polymer papers

Neutron scattering by multiblock copolymers of structure $(A\text{–}B)_N\text{–}A$

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(Received 4 July 1991; revised 18 February 1992; accepted 2 March 1992)

Multiblock copolymers were prepared by anionic copolymerization of deuterated and classical styrene monomers. The use of bifunctional initiators gives copolymers with an odd number of sequences. Neutron scattering experiments were performed on these samples in order to check the existing theories which are extended in the first part to multiblock copolymers with an odd number of blocks. The agreement between theory and experiment is excellent and, surprisingly, the height of the maximum of the curves: scattered intensity *versus* scattering angle, does not depend on the number of blocks.

(Keywords: copolymers; neutron scattering; deuteration; polystyrene)

INTRODUCTION

In a recent paper[1] the scattering properties of even multiblock copolymers of the form $(A\text{–}B)_N$ were calculated, based on the random-phase approximation. The technique is applied here to odd copolymers of the type $(A\text{–}B)_N\text{–}A$ and compared to experimental results. Experiments were performed using a model copolymer system consisting of alternating blocks of perdeuterated and normal polystyrene. This system is ideally suited for testing the theoretical predictions because the contrast factor for neutral scattering from hydrogen and deuterium is significant, yet the thermodynamic interaction between the blocks is quite small and can be neglected for the block molecular weights used. Block copolymer mesophases are therefore not formed and the chain statistics is Gaussian. Symmetric block copolymers were synthesized via anionic polymerization using a difunctional initiator, a procedure that cannot be used to produce even (asymmetric) copolymers. Theoretical results for even and odd copolymers are evidently identical at the limit of very high N, but are different for low values of N. The theoretical treatment of the odd case is outlined in the first part of this paper, as a complement to ref. 1, where the even case was developed, and is followed by a discussion of the experimental results.

THEORETICAL

The random-phase approximation theory allows one to evaluate the scattered intensity by a copolymer in bulk knowing the form factors of part A, P_A, and part B, P_B, as well as the cross form factor, $P_{AB}(q)$. It takes a simple form if one assumes that the system is monodisperse and that one has divided both parts A and B into units having the same volume:

$$\frac{(b_A - b_B)^2}{i(q)} = \frac{(z_A + z_B)^3}{z_A^2 z_B^2} \frac{P_T}{P_A P_B - P_{AB}^2} - 2\chi \qquad (1)$$

In this expression b_A and b_B are the coherent scattering lengths of the monomers of type A and B, which are supposed to have the same volume; $i(q)$ is the scattered intensity per monomeric unit; χ is the interaction parameter between monomers of type A and B; and z_A and z_B are the numbers of monomers of type A and B in a molecule of copolymer.

P_A is the form factor of part A, i.e. the quantity:

$$P_A(q) = \frac{1}{z_A^2} \left\langle \sum_{l=1}^{z_A} \sum_{k=1}^{z_A} \exp(-i\boldsymbol{q}\cdot\boldsymbol{r}_{k_A l_A}) \right\rangle \qquad (2)$$

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where the indices k and l run over part A of the copolymer. The quantity $\boldsymbol{q}$ is the scattering vector $[|\boldsymbol{q}| = (4\pi/\lambda)\sin\theta/2]$ and the vector $\boldsymbol{r}_{kl}$ is the vector joining the scattering centres k and l. A similar definition can be given for part B of the copolymer. The cross term $P_{\mathrm{AB}}(q)$ is defined as:

$$P_{\mathrm{AB}}(q) = \frac{1}{z_{\mathrm{A}} z_{\mathrm{B}}} \left\langle \sum_{l_{\mathrm{A}}=1}^{z_{\mathrm{A}}} \sum_{k_{\mathrm{B}}=1}^{z_{\mathrm{B}}} \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{k_{\mathrm{A}} l_{\mathrm{B}}}) \right\rangle \tag{3}$$

It represents the interference between the radiation scattered by monomers A and B. Finally, P_{T} is the form factor of the whole polymer and one has the simple relation:

$$(z_{\mathrm{A}} + z_{\mathrm{B}})^2 P_{\mathrm{T}}(q) = z_{\mathrm{A}}^2 P_{\mathrm{A}}(q) + z_{\mathrm{B}}^2 P_{\mathrm{B}}(q) + 2 z_{\mathrm{A}} z_{\mathrm{B}} P_{\mathrm{AB}}(q) \tag{4}$$

Now let us consider our block copolymer. If we call $N + 1$ the number of blocks of type A, each of them made of n_{A} units, and N the number of blocks B, each made of n_{B} units, one has:

$$z_{\mathrm{A}} = (N + 1)n_{\mathrm{A}} \quad \text{and} \quad z_{\mathrm{B}} = N n_{\mathrm{B}}$$

This leads to the rearrangement of equation (1) in the form:

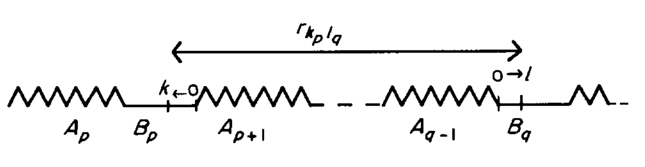
$$\frac{(b_{\mathrm{A}} - b_{\mathrm{B}})^2}{i(q)} = \frac{[(N + 1)n_{\mathrm{A}} + N n_{\mathrm{B}}]^3}{(N + 1)^2 n_{\mathrm{A}}^2 N^2 n_{\mathrm{B}}^2} \times \frac{P_{\mathrm{T}}(q)}{P_{\mathrm{A}}(q) P_{\mathrm{B}}(q) - P_{\mathrm{AB}}^2(q)} - 2\chi \tag{5}$$

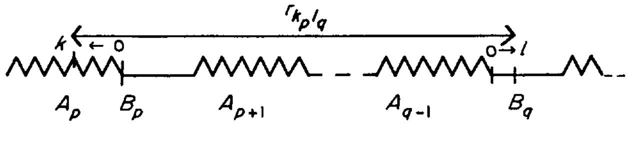
The problem now is to evaluate the three quantities P_{A}, P_{B} and P_{AB}. If N is large they are evidently identical and equal to the form factor of the whole polymer as in a statistical copolymer. However, we are interested in the cases where N is small and this requires a rigorous calculation in the frame of the Gaussian approximation. This has already been done in ref. 1 and we shall briefly summarize the method.

The case of P$_B$ *and* P$_A$

Let us define a point A by two indices k and p; k_p is the kth point on the block p. The vector $\boldsymbol{r}_{k_p l_q}$ joins point k on block p to point l on block q. Assuming $k < l$, $p < q$ and counting k from the right to the left and l from the left to the right (see diagram), one sees immediately that the number of segments d between k and l is:

$$\begin{aligned} d &= k + n_{\mathrm{B}}(q - p - 1) + n_{\mathrm{A}}(q - p) + 1 \\ &= k + l + (n_{\mathrm{A}} + n_{\mathrm{B}})(q - p - 1) + n_{\mathrm{A}} \end{aligned} \tag{6}$$





Extracting from the double sum the terms for which $p = q$ leads to:

$$P_{\mathrm{B}}(q) = \frac{1}{N} p_{\mathrm{B}}(q) + \frac{2}{N^2 n_{\mathrm{B}}^2} \sum_{p<q}^{N} \sum^{N} \sum_{k_p}^{n_{\mathrm{B}}} \sum_{l_q}^{n_{\mathrm{B}}} \times \exp\left\{ -\frac{q^2 \ell^2}{6} [k + l + (n_{\mathrm{A}} + n_{\mathrm{B}})(q - p - 1) + n_{\mathrm{A}}] \right\} \tag{7}$$

where $p_{\mathrm{B}}(q)$ is the form factor of one block B and ℓ is the length of the statistical element. (This formula is obtained using the classical result that the Fourier transform of a random walk of n steps equals $\exp(-q^2 n\overline{\ell^2}/6)$, where $\overline{\ell^2}$ is the statistical length of one step.) The quadruple sum is a simple geometrical one but some care has to be taken in order to obtain the correct formula for any value of N. We give only the final result because these calculations are explained in detail in ref. 1:

$$P_{\mathrm{B}}(q) = \frac{1}{N} p_{\mathrm{B}}(q) + \frac{2B^2(q) x_{\mathrm{A}}}{N^2} \left[\frac{N}{1 - x} - \frac{1 - x^N}{(1 - x)^2} \right] \tag{8}$$

Here we have introduced for simplification the quantities:

$$x_{\mathrm{A}} = \langle \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{0;n_{\mathrm{A}}}) \rangle = \exp(-q^2 n_{\mathrm{A}} \ell^2/6) \tag{9}$$

$$x_{\mathrm{B}} = \langle \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{0;n_{\mathrm{B}}}) \rangle = \exp(-q^2 n_{\mathrm{B}} \ell^2/6) \tag{10}$$

and

$$x = x_{\mathrm{A}} x_{\mathrm{B}}$$

The quantity x_{A} or x_{B} represents the phase shift going from one end of a block to the other:

$$A(q) = \sum_{1}^{k_{\mathrm{A}}} \exp\left(-\frac{q^2 n_{\mathrm{A}} \ell^2}{6} \right) = \frac{1 - \exp[-(q^2 \ell^2/6) n_{\mathrm{A}}]}{(q^2 \ell^2/6) n_{\mathrm{A}}} \tag{11}$$

$$B(q) = \frac{1 - \exp[-(q^2 \ell^2/6) n_{\mathrm{B}}]}{(q^2 \ell^2/6) n_{\mathrm{B}}} \tag{12}$$

The quantities $A(q)$ and $B(q)$ are the amplitudes scattered by block A or B.

In order to obtain the value of $P_{\mathrm{A}}(q)$ it is sufficient to transform A into B and to replace N by $N + 1$. This gives:

$$P_{\mathrm{A}}(q) = \frac{1}{N + 1} p_{\mathrm{A}}(q) + \frac{2A^2(q) x_{\mathrm{B}}}{(N + 1)^2} \left[\frac{N + 1}{1 - x} - \frac{1 - x^{N+1}}{(1 - x)^2} \right] \tag{13}$$

The case of P$_{AB}$

The calculation of $P_{\mathrm{AB}}(q)$ follows the same lines. Nevertheless there is one difference: it is not possible to assume $p < q$ and to double the rectangular terms as done in equation (8). Both cases $p < q$ and $p > q$ should be considered in order to evaluate the number of segments between the scattering centres k_p on A and l_q on B. One finds:

$$d = k + l + (n_{\mathrm{A}} + n_{\mathrm{B}})(q - p) \qquad \text{if } p \leqslant q \tag{14}$$

$$d = k + l + (n_{\mathrm{A}} + n_{\mathrm{B}})(q - p - 1) \qquad \text{if } p > q \tag{15}$$

The calculation proceeds on the same lines to obtain:

$$P_{\mathrm{AB}}(q) = \frac{2A(q)B(q)}{N(N + 1)} \left[\frac{N + 1}{1 - x} - \frac{1 - x^{N+1}}{(1 - x)^2} \right] \tag{16}$$

Equations (13) and (16) are very similar; they are also similar to the result obtained for a Gaussian chain:

$$P(q) = \frac{1}{N} + \frac{2}{N^2} \sum_{p<q}^{N} \sum^{N} \exp\left[-\frac{q^2\ell^2}{6}(q-p) \right] \quad (17)$$

for which the double sum is, without making any assumption on N:

$$P(q) = \frac{1}{N} + \frac{2}{N^2}\left[N\frac{1+x}{1-x} - 2\frac{x}{(1-x)^2}(1-x^N) \right] \quad (18)$$

where we have written $x = \exp(-q^2\ell^2/6)$. It is evident that when N is large and x small it reduces to the classical Debye formula.

Behaviour at small q *values*

Expanding these expressions as a function of q gives:

$$\begin{aligned} R_A^2 &= (N+1)(r_A^2 + r_B^2) - \frac{1}{N+1} r_B^2 \\ R_B^2 &= N(r_A^2 + r_B^2) - \frac{1}{N} r_A^2 \quad (19) \\ R_{AB}^2 &= (N + \tfrac{1}{2})(r_A^2 + r_B^2) \end{aligned}$$

where R_A^2 and R_B^2 are the radii of gyration of the parts A and B of the copolymer and r_A^2 and r_B^2 the radii of gyration of each of the blocks A and B. One can now evaluate the quantity $\overline{L^2}$, the average value of the distance between the centre of masses of the parts A and B of the copolymer:

$$\overline{L^2} = 2\left(\frac{r_A^2}{N} + \frac{r_B^2}{N+1} \right) \quad (20)$$

This quantity is similar to the corresponding result in the case of even copolymers:

$$\overline{L^2} = 2\left(\frac{r_A^2}{N} + \frac{r_B^2}{N} \right) \quad (21)$$

and, as expected, the difference disappears when N becomes large. It confirms that even and odd block copolymers have similar behaviours.

The behaviour at large angles

As can be deduced from the general laws of scattering, the cross term $P_{AB}(q)$ decreases faster than $P_A(q)$ and $P_B(q)$ and can be neglected when one reaches the intermediate range. One obtains after these simplifications:

$$\frac{(b_A - b_B)^2}{i(q)} = \frac{[(N+1)n_A + Nn_B]^3}{(N+1)^2 n_A^2 N^2 n_B^2} \frac{P_T(q)}{P_A(q)P_B(q)} \quad (22)$$

where $P_T(q)$ is the form factor of the whole molecule. If one looks at the expressions for $P_A(q)$ and $P_B(q)$ one realizes, assuming Gaussian statistics, that the two leading terms come from $P_A(q)$ and $P_B(q)$, the structure factors of the blocks. One thus obtains:

$$\begin{aligned} P_A(q) &= \frac{p_A(q)}{N+1} = \frac{2}{\lambda n_A(N+1)}\left(1 - \frac{1}{\lambda n_A}\right) \\ P_B(q) &= \frac{p_B(q)}{N} = \frac{2}{N\lambda n_B}\left(1 - \frac{1}{\lambda n_B}\right) \quad (23) \end{aligned}$$

and also

$$P_T(q) = \frac{2}{\lambda N_T}\left(1 - \frac{1}{\lambda N_T}\right)$$

where we have used the classical expansion of the Debye form factor for a Gaussian chain and defined λ as $q^2\ell^2/6$.

If one defines the following quantities:

$$u = \frac{(N+1)n_A}{N_T} \qquad v = 1 - u = \frac{Nn_B}{N_T} \quad (24)$$

these quantities being the number (and volume) fractions of monomers A and B in the sample one obtains:

$$\frac{(b_A - b_B)^2}{i(q)} = \frac{1}{2uv}\left(\lambda + \frac{1}{n_A} + \frac{1}{n_B} - \frac{1}{N_T} \right) \quad (25)$$

This formula is identical to the expression obtained for an even number of blocks and to the formula that was used to study the problem of transesterification[2]: it should be added that this result is valid even if the system is polydisperse. In this case one has to replace the quantities n_A, n_B and N_T by the corresponding number-average values and to remember that the definition of u and v as the composition of the copolymer has to be replaced by the composition of the sample.

It is evident that, if one plots $(b_A - b_B)^2/i(q)$ as a function of q^2 or λ one obtains, in the intermediate range, a straight line; the number of blocks in the copolymer, knowing its composition and its degree of polymerization, can be obtained directly from its intercept. Assuming the system to be monodisperse one has:

$$n_A = N_T u/(N+1) \qquad n_B = N_T v/N$$

Putting these values in equation (25) one obtains:

$$uv\frac{(b_A - b_B)^2}{i(q)} = \frac{1}{2}\left[\lambda + \frac{1}{N_T}\left(\frac{N}{uv} + \frac{1}{u} - 1 \right) \right] \quad (26)$$

If the copolymer is symmetric one has just to suppress the coefficient $1/u$ on the right-hand side of equation (26). This procedure is difficult to use, for experimental reasons, if N is not small compared to N_T.

The position and the height of the maximum

For simplicity we shall limit our discussion to the case where the sequences are of the same length ($n_A = n_B$), knowing that the results can be extended easily to the general case. For this purpose we have plotted the curves $i(q)$ *versus* qr_A (calling r_A the radius of gyration of the blocks A). It is known, in the even case, that the maximum is shifted slightly towards high angles and that its height decreases noticeably when N increases (this decrease is of the order of 30% when N goes from 1 to infinity). The situation is rather different for odd copolymers. As an example we show in *Figure 1* the results obtained for $i(q)/n_A(a-b)^2$ as a function of q for three cases: the copolymer A–B, the copolymer A–B–A and the copolymer $(A{-}B)_N$ with $N = \infty$. One sees clearly that the curve for the sample A–B–A ($N = 1$) is very near to the curve corresponding to $N = \infty$. We did not plot the curves corresponding to intermediate values of N; they fill the interval between the odd curve $N = 1$ and the curve $N = \infty$ making the diagram difficult to read. The fact that the maximum of the curves does not decrease for odd polymers but decreases appreciably for even polymers is, at first sight, surprising. Let us call y_m the height of the

Table 1

			H		*D*	
Type	M_w	M_w/M_n	Estim.	Meas.	Estim.	Meas.
H–D	86 600	1.07	62		38	
H–D–H	75 000	1.11	68.9	68.1	31.1	31.9
D–H–D–H–D	125 000	1.12	42.5	42.1	57.5	57.9

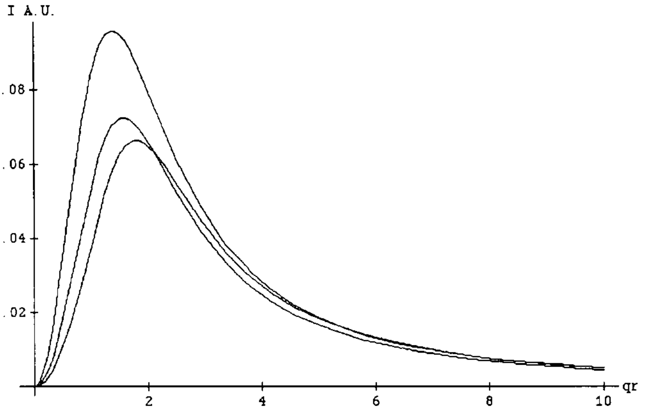


Figure 1 Scattering intensity (in arbitrary units) as a function qr (r being the radius of gyration of one block) for the copolymers (from top to bottom) A–B, A–B–A and $(A–B)_N$

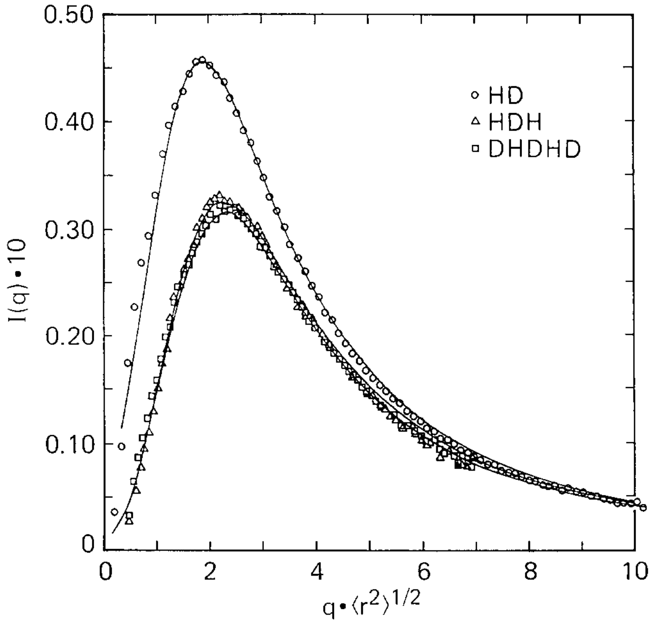


Figure 2 Experimental curves obtained for the three polymers described in *Table 1*. The abscissa corresponding to these polymers has been adjusted in order to use the universal quantity $q[\langle r^2\rangle^{1/2}]$ where r is the radius of gyration of one block

maximum of these curves. One knows that $1/y_m = 2\chi_c$, calling χ_c the value of the Flory interaction parameter for which phase separation occurs. It has been shown[1] that, for multiblock linear copolymers, χ_c depends on two parameters: the total number of blocks N and the composition u. It was shown also that, at u constant, y_m decreases with N. If keeping N constant, $|u - \frac{1}{2}|t$ increases then y_m decreases. In the case of even copolymers when one changes N one keeps u constant. This is no longer true for odd copolymers when all the sequences are identical. In this case one finds that $u = \frac{1}{2} + 1/(4N + 2)$ and reaches $\frac{1}{2}$ only for large N. Consequently, when N increases the height of the peak decreases due to the influence of N but increases due to the effect of u. This explains, at least qualitatively, the results and would not have been observed if one had kept the composition constant. It is also interesting to note that the effect of polydispersity can be treated in this case following exactly the same method as for the even copolymer.

EXPERIMENTAL

Our aim was to verify the theory established in ref. 1 measuring the neutron scattering by multiblock copolymers. The anionic polymerization technique was employed in order to prepare model alternating block copolymers. The polymerization took place in tetrahydrofuran at −55°C. As a matter of convenience, we used naphthalene potassium as initiator since, after the first block, we could add sequentially two blocks at each step of the reaction. This leads to copolymers with an odd number of blocks. Thus we modified the previous theoretical treatment[1] of the even copolymer $(A–B)_N$ to an odd one $(A–B)_N–A$ and established the corresponding rules of scattering behaviour as described in the first part of this paper. We prepared polystyrene block copolymers with alternating ordinary (H) and perdeuterated (D) blocks. The molecular weights and the polydispersity of the final copolymers and the aliquots were measured with size exclusion chromatography (s.e.c.) (*Table 1*). The volume compositions reported in *Table 1* were estimated from the molecular weights and measured with forward recoil spectrometry[3,4] which allows a measurement of the composition of the hydrogen and deuterium content of the polymer to within ±2%. The agreement between the estimated and measured volume composition is excellent.

The neutron scattering experiments were performed at the National Institute of Standards and Technology (NIST) (Gaithersburg) Small Angle Neutron Facility. The raw data were corrected for the instrumental and incoherent background. The absolute intensity measurements were made against a silica secondary standard specimen[5]. The data, after further renormalization for the square of the scattering length density difference of the two components, $(a_D - a_H)^2$, the degree of polymerization of each block and the number of blocks, are reported on *Figure 2*. The points on the graph represent the experimental data and the lines the values evaluated using equation (5) and the calculated values of the corresponding form factors, without any adjustable parameter.

The agreement is remarkably good, confirming both the quality of the samples and the validity of the equations. The curves practically reach the asymptotic values for $N = 3$ so it was of no interest to report results for samples having more than five blocks.

CONCLUSION

These results confirm first that the random-phase approximation theory can be applied safely to multiblock copolymers with an even or an odd number of sequences. This could have been foreseen since one can show that for a 50/50 block copolymer one does not need any approximation to obtain equation (1). Since the odd copolymer is not very far from symmetric and since the interaction coefficient between deuterated and ordinary polystyrene is negligible, considering the molecular weight of the blocks, one is in a case where the formula can be used safely. The only and important point which has been obtained in these experiments is that the critical point for the appearance of mesophases does not depend on the number of blocks for odd copolymers and that the technique of preparation leads to copolymers having really the desired structure.

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