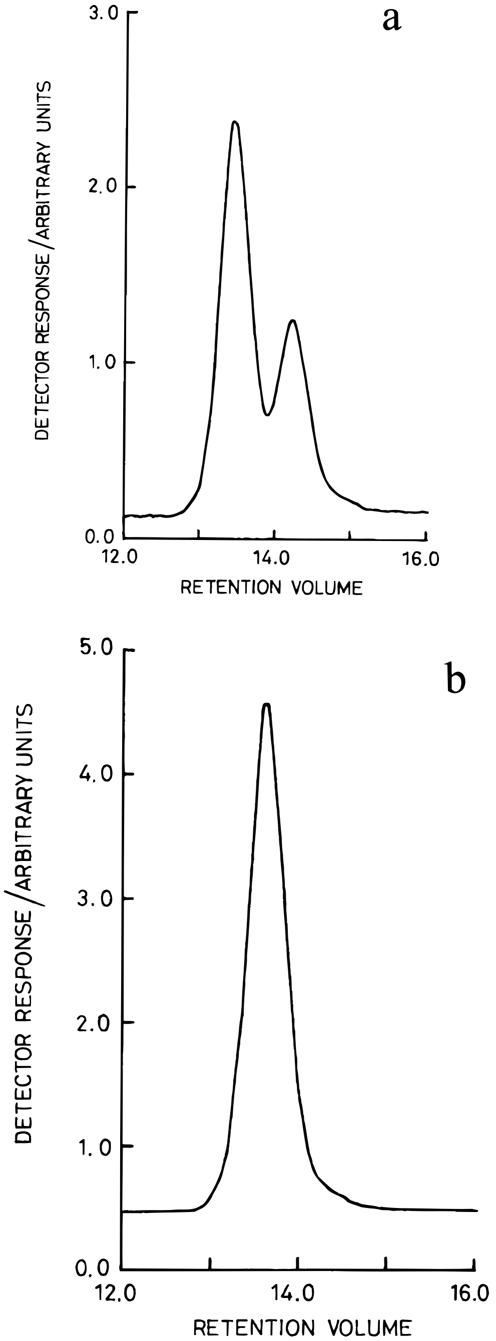

Figure 3. Size-exclusion chromatograms of the partially labeled four-arm star polymer (a) before fractionation to remove excess hydrogenous arm polymer and (b) after fractionation.

at least twice before final removal of all traces of methanol by distillation on the vacuum line. All these operations were carried out in the reaction flask. Benzene was add to redissolve the silane-capped polymer before a benzene solution with an excess of living hydrogenous polybutadiene was added to react with the remaining sites on the core.

Linear deuterio and hydrogenous polybutadiene were prepared by anionic polymerization with benzene as solvent and s-BuLi as initiator. The reaction was terminated with degassed methanol and the polymers were precipitated out in methanol. Hydrogenous star polymer was prepared by adding tetrachlorosilane to an excess of living hydrogenous polybutadiene and removing unreacted polybutadiene by fractionation. Table 1 reports the molecular weights and molecular weight distributions obtained by size-exclusion chromatography with in-line refractive index, viscometry, and light scattering detectors.

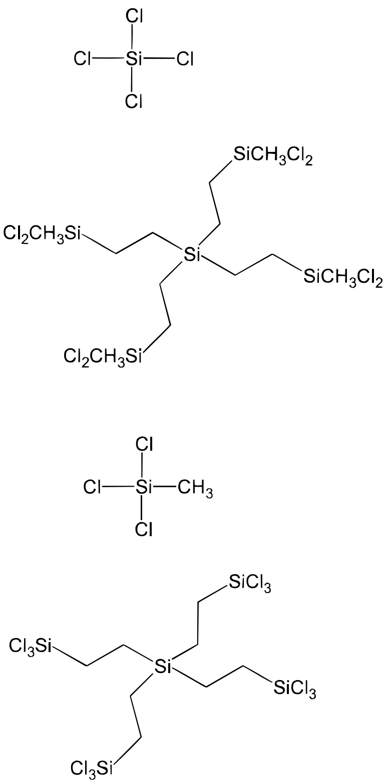

Figure 4. Sketches of the silane cores of the 4-, 8-, and 12-arm stars.

Table 1. Molecular Weights and Molecular Weight Distributions of Polybutadiene Polymers and Average Functionality of Star Polymers

polymer	$\bar{M}_w/10^3$	$\bar{M}_w/\bar{M}_n$	average functionality
linear H	28.4	1.01	
linear D	36.0	1.03	
3 arm star D arm	33.2	1.02	
3 arm star H arm	31.7	1.02	2.8
4 arm star D arm	30.1	1.02	
4 arm star H arm	31.2	1.01	3.8
linear H high MW	112.3	1.04	
H 4 arm star	110	1.01	3.7
8 arm star D arm	33.3	1.07	
8 arm star H arm	33.5	1.01	7.8
12 arm star D arm	30.9	1.02	
12 arm star H arm	33.8	1.01	11.7

Small-Angle Neutron Scattering. Small-angle neutron scattering data were obtained by using the D22 diffractometer at the Institut Laue-Langevin, Grenoble, France. Two sample–detector distances were used and the incident neutron beam wavelength was 10 Å; the range of scattering vector, Q, covered was $3 \times 10^{-3} \leq Q\ (\text{Å}^{-1}) \leq 0.2$. In all cases samples, 1 mm thick, were held between quartz windows and the temperature used for all the SANS experiments was 298 K. Scattering due to the quartz was subtracted and the data were normalized to the scattering of a 1 mm path length specimen of light water.

Star polymers of polybutadiene with 3, 4, 8, and 12 arms in total, each with one arm fully deuterated, were examined in the pure state by SANS. Mixtures of the partially labeled four-arm star polymer with each of the hydrogenous polymers were prepared by codissolving the two polymers in toluene and precipitating the solution into methanol followed by drying to constant weight under vacuum. The mixtures investigated were (a) partially labeled four-arm star in linear hydrogenous polybutadiene of the same degree of polymerization as a single arm over a nominal concentration range of star polymer of 5–50% (w/w); (b) the same four-arm star polymer in linear polymer with a degree of polymerization of the whole star; and

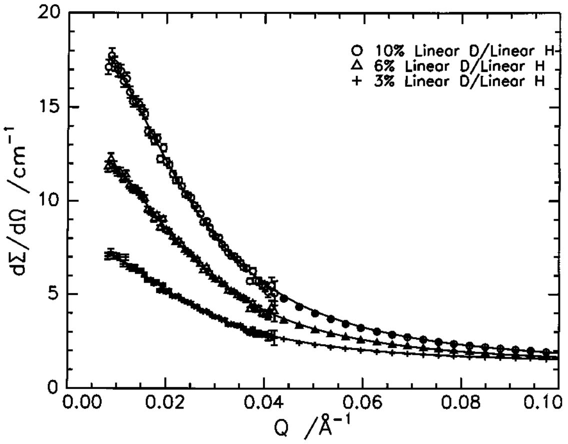

Figure 5. Scattering cross sections for mixtures of linear deuteriopolybutadiene in hydrogenous polybutadiene. The lines are fits to the data with the RPA expression for homopolymer mixtures.

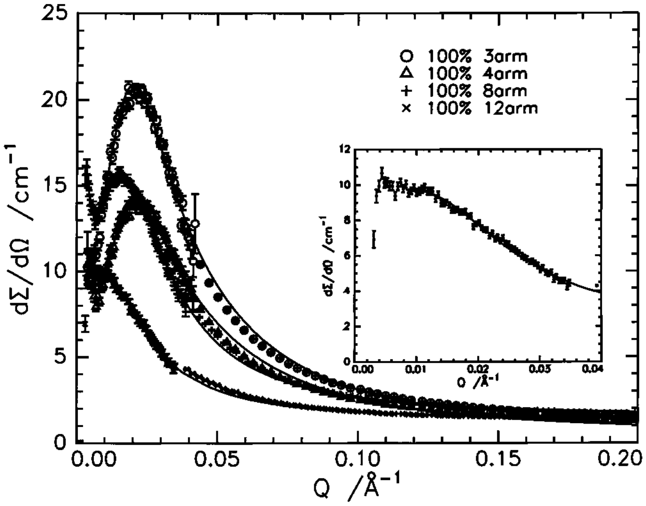

Figure 6. Scattering cross sections for the pure partially labeled stars. The lines are fits to the data with the RPA expression obtained for partially labeled stars. The inset shows the low Q region of the scattering cross section for the 12-arm star.

Table 2. Radii of Gyration and Interaction Parameters Obtained from SANS Data

(a) Mixtures of Linear D and H Polybutadienes

ϕ D polymer	R_g (Å)	χ
0.029	66	1.04×10^{-3}
0.055	64	5.12×10^{-4}
0.088	66	2.0×10^{-4}

(b) Pure Partially Labeled Star Polymers

no. of arms	R_g (Å) of labeled arm	χ_{HD}	χ_{DM}
3	68	6.2×10^{-3}	-5.1×10^{-3}
4	66	4.1×10^{-3}	-7.8×10^{-3}
8	72	-1.5×10^{-3}	7.7×10^{-4}
12	91	4.6×10^{-3}	-4.8×10^{-3}

(c) Partially Labeled 4 Arm Star in Linear Polybutadiene with Molecular Weight Equal to the Arm

ϕ star polymer	R_g (Å) of labeled arm	χ_{HD}	χ_{DM}
0.05	65	3.8×10^{-2}	-2.9×10^{-2}
0.9_6	66	2.2×10^{-2}	-1.5×10^{-2}
0.14	63	1.5×10^{-2}	-0.9×10^{-2}
0.18	66	1.3×10^{-2}	-0.8×10^{-2}
0.29	64	1.0×10^{-2}	-0.5×10^{-2}
0.49	62	6.5×10^{-3}	-0.1×10^{-2}

(d) Partially Labeled 4 Arm Star in Linear Polybutadiene with Molecular Weight Equal to the Whole Star

ϕ star polymer	R_g (Å) of labeled arm	χ_{HD}	χ_{DM}
0.05	57	-5×10^{-4}	6×10^{-3}
0.1	59	-5×10^{-3}	7×10^{-3}
0.15	61	-5×10^{-3}	6×10^{-3}
0.2	65	6×10^{-4}	1×10^{-3}
0.3	59	-3×10^{-3}	5×10^{-3}
0.5	61	-1×10^{-4}	3×10^{-3}

(c) the partially labeled four-arm star polymer in the equivalent fully hydrogenous four-arm star polybutadiene.

In the latter case the concentration range was 10–30% (w/w). In addition to these star polymer mixtures, dilute mixtures of linear deuteriopolybutadiene in linear hydrogenous polybutadiene [3–10% (w/w)] were investigated to ensure that the method of obtaining the cross sections as a function of *Q* was correct. To aid identification of the various mixtures, the following coding has been used: linear d polybutadiene in linear h polybutadiene, LDLH; four-arm partially labeled star in linear h polybutadiene of the same degree of polymerization as a single arm, 4ALH; four-arm partially labeled star in linear h polybutadiene of the same degree of polymerization as the star, 4A4L; and four-arm partially labeled star in hydrogenous star polybutadiene, 4A4H.

Results

Mixtures of Linear Polybutadiene. Figure 5 shows the scattering cross sections for the three mixtures of linear deuteriopolybutadiene in linear hydrogenous polybutadiene. As anticipated, the amplitude of the scattering decreases as the deuterium content of the mixtures decreases. For *Q* values greater than ~ 0.15 $Å^{-1}$ the scattering cross section was essentially constant. The solid lines through these data are fits of the RPA expression to the data when the volume fraction composition of the mixtures and scattering length densities have been incorporated. The only adjustable parameters in obtaining these fits were the radius of gyration and the interaction parameter χ in each case. In fitting the data for the linear mixtures with the appropriate RPA expression, the radius of gyration for the hydrogenous polybutadiene was fixed at the unperturbed value for the molecular weight of hydrogenous polybutadiene used (63.3 Å). From this same relation we anticipated that the radius of gyration of the deuterio polymer should be ca. 70 Å. We would expect the value of χ to be ca. $(7-10) \times 10^{-4}$ at this temperature.[16,17] From the fits to the data for all three concentrations we obtain an average radius of gyration of 65.2 Å. The values of χ obtained are in the range anticipated for this polymer from values reported by others (Table 2).

Pure Partially Labeled Stars. Figure 6 shows the absolute scattering cross section of the four partially labeled stars: for the 8- and 12-arm stars there is a clear shift of the scattered intensity maximum to lower *Q* values, i.e., an increase in the radius of gyration of the star arms as the functionality increases. This is particularly evident for the 12-arm star where the molecular weight of the labeled arm is somewhat smaller than that in the stars of lower functionality. Fitting these data with the appropriate RPA expression required the incorporation of two interaction parameters between the deuterated arm and its surrounding. One interaction parameter (χ_{HD}) is associated with intramolecular interactions; the second (χ_{DM}) is associated with the

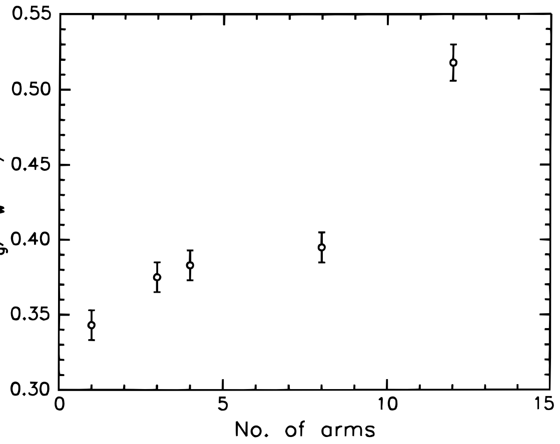

Figure 7. $R_g/M_w^{1/2}$ as a function of the number of arms of the partially labeled star polybutadienes.

interaction of the labeled arm with the surrounding matrix, which is made up of identical partially labeled star molecules. The fits obtained are shown as the lines in Figure 6 and the radii of gyration and interaction parameters obtained are given in Table 2. To remove any influence of the small variations in molecular weight the dimensions are plotted as $R_g/M_w^{1/2}$, as a function of the star functionality in Figure 7. There is clear evidence of an increase in size of the arm as the star functionality increases and we note a significant increase in $R_g/M_w^{1/2}$ between stars with 8 and 12 arms.

Mixtures of Partially Labeled Four-Arm Stars with Hydrogenous Polymer. Mixing the partially labeled four-arm star with the linear polybutadiene results in a fall in the intensity (Figure 8a) compared to that of the pure partially labeled four-arm star due to dilution of the deuterio polymer and shifts the maximum to lower Q due to convolution of the partial structure factors. At ca. 20% content of the partially labeled star, the maximum in the scattering cross section is just evident as a small shoulder on a continuously rising scattering cross section with reduction in Q. When the molecular weight of the linear matrix is increased to equal the total molecular weight of the star polymer, only the mixture containing 50% of the partially labeled star polymer has any hint of an underlying maximum, in the form again of a weak shoulder (Figure 8b). Decreasing the star content below 50% results in a continuously increasing scattered intensity as Q decreases, but this region of excess scattering above the flat background becomes confined to a successively smaller range of Q as the concentration of star polymer decreases. These general observations also apply when the partially labeled star polymer is mixed with the equivalent hydrogenous star polymer (Figure 8c).

In fitting the RPA expression to the SANS data for blends of the partially labeled four-arm star polymer mixed with hydrogenous polybutadiene, we have set the interaction parameter between H arms and H matrix (of whatever type) as zero and we have allowed for the possibility of two different interaction parameters between the labeled arm and the hydrogenous arms completing the star (χ_{HD}) and the labeled arm and the surrounding matrix (χ_{DM}). This is in the spirit of the liquid state theory for star polymers developed by Grayce and Schweizer.[10] For the two linear polybutadiene matrixes, the radius of gyration of each matrix polymer was fixed at the value obtained from literature values of the unperturbed dimensions. Figure 8a shows typical fits (solid lines) to the data where the only adjustable variables are the two interaction parameters mentioned and the radius of gyration of the arms of the star. When the partially labeled four-arm star is mixed with the hydrogenous four-arm star matrix, the scattering law requires the form factor for a regular star derived by Benoit. In its turn this form factor needs a value for the radius of gyration of each arm in the star. On the basis of the evidence for expansion of arms set

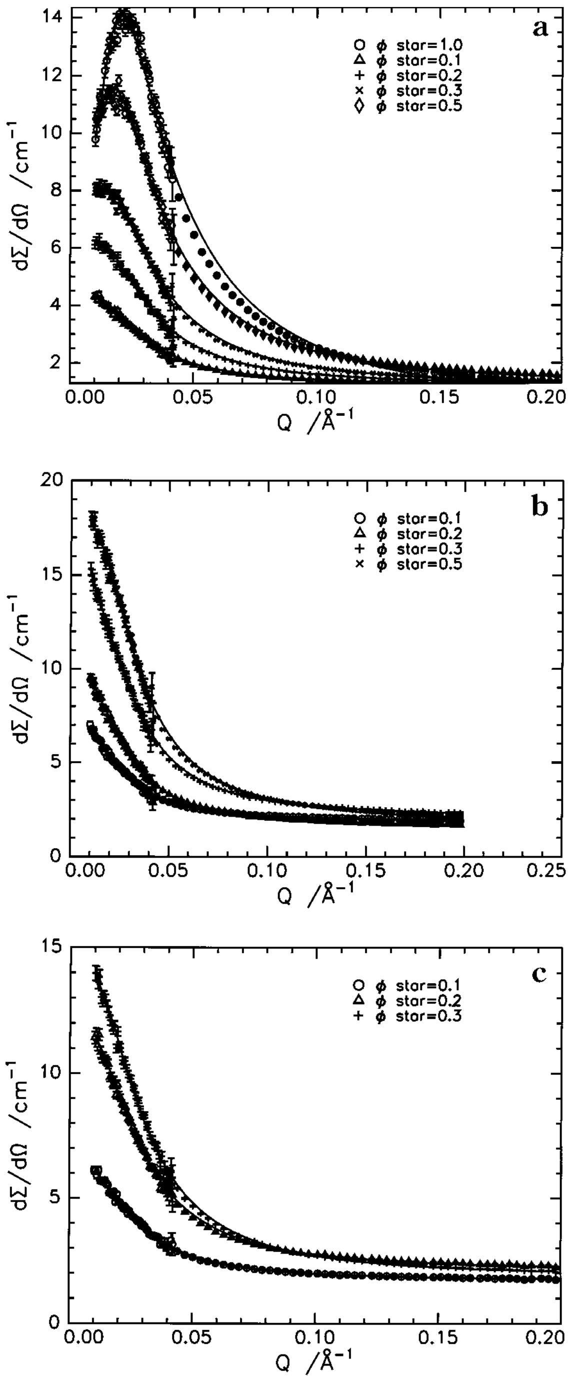

Figure 8. (a) Scattering cross sections for mixtures of the four-arm partially labeled star polymers in linear hydrogenous polybutadiene of the same molecular weight as the arms. (b) Scattering cross sections for mixtures of the four-arm partially labeled star polymers in linear hydrogenous polybutadiene of the same molecular weight as the star polymer. (c) Scattering cross section for mixtures of the four-arm partially labeled star polymer mixed with hydrogenous four-arm star polymer. Solid lines in panels a and b are fits to the data with the RPA expressions for the structure factor.

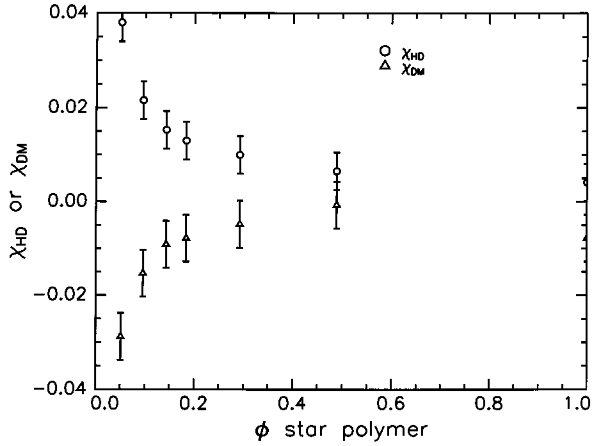

Figure 9. Interaction parameters, χ_{HD} and χ_{DM}, as a function of the star polymer content for mixtures of the four-arm partially labeled star polymer mixed with linear polybutadiene of the same molecular weight as the star arms.

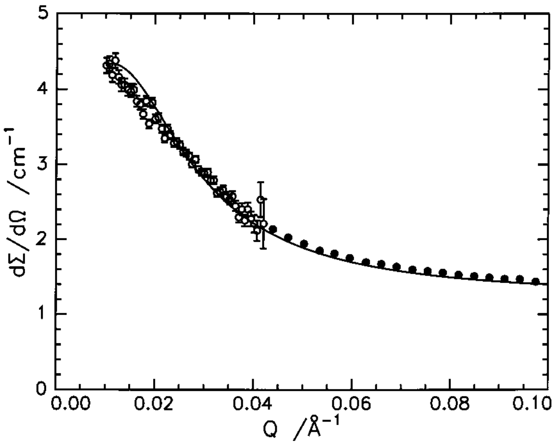

Figure 10. Attempted fit to the scattering cross section fixing the interaction parameters at zero for a mixture of the four-arm partially labeled star in linear polybutadiene; volume fraction of star polymer is 0.14.

out earlier, then strictly we should not use R_g values pertaining to the linear polymer. However, for a four-arm star the expansion of the arms over the linear polymer of equivalent molecular weight is not great and we have used values based on $R_g/M_w^{1/2}$ for linear polybutadiene. When the linear hydrogenous matrix has a molecular weight equal to or greater than the molecular weight of an arm, there appears to be a negligible influence of composition on the radius of gyration of the labeled arm in a four-arm star.

The dependence of χ_{HD} and χ_{DM} on the content of partially labeled four-arm star polymer in mixtures with hydrogenous linear polybutadiene of the same molecular weight as the star arms is shown in Figure 9, the lines being guides to the eye. Clearly the variation of both χ values is highly correlated with the composition of the mixture. Although the two curves appear to be mirror images of each other, due to the form of the equation for the scattered intensity these two values are *not* equivalent to having $\chi_{HD} = \chi_{DM} = 0$. A fit to the data cannot be obtained if these two χ parameters are set to zero and this is especially true when the volume fraction of star polymer is low (Figure 10). Comparing these values of χ_{HD} and χ_{DM} with the interaction parameter obtained for the linear polymer (Table 2), we note that the modulus of each interaction parameter is at least an order of magnitude greater than that for the linear polymers. Indeed, where mixture compositions can be directly compared the moduli of the interaction parameters for the star–linear mixtures are 2 orders of magnitude larger than those of the linear polymer.

Discussion

Radius of Gyration of a Single Arm. The stretching of polymer molecules attached by one end (grafted or tethered) to a surface and surrounded by identical molecules also attached to the same surface has been discussed many times from theoretical viewpoints.[34−36] When the surrounding matrix is a thermodynamically favorable solvent, the expansion of the tethered molecules leads to unfavorable intermolecular interactions between the arms that are relieved by a stretching of the molecules normal to the surface. This stretching has also been invoked for polymers surrounded by a polymeric matrix and such descriptions are covered by the generic term brush-like layers. In the main, polymer brushes are generally discussed when the molecules are attached to a planar surface and experimental studies in both bulk melts and dilute solutions have been reported.[37−46] Initially, the concept of stretching was confined to stars in dilute solution, but given the theoretical predictions, confirmed to some extent by experiment, of the stretched dry brush state, it is perhaps not surprising that we have observed stretching of the single labeled arm in the multiarm stars. Past experimental work has inferred the stretching of star arms from the global dimensions of the star polymers;[3,9,47] we have reported here a direct observation of this stretching for *one arm* of the star. In the liquid state theory for star polymers the basic source for the stretching of the arms, even at bulk melt density, is a failure of complete screening of excluded volume interactions. For segments near the core, their shielding by corona segments reduces the intermolecular interactions responsible for screening. Furthermore, excluded volume interactions continue to exist between core segments and corona segments on different arms and particularly between corona segments on different arms. Relief of such interactions is obtained by stretching of the star arms. Grayce and Schweizer[10] calculate a number of parameters quantifying the conformational properties of star polymers, and of particular relevance here is their parameter g_{arm}, the ratio of the mean square end-to-end distance for a star arm to that of the equivalent unattached polymer. Gaussian chain behavior was not assumed in obtaining this parameter (and others), and if stretching becomes sufficiently large, non-Gaussian behavior eventually supervenes in any event. Because of this possibility of non-Gaussian behavior we cannot use the Gaussian relation ($\langle r^2\rangle = 6\langle R_g^2\rangle$) to calculate values of g_{arm}. In Figure 11 we plot $[(R_g/M_w^{1/2})_{star}/(R_g/M_w^{1/2})_{lin}]^2$ as a function of the star functionality and compare it with g_{arm} values from Grayce and Schweizer. Clearly the two dependencies diverge even at modest values of f. From the experimental data we again note that somewhere between f=8 and f=12 a critical functionality is reached where the extension of the arm increases markedly above the expectations of theory. However, the main contention of Grayce and Schweizer that there is a stretching of the arms, even in bulk melt conditions, is borne out for the partially labeled stars reported here. A feature of these stars is that the silane cores in each do not have a wide size range variation, and from the viewpoint of early theories of star polymers, this factor is important because it was

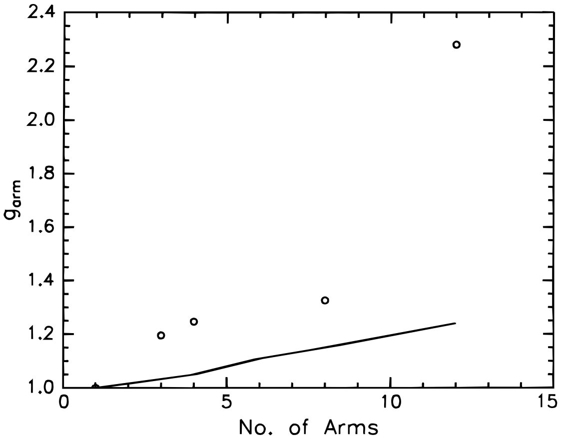

Figure 11. Single-arm stretching factor calculated as $[(R_g/M_w^{1/2})_{star}/(R_g/M_w^{1/2})_{lin}]^2$ (○) compared with the g_{arm} values calculated by Grayce and Schweizer (solid line).

the aversion to each other of segments near the core to which the stretching of chains was attributed. This view is not supported by the calculations of Grayce and Schweizer, which reveal that excluded volume interactions between core and corona sites, which *pull* the core regions outward toward the corona region, protect the core regions from being fully screened under bulk conditions. However, for stars with significantly larger number of arms, a larger silane nucleus has to be used and these more open cores may be less well protected from screening and thus the stretching in very many arm star polymers may be reduced.

Interaction Parameters. The concept of differential screening for core and corona segments rationalizes the experimental observation that to obtain a fit to the scattering data, with the RPA scattering laws, the most general form of the scattering law had to be used, i.e., one that included an interaction parameter between H and arms within the star and between D arm and surrounding matrix. These two interaction parameters are probably better interpreted as quantifying the interactions between core and corona regions and between corona regions on different stars in some way. The accuracy of the χ values depends on using absolute cross sections and observing a sufficient range of the scattering law so that the fitting to the data is unambiguous, and for the data reported here this is only true for the pure partially labeled star polymers and the four-arm star in the linear polybutadiene matrixes. The dependence of the two interaction parameters on star functionality is shown in Figure 12 for all the pure star copolymers, i.e., in the absence of any added hydrogenous linear polymer. Although these data are somewhat scattered, the general trend is an increase in χ_{HD} and a possible decrease in χ_{DM} as the functionality increases (i.e., as the volume fraction of deuterium in the polymer decreases). The interaction parameters for the eight-arm star do not fit the general trend well, and despite repeated fitting of the data (from different starting points), the values for the interaction parameters returned were always the same.

By contrast, the interaction parameters obtained for the partially labeled four-arm star in hydrogenous polymer of the same molecular weight as the arm exhibit highly correlated dependencies on the composition of the matrix (Figure 9). These highly correlated dependencies on composition are not evident in the interaction parameters for the partially labeled star in

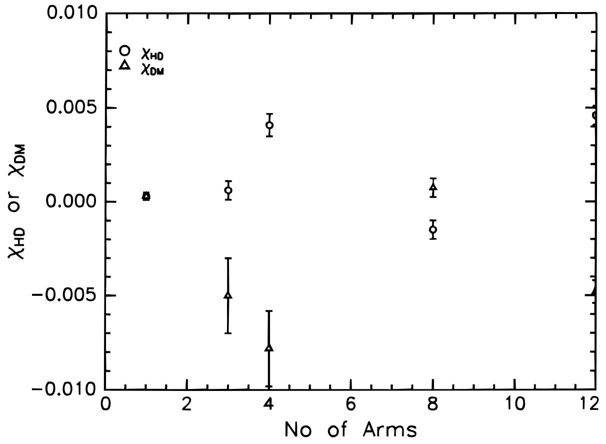

Figure 12. Interaction parameters for the star polymers as a function of the number of arms.

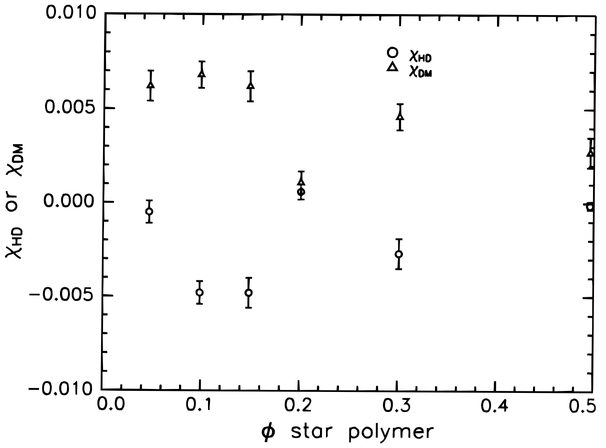

Figure 13. Dependence of the interaction parameters on composition for mixtures of the partially labeled four-arm star polymer in linear hydrogenous polybutadiene of the same molecular weight as the star polymer.

a hydrogenous matrix whose molecular weight equals that of the star (Figure 13). Evidently the interaction parameter behavior is highly dependent on the nature of the system and no trend even in general behavior is apparent in Figures 11, 14, and 15. The composition dependencies seen in Figure 9 are quite often observed for mixtures of linear polymers and a view has been expressed that this is due to errors becoming increasingly significant as the content of labeled polymer decreases. After careful consideration of the sources of error and noting the extremely low signal-to-noise errors on our SANS data, we believe the errors in χ_{HD} and χ_{DM} are correctly expressed in Figures 11, 14, and 15. Additionally, if such behavior were due to increased errors at low composition, then it should also be evident in Figure 13 for the star polymer in the linear matrix of molecular weight equal to that of the star.

Although the influence of composition on the interaction parameters has been the subject of some investigations for linear polymers and the focus of some theoretical effort,[48−50] there has been no equivalent attention paid to the role that molecular architecture plays. Indeed, most experimental work investigates the temperature dependence of χ. There have been some discussions of structural effects on χ but these have been confined to relatively minor perturbations on the linear configuration, e.g., linear and branched polyethylenes.[51] It was noted that phase separation could be driven by a branch content greater than a critical average number per molecule. Graessley and co-workers[24] used hydrogenated and partially deuterated polydienes where the statistical segment length varied and found that the values of the interaction parameters had some consistency with a proposal that mismatch in statistical segment length decreases the entropy of mixing.[28] However, the authors remarked on notable exceptions, and moreover only the temperature dependence of χ was examined.

Fredrickson et al.[27] have expanded on the original suggestion regarding mismatch in step lengths restricting the entropy by considering the contribution that nonlocal correlations may make to χ. Such nonlocal correlations would be universal and independent of the chemistry of the monomer units making up the polymer, being dependent on R_g and molecular architecture only. The cogent critique of this approach by Singh and Schweizer[52] notwithstanding, we have applied their relation to our data for the partially labeled four-arm star in the two linear matrixes. The expression obtained for the interaction energy density ($\equiv \chi/(v_1v_2)^{1/2}$, where v_1 and v_2 are the volumes of the monomer units in the polymer) for a blend of linear polymers is a product of a local term dependent on chemistry of the monomer units and a term composed of volume fractions and invariant parameters (β_i) defined by Helfand and Sapse[53]

$$\frac{\chi}{(v_1v_2)^{1/2}} = \frac{\Lambda_a{}^3}{24\pi^2}\left[\frac{1-(\beta_1/\beta_2)^2}{\phi+(1-\phi)(\beta_1\beta_2)^2}\right]^2 \qquad (5)$$

and

$$\beta_i{}^2 \equiv a_i{}^2/6v_i$$

where a_i is the statistical segment length of species i and $\Lambda_a = (a_1a_2)^{-1/2}$. If eq 5 above is valid for the mixtures of linear h and d polybutadiene, then we expect (β_1/β_2) to have a value very near 1 and the value of a_i should not be too distant from the generally accepted statistical segment length for polybutadiene of ~6.9 Å. Analyzing the three values of χ obtained for the linear polybutadiene mixtures according to eq 5, we obtained $a = 5.8$ Å and $(\beta_1/\beta_2) = 0.98$. The statistical step length is smaller than anticipated, but since only three data points for compositions over a narrow range have been used, the values obtained for a and (β_1/β_2) are satisfactorily close to the expected values. Clearly, the validity of eq 5 needs to be examined over a wider range of mixture composition for linear polymers.

Entropic corrections are also associated with architectural asymmetry such as would be exhibited by mixtures of star and linear polymers. For a star of f arms mixed with a linear polymer and for cases where either f is large or the linear polymer has a radius of gyration greater than that of the arms, then

$$\frac{\chi}{(v_1v_2)^{1/2}} \simeq \frac{(f-3)^{3/2}}{(1-\phi)^{1/2}} \qquad (6)$$

For partially labeled star polymer in both linear hydrogenous polybutadiene matrixes, both χ_{HD} and χ_{DM} have been plotted in Figure 14 as a function of $(1-0)^{-1/2}$ where ϕ is the volume fraction of star polymer in the mixture. Linear dependencies of χ on $(1-0)^{-1/2}$ are only observed for mixtures with the higher molecular weight linear polybutadiene. The combination of the star polymer in a linear matrix whose molecular weight is equal to that of the whole star more closely fulfils the conditions set down by Fredrickson et al.[27]

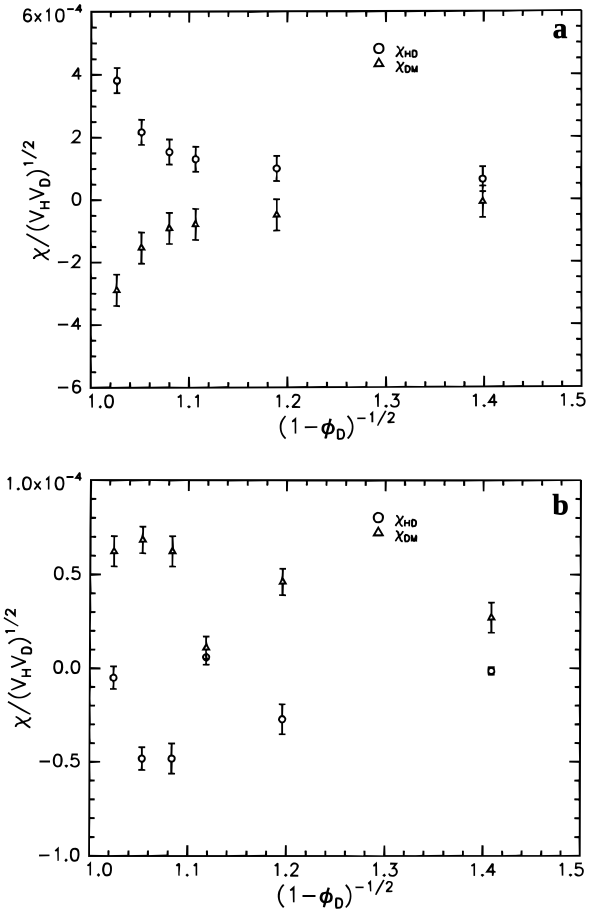

Figure 14. Interaction parameters for the four-arm star polymer in the low molecular weight (a) and the high molecular weight (b) hydrogenous polybutadiene plotted in the manner suggested by Fredrickson et al.[27]

Kumar[50] has used Monte Carlo simulations to assess the composition dependence of χ for blends of *linear* polymers. He attributes the parabolic variation of χ observed by SANS to the disregard of excess volume changes on mixing in the incompressible RPA theory. From such considerations Kumar obtained a relation for SANS-determined χ values, which can be represented for the star (s)−linear (l) combinations here as

$$-\chi \propto \phi_s\phi_l$$

where ϕ_s and ϕ_l are the volume fraction of the star and linear polymer, respectively. For the partially labeled four-arm star polymer in a linear polybutadiene with a molecular weight equal to that of the arms, the linear dependence predicted by the Kumar relation is observed for both χ_{HD} and χ_{DM} (Figure 15). This linear dependence is *not* evident for the interaction parameters when the matrix is the higher molecular weight linear polybutadiene.

From these data no clear view of the relation between the interaction parameters and the architecture or composition of the mixture containing the star polymers is evident. This may be because what are reported as interaction parameters are not as defined in the original Flory−Huggins theory. These χ values may be *effective*

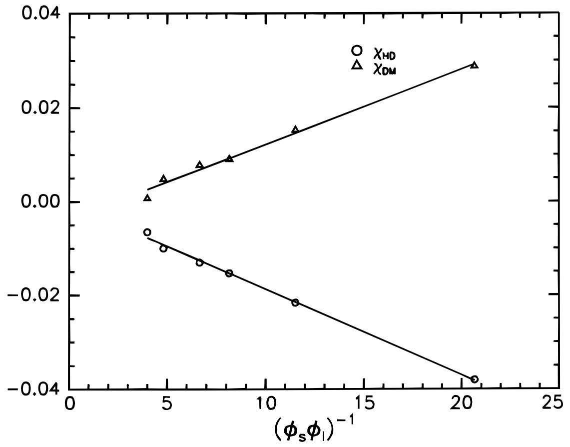

Figure 15. Dependence of interaction parameters for the mixtures of the partially labeled four-arm star polymer in hydrogenous polybutadiene of the same molecular weight as the arms plotted according to the relation derived by Kumar. The lines are the best linear fits to the data.

values. The RPA theory on which the scattering laws used are based may not properly account for the different levels of screening in star polymers of the core and corona segments. Hence the fluctuations in monomer density responsible for the scattering will differ between core and corona regions. These fluctuations will clearly be modified by the presence of homopolymer, and the differential screening between core and corona will also be changed. The RPA expressions for the scattering are insufficiently able to cope with these differing level of fluctuations in a *proper* manner, but a fit can be obtained by adjusting the interaction parameters. The dependence of the interaction parameters on composition reflects the change in the excluded volume effects between core and corona but it is most probably incorrect to view them as true χ values in the generally accepted sense.

Conclusions

Definitive evidence for the stretching of the arms in star polymers has been obtained from SANS data for star polybutadienes with one deuterium-labeled arm. The stretching of the arms increases with the number of arms. There is some evidence for an enhanced stretching of arms at some star functionality between 8 and 12. Although the increase in arm dimensions has been theoretically predicted by Grayce and Schweizer, the experimental values of the stretching factor (g_{arm}) are much larger than those predicted by the liquid state theory.

By use of a random phase approximation approach, the generalized scattering law for partially labeled star polymers and their mixtures with linear and star polymers has been obtained. In its most general form (where the matrix is chemically distinct from the labeled star), two interaction parameters are required; which describe intrastar and star−matrix thermodynamics, respectively. Acceptable fits to the SANS data were only obtained when both interaction parameters were retained, the identical chemical nature of the unlabeled arms and the matrix polymer notwithstanding. Although the dependence of both interaction parameters on the composition of mixtures of the four-arm star with linear polybutadienes was describable by current theories, no common pattern is discernible as the labeled polymer content is diluted either by increasing the number of arms or by adding hydrogenous polymer. The need to use two interaction parameters can be rationalized by appeal to the liquid state theory of star polymers, which predicts differential screening between core and corona segments in stars. It therefore seems more probable that the interaction parameters obtained are *effective* quantities reflecting the change in screening as the number of arms and/or mixture composition changes.

All of the parameters discussed (interaction parameter values and radius of gyration) have relied on the use of random phase theory, which presumes that the polymer is incompressible. Liquid state theory of star polymers does *not* make this assumption; consequently, the observations made by using values from an RPA theory approach and the comparison to the predictions of liquid state theory may be questionable. In the absence of structure factor expressions derived directly from liquid state theory, there is no alternative and a rigorous examination fully based on the latter theory awaits the development of such structure factors.

Acknowledgment. We thank the EPSRC for support of the research program of which this work forms part and for their support of the Institut Laue-Langevin, Grenoble, France.

Appendix

The general form of the scattering cross section for a three component system is given by

$$\frac{\mathrm{d}\sum(Q)}{\mathrm{d}\Omega} = K_{\mathrm{HM}}S_{\mathrm{AA}}(Q) + 2K_{\mathrm{DM}}K_{\mathrm{HM}}S_{\mathrm{AB}}(Q) + K_{\mathrm{DM}}S_{\mathrm{BB}}(Q)$$

$$S_{\mathrm{AA}}(Q) = \frac{S1_{\mathrm{BB}}(Q)}{S1_{\mathrm{AA}}(Q)S1_{\mathrm{BB}}(Q) - S1_{\mathrm{AB}}{}^{2}(Q)}$$

$$S1_{\mathrm{BB}}(Q) = SO1_{\mathrm{BB}}(Q) + V_{\mathrm{BB}}(Q)$$

$$SO1_{\mathrm{BB}}(Q) = \frac{SO_{\mathrm{AA}}(Q)}{SO_{\mathrm{AA}}(Q)SO_{\mathrm{BB}}(Q) - SO_{\mathrm{BB}}{}^{2}(Q)}$$

$$SO_{\mathrm{AA}}(Q) = n_{\mathrm{H}}D_{\mathrm{H}}\phi_{\mathrm{H}}v_{\mathrm{H}}\left(g_{\mathrm{dH}} + (n_{\mathrm{H}} - 1)\left[\left(\frac{1}{u_{\mathrm{H}}}\right)(1 - \exp(u_{\mathrm{H}}))\right]^{2}\right)$$

$$SO_{\mathrm{BB}}(Q) = n_{\mathrm{D}}D_{\mathrm{D}}\phi_{\mathrm{D}}v_{\mathrm{D}}\left(g_{\mathrm{dD}} + (n_{\mathrm{D}} - 1)\left[\left(\frac{1}{u_{\mathrm{D}}}\right)(1 - \exp(u_{\mathrm{D}}))\right]^{2}\right)$$

$$SO_{\mathrm{AB}}(Q) = \sqrt{n_{\mathrm{D}}n_{\mathrm{D}}D_{\mathrm{H}}D_{\mathrm{D}}v_{\mathrm{H}}v_{\mathrm{D}}\phi_{\mathrm{H}}\phi_{\mathrm{D}}} \times \left[\left(\frac{1}{u_{\mathrm{H}}}\right)(1 - \exp(u_{\mathrm{H}}))\right]\left[\left(\frac{1}{u_{\mathrm{D}}}\right)(1 - \exp(u_{\mathrm{D}}))\right]$$

$$V_{\mathrm{BB}}(Q) = \frac{1}{D_{\mathrm{M}}\phi_{\mathrm{M}}v_{\mathrm{M}}g_{\mathrm{dM}}} - \frac{2\chi_{\mathrm{DM}}}{v_{\mathrm{norm}}}$$

The term $S_{\mathrm{BB}}(Q)$ is constructed in a similar manner as that above for $S_{\mathrm{AA}}(Q)$. The cross term $S_{\mathrm{AB}}(Q)$ is given by

$$S_{AB}(Q) = \frac{-S1_{AB}(Q)}{S1_{AA}(Q)S1_{BB}(Q) - S1_{AB}{}^{2}(Q)}$$

$$S1_{AB}(Q) = SO1_{AB}(Q) + V_{AB}(Q)$$

$$SO1_{AB}(Q) = \frac{-SO_{AB}(Q)}{SO_{AA}(Q)SO_{BB}(Q) - SO_{AB}{}^{2}(Q)}$$

$$V_{AB}(Q) = \frac{1}{(D_{M}\phi_{M}v_{M}g_{dM})} - \frac{\chi_{HM} + \chi_{DM} + \chi_{HD}}{v_{norm}}$$

where K_{IJ} is the contrast factor between species I and J and D, H, and M refer to deuterio, hydrogenous, and matrix species, respectively. n, D, ϕ, and v are the number of arms, degree of polymerization, volume fraction, and monomer unit volume, respectively, of the species signified by the subscript. v_{norm} is a reference volume calculated as the appropriate root of the product of the individual monomer unit volumes [square root for $V_{II}(Q)$ terms and cube root for $V_{IJ}(Q)$ terms]. The Debye function for the scattering of a Gaussian coil is represented by g_{dI} for species I.

References and Notes

(1) Grest, G. S.; Fetters, L. J.; Huang, J. S.; Richter, D. *Adv. Chem. Phys.* **1996**, *94*, 67.
(2) Daoud, M.; Cotton, J. P. *J Phys. (Paris)* **1982**, *43*, 531.
(3) Horton, J. C.; Squires, G. L.; Boothroyd, A. T.; Fetters, L. J.; Rennie, A. R.; Glinka, C. J.; Robinson, R. A. *Macromolecules* **1989**, *22*, 681.
(4) Boothroyd, A. T.; Squires, G. L.; Fetters, L. J.; Rennie, A. R.; Horton, J. C.; de Vallera, A. M. B. G. *Macromolecules* **1989**, *22*, 3130.
(5) Wiilner, L.; Jucknischke, O.; Richter, D.; Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; Fetters, L. J.; Huang, J. S.; Lin, M. Y.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 3821.
(6) Boothroyd, A. T.; Ball, R. C. *Macromolecules* **1990**, *23*, 1729.
(7) Richter, D.; Jucknischke, O.; Willner, L.; Fetters, L. J.; Lin, M.; Huang, J. S.; Roovers, J.; Toporowski, P.; Zhou, L.-L. *Polym. Mater. Sci. Eng.* **1994**, *67*, 425.
(8) Lantman, C. W.; MacKnight, W. J.; Rennie, A. R.; Tassin, J.; Monnerie, L.; Fetters, L. J. *Macromolecules* **1990**, *23*, 836.
(9) Richter, D.; Farago, B.; Huang, J. S.; Fetters, L. J.; Ewen, B. *Macromolecules* **1989**, *22*, 468.
(10) Grayce, C. J.; Schweizer, K. S. *Macromolecules* **1995**, *28*, 7461.
(11) Schweizer, K. S.; Curro, J. G. *Adv. Chem. Phys.* **1997**, *98*, 1.
(12) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(13) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(14) Mori, K.; Tanaka, H.; Hashimoto, T. *Macromolecules* **1987**, *20*, 381.
(15) Benoit, H.; Hadzioannou, G. *Macromolecules* **1988**, *21*, 1449.
(16) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.
(17) Bates, F. S.; Dierker, S. B.; Wignall, G. D. *Macromolecules* **1986**, *19*, 1938.
(18) Krishnamoorti, R.; Graessley, W. W.; Fetters, L. J.; Garner, R. T.; Lohse, D. J. *Macromolecules* **1995**, *28*, 1252.
(19) Krishnamoorti, R.; Graessley, W. W.; Dee, G. T.; Walsh, D. J.; Fetters, L. J.; Lohse, D. J. *Macromolecules* **1996**, *29*, 367.
(20) Taylor-Maranas, J. K.; Debenedetti, P. G.; Graessley, W. W.; Kumar, S. K. *Macromolecules* **1997**, *30*, 6943.
(21) Taylor, J. K.; Debenedetti, P. G.; Graessley, W. W.; Kumar, S. *Macromolecules* **1996**, *29*, 764.
(22) Hopkinson, I.; Kiff, F. T.; Richards, R. W.; King, S. M.; Farren, T. *Polymer* **1995**, *36*, 3523.
(23) Balsara, N. P.; Jonnalagadda, S. V.; Lin, C. C.; Hanc, C.; Krishnamoorti, R. *J. Chem. Phys.* **1993**, *99*, 10011.
(24) Krishnamoorti, R.; Graessley, W. W.; Balsara, N. P.; Lohse, D. J. *Macromolecules* **1994**, *27*, 3073.
(25) Lin, C. C.; Jonnalagadda, S. V.; Kesani, P. K.; Dai, H. J.; Balsara, N. P. *Macromolecules* **1994**, *27*, 7769.
(26) Lin, C. V.; Jonnalagadda, S. V.; Balsara, N. P.; Han, C. C.; Krishnamoorti, R. *Macromolecules* **1996**, *29*, 661.
(27) Fredrickson, G. H.; Liu, A. J.; Bates, F. S. *Macromolecules* **1994**, *27*, 2503.
(28) Bates, F. S.; Fredrickson, G. H. *Macromolecules* **1994**, *27*, 1065.
(29) Benoit, H. *J. Polym. Sci.* **1953**, *11*, 507.
(30) Balsara, N. P.; Jonnalagadda, S. V.; Lin, C. C.; Han, C. C.; Krishnamoorti, R. *J. Chem. Phys.* **1993**, *99*, 10011.
(31) Read, D. J. *Macromolecules* **1998**, *31*, 899.
(32) Akcasu, A. Z.; Tombaklogu, T. *Macromolecules* **1990**, *23*, 607.
(33) Hutchings, L. R.; Richards, R. W. *Polym. Bull.* **1998**, *41*, 283.
(34) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(35) Shull, K. R. *J. Chem. Phys.* **1991**, *94*, 5723.
(36) Fleer, G. J.; Cohen-Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman and Hall: London, 1993.
(37) Klein, J.; Luckham, P. F. *Macromolecules* **1984**, *17*, 1041.
(38) Luckham, P. F.; Klein, J. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86*, 1363.
(39) Klein, J.; Kumacheva, E.; Perahia, D.; Mahalu, D.; Warburg, S. *Faraday Discuss.* **1994**, *98*, 173.
(40) Patel, S.; Tirrell, M.; Hadziioannou, G. *Colloids and Surfaces* **1988**, *31*, 157.
(41) Patel, S.; Tirrell, M. *Annu. Rev. Phys. Chem.* **1989**, *40*, 597.
(42) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571.
(43) Dan, N. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 48.
(44) Kiff, F. T.; Richards, R. W.; Thompson, H. L.; Bucknall, D. G.; Webster, J. P. R. *J. Phys. II France* **1997**, *7*, 1871.
(45) Jones, R. A. L.; Kramer, E. J.; Norton, L.; Fetters, L. J. *Macromolecules* **1992**, *25*, 2359.
(46) Hopkinson, I.; Kiff, F. T.; Richards, R. W.; Clough, A.; Bucknall, D. G. *Polymer* **1997**, *38*, 87.
(47) Richter, D.; Farago, B.; Fetters, L. J.; Huang, J. S.; Ewen, B. *Macromolecules* **1990**, *23*, 1845.
(48) Bates, F. S.; Muthukumar, M.; Wignall, G. D.; Fetters, L. J. *J. Chem. Phys.* **1988**, *89*, 535.
(49) Muthukumar, M. *J. Chem. Phys.* **1986**, *85*, 4722.
(50) Kumar, S. K. *Macromolecules* **1994**, *27*, 260.
(51) Alamo, R. G.; Graessley, W. W.; Krishnamoorti, R.; Lohse, D. J.; Londono, J. D.; Mandelkern, L.; Stehling, F. C.; Wignall, G. D. *Macromolecules* **1997**, *30*, 561.
(52) Singh, C.; Schweizer, K. S. *J. Chem. Phys.* **1995**, *103*, 5814.
(53) Helfand, E.; Sapse, A. M. *J. Chem. Phys.* **1975**, *62*, 1327.

MA980980W