Small-Angle Neutron Scattering from Single Arm Labeled Polybutadiene Star Polymers in Dilute Solution

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ABSTRACT: Dilute cyclohexane solutions of polybutadiene star polymers with 3, 4, 8, and 12 arms wherein one arm is perdeuterated have been investigated by small-angle neutron scattering. The scattering cross sections obtained showed a characteristic peak at finite values of the scattering vector, Q. This maximum is not a structure factor arising from intermolecular interactions but is intrinsic to the scattering law of star molecules with one arm of a different isotopic composition to the other arms. The theoretical scattering law developed for such isotopic copolymers was found to fit the observed scattering well and provided values of the radius of gyration of the labeled arm. No dependence of the radius of gyration on star polymer concentration was noted, but the radius of gyration of the labeled arm increased as the functionality of the star increased from 3 to 12, the increase in dimensions in the 12-arm star being ca. 25% greater than the radius of gyration obtained for the three-arm star. In these dilute solutions the radii of gyration were larger than obtained for the bulk melt state of the stars. The data have been compared with theoretical predictions, but generally a much stronger dependence of the radius of gyration on star functionality is observed than is predicted.

Introduction

Star polymers have been the focus of theoretical and experimental interest for over 20 years.[1−4] The understanding of the properties in dilute solution and in the bulk state has been aided by the development of synthetic methods of great precision that produce star polymers with a known number of arms with an exact molecular weight and a very narrow molecular weight distribution. A considerable amount of experimental data has been reported on the size as a function of number of arms and their molecular weight, their diffusion and viscosity in solution, excluded-volume effects,[2,4−19] and comparison of all these data with theoretical models and simulations.[1,20−34] The theoretical background is summarized below, and the majority of the experimental data pertains to stars wherein all the arms are identical in molecular weight and chemical and isotopic purity. Much of the data is from small-angle neutron scattering, and considerable theoretical attention is focused on the scattering law or form factor of the star polymers. However, the theoretical descriptions very often are based on the behavior of a single arm, and experimental verification of this aspect has not been reported to a significant extent.

The absence of data on the single-arm behavior of multiarm stars is, to an extent, due to the difficulty in synthesizing star polymers where one arm can be investigated uniquely but without making the arm significantly different in nature to the others. Hence, the “mikto” arm copolymer synthesis pioneered by Hadjichristidis is not suitable for such investigations. We reported earlier the development of a synthetic method[35] that allows us to prepare star polymers where only one arm is deuterated. This led to the successful preparation of polybutadiene star polymers with up to 12 arms, one of which was deuterated and the remainder being hydrogenous. Earlier small-angle neutron scattering from the bulk state and mixtures with linear polymers[36] was successfully interpreted using a scattering law obtained by combining a method developed by Read[37] and the correct incorporation of contrast factors due to Akcasu and Tombakoglu.[38] The results gave some support to the PRISM theory of dense star fluids;[32] however, the expansion of the single labeled arm was considerably larger than that predicted by the theory. We now turn our attention to dilute solutions of the same polybutadiene star polymers in cyclohexane where the expansion of linear polybutadiene approaches the excluded-volume limit.

Theoretical Background

Although the solutions of star polymers investigated may be dilute in terms of number of star molecules per unit volume, this dilute picture does not prevail within any one star. The fundamental aspects and analysis of the concentration regimes within a star polymer were set out by Daoud and Cotton[23] some 20 years ago. A star molecule with sufficiently long arms and dissolved in a thermodynamically good solvent has three regions. At the core is a region corresponding to bulk, melt conditions, i.e., number density of monomers $\rho(r) = 1$ and absence of any excluded-volume effects that produce expansion of the arm dimensions. The radius of this region is given by the scaling relation

$$r_{\text{core}} \sim f^{1/2} a \tag{1}$$

f is the number of arms in the star and a the statistical step length of the polymer. At distances greater than r_{core} but less than a radius, r_1, the number density of monomers is still high, and the conditions for a concentrated solution prevail. The chain configuration is described using the “blob” model, but the blobs are

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unswollen and the portion of the chain within each blob behaves as an ideal, unperturbed chain. The number density of monomer units varies with the radius and is given by

$$\rho(r) \sim (r/a)^{-1} f^{1/2} \tag{2}$$

and the radius, r_1, where this ideal blob behavior persists to is

$$r_1 \sim a f^{1/2} (V/a^3)^{-1} \tag{3}$$

where V is the excluded-volume parameter determined by the polymer−solvent interaction parameter χ, i.e.

$$V = a^3(^1/_2 - \chi) \tag{4}$$

For radii greater than r_1 the monomer number density falls sufficiently that semidilute solution conditions are met and the blobs become swollen. In this outer region the monomer number density is

$$\rho(r) \sim f^{(3\nu-1)/2\nu} \left(\frac{r}{a}\right)^{(1-3\nu)/\nu} \left(\frac{V}{a^3}\right)^{(1-2\nu)/\nu} \tag{5}$$

where ν is the molecular weight exponent in the relation between radius of gyration and molecular weight.

When the star arms are long, then the center-to-end distance of the arm ($\equiv$ star radius) is

$$R \sim aN^{\nu} f^{(1-\nu)/2} \left(\frac{V}{a^3}\right)^{2\nu-1} \tag{6}$$

and adopting the Flory value for ν ($^3/_5$) then

$$R \sim aN^{3/5} f^{1/5} \left(\frac{V}{a^3}\right)^{1/5} \tag{7}$$

The different length scales that characterize a star polymer are the radius (R), the size of the largest blob in the outer portion of the star, i.e., the correlation length, ξ, and the monomer size, a. The existence of these length scales becomes apparent in the scattering vector (Q) dependence of the scattered intensity. For $Q < R^{-1}$ the scattering is independent of Q since it is determined by the global dimensions of the star. For $\xi^{-1} \le Q \le a$ the scattering should have a $Q^{-(1/\nu)}$ dependence, i.e., $Q^{-5/3}$ where excluded-volume effects are present and Q^{-2} under Θ conditions.

Form factors for the scattering by the whole star molecule have been derived by Benoit[21] and Alessandrini and Carignano,[20] that by the latter incorporating excluded-volume effects. Neither of these fits the experimental scattered intensity over the entire Q range; however, the equation of Alessandrini and Carignano does reproduce the maximum observed when the data are plotted as $Q^{5/3}\,\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega$ as a function of Q, from which the radii of gyration of the stars are obtained. Dozier et al.[7] have also produced a form factor expression that incorporates excluded-volume behavior. An early attempt at a different observation of the dimensions of a single arm (as opposed to inferring it from the global properties) was reported by Richter et al.[12] A $Q^{-3/2}$ dependence was observed for a 12-arm polystyrene star, the small exponent being cited as evidence for a stronger stretching of the arms than that due to excluded-volume effects. The difficulty with accepting this conclusion is that it is clear from the synthesis procedure that the polymer did not consist of stars wherein just one arm was deuterium labeled. The "smearing" of the scattering due to this distribution of labeled arms is more severe than is implied, and thus the conclusions may not be firmly based. Moreover, the scattering law used to interpret the data for these one-armed stars was not correct.

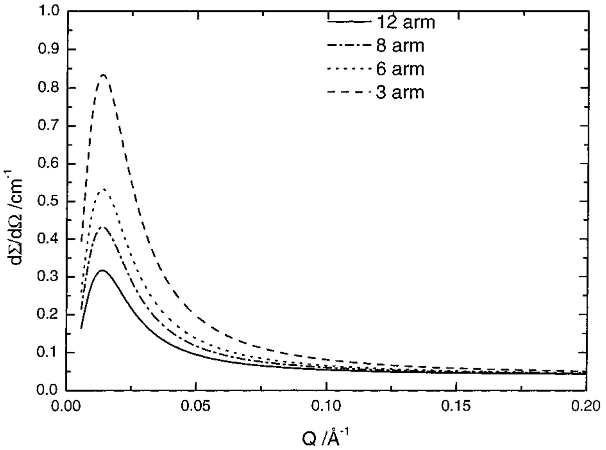

Figure 1. Calculated scattering cross sections for polybutadiene star polymers with the functionalities indicated with each having one deuterium-labeled arm. All arms have the same radius of gyration of 100 Å.

The proper form of the scattering law for stars where one or more arms differs in scattering power from the remaining arms has been set out by Read.[37] This form of the scattering law for the system has been previously used by us in the analysis of the small-angle neutron scattering from the bulk state of the star polymers discussed here and for the analysis of scattering from star diblock copolymers wherein one block of each diblock arm is deuterated.[36,39]

The precise form of the scattering law has been fully described in an earlier publication,[36] but we reiterate the essential aspects here and point out the modifications from the use of dilute solutions rather than the bulk state experiments reported earlier. Inherent in the scattering law obtained (as in the majority of published scattering laws) is the assumption of incompressibility; the general form of the scattering cross section is given by

$$\frac{\mathrm{d}\Sigma(Q)}{\mathrm{d}\Omega} = B_{\mathrm{is}}^{\mathrm{T}} S B_{\mathrm{is}} \tag{8}$$

where B_{is} is the $(1 \times n)$ matrix of contrast factors (K_{is}) between each component, i, in the star polymer and the solvent, s. $B_{\mathrm{is}}^{\mathrm{T}}$ is the transpose of this matrix. The number, n, is the total number of components in the system in addition to the solvent, and the vector S is an $(n \times n)$ matrix containing the scattering laws for each component and the influence of excluded-volume interactions via polymer−solvent interaction and polymer−polymer interaction parameters. For the case at issue here, i.e., stars with one arm deuterium labeled, $n = 2$, and we presume that the polymer−solvent interaction parameter is the same for hydrogenous and deuterated arms. Moreover, the influence of excluded volume is only encompassed in the value of the interaction parameters; i.e., the forms of the scattering laws and co-terms retain their original Debye and Leibler forms. The form of the scattering cross section for a three-component system as considered here is given by

$$\frac{d\Sigma(Q)}{d\Omega} = K_{HS}S_{AA}(Q) + 2K_{DS}K_{HS}S_{AB}(Q) + K_{DS}S_{BB}(Q) \tag{9}$$

and

$$S_{AA}(Q) = \frac{S1_{BB}(Q)}{S1_{AA}(Q)\,S1_{BB}(Q) - S1^2_{AB}(Q)}$$

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

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

$$SO_{AA}(Q) = n_H D_H \phi_H v_H \left(g_{dH} + (n_H - 1)\left[\left(\frac{1}{u_H}\right)(1 - \exp(u_H))\right]^2 \right)$$

$$SO_{BB}(Q) = n_D D_D \phi_D v_D \left(g_{dD} + (n_D - 1)\left[\left(\frac{1}{u_D}\right)(1 - \exp(u_D))\right]^2 \right)$$

$$SO_{AB}(Q) = n_D n_H \sqrt{D_H D_D v_H v_D \phi_H \phi_D}\left[\left(\frac{1}{u_H}\right)(1 - \exp(u_H))\right] \times \left[\left(\frac{1}{u_D}\right)(1 - \exp(u_D))\right]$$

$$V_{BB}(Q) = \frac{1}{\phi_s v_s} - \frac{2\chi_{DS}}{v_{norm}}$$

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

$$S_{AB}(Q) = \frac{-S1_{AB}(Q)}{S1_{AA}(Q)\,S1_{BB}(Q) - S1^2_{AB}(Q)}$$

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

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

$$V_{AB}(Q) = \frac{1}{\phi_s v_s g_{dS}} - \frac{\chi_{HS} + \chi_{DS} + \chi_{HD}}{v_{norm}}$$

where K_{IJ} is the contrast factor between species I and J for which D, H, and S refer to deuterio, hydrogenous, and solvent species, respectively, $u_I = Q^2 R_{gI}{}^2$ for the species I where R_g is the radius of gyration, n_I, D, ϕ, and v are the number of arms of species I (either H or D), degree of polymerization, volume fraction, and monomer unit or solvent molecule volume, respectively, for 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 and $g_{dI} = (2/u_I{}^2)[u_I{}^2 + 1 - \exp(-u_I{}^2)]$.

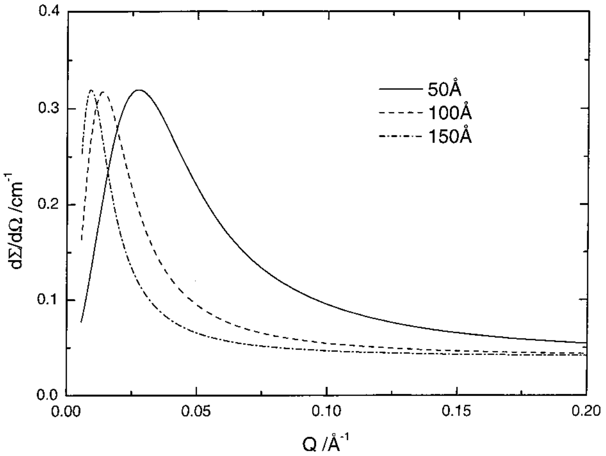

Figure 2. Influence of changing arm radius of gyration on the scattering cross section for a 12-arm star polymer with one arm deuterium labeled.

The scattering law obtained conforms in structure to the more general forms derived by Benoit et al. some years ago but where precise expressions for star polymers were not given. In particular, the influence of excluded-volume effects is incorporated via interaction parameters, χ_{IJ}, χ_{IS}, and χ_{JS} where I and J are the polymeric components, H and D arms in the specific case here, and S is the solvent.

In view of the stress laid upon the exponents in scattering cross section−scattering vector relationships outlined above, it is pertinent to examine the form of the scattering law obtained. A major problem as pointed out by Benoit et al.[21] is that values of χ_{IJ} etc. are unknown (generally). Furthermore, if the assumption that $\chi_{IS} = \chi_{JS}$ (reasonable if I and J only refer to H and D isotopes of the polymer) is made, then the scattering law is insensitive to the absolute values of χ_{IS} (or χ_{JS}).

Consequently, we compare predicted scattering curves for $\chi_{IJ} = \chi_{IS} = \chi_{JS} = 0$ for a fixed arm radius of gyration for stars with increasing number of arms at a volume fraction corresponding to a 5% solution in a low molecular weight matrix whose scattering length density is the same as the hydrogenous arms (Figure 1). We note as the star functionality decreases the scattering cross section increases, as is expected due to the increasing percentage of deuterated material in the polymer as the arm number decreases. The maximum in the scattering is not dependent on the arm number because we have fixed the arm radius of gyration. If this radius of gyration is altered, then it has a profound influence on the position of the maximum (Figure 2). What is perhaps more revealing is the change in the Q dependence of the scattering cross section evident in the double-logarithmic plot of Figure 3. For Q values of 0.02 Å^{-1} and greater there are two regions of differing behavior, and this becomes increasingly evident as the star functionality increases. In the Q range from $0.02 \leq Q/\text{Å}^{-1} \leq 0.07$, then

$$d\Sigma/d\Omega \sim Q^{-1.1}$$

and for $0.1 \leq Q/\text{Å} \leq 0.2$ the scaling law that is approached is

$$d\Sigma/d\Omega \sim Q^{-0.28}$$

These exponents are not what would be expected from the use of Debye and Leibler expressions in the deriva-

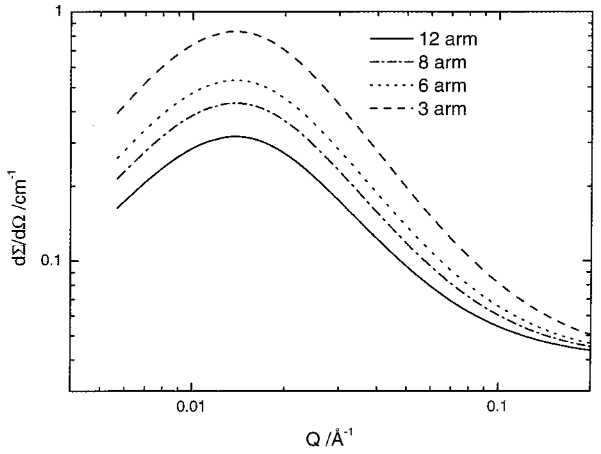

Figure 3. Double-logarithmic plot of the data in Figure 1 showing change of Q dependence in different ranges of Q.

tion of the scattering law and the assumption of athermal conditions. Moreover, there is a direct relationship between Q_{max} and the arm radius of gyration

$$R_g \sim Q_{max}^{-1}$$

However, excluded-volume effects *do* have an influence on the exponent for the Q dependence of the scattering cross section in this mid-Q range ($0.02 \leq Q \leq 0.07$). Inserting values of −0.5, 0, and 0.5 for χ_{ij} gives values of −2.16, −1.10, and −0.95, respectively, for the exponent β in the relation

$$d\Sigma/d\Omega \sim Q^{\beta} \quad (10)$$

In summary, the Q dependence of the scattering from the one labeled arm in a star polymer, although exhibiting some influence from excluded-volume effects, has behavior that is intrinsic to the scattering law. Consequently, although the observed experimental scattering may contain within it the variations in excluded-volume behavior predicted in the Daoud−Cotton[23] model, the identification of exponents with a particular length scale behavior is not transparent and caution needs to be exercised in such attempts.

Experimental Section

Star Polymer Synthesis. Polybutadiene star polymers with arm numbers (f) of 3, 4, 8, and 12 in which one arm was perdeuterated and ($f - 1$) arms hydrogenous were synthesized by the procedures detailed in earlier publications.[35,36] The synthetic route is a variation of the well-established use of chlorosilane linking of living polymers, but we emphasize here that all manipulations (fractionation, linking, etc.) were carried out under high vacuum. Completion of functionalization by the hydrogenous arms required a reaction time of up to 1 month for the 12-arm stars. Only after termination of any remaining living polymer was the solution exposed to air, and thus the possible reaction of chlorosilane units with moisture to form Si−OH units, thus possibly reducing the efficiency of functionalization was reduced to the barest minimum. The values of the functionality obtained given in Table 1 attest to the efficiency of this procedure. Molecular weights of the hydrogenous (H) and deuterated (D) arms and the resultant star polymers were obtained from size exclusion chromatography with triple detection (refractive index, viscosity, and light scattering detectors). From comparison of the star polymer molecular weights to that of the precursors, the average functionality of the star polymers was obtained. The individual arm molecular weights, their molecular weight distribution, and the functionalities are given in Table 1.

Table 1. Star Polybutadiene Arm Molecular Weights and Average Functionalities

av functionality	$\bar{M}_w/10^3$ g mol^{-1}	$\bar{M}_w/\bar{M}_n$	av functionality	$\bar{M}_w/10^3$ g mol^{-1}	$\bar{M}_w/\bar{M}_n$
2.8	33.2 (D)	1.02	7.8	33.3 (D)	1.07
	31.7 (H)	1.02		33.5 (H)	1.01
3.7	30.1 (D)	1.02	11.7	30.9 (D)	1.02
	31.2 (H)	1.01		33.8 (H)	1.01

Small-Angle Neutron Scattering. All small-angle neutron scattering data were obtained using the D22 diffractometer at the Institut Laue-Langevin, Grenoble, France. Two sample−detector distances were utilized, and by placing the detector slightly off the incident beam direction, the scattering vector, Q, range covered was $3 \times 10^{-3} \leq Q$/Å$^{-1} \leq 0.2$ for the incident neutron beam wavelength of 8 Å.

For each star polymer, the range of concentrations explored was between ca. 1% to 8% (w/v). The highest concentration of 8% was only used for the 8- and 12-arm stars to improve signal-to-noise ratio in these polymers with a very small volume fraction of deuterated material. The scattering data were normalized to the scattered intensity from a 1 mm thick light water specimen (for which the absolute scattering intensity is known) and the contributions due to electronic noise, solvent, and cell scattering subtracted.

Results and Discussion

Figure 4 shows double-logarithmic plots of the differential scattering cross section as a function of scattering vector for the most concentrated solution of each star polymer. As the number of arms increases, we note that the maximum clearly evident at finite Q value for the 3- and 4-arm star is barely evident for the 8-arm star and essentially nonexistent in the scattering profile of the 12-arm star. Additionally, it is evident that a different dependence on Q prevails at high Q for the 12-arm star (for $Q \geq 0.1$) but which is barely noticeable in the 3-arm star. This change in Q dependence of the scattering is not apparent in the linear scale plots of Figure 5. The maximum in each scattering curve is now clearly evident in the 3-, 4-, and 8-arm star data, but there is no evidence at all for a maximum in the data for the 12-arm star at this highest concentration. The maximum does become evident for the lower concentration solutions. In the midrange of $Q \sim 3 \times 10^{-2}$ Å$^{-1} \leq Q \leq 0.1$, the exponent in the scaling relation between $d\Sigma/d\Omega$ and Q is −1.45 ± 0.05 for the 3-, 4-, and 8-arm stars but has increased to −1.2 for the 12-arm star. For the high-Q range $0.1 \leq Q$/Å$^{-1} \leq 0.2$, the 4- and 8-arm star have an exponent of −1.25 ± 0.05, but the 12-arm star has a more positive exponent of −0.6.

Nonlinear least-squares fits to the scattering cross sections were obtained using the theoretical expression,[37] eq 9, and varying the radius of gyration of the labeled arm and χ_{HD}. The values of χ_{HS} and χ_{DS} were made equal to each other at zero; evidently this is not a correct description of the large positive excluded-volume effects for polybutadiene in cyclohexane. However, as noted earlier, the absolute values of χ_{HS} and χ_{DS} have no influence on the scattering cross section as long as they are equal. Typical fits are shown in Figure 6, and the average radii of gyration obtained for all concentrations of all stars are given in Table 2. There was no significant dependence of the radius of gyration on star polymer concentration for any of the star polymers investigated here. We pointed out earlier that the expression used employs the original Debye−Gaussian coil scattering law, and in view of the excluded-

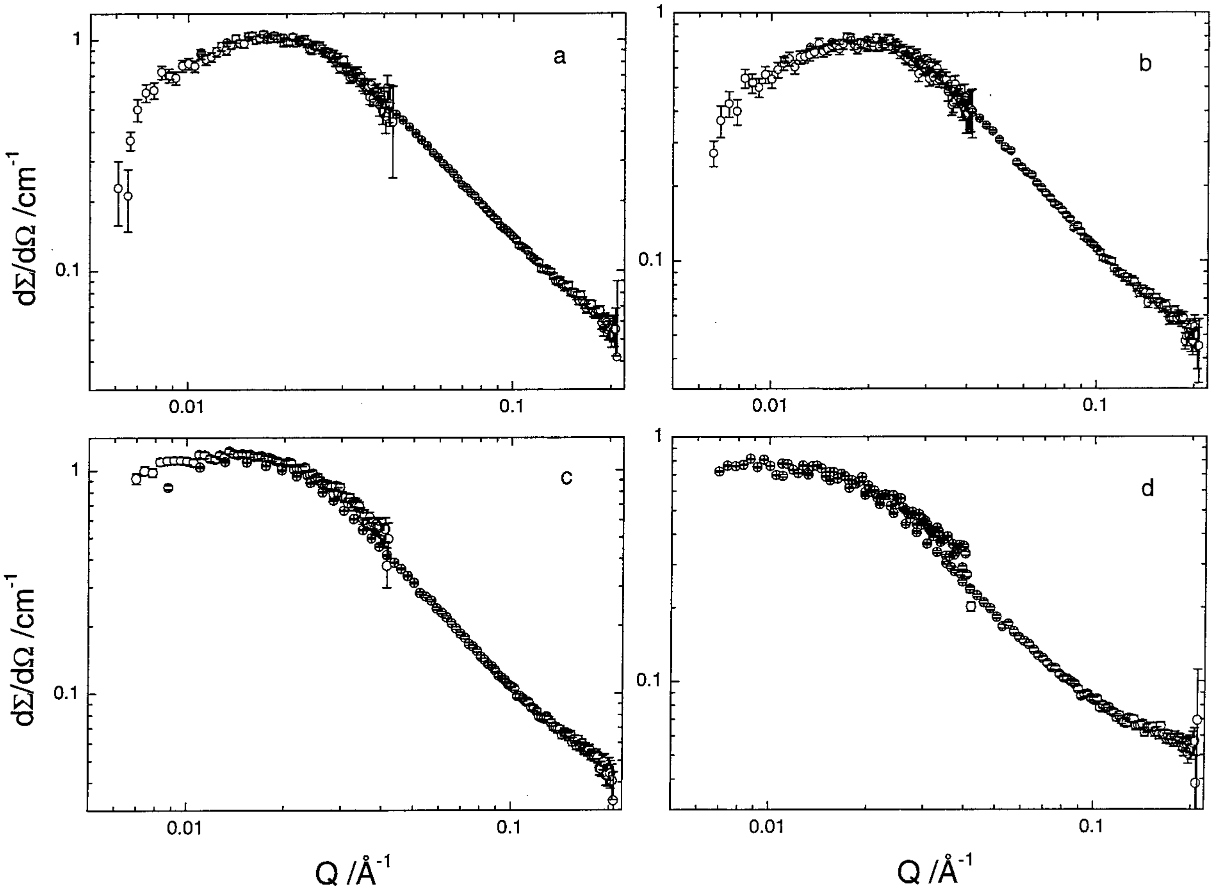

Figure 4. Double-logarithmic plots of the experimental scattering cross sections obtained for cyclohexane solutions of the star polybutadienes: (a) 5% three-am star; (b) 5% four-arm star; (c) 8% eight-arm star; (d) 8% 12-arm star.

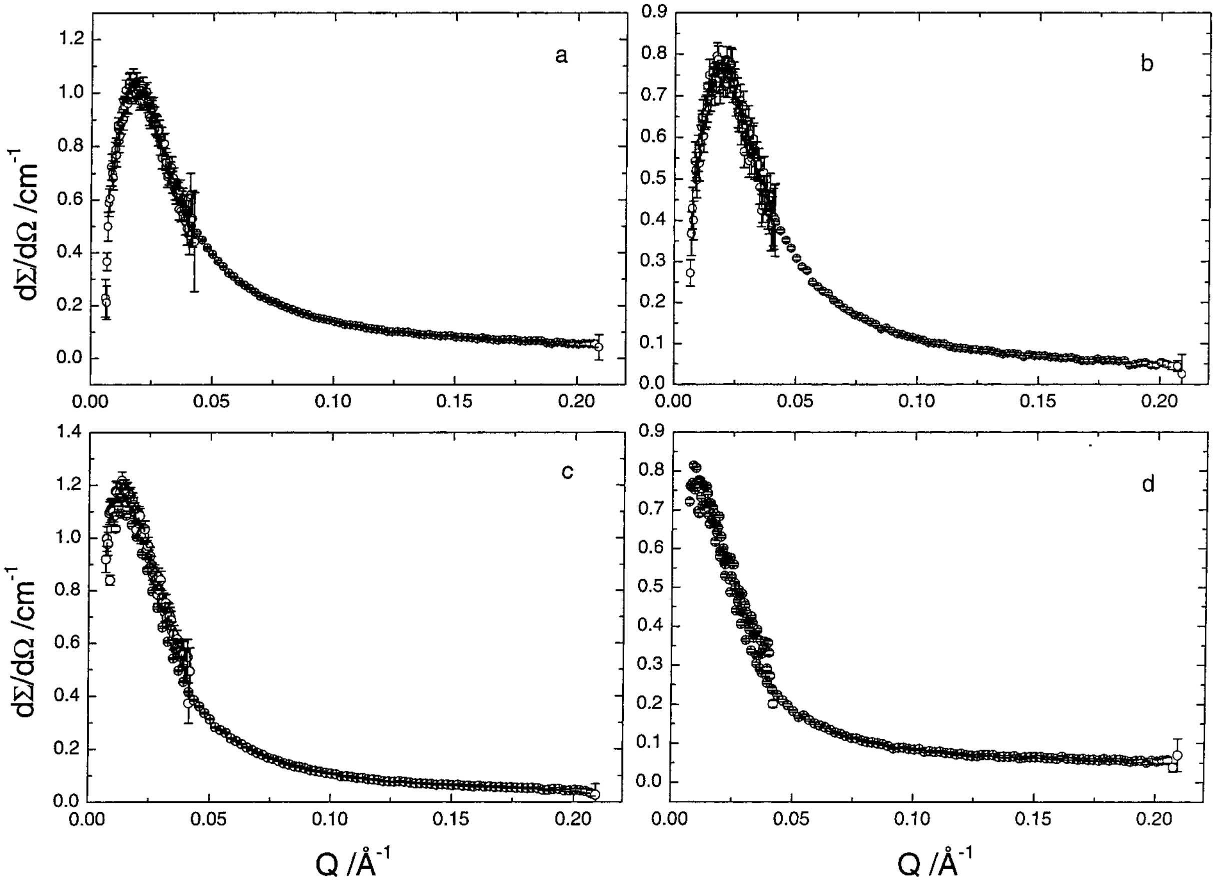

Figure 5. Linear plots of the same data sets as in Figure 4.

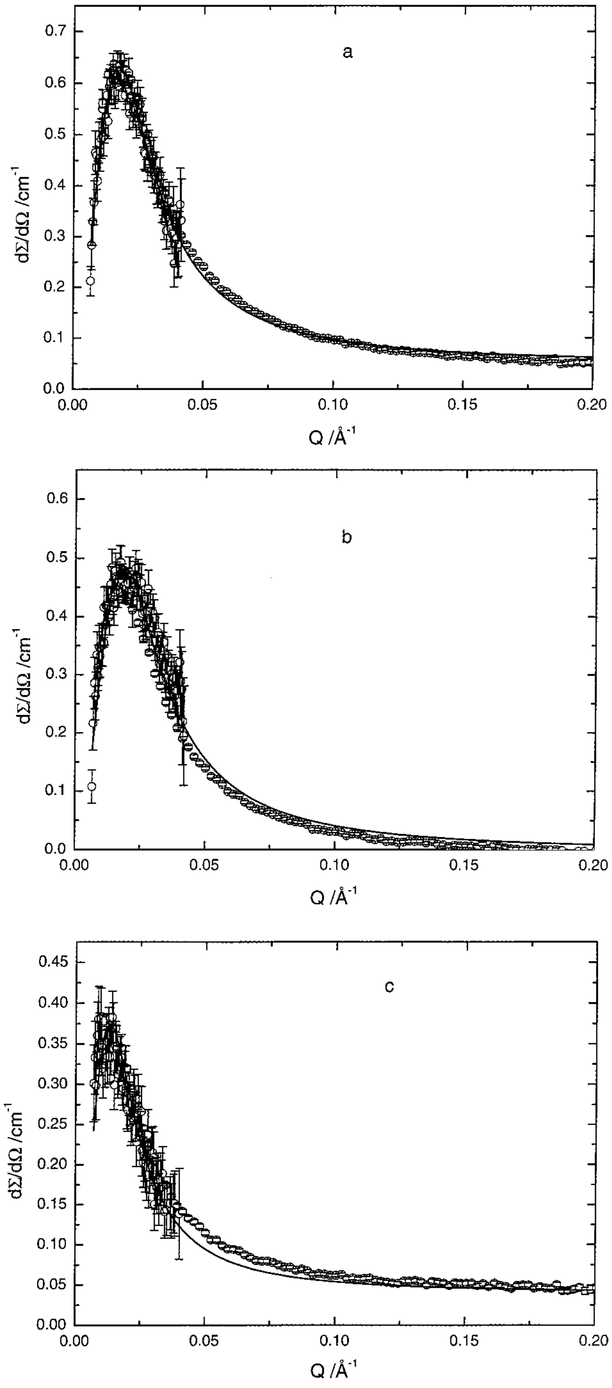

Figure 6. Nonlinear least-squares fits to selected scattering cross section data for cyclohexane solutions of star polybutadienes: (a) 5% three-arm star; (b) 3% four-arm star; (c) 5% 12-arm star.

volume effects this may not be appropriate especially in the high-Q range. Fits were also attempted using the scattering law for swollen chains:[40−42]

$$P(\alpha,N) = [1/(\nu X^{1/(2\nu)})]\{\gamma({}^{1}/_{2}\nu),X) - [1/(X^{1/(2\nu)})]\gamma(1/(\nu),X)\}$$

where $X = (Q^2a^2N^{2\nu})/6$ and $\gamma(A,X)$ is the incomplete gamma function. The values of the radii of gyration obtained with this more complicated expression were little different to those obtained using the Debye function set out earlier, and there was no apparent improvement to the fit at higher Q.

Table 2. Radii of Gyration of Labeled Arms

	R_g/Å		
functionality	cyclohexane	bulk[36]	linear unperturbed
3	79 ± 2	68	61
4	75 ± 2	66	58
8	92 ± 3	72	61
12	104 ± 4	91	59

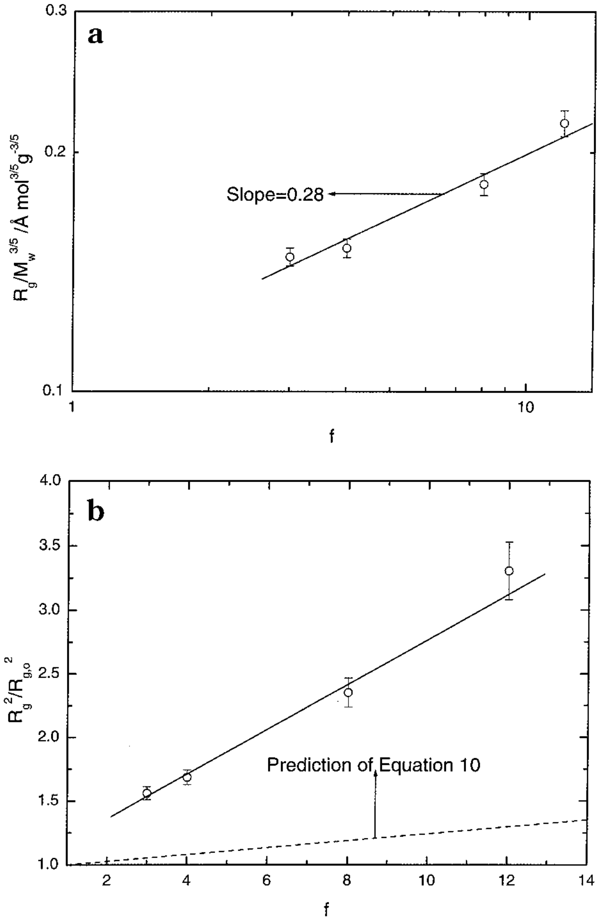

Figure 7. (a) Radius of gyration as a function of star functionality plotted according to the Daoud−Cotton model for stars in good solvents. (b) Expansion factor of labeled arm as a function of star functionality. Solid line is the linear least-squares fit to the data, and the dashed line is the prediction of the Allesandrini and Carignano model of eq 10.

Direct comparison of the radii of gyration with star functionality cannot be made because of the small variations in the labeled arm molecular weight from star to star. This molecular weight variation can be normalized out by dividing each R_g value by the arm molecular weight raised to the power (3/5), i.e., adopting the Daoud−Cotton relation of eq 7. Figure 7a is a double-logarithmic plot of the normalized R_g values as a function of f, the star functionality, the best linear fit to the data has a slope of 0.3, larger than the 0.2 predicted by the Daoud−Cotton model. Moreover, the data appear to be more on a convex curve rather than having a linear dependence on the star functionality, f. A second way of normalizing for the difference in molecular weights is to divide the R_g values by the unperturbed radius of gyration of the linear polymer of equivalent molecular weight as the arm. These values (calculated from relationships in the literature) are given in Table 2. Alessandrini and Carignano[20] have

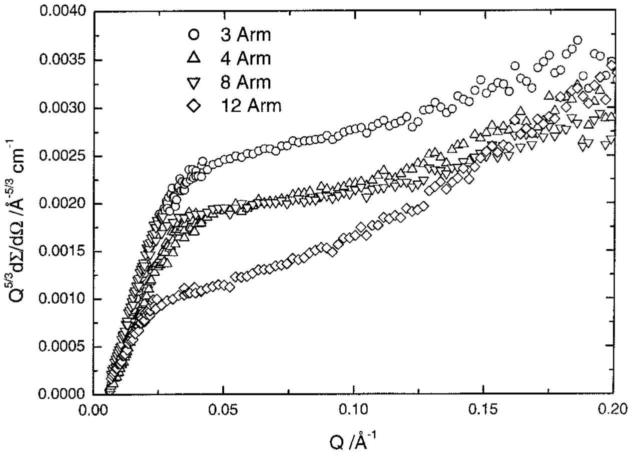

Figure 8. Kratky plot of scattering cross sections for the most concentrated solutions in cyclohexane of all star polymers with one labeled arm investigated using excluded volume adjusted exponent for Q.

given an analytical expression for the expansion factor of the labeled arm in an f functional star

$$R_g^{\,2}/R_{g,0}^{\,2} = 1 + (f - 1)\left[\frac{35}{64} - \frac{3}{4}\ln 2\right] \qquad (11)$$

The data are plotted in this matter in Figure 7b and compared with the predictions of eq 10. Although a linear plot is obtained, the magnitude of the expansion factors are clearly much greater than those predicted. We close this section by considering the Kratky (or pseudo-Kratky) plots of the SANS data. Commonly for stars in solution where all the arms are identical, the radii of gyration are obtained from the position of the maximum in the pseudo-Kratky plot, i.e., $Q^{5/3}$ dΣ/dΩ as a function of Q. Figure 8 shows representative data plotted in this way after subtraction of the residual incoherent background. The value used for this was that obtained from the fits to the data as shown in Figure 6; we note that the slope of the plateau region of Kratky plots can be extremely sensitive to the value of the background subtracted. These cautionary comments do not obscure the fact that no maximum is evident in the plots as is commonly observed when there is contrast from *all* the arms of the star rather than just the one labeled arm in our star polymers. Moreover, a horizontal region is not observed over any range of Q. Reducing the value of the Q exponent does produce a horizontal plot for $0.04 \leq Q/\text{Å}^{-1} \leq 0.14$, and this would normally be interpreted as a greater influence of excluded-volume effects leading to an expansion of the star arm. However, in view of the findings concerning the Q dependence of the scattering cross section in the simulations discussed earlier, such an explanation cannot be adopted without reservation. What is clear is the enhanced slope for $Q > 0.04$ Å^{-1} for the 12-arm polymer, an aspect that was predicted by Alessandrini and Carignano for single-arm labeled stars.

Conclusions

Solutions of star polybutadienes wherein one arm was fully perdeuterated have been investigated by small-angle neutron scattering. In cyclohexane, a thermodynamically favorable solvent for polybutadiene, the observed scattering cross section conforms well to the predictions of a recently developed method of deriving scattering laws for polymers and copolymers with different architectures. The radii of gyration obtained have a dependence on star functionality that agrees reasonably well with the predictions of Daoud and Cotton, but better qualitative agreement is obtained with the theory of Allesandrini and Carignano but with the expansion of the arms being much greater than predicted. The scattering from these polymers is intrinsically different from the scattering for the whole star; in particular, plotting the scattering cross sections in pseudo-Kratky form does not exhibit the characteristic maximum associated with scattering by the whole star. Caution needs to be exercised in interpreting such plots for singly arm labeled stars because a change in Q dependence of the scattering is intrinsic in the scattering function.

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