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Elastic Coherent Neutron Scattering from Mixtures of Triblock Copolymers and Homopolymers in the Homogeneous Bulk State

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ABSTRACT: The coherent elastic scattering structure factor for mixtures of triblock copolymers and homopolymers in the homogeneous bulk state is described using the random-phase approximation and incompressibility constraint. Mathematical expressions have been developed for the small q-region as well as for the large q-limit. Small-angle neutron scattering experiments were performed on mixtures of triblock copolymers made of deuterated and hydrogenated poly(dimethylsiloxane) (PDMS) blocks and deuterated PDMS homopolymers. The experimental results are in good agreement with the theoretical predictions.

Introduction

The properties of diblock copolymers have been extensively explored by scattering experiments using essentially neutrons.[1–7] The data are successfully interpretated using the random-phase approximation (RPA) method developed by de Gennes, Leibler, and others.[8–13] Both theory and experiments show that the scattering intensity exhibits a peak at a finite wave vector $Q_{\max}$, which depends on the radius of gyration of the total copolymer roughly as $2/\langle R_g^2\rangle^{1/2}$ in the case of a symmetrical diblock. The properties of multiblock copolymers however were much less explored, and very little information is known about their static behavior.[14–16]

The purpose of the present paper is to test the RPA method from mixtures of triblock copolymers and homopolymers in the homogeneous bulk state. Investigations of the small-angle scattering properties were carried out on mixtures of entirely deuterated poly(dimethylsiloxane) (PDMS) homopolymers and triblock copolymers made of deuterated and protonated PDMS blocks. In particular, the scattering behavior as dependent on the distribution of the hydrogenated and the deuterated blocks will be reported. For this purpose experiments using the small-angle neutron scattering facilities in Jülich (Germany) were performed.

Monodisperse mixtures made of each of two different types of triblock copolymers (HDH and DHD) with entirely deuterated PDMS homopolymers (D-PDMS) were examined. In the case of DHD the center part is hydrogenated ($[(CH_3)_6SiO]_x$ units), whereas the outer parts are deuterated ($[(CD_3)_6SiO]_y$ units). The other triblock copolymer HDH consists of a deuterated inner part and hydrogenated wings.

In the first part of this paper, we briefly summarize the method of calculation of the scattering properties of mixtures of triblock copolymers and homopolymers.[17–22] The second part describes the experiments made by small-angle neutron scattering (SANS) on these mixtures. The theoretical results will be applied to interpret the experimental data.

Theoretical Section

Scattering Equations of Mixtures of Triblock Copolymers and Homopolymers. Assuming that the scattering due to the compressibility is negligible, the general expression for the coherent scattering intensity of a mixture of homopolymers with partly labeled chains in the bulk state is described by the random-phase approximation

$$I(q) = a^2S_{AA}(q) + 2abS_{AB}(q) + b^2S_{BB}(q) \qquad (1)$$

where $S_{AA}(q)$, $S_{AB}(q)$, and $S_{BB}(q)$ are the Fourier transforms of the monomer density correlation functions and a,b are the coherent scattering lengths of monomers of type A,B.

From the definition of the correlation functions we get

$$S_{AA}(q) = S_{BB}(q) = -S_{AB}(q) = -S_{BA}(q) = S(q) \qquad (2)$$

and

$$I(q) = (a_D - a_H)^2S(q) \qquad (3)$$

a_D and a_H represent the coherent scattering length densities of the deuterated and the ordinary monomeric units, respectively. The contrast factor $(a_D - a_H)^2$ should be corrected for the difference in specific volumes. The scattered coherent intensity was measured as a function of the scattering vector $q = 4\pi\,\sin(\theta/2)/\lambda_0$ (λ_0 is the wavelength of the incident beam and θ is the scattering angle).

For a ternary mixture of a triblock copolymer ABA and homopolymer C, we have

$$S_{AA}(q) = [S^\circ{}_{AA}(1 + V_{BA}S^\circ{}_{AB} + V_{BB}S^\circ{}_{BB}) - S^\circ{}_{AB}(V_{BA}S^\circ{}_{AA} + V_{BB}S^\circ{}_{BA})]/D \qquad (4)$$

$$S_{BB}(q) = [S^\circ{}_{BB}(1 + V_{AB}S^\circ{}_{BA} + V_{AA}S^\circ{}_{AA}) - S^\circ{}_{BA}(V_{AB}S^\circ{}_{BB} + V_{AA}S^\circ{}_{AB})]/D \qquad (5)$$

$$S_{AB}(q) = [-S^\circ{}_{AA}(V_{AA}S^\circ{}_{AB} + V_{AB}S^\circ{}_{BB}) + S^\circ{}_{AB}(1 + V_{AA}S^\circ{}_{AA} + V_{AB}S^\circ{}_{BA})]/D \qquad (6)$$

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where

$$D = (1 + V_{AA}S^\circ_{AA} + V_{AB}S^\circ_{BA})(1 + V_{BA}S^\circ_{AB} + V_{BB}S^\circ_{BB}) - (V_{AA}S^\circ_{AB} + V_{AB}S^\circ_{BB})(V_{BA}S^\circ_{AA} + V_{BB}S^\circ_{BA}) \quad (7)$$

We assume that the interaction parameter χ between monomers of different type is zero.[23,24] All excluded volumes $V_{I,J}$ (I,J = A,B) are, therefore, the same, $V_{I,J} = 1/S^\circ_{CC}$. The quantities $S^\circ_{AA}(q)$, $S^\circ_{BB}(q)$, $S^\circ_{CC}(q)$, $S^\circ_{AB}(q)$, and $S^\circ_{BA}(q)$ are bare structure factors which will be given later for each system.

In our work two types of mixtures are considered: The first one is made of HDH triblock copolymers in D-homopolymers. A will be the hydrogenated species and B the deuterated species in the copolymer. C will be the deuterated homopolymer.

The coherent scattered intensity of the first system can be written as

$$I(q) = (a_D - a_H)^2 \frac{S^\circ_{AA}S^\circ_{CC} + S^\circ_{AA}S^\circ_{BB} - S^\circ_{AB}{}^2}{S^\circ_{CC} + S^\circ_{AA} + S^\circ_{BB} + 2S^\circ_{AB}} \quad (8)$$

The second mixture is made of DHD triblock copolymers in the same D-homopolymers used in the first sample. A will be the deuterated species and B the protonated species in the copolymer. C will be the deuterated homopolymer.

$$I(q) = (a_D - a_H)^2 \frac{S^\circ_{BB}{}'S^\circ_{CC}{}' + S^\circ_{AA}{}'S^\circ_{BB}{}' - S^\circ_{AB}{}'^2}{S^\circ_{CC}{}' + S^\circ_{AA}{}' + S^\circ_{BB}{}' + 2S^\circ_{AB}{}'} \quad (9)$$

To avoid difficulties in distinguishing the bare structure factors of the first and the second systems, we keep the unprimed quantities for describing the first system and the primed quantities for describing the second system. It is obvious that in the special case n_A(system 1) = n_A(system 2), n_B(system 1) = n_B(system 2), and N_A(system 1) = N_A(system 2), the corresponding bare structure factors of the two systems considered will be identical.

The quantities appearing in eq 8 are defined as follows: $S^\circ_{CC}(q)$ is the bare structure factor of the deuterated homopolymer

$$S^\circ_{CC}(q) = N_C n_C{}^2 P_C(q) \quad (10)$$

N_C represents the number of homopolymers per unit volume and n_C their degree of polymerization. $P_C(q)$ is the form factor of the homopolymer with the normalization $P_C(q{=}0) = 1$. Assuming that the chains are Gaussian, $P_C(q)$ can be represented reasonably well by the Debye function:

$$P_C(q) = (2/z^2)(z - 1 + \exp(-z)) \quad (11)$$

where $z = \lambda n_C$ and $\lambda = q^2l^2/6$.

The average square statistical length $\langle l^2\rangle = l^2$ of the deuterated and the hydrogenated monomeric species is assumed to be the same.

The other bare structure factors of eq 8 are defined as follows:[16]

$$S^\circ_{AA}(q) = 2N_A n_A{}^2\left(B_A(q) + \frac{(1 - \exp(-\lambda n_A))^2}{\lambda^2 n_A{}^2}\exp(-\lambda n_B)\right) \quad (12)$$

$$S^\circ_{BB}(q) = N_A n_B{}^2 B_B(q) \quad (13)$$

$$S^\circ_{AB}(q) = 2N_A n_A n_B \frac{1 - \exp(-\lambda n_A)}{\lambda n_A}\frac{1 - \exp(-\lambda n_B)}{\lambda n_B} \quad (14)$$

where N_A is the number of copolymer chains per unit volume and n_A and n_B are the degrees of polymerization of the H/D-block, respectively. The quantities $B_A(q)$ ($B_B(q)$) are the form factors of one H-block (D-block), which are defined in the same way as eq 11, where the quantity z is given by $z = \lambda n_A$ ($z = \lambda n_B$).

For the second system the bare structure factors will be designated by primes: $S^\circ_{CC}{}'(q)$, $S^\circ_{AA}{}'(q)$, $S^\circ_{BB}{}'(q)$, $S^\circ_{AB}{}'(q)$. The quantities N_C', N_A', n_A', n_B', $B_A'(q)$, and $B_B'(q)$ are defined in a similar way as explained above for system 1.

If we limit ourselves to the case where the degrees of polymerization of the blocks are the same in the two systems i.e., $n_A' = n_A = n_B' = n_B$, $N_A' = N_A$, and $N_C' = N_C$, we recover the expected identities:

$$S^\circ_{AB}(q) = S^\circ_{AB}{}'(q)$$
$$S^\circ_{AA}(q) = S^\circ_{AA}{}'(q) \quad (15)$$
$$S^\circ_{BB}(q) = S^\circ_{BB}{}'(q)$$

It is worthwhile to note that in this case and for monodisperse samples the coherent scattering intensities should be identical for both systems considered.

Behavior at Small Angles. If we expand $I(q)$ as a function of q in the range of q-values smaller than the inverse radius of gyration of the most extended chains, $q < R_{g,max}{}^{-1}$ (eqs 8–14), we obtain

$$\frac{(a_D - a_H)^2}{I(q)} = \alpha\left[1 + \frac{q^2\langle R_{app}{}^2\rangle}{3}\right] \quad (16)$$

This expression defines $\langle R_{app}{}^2\rangle$ as the mean square apparent radius of gyration which depends on all the properties characterizing the mixture. This quantity can be written as

$$\langle R_{app}{}^2\rangle = (x_1 - x_2)/x_3 \quad (17)$$

Equations 16 and 17 are valid for both systems with different expressions for α and x_i (i = 1–3). For the first system, one obtains

$$x_1 = D(N_C n_C{}^2\, 4N_A n_A{}^2(\mathbf{R}_C{}^2 + \mathbf{R}_A{}^2) - 4N_A{}^2 n_A{}^2 n_B{}^2\langle L^2\rangle) \quad (18a)$$

$$x_2 = N_C n_C{}^2\, 4N_A n_A{}^2(N_C n_C{}^2\mathbf{R}_C{}^2 + 4N_A n_A{}^2\mathbf{R}_A{}^2 + N_A n_B{}^2\mathbf{R}_B{}^2 + 4N_A n_A n_B\mathbf{R}_{AB}{}^2) \quad (18b)$$

$$x_3 = D(N_C n_C{}^2\, 4N_A n_A{}^2) \quad (18c)$$

The quantity α is defined by

$$\alpha = D/(N_C n_C{}^2\, 4N_A n_A{}^2) \quad (19a)$$

where

$$D = N_C n_C{}^2 + N_A n_B{}^2 + 4N_A n_A{}^2 + 4N_A n_A n_B \quad (19b)$$

$\mathbf{R}_A{}^2$ and $\mathbf{R}_B{}^2$ are the mean square radii of gyration of the normal and deuterated sections of the copolymer chains. This must be distinguished from the radii of gyration of the individual blocks, which will be denoted by the small letter r. $\mathbf{R}_C{}^2$ is the mean square radius of gyration of the homopolymer. $\mathbf{R}_{AB}{}^2$ is the cross-term contribution of the copolymer. The quantity $\langle L^2\rangle$ is the average value of the square distance between the center of mass of the H and D parts of the copolymer:[25]

$$\langle L^2\rangle = 2\mathbf{R}_{AB}{}^2 - \mathbf{R}_A{}^2 - \mathbf{R}_B{}^2 \quad (20)$$

With these notations, we have for the first system

$$\mathbf{R}_A^2 = {}^3/_2 r_B^2 + 2r_A^2 \tag{21a}$$

$$\mathbf{R}_B^2 = r_B^2 \tag{21b}$$

$$\mathbf{R}_{AB}^2 = {}^3/_2(r_A^2 + r_B^2) \tag{21c}$$

$$\langle L^2 \rangle = r_A^2 + {}^1/_2 r_B^2 \tag{22}$$

where r_A^2 and r_B^2 are the radii of gyration of the H and D blocks individually.

For the second system we have

$$x_1 = D'(N_C'n_C^2N_A'n_B'^2(\mathbf{R}_C^2 + \mathbf{R}_B'^2) - 4N_A'^2n_B'^2n_A'^2\langle L'^2 \rangle) \tag{23a}$$

$$x_2 = N_C'n_C^2N_A'n_B'^2(N_C'n_C'^2\mathbf{R}_C^2 + N_A'n_B'^2\mathbf{R}_B'^2 + 4N_A'n_A'^2\mathbf{R}_A'^2 + 4N_A'n_A'n_B'\mathbf{R}_{AB}'^2) \tag{23b}$$

$$x_3 = D'(N_C'n_C^2N_A'n_B'^2) \tag{23c}$$

The quantity α is defined by

$$\alpha = D'/(N_C'n_C^2N_A'n_B'^2) \tag{24a}$$

where

$$D' = N_C'n_C^2 + 4N_A'n_A'^2 + N_A'n_B'^2 + 4N_A'n_A'n_B' \tag{24b}$$

$\langle L'^2 \rangle$ is defined similarly in terms of the new quantities

$$\langle L'^2 \rangle = 2\mathbf{R}_{AB}'^2 - \mathbf{R}_B'^2 - \mathbf{R}_A'^2 \tag{25}$$

where

$$\mathbf{R}_B'^2 = r_B'^2 \tag{26a}$$

$$\mathbf{R}_A'^2 = {}^3/_2 r_B'^2 + 2r_A'^2 \tag{26b}$$

$$\mathbf{R}_{AB}'^2 = {}^3/_2(r_B'^2 + r_A'^2) \tag{26c}$$

Substituting the latter results into eq 25 yields

$$\langle L'^2 \rangle = r_A'^2 + {}^1/_2 r_B'^2 \tag{27}$$

Behavior at Intermediate q-Values. In the range of q-values $q > R_{g,\min}^{-1}$, where $R_{g,\min}$ is the smallest radius of gyration, the exponential functions in the form factors (eqs 11–14) together with the terms proportional to $1/\lambda^2$ can be neglected and one obtains for the first system

$$I(q) = (a_D - a_H)^2 \frac{4(N_Cn_C + N_An_B)N_An_A}{\lambda(N_Cn_C + N_An_B + 2N_An_A)} \tag{28}$$

Likewise, in the case of system 2, we have

$$I(q) = (a_D - a_H)^2 \frac{2(N_C'n_C + 2N_A'n_A')N_A'n_B'}{\lambda(N_C'n_C + 2N_A'n_A' + N_A'n_B')} \tag{29}$$

At this stage, we need to introduce some relationships between experimental and microscopic quantities. First we have

$$\rho_N^H = \rho_m^H N_L/M_0^H \tag{30}$$

$$\rho_N^D = \rho_m^D N_L/M_0^D$$

where $\rho_m^{H/D}$ are the macroscopic densities in g/cm^3 and $\rho_N^{H/D}$ the number of molecules per unit volume of the hydrogenated/deuterated species. $M_0^{H/D}$ are the molecular weights of a hydrogenated/deuterated subunit,[26] and N_L is the Avogadro number.

To obtain a suitable form for the calculations and comparison of the scattering data for the two systems, we further introduce for the first system

$$N_Cn_C = \Phi_C\rho_N^D \tag{31}$$

$$N_An_B = \Phi_B\rho_N^D \tag{32}$$

$$2N_An_A = \Phi_A\rho_N^H \tag{33}$$

where Φ_C is the volume fraction of the homopolymer and Φ_A and Φ_B are the volume fractions of the hydrogenated and deuterated parts of the copolymer. The Φ_I are normalized by writing the incompressibility condition:

$$\Phi_C + \Phi_A + \Phi_B = 1 \tag{34}$$

According to eq 29 the expressions for the second system are

$$N_C'n_C = \Phi_C'\rho_N^D \tag{35}$$

$$2N_A'n_A' = \Phi_A'\rho_N^D \tag{36}$$

$$N_A'n_B' = \Phi_B'\rho_N^H \tag{37}$$

The incompressibility assumption yields

$$\Phi_C' + \Phi_A' + \Phi_B' = 1 \tag{38}$$

Assuming $\rho_N^H = \rho_N^D = \rho_N$ and $n_A' = n_A = n_B' = n_B$, one obtains for the first system

$$I(q) = (a_D - a_H)^2 \frac{2}{\lambda}\rho_N\Phi_A(\Phi_C + \Phi_B) \tag{39}$$

whereas for the second system one has

$$I(q) = (a_D - a_H)^2 \frac{2}{\lambda}\rho_N\Phi_B'(\Phi_C' + \Phi_A') \tag{40}$$

These results are further compared with the theoretical predictions concerning a mixture of monodisperse hydrogenated and deuterated homopolymers (called system 3)

$$N_Hn_H = \Phi_H\rho_N^H \tag{41}$$

$$N_Dn_D = \Phi_D\rho_N^D \tag{42}$$

where $N_{H/D}$ are the number of homopolymer molecules per unit volume, $n_{H/D}$ are the degrees of polymerization, and $\Phi_{H/D}$ are the volume fractions of the hydrogenated and deuterated hompolymers. The Φ_I satisfy the incompressibility requirement:

$$\Phi_H + \Phi_D = 1 \tag{43}$$

In this case the coherent scattered intensity can be written as

$$I(q) = (a_D - a_H)^2 \frac{2}{\lambda}\rho_N\Phi_H\Phi_D \tag{44}$$

These results (eqs 39, 40, and 44) clearly indicate that the q-dependence of the coherent scattered intensity at large q-values remains the same regardless of the architecture of the chains in the mixtures. This is to be expected since, at high q-values, one sees only short distances and the scattering becomes independent of molecular weight and also of the existence of junctions between the different blocks of the copolymer.

Experimental Section

Our experiments were carried out with two kinds of monodisperse mixtures made of two different PDMS triblock copolymers and completely deuterated PDMS homopolymer (D-PDMS). The anionic polymerization technique was employed to prepare the samples. The method of synthesis and charac-

Table I

sample	polymer	$M_n \times 10^{-3}$	M_w/M_n	wt % H in polymer	wt % polymer in sample
system 1	triblock copolymer HDH	190	1.22	78	13.7
	D-PDMS[a]	113	1.03	0	86.3
system 2	triblock copolymer DHD	176	1.27	37	23.6
	D-PDMS[a]	113	1.03	0	76.4
matrix-D	D-PDMS[a]	113	1.03	0	100
matrix-H	H-PDMS[b]	154	1.06	100	100

[a] Entirely deuterated PDMS homopolymer. [b] Entirely hydrogenated PDMS homopolymer.

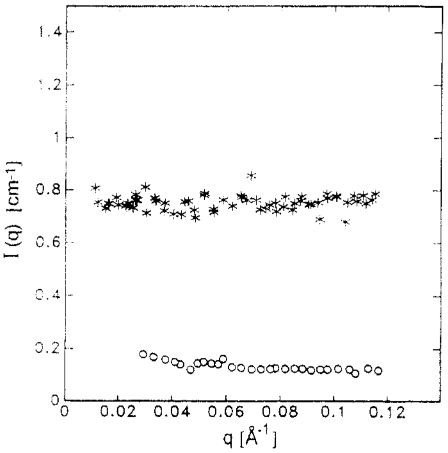

Figure 1. Scattered intensity $I(q)$ at $T = 200$ °C as a function of q for the D-matrix (○) and the H-matrix (*).

terization are detailed in refs 27–30. The molecular weights, polydispersities, and weight fractions of the polymers in the samples are given in Table I.

Samples of systems 1 and 2 of the H-PDMS and D-PDMS were placed in 1-mm-thick quartz cells. The samples were kept for 24 h at $T = 200$ °C in vacuum. After this treatment, gel permeation chromatography (GPC) measurements were carried out to check for degradation, which was not the case. For the SANS system itself, all samples were annealed at $T = 200$ °C for 4 h.

The SANS experiments were performed on the KWS II diffractometer at the cold source of the Jülich research reactor FRJ-2.[31] The wavelength of the incident neutron beam was fixed at $\lambda = 7$ Å with a resolution of $\delta\lambda/\lambda = 18\%$. The sample–detector distances were 2 and 8 m, allowing measurements in a range of momentum transfer between 0.68×10^{-2} Å and 0.12 Å. Absolute units for the intensities were obtained by using an incoherent scattering sample, called Lupolen. The calibrations with a vanadium single crystal on this material were done before in ref 32. This calibration method provides a reported precision of ±5%. All measurements were carried out at $T = 200 \pm 0.1$ °C.

The raw data were corrected for detector efficiency, transmissions, sample thickness, etc. and for the appropriate incoherent background using a pure hydrogenated PDMS homopolymer as the H-matrix. Figure 1 shows the intensity scattered as a function of q for the H-matrix (*) and for the D-matrix (○). The weight of the coherent scattering of the deuterated homopolymer in systems 1 and 2 is included in the theoretical calculations. As expected, the D-matrix produced only a weak scattering behavior. We neglect therefore the effect of incoherent scattering of the pure deuterated homopolymer.

The contribution of the H-matrix, which is q-independent can be compared with the scattering behavior of the systems 1 and 2 (Figure 3). It is seen that the full weight of the H-matrix signal is of more than an order of magnitude less than the signals of each of the two systems.

No corrections for multiple scattering were necessary in the present case since the transmission coefficients were always above 85%.

Values for the densities of the deuterated and the hydrogenated PDMS were taken from the literature.[33-35] The coherent scattering length densities of the hydrogenated and deuterated monomeric unit are given as $a_H = 8.2 \times 10^{-16}$ m and $a_D = 632.8 \times 10^{-16}$ m, respectively.[36]

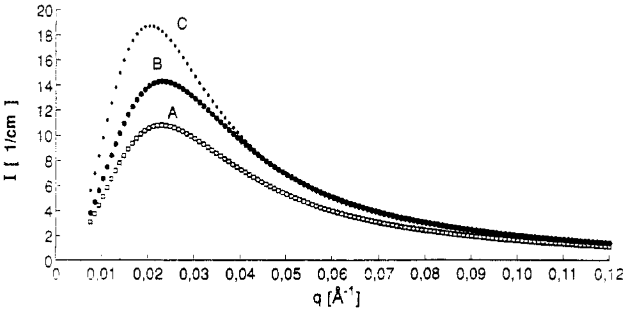

Figure 2. Theoretical values (RPA theory) of the coherent scattered intensity for the pure triblock copolymers HDH (curve A) and DHD (curve B) in the conditions of the experiment (without homopolymer) and for a triblock copolymer made of equal size blocks HDH or DHD (curve C; see text for details) plotted against q.

Results and Discussion

To illustrate the effects of the matrix homopolymer D on the coherent scattered intensity, we have plotted in Figure 2 the theoretical variation of $I(q)$ as a function of q for the pure triblock copolymers HDH (curve A) and DHD (curve B). The parameters chosen for the copolymers in this plot were consistent with the experimental conditions described in Table I except of course the composition of deuterated homopolymers (D-PDMS), which is zero.

One observes a clear maximum for the pure triblock copolymer in the absence of the homopolymer matrix. The position of the maximum ($q_{max} = 0.02$ Å^{-1}) is approximately given by $2/R_{gT}$, where R_{gT} is roughly estimated from $\langle R_g^2\rangle^{1/2} = (n_T l^2/6)^{1/2} = 120$ Å assuming that n_T is equal to 180 000 g/mol and l is 6 Å.[37] The intensity of the peak maximum is different because the molecular weight of the hydrogenated and the deuterated parts of the two triblock copolymers are different. From a theoretical point of view, for triblock copolymers made of equal size blocks HDH or DHD, one would expect the two curves to be superposed. This is indeed the case as illustrated by curve C in Figure 2. The degrees of polymerization herein are $n_A' = n_A = n_B' = n_B = 1000$. The compositions for the triblock copolymer HDH were chosen as $\Phi_A = 0.67$ and $\Phi_B = 0.33$ and for DHD, $\Phi_A' = 0.67$ and $\Phi_B' = 0.33$.

If the deuterated homopolymer is added to the copolymer like in our experiments, the peak disappears in the q-range of the experiments and the intensity at small q increases dramatically, which can be seen from eqs 8–14. For higher homopolymer contents the fluctuations in the compositions of H and D species are reduced and the absolute intensity is also reduced. Ultimately, when the composition of deuterated homopolymer is 100%, the scattering intensity vanishes, assuming that the system is incompressible.

All calculations presented herein take into account the effect of polydispersity using corrected equations for the different structure factors.[38] It has to be noted that the additional contributions to the theoretical predicted scattered intensity are small because of the low polydispersity (Table I).

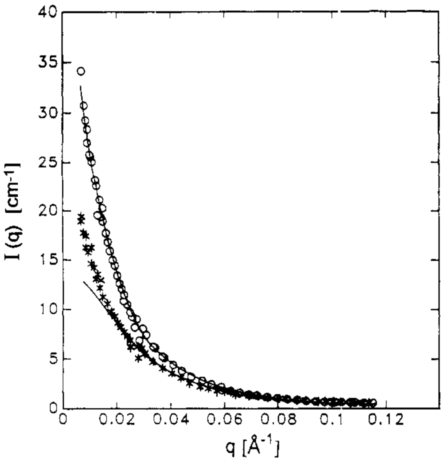

Figure 3. Experimentally observed coherent scattered intensity of the system 1 (O) and system 2 (*) at $T = 200$ °C as a function of q. The full lines represent calculations of the RPA theory (eqs 7–14).

Figure 3 represents the coherent scattering intensities for systems 1 and 2 as a function of q. One observes that the maximum predicted in the pure copolymer system (Figure 2) disappears in the presence of the deuterated homopolymer matrix in the range of q explored. The two curves meet for q-values larger than about 0.04 $Å^{-1}$, which is consistent with the result in eq 44 where we have obtained the same behavior regardless of the chain architecture. As q decreases from this value, the two systems show different scattering curves because of the different molecular weights of the block parts. It should be noted that the difference in the intensities of both systems is not due to contrast factors because these are the same.

The continuous lines in Figure 3 represent the theoretical predictions given by eqs 8–14 in the conditions of the experiments. One observes a good agreement between the theoretical curves and the experimental data. The slight discrepancy in the small q-range of the lower curve may be due to the higher sensitivity on the intensity in this region. The bending of the theoretical curve in the small q-limit, which is not observed in the experiments, indicates a stronger effect due to the copolymer component. A similar behavior is described in ref 6. In this data treatment it is not necessary to introduce the interaction parameter χ and yet the agreement between theory and experiments is fairly good.

To extract the apparent radius of gyration for the two systems, we have made a plot in Figure 4 where the inverse intensity is represented as a function of q^2 in the small q-range. The lines give directly access to the apparent radii of gyration for the two systems (eq 16). From the slopes of Figure 4 one extracts after corrections due to the contrast factor in the case of system 1 $\langle R_{app}^2 \rangle = 118 \pm 1$ $Å^2$ and in the case of system 2 $\langle R_{app}^2 \rangle = 133 \pm 2$ $Å^2$. From eqs 16–22, defining the theoretical apparent radii of gyration, we get $\langle R_{app}^2 \rangle_{theor} = 122$ $Å^2$ for system 1. Within the experimental errors, one observes here a good agreement between the theoretical value and the experimental one. The intercept obtained from Figure 4 is also in agreement with the theoretically predicted on (eq 19).

The discrepancy between the experimental values and the theoretical curve does not allow one to define a theoretical apparent radius of gyration in the small q-region in the case of system 2.

The same data are represented in Figure 5 in Kratky plots. The plateau region is clearly reached in the intermediate range of q which is explored here. This shows that in the high q-region $I(q)$ behaves as $1/q^2$, which indicates that the Gaussian approximation for the coils is a good representation of the form factor of the chains. The discrepancy in the plateau values of the two systems is due to the differences in the apparent radii of gyration. The continuous lines in Figure 5 represent the theoretical curves given by eqs 8–14 and 28–38.

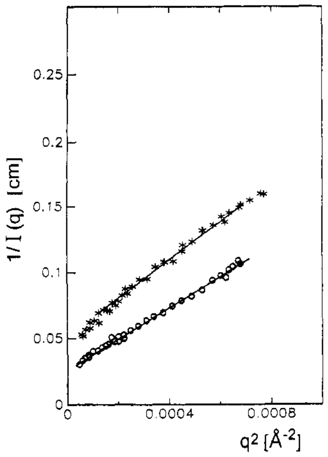

Figure 4. Inverse coherent scattered intensity as a function of q^2 for system 1 (O) and system 2 (*) considering only the small q-range at $T = 200$ °C. The continuous lines represent linear fits of the experimental values.

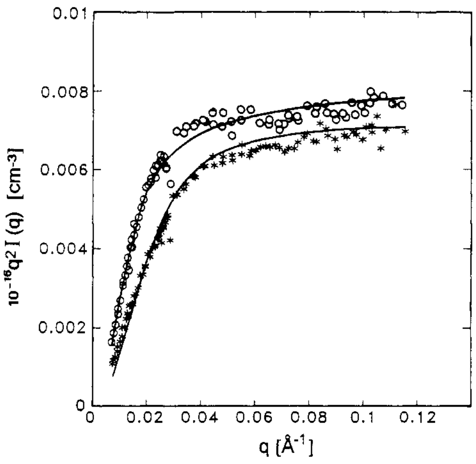

Figure 5. Kratky plot (Iq^2 versus q) for system 1 (O) and system 2 (*) ($T = 200$ °C). The full lines represent calculations of the RPA theory (eqs 8–14 and 28–38).

Conclusion

In this work an attempt is made to characterize experimentally the scattering behavior of systems made of triblock copolymers HDH and DHD in matrices made of deuterated homopolymers. Since it is known that triblock copolymers have some features of the multiblock copolymers, this study can provide the essential basis for the difference expected between diblock and multiblock copolymers.

We have examined the effect of adding deuterated homopolymers to the triblock copolymers and explored the changes in the intensities when the concentration of homopolymers is increased. It is shown that the effect of adding a homopolymer removes the maximum and the intensity at small q-values is dramatically increased. The experimental observations can be analyzed qualitatively and in many cases quantitatively with the simple model based on the random-phase approximation.

This investigation provides useful information which constitutes a prelude to the investigation of the dynamic properties of these systems as obtained by the neutron spin–echo technique.[39]

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References and Notes

(1) Bates, F. S.; Hartney, M. A. *Macromolecules* **1987**, *18*, 2478.
(2) Richards, R. W. *Adv. Polym. Sci.* **1985**, *71*, 2.
(3) Mori, K.; Hasegawa, H.; Hashimoto, T. *Polym. J.* **1985**, *17*, 799.
(4) Fischer, E. W. In *Frontiers of Macromolecular Science, IUPAC 32nd International Symposium on Macromolecules*; Saegusa, T., Higashimura, T., Abe, A., Eds.; Blackwell Scientific Publications: Oxford, London, Edinburgh, Boston, Melbourne, 1989; pp 9–19.
(5) Ionescu, L.; Picot, C.; Duval, M.; Duplessix, R.; Benoît, H.; Cotton, J. P. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1019.
(6) Stühn, B.; Rennie, A. R. *Macromolecules* **1989**, *22*, 2460.
(7) Connell, J. G.; Richards, R. W. *Eur. Polym. J.* **1993**, *29*, 331.
(8) de Gennes, P.-G. *J. Phys.* (*Paris*) **1970**, *31*, 235.
(9) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(10) Legrand, A. D.; Legrand, D. G. *Macromolecules* **1979**, *12*, 450.
(11) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(12) Leibler, L.; Benoît, H. *Polymer* **1981**, *22*, 195.
(13) Kim, J. K.; Kimishima, K.; Hashimoto, T. *Macromolecules* **1993**, *26*, 125.
(14) Boué, F.; Daoud, M.; Nierlich, M.; Williams, C.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Benoît, H.; Duplessix, P.; Picot, C. In *IAEA*: Vienna, 1978; Vol. 1, p 563.
(15) Duplessix, P.; Cotton, J. P.; Benoît, H.; Picot, C. *Polymer* **1979**, *20*, 1181.
(16) Hadziioannou, G.; Benoît, H.; Tang, W.; Shull, K.; Han, C. C. *Polymer* **1992**, *33*, 4677.
(17) Benoît, H.; Koberstein, J.; Leibler, L. *Makromol. Chem., Suppl.* 1981, *4*, 85.
(18) Benmouna, M.; Benoît, H. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1227.
(19) Benoît, H.; Benmouna, M. *Macromolecules* **1984**, *17*, 535.
(20) Benoît, H.; Wu, W.; Benmouna, M.; Mozer, B.; Bauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986.
(21) Benoît, H.; Hadziioannou, G. *Macromolecules* **1988**, *21*, 1449.
(22) Benoît, H.; Benmouna, M.; Wu, W.-L. *Macromolecules* **1990**, *23*, 1511
(23) Kirste, R. G.; Lehnen, B. R. *Makromol. Chem.* **1976**, *177*, 1137.
(24) Lapp, A.; Picot, C.; Benoît, H. *Macromolecules* **1985**, *18*, 2437.
(25) Leng, M.; Benoît, H. *J. Polym. Sci.* **1962**, *57*, 263.
(26) It has to be noted that in the case of poly(dimethylsiloxane) the molecular weight of the monomer (1,1,3,3,5,5-hexamethylcyclotrisiloxane, molecular weight 222.48) is 3 times larger than the molecular weight of a PDMS chain unit (molecular weight 74.16).
(27) Maschke, U. Ph.D. Dissertation, University of Mainz, Germany, 1992.
(28) Maschke, U.; Wagner, T.; Coqueret, X. *Makromol. Chem.* **1992**, *193*, 2453.
(29) Coqueret, X.; Maschke, U. Submitted for publication.
(30) Wagner, T.; Maschke, U. To be published.
(31) In *Experimentiereinrichtungen im Forschungsreaktor und im Neutronenleiterlabor*; Springer, T., Ed.; Kernforschungsanlage Jülich GmbH, KFA Bericht: Jülich, Germany, 1986.
(32) Schwahn, D.; Hahn, K.; Streib, J.; Springer, T. *J. Chem. Phys.* **1990**, *93*, 8383.
(33) Shih, H.; Flory, P. J. *Macromolecules* **1972**, *6*, 758.
(34) Hurd, C. B. *J. Am. Chem. Soc.* **1946**, *68*, 364.
(35) Lehnen, B. R. Ph.D. Dissertation, University of Mainz, Germany, 1977.
(36) Koester, L.; Rauch, H. *Neutron Scattering Length*, IAEA Contract 2517/RB, Vienna, 1981.
(37) In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1991.
(38) (a) Greschner, G. S. *Makromol. Chem.* **1973**, *168*, 273. (b) Greschner, G. S. *Makromol Chem.* **1973**, *170*, 203.
(39) Maschke, U.; Ewen, B.; Benmouna, M.; Farago, B. To be published.