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SANS Study of Star Block Copolymers

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ABSTRACT: Small-angle neutron scattering (SANS) measurements have been carried out on two star polymers. In one case, deuterated blocks have been placed at the core of the star, and, in the other, deuterated blocks have been placed at the extremities of each arm. The measurements yielded values for the radius of gyration, screening length, and persistence length of each labeled block. The results indicate that, for six-armed polystyrene stars dissolved in toluene, the chains are somewhat extended by steric exclusion close to the core but that sufficient flexibility is present for the ends of the star arms to behave as random coils. The inherent chain flexibility is independent of position, and the radial concentration dependence is in qualitative agreement with the blob model.

The molecular structure of star-shaped polymers is currently an area of rapidly developing interest. Star polymers provide an opportunity to study the effects of molecular architecture on a variety of properties such as internal modes of relaxation,[1] chain conformation,[2] and hydrodynamic behavior.[3,4] Of utmost importance to these studies is the interior structure of the star molecule. This paper reports structural information for isolated six-armed polystyrene stars in toluene which is a good solvent. By use of block copolymers of hydrogenous and perdeuteriostyrene, it is possible to describe different regions within a star polymer for the first time.

It has been suggested by Daoud and Cotton[5] and Birshtein et al.[6] that the internal concentration of a star will vary radially. Each arm of the star can be visualized as a succession of blobs with size ξ which increases from the center of the star to the outside. Hence the molecule will be much more concentrated at its core than in its outer shells. This variation of the local concentration will govern the resulting properties.

Small-angle neutron scattering (SANS) proves to be an ideal tool for measuring the radial variation in molecular conformation. Since hydrogenous and perdueteriated polymers scatter neutrons very differently, the use of perdeuteriated block copolymers allows the site specific labeling of different sections of the star polymer. In this paper, the scattering profiles of two star molecules are compared. In one case the labeled blocks are located at the core of the star, and in the second case the labels are placed at the extremities of each arm. By measuring the intensity of scattered neutrons in the appropriate angular ranges, it is possible to compare the behavior of the two materials on different length scales. This paper presents results for the radius of gyration R_g and internal screening length ξ of each labeled block.

The synthesis of star polymers involving styrene has been reported previously.[2–4,7] Two six-armed star block copolymers were prepared for this study. The first, called star A, is composed of polystyrene arms ($M_n = 1.79 \times 10^5$, $M_w/M_n = 1.05$) which are tipped with blocks of perdeuteriated polystyrene ($M_n = 3.50 \times 10^4$, $M_w/M_n = 1.06$). In the second material, star B, the organization is reversed and the perdeuteriated blocks ($M_n = 2.94 \times 10^4$, $M_w/M_n = 1.04$) are at the core of the star while the remainder of the arms are hydrogenous polystyrene ($M_n = 2.07 \times 10^5$, $M_w/M_n = 1.05$). These materials are shown schematically in Figure 1. Each star block copolymer was dissolved at 1.0 g/dL in toluene. Previous measurements[8] have shown this concentration to be below the overlap concentration, and so each solution contains isolated star molecules.

The SANS measurements were performed on the D17 spectrometer of the high flux reactor at the Institut Laue Langevin in Grenoble, France. For these experiments, a wavelength of $\lambda = 8$ Å was used and two different sample-to-detector distances were chosen to obtain a large range of scattering wavevector. These distances were 10 and 2 m with 10 and 2.5 m collimation, respectively. The resulting wavevector range of the two configurations was $0.006 \leq q \leq 0.137$ Å^{-1} where $q = 4\pi/\lambda \sin \theta/2$ and θ is the scattering angle. The data were corrected for detector efficiency. The scattering due to the empty cell and solvent was subtracted. The contrast between protonated polymer and solvent and the small residual incoherent background were assumed negligible.

The q dependence of the measured scattering intensities for star polymers A and B are shown in Figure 2. These data were analyzed assuming various functional forms,[9–11] but none of the resulting fits were satisfactory. For this reason, the scattered intensity was analyzed by the classical Zimm methodology[12] to obtain R_g measurements that are independent of any assumed functional form for the star conformation. In this analysis, the scattered intensity $I(q)$ from a dilute polymer solu-

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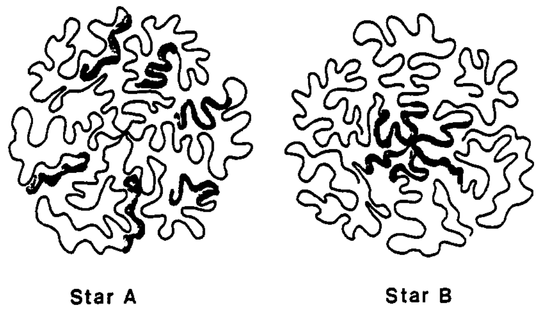

Figure 1. Schematic of star block copolymers of styrene (—) and perdeuteriostyrene (—).

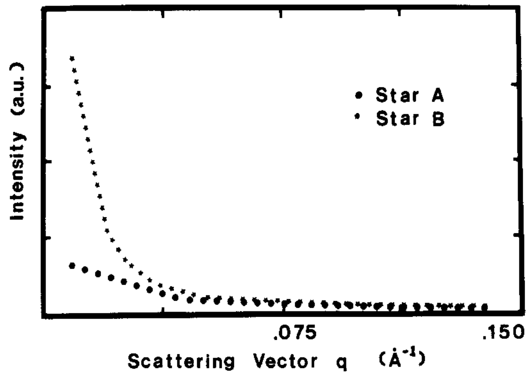

Figure 2. Angular variation of scattered intensity for stars A and B in toluene.

tion with concentration C is

$$\frac{KC}{I(q)} = \frac{1}{M}\left[\frac{2}{u^2}(e^{-u} - 1 + u)\right]^{-1} + 2A_2C \qquad (1)$$

where $u = q^2R_g^2$, M is the polymer molecular weight, and A_2 is the second virial coefficient. The constant K contains machine parameters and contrast factors. The radius of gyration can be determined from the ratio of slope to intercept of a linear $C/I(q)$ vs q^2 plot and is independent of normalization and the constant K. The concentration of labeled monomers within these solutions is sufficiently low that the second term in eq 1 is negligible. The resulting plots are shown in Figure 3.

Least-squares line fitting of the scattered intensity from the labeled core yields an $R_{g_{\text{core}}}$ of 119 Å. This value must be corrected for the angular range of measurement since Zimm analysis is restricted to the range $qR_g \ll 1$. Such corrections have been described by Ullman[13] and yield a value of $R_{g_{\text{core}}} = 102 \pm 5$ Å. Using this value, it is possible to calculate the contraction factor $g = \langle R_g^2\rangle_{\text{core}}/\langle R_g^2\rangle_{\text{linear}}$. The radius of gyration for a linear chain whose degree of polymerization equals that of the labeled core can be determined from published relationships[4,14] and is equal to $R_{g_{\text{linear}}} = 148$ Å. Hence a value of $g = 0.47$ is obtained. This value is virtually identical with that found (0.46) for a hydrogenous six-arm polystyrene star in toluene.[14] Good agreement is also found with the result from recent scaling predictions[15] and experimental results[16] for polyisoprene stars in good solvents. Within experimental precision, the core of a six-armed star exhibits the same contraction factor as measured for the overall molecule.

Knowing the radius of gyration of the core, the radius of gyration of the individual blocks within that core can be determined[9,17] from the relationship $\langle R_g^2\rangle_{\text{star}}/\langle R_g^2\rangle_{\text{arm}} = (3f - 2)/f$. For the present case, a value for the inner blocks of star B of $R_{g_i} = 62 \pm 3$ Å is obtained. This value is considerably larger than calculated for a free block of equivalent mass. The results imply a 22% expansion of the block due to steric exclusion at the hexafunctional branch point. This is in qualitative agreement with recent infrared spectroscopy studies of six-armed polystyrene stars in the melt.[18]

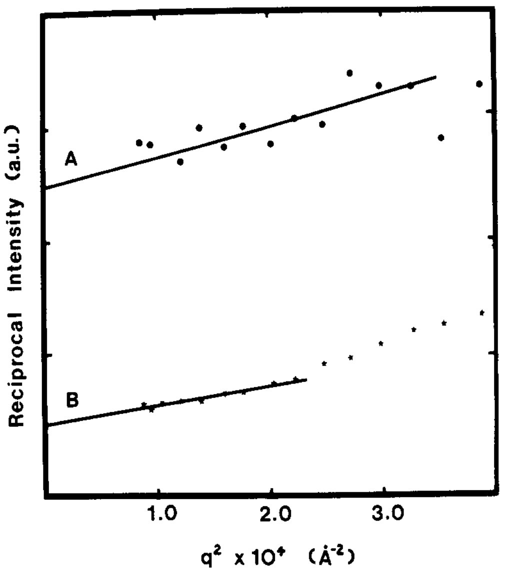

Figure 3. Determination of radius of gyration for stars A and B in toluene.

Table I

material	structural parameter		
	$R_{g_{\text{core}}}$	$R_{g_{\text{linear}}}$	g
star B	102 ± 5 Å	148 Å	0.47
	R_{g_i}	$R_{g_{\text{linear}}}$	% expansion
star B	62 ± 3 Å	51 Å	22
	R_{g_o}	$R_{g_{\text{linear}}}$	% expansion
star A	57 ± 3 Å	57 Å	0
	ξ_i	l_i	
star B	28 ± 3 Å	33 ± 3 Å	
	ξ_o	l_o	
star A	35 ± 3 Å	30 ± 3 Å	

If the Zimm plot in Figure 3 for star A is now considered, it is apparent that the scattering from the terminal perdeuteriated blocks is uncorrelated between the six arms since an intercept (and hence a molecular weight of the block) is determined which differs from that of the core by roughly a factor of 6. This is an important result since it demonstrates that a functionality of six is too low to cause a hollow sphere structure for star materials containing relatively long flexible arms and short terminal blocks. This finding is further supported by the measured value of the radius of gyration of the outer block $R_{g_o} = 57 \pm 3$ Å. In this case, no corrections for limited angular range were necessary. When the relationship in ref 19 is used to calculate the R_g expected for a free block of this molecular weight, the values match exactly. These values of R_g are compiled in Table I. Since no expansion is observed for the terminal perdeuteriated block, it must be too far from the branch point to be affected by steric exclusion from the core.

By examining the scattered intensity in the appropriate angular range, it is also possible to measure an internal screening length ξ. It is important to recall that dilute conditions have been chosen so that the macromolecules exist as isolated species. According to the blob model, individual star molecules will possess an internal concentration variation; the local concentration being greater in the core than in the outer shells. This proposed vari-

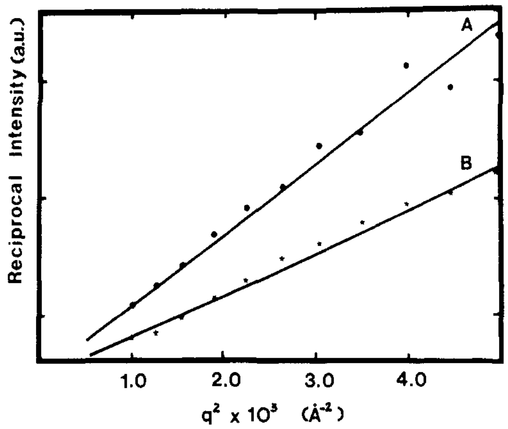

Figure 4. Determination of screening length for stars A and B in toluene.

ation in local concentration will be directly expressed in the internal screening length of the chain. In the present case, the screening length is determined from the following Lorentzian equation[19,20] for the angular dependence of scattered intensity in the range $1/\langle R_g^2\rangle^{1/2} < q < 1/b$

$$I(q) \propto \frac{1}{1 + q^2\xi^2} \tag{2}$$

where b is the statistical segment length of the polymer. The screening length is obtained by fitting a straight line to inverse intensity versus q-squared plots.

The resulting plots for the two star copolymers are shown in Figure 4, and the measured values of ξ are listed in Table I. The first value to note is that of the inner block $\xi_i = 28 \pm 3$ Å. From this value of ξ_i, it is possible to calculate the effective local concentration using the relationship of Brown and Mortensen.[8] The value $\xi_i = 28$ Å implies a local concentration of 4.45 g/dL at the core of the star. This is internally consistent with the concentration calculated from the ratio of total inner block mass to spherical core volume using the measured $R_{g_{\mathrm{core}}}$.

If the general blob model for star polymers is correct, then the local concentration within the star should decrease with radial distance from the branch point and hence the internal screening length should increase. This is observed in the screening length of the outer labeled block $\xi_o = 35 \pm 3$ Å. This increase in screening length with radial distance is consistent with the blob model. The amount of increase is also consistent with the measured variation in R_g. The observed value of ξ_o is larger than ξ_i but not as large as anticipated for the outer shells of the star polymer. Hence the arms of this star have sufficient flexibility that the chain ends can occupy a position intermediate between the core and the outermost layers of the star. This is equivalent to the previous statement that a functionality of six is not high enough to cause the exclusion of the polystyrene arm's extremity to the outer surface of the star. Clearly, this is consistent with the absence of correlation between the outer blocks as already discussed in the R_g determination.

In conclusion, it has been possible to measure the radius of gyration and screening length of perdeuteriated polystyrene blocks within isolated six-armed polystyrene stars dissolved in toluene. The results show that the chains are somewhat extended by steric exclusion close to the core but that sufficient flexibility is present for the free chains ends to infiltrate the star in a manner analogous to the ends of a random coil. A radial variation in local concentration is found which is in qualitative agreement with the blob model of star polymers.

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