Method of variation of contrast in neutron scattering studies of conformations of block copolymers forming a microdomain structure*

A. D. Vilesov†, L. V. Vinogradova, N. V. Gazdina, G. A. Evmenenko‡, V. N. Zgonnik, V. V. Nesterov and S. Frenkel
Institute of Macromolecular Compounds and ‡Nuclear Physics Institute, Academy of Sciences, 199004 St Petersburg, Bolshoi 31, Russia
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The registration of the signal of small angle neutron scattering from a single deuterated chain in a superstructure formed by block copolymers is difficult due to Bragg diffraction. A method is proposed to avoid this diffraction by turning the interdomain neutron contrast to zero. This is attained by means of synthesis of each block of the polystyrene–polybutadiene–polystyrene block copolymer as a statistical copolymer of H and D monomers. The radius of gyration of the deuterated polybutadiene block was measured by neutron scattering.

(Keywords: neutron scattering; block copolymer; superstructure; macromolecule; radius of gyration)

INTRODUCTION

The methods of small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) are widely applied in structural studies of block copolymers in the solid state[1,2]. The main results correspond to the morphologies of superstructures originated due to segregation of blocks into microdomains.

In addition, information on the conformational state of single blocks of macromolecules in such structures can be of great interest since it may enlighten general considerations on the states of chains linked to interfaces or included in restricted volumes[3].

SANS is practically the only method allowing data to be obtained on the conformation of a single chain in a bulk polymer by means of deuterium contrasting. Several per cent of macromolecules consisting of D monomers are introduced into the sample. The method of H–D contrasting minimally distorts the physical properties of a given macromolecule simultaneously creating good contrast due to a large difference in amplitudes of coherent nuclear scattering for hydrogen and deuterium. Subtracting the scattering curves for samples containing the marked and unmarked macromolecules and treating the data by the method of Guinier[4], one can obtain the value of the mean-square radius of gyration R_g of the deuterated macromolecule. However, in some cases it is necessary to use more refined methods of contrasting. Reference 5 uses a combined SANS–SAXS method in the study of blends of polystyrene (PS)–polybutadiene (PB) block copolymers with deuterated PB. The SANS arose as a result of the contrast between D-PB and H-BC while the SAXS arose as a result of the electron density contrast between the PS and PB components.

Using a mixture of deuterated and hydrogenated solvents one can mark specific parts of the scattering particle[6]. This technique of contrast variation is widely used in biological applications of SANS[7].

The estimation of R_g of a single block in a microdomain structure is greatly complicated by the Bragg diffraction of such a structure superimposed on the weak scattering signal from a single marked macromolecule. Such a problem was initially investigated by a research group from Strasbourg[8] and by us[9]. In reference 8, for a diblock copolymer of PS–polyisoprene forming a lamella superstructure, the R_g value for the PS block was obtained in the direction normal to the face of the lamella. For that particular orientation diffraction does not occur and the subtracting procedure can be realized with high precision. In reference 9 we estimated R_g of the PB block in a PS–PB–PS block copolymer forming a polycrystalline-type superstructure. Two scattering curves were subtracted containing Bragg maxima. This led to a low precision in estimating R_g. An analogous problem for a PS–PI block copolymer has been investigated in reference 10.

In this study a method is proposed which allows accurate R_g values for a single macromolecular block to be obtained in different directions for monocrystalline-type samples or average values for polycrystalline-type samples. The principle of this method is to extinguish the relative neutron contrast of the domains which naturally excludes the diffraction since the scattering intensity is proportional to the square of the interblock contrast $\Delta\rho^2$ and makes the scattering curves monotonous (*Figure 1*). A triblock copolymer PS–PB–PS was studied. The PS–PB interdomain contrast is determined by the difference in the densities of the amplitudes of the coherent nuclear scattering[4]:

$$\Delta\rho = \rho_{PS} - \rho_{PB} \qquad (1)$$

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†To whom correspondence should be addressed

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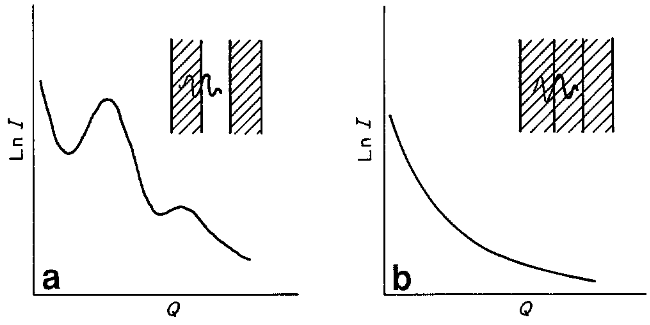

Figure 1 SANS profiles: (a) contrast differs from zero; (b) contrast equal to zero

The density of the amplitude of scattering ρ is related to the density of the material d and the sum of scattering amplitudes of the atomic nuclei b_i contained in the monomeric unit by the expression:

$$\rho = N_A d M^{-1} \sum_i b_i \tag{2}$$

where M is the molecular weight of the monomeric unit and N_A is Avogadro's number. For the realization of the condition $\Delta\rho \to 0$ the PS and PB blocks were synthesized in the form of statistical copolymers of H and D monomers of corresponding composition. Averaging of the type shown in equation (2) for the calculation of block compositions was carried out for ~100 monomeric units. A scattering theory for such copolymers was developed in reference 11. Scattering for multiblock copolymers was studied including the limit when the number of blocks was infinite. That case corresponded to a statistical copolymer.

As the marked particle for our experiment a block copolymer was synthesized with a PB block consisting only of D monomers. The other blocks were similar to those of the background sample.

SYNTHESIS AND CHARACTERIZATION OF THE SAMPLES

The synthesis of block copolymers was carried out in glass high vacuum systems (10^{-6} mm Hg) at 20°C in a benzene solution. The polymerization was promoted by a living chain oligomer oligostyryllithium. The synthesis involved three stages. In the first stage an H–D copolymer of styrene was formed. Then the butadiene block was polymerized in the same way. In the last stage the second H–D styrene block was obtained.

The calculated composition (in weight per cent) of the blocks necessary to fulfil the condition $\Delta\rho \simeq 0$ was obtained from the expression:

$$\rho_{\mathrm{PS}^{\mathrm{H}}_{\mathrm{D}}} = \rho_{\mathrm{PB}^{\mathrm{H}}_{\mathrm{D}}} = \tfrac{1}{4}(\rho_{\mathrm{PS}^{\mathrm{H}}} + \rho_{\mathrm{PS}^{\mathrm{D}}} + \rho_{\mathrm{PB}^{\mathrm{H}}} + \rho_{\mathrm{PB}^{\mathrm{D}}}) = \rho^* \tag{3}$$

where ρ is the amplitude density (unit: $10^{-10}\ \mathrm{cm}^{-2}$) and $\rho_{\mathrm{PS}^{\mathrm{H}}} = 1.40$, $\rho_{\mathrm{PS}^{\mathrm{D}}} = 6.42$, $\rho_{\mathrm{PB}^{\mathrm{H}}} = 0.45$ and $\rho_{\mathrm{PB}^{\mathrm{D}}} = 7.16$ are the amplitude densities of scattering by H- and D-PS and PB, respectively. The presumed optimal density of the scattering amplitude $\rho^* = 3.86 \times 10^{10}\ \mathrm{cm}^{-2}$ corresponds to the following composition of blocks controlled in the course of polymerization: 51.0% H–styrene and 49.0% D–styrene for PS blocks and 49.2% H–butadiene and 50.8% D–butadiene for PB blocks.

Evaluation of the molecular weight characteristics of the block copolymers was carried out by means of two-detector exclusion liquid chromatography. One of the detectors, a differential refractometer, registered both blocks and the second, a spectrophotometer, registered only the PS block at a wavelength of 269.5 nm. Tetrahydrofuran was used as eluent. A system of chromatographic columns was filled with macroporous glass particles with linear calibration. Calculations of the molecular weight characteristics from these data were carried out assuming a segregated conformation of the blocks of the copolymer when:

$$R^2_{\mathrm{g,BC}} = R^2_{\mathrm{g,PS}} + R^2_{\mathrm{g,PB}} \tag{4}$$

The PS fraction P in the copolymer equals the ratio of the corresponding molecular weights of the PS and PB blocks, i.e.

$$P = M_{\mathrm{PS}}/M_{\mathrm{PB}}$$

This ratio is evaluated directly from the ratio of chromatographic peak heights given by the refractometric (h_R) and spectrophotometric (h_{SP}) detectors as:

$$P = \left(\frac{h_R \alpha_{\mathrm{PS,SP}}}{h_{SP}\alpha_{\mathrm{PB,R}}} - \frac{\alpha_{\mathrm{PS,R}}}{\alpha_{\mathrm{PB,R}}}\right)^{-1} \tag{5}$$

The values of the sensitivity coefficients of the detectors in the linear range being (mm cm^3 g^{-1}): $\alpha_{\mathrm{PS,R}} = 55$, $\alpha_{\mathrm{PS,SP}} = 54$ and $\alpha_{\mathrm{PB,R}} = 27$. The chromatogram registered by the refractometric detector is corrected preliminarily taking into account the different sensitivities of the refractor towards the copolymer components:

$$w_R = h_R[\alpha_{\mathrm{PS,R}}P + \alpha_{\mathrm{PB,R}}(1-P)]^{-1} \tag{6}$$

where w_R is the corrected chromatogram. Using the universal calibration principle[12] and the Flory–Fox relation for the dependence of intrinsic viscosity on molecular weight[13] the calibration expression for the block copolymer is obtained in the form:

$$\begin{aligned} A = M_{\mathrm{BC}}[&K_{\mathrm{PS}}^{2/3} P^{2/3(a_{\mathrm{PS}}+1)} M_{\mathrm{BC}}^{2/3 a_{\mathrm{PS}}} \\ &+ K_{\mathrm{PB}}^{2/3}(1-P)^{2/3(a_{\mathrm{PB}}+1)} M_{\mathrm{BC}}^{2/3 a_{\mathrm{PB}}}]^{3/2} \end{aligned} \tag{7}$$

where A is the known value for the polymer standard, M_{BC} is the molecular weight of the block copolymer and a_{PS}, a_{PB}, K_{PS} and K_{PB} are the Mark–Kuhn–Houwink constants for the copolymer components. The subsequent calculation of the molecular weight characteristics using this calibration is carried out in the usual way[14,15].

Table 1 gives the calculated molecular weight characteristics by the described procedures for both samples. One can see that their chacteristics are quite close. It should be pointed out that both samples had a bimodal molecular weight distribution. It was found to be impossible to obtain a unimodal distribution by the method of synthesis used.

NEUTRON SCATTERING STUDY

The SANS experiments were carried out using the SANS diffractometer 'Membrana-2' at the Nuclear Physics Institute, Academy of Sciences, St Petersburg, Russia[16]. The range of scattering vectors $|\mathbf{Q}| = Q = (4\pi/\lambda)\sin\theta$ was 1.3×10^{-3}–0.6 Å^{-1}). The average wavelength of the incident beam λ was 2.3 Å and the halfwidth of the spectrum $\Delta\lambda/\lambda$ was $\simeq 0.1$ (2θ is the scattering angle).

Table 1 Molecular weight characteristics of block copolymers

Sample	$\frac{M_w}{M_n}$	Fraction of PS (%)	M_{PS} ($\times 10^{-3}$) (g mol^{-1})	M_{PB} ($\times 10^{-3}$) (g mol^{-1})	Fraction in sample
1 PS–PB–PS	1.10	23	19.3	64.7	2/3
(H + D) (H + D) (H + D)	1.08	35	73.5	136.5	1/3
2 PS–PB–PS	1.10	25	20.3	60.7	2/3
(H + D) (D) (H + D)	1.07	33	68.3	138.7	1/3

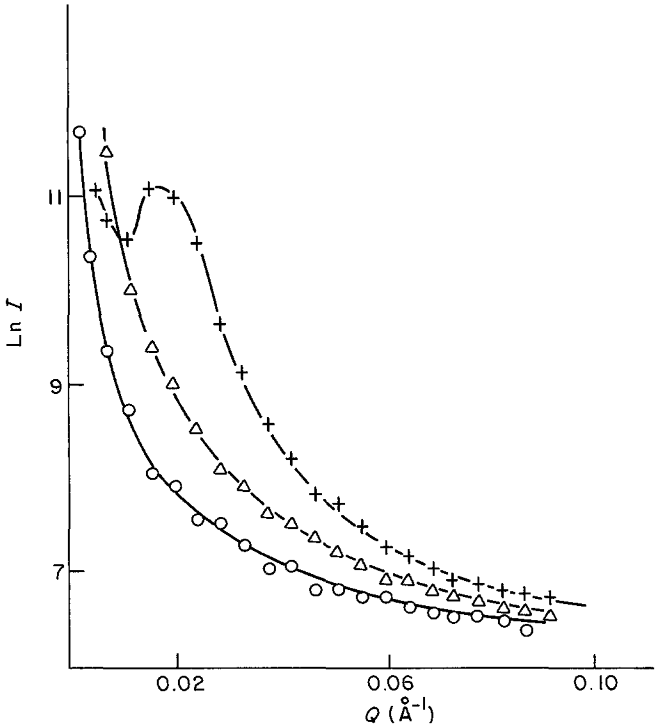

Figure 2 SANS profiles of samples 1 (○), 2 (+) and the system consisting of 97% sample 1 and 3% sample 2 (sample 3, △)

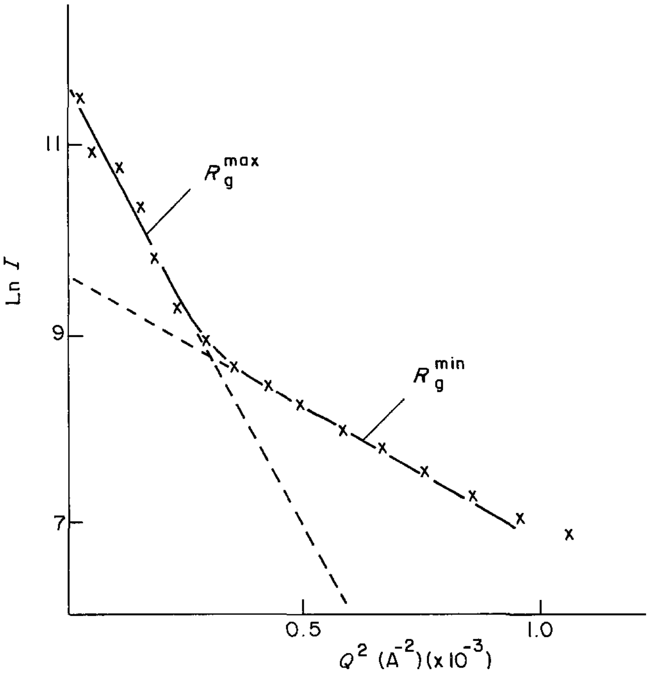

Figure 3 Guinier plot of the difference scattering curve of samples 3 and 1

The samples were cast as films from 5% toluene solutions on a solid surface. Sample 1 (background) consisted only of type 1 molecules (*Table 1*). Sample 2 consisted only of type 2 molecules and sample 3 consisted mainly of type 1 molecules but contained 3% type 2 molecules. The measured values do not depend on the concentration of marked molecules in the range of 1–5%. *Figure 2* shows the dependence of the natural logarithm of the scattering intensity I on Q. The curve corresponding to sample 2 contains a Bragg maximum. Its intensity does not depend on the orientation of the sample. A characteristic period of the structure $d = 2\pi/Q_{max}$ is equal to 363 ± 10 Å. The curve corresponding to sample 1 does not contain Bragg maxima. Hence, the aim to create a background sample with a domain structure 'invisible' in the neutron beam was achieved.

For a polydisperse system of scattering particles small with respect to interparticle distances the intensity of scattering is given by[4]:

$$I(Q) = \int_0^\infty N(R_g) R_g^6 F(QR_g) \, dR_g \Big/ \int_0^\infty N(R_g) R_g^6 \, dR_g \tag{8}$$

where $N(R_g)$ is the distribution function of the dimensions, $F(QR_g)$ is the form factor of a scattering centre [in our case $F(QR_g) = \exp(-Q^2R_g^2/3)$]. The aim is to establish the form of $N(R_g)$ which was assumed bimodal with a normal distribution function for each mode:

$$N(R_g) = \sigma^i \frac{1}{\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{R_g - R_g^i}{\sigma^i}\right)^2\right] \tag{9}$$

where R_g^i is the variable parameter of the distribution ($i = 1, 2$). The dispersion σ^i was estimated from the molecular weight characteristics (*Table 1*). R_g^1 and R_g^2 were determined by comparison of the experimentally obtained difference between the scattering curves for samples 3 and 1 (*Figure 3*) with those calculated from equation (8). The integral R_I factor was chosen as a criterion for comparison[4]:

$$R_I = \int_{Q_1}^{Q_2} Q^4 (I_e - I_c)^2 \, dQ \Big/ \int_{Q_1}^{Q_2} Q^4 I_e \, dQ \tag{10}$$

where I_e and I_c are the experimental and calculated values of the scattering intensity. The iteration was carried out up to $R_I \sim 10^{-3}$.

The model curve corresponding to the best coincidence with the experimental curve is shown in *Figure 3* by a solid line. As a result of the calculations one obtains the maximal and the minimal values of R_g of marked blocks at a random orientation of the chain coils:

$$R_g^{\min} = 92 \pm 5\,\text{Å} \qquad R_g^{\max} = 160 \pm 8\,\text{Å}$$

which approximately corresponds to the molecular weights of the PB blocks in each of the fractions.

CONCLUSIONS

This paper shows the possibility of measuring R_g of a single chain in a superstructure giving, without special contrasting, a Bragg scattering pattern. This was achieved by a special technique involving the variation of contrast which led to 'invisibility' for Bragg reflections.

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