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Small-Angle X-Ray Scattering from Block Copolymers

G. G. Vitale and D. G. LeGrand*

General Electric Company, Corporate Research and Development Center,
Synthesis and Characterization Branch, Chemical Laboratory,
Schenectady, New York 12301.

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ABSTRACT: Debye's theory of scattering from dilute solutions of homopolymer coils and rods is extended to block copolymers. The angular dependence of scattering is dependent (1) on the electron density difference between the solvent and the different blocks in the molecule, (2) on structure, and (3) on conformation. Results indicate that small-angle x-ray data from solutions made with appropriate solvents should provide information about copolymer structure.

Recent advances in polymer technology have made possible the synthesis of a large variety of block and graft copolymers. During the past several years, many of the properties of silicone-containing alternating block copolymers have been studied in our laboratories[1-3] to determine the feasibility of designing materials to meet specific needs. Characterization of these materials by viscometry, osmometry, and NMR proved inadequate because copolymer physical properties were found to be dependent not only on their composition and molecular weight but also on their molecular structure and the larger inter- and intramolecular structures which they form.

In an attempt to overcome this deficiency, we have used small-angle x-ray scattering (SAXS) as a tool to study the structure of copolymers in the bulk and swollen states and have initiated studies in solution to further characterize these materials and to understand their properties.[4-6] Previous workers have treated scattering from copolymers, but in the light-scattering region, so that the scattering due to the polymer's structure has not been important. In many cases, the molecule is then treated like a homogeneous particle whose refractive index and refractive index increment are weighted averages of the values for the two homopolymers.[7] Benoit et al.[8-11] have treated copolymer scattering in greater detail, even deriving structure-dependent expressions for several simple copolymer molecules.

Because many different models can account for similar scattering phenomena, other techniques must supplement SAXS data in order to confirm any proposed model. It is the objective of this paper to propose and analyze a model which might be used to interpret data from dilute solutions of coils or rigid rods. We assume that the alternating block copolymer molecule is monodisperse in structure, composition, and molecular weight and consists of alternating A and B blocks. Extension of the work to polydisperse material is currently under investigation and will be reported later.

Scattering from Copolymer Solutions. We consider a small volume in which we suppose a single copolymer molecule, N units long, can be found. The intensity of x-ray scattering by this molecule will be dependent upon its size, shape, composition, and the electron density difference between the various species within the molecule and their surroundings.

We assume for simplicity that the electron density of the material surrounding the ith species is equal to that of the solvent.

According to the Debye equation for scattering[12]

$$I = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i f_j \frac{\sin (ksr_{ij})}{ksr_{ij}} \tag{1}$$

where f_i and f_j are scattering coefficients for the ith and jth particles and are related to the electron density difference between these species and their surroundings, $k = 2\pi/\lambda$ is the wavenumber in the medium, $s = 2 \sin \theta/2$ where θ is the scattering angle, and r_{ij} is the distance between the ith and jth species.

This equation can be rewritten as

$$I = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i f_j t_{|i-j|} \tag{2}$$

For random coils

$$t_{|i-j|} = e^{-bz} \tag{3}$$

and

$$b = \frac{k^2 s^2 a^2}{6} \left(\frac{1+q}{1-q}\right) \tag{4}$$

Here, $z = |i - j|$ is the number of segments between the ith and jth points, a is the size of a segment, and the quantity $(1 + q)/(1 - q)$ is related to the rotational freedom of the chain. For a rigid rod,

$$t_{|i-j|} = \frac{\sin (ksaz)}{ksaz} \tag{5}$$

Debye wrote eq 2 as an array:

$$I = f^2 \left| \begin{array}{l} t_0 + t_1 + t_2 + \ldots + t_{N-1} \\ t_1 + t_0 + t_1 + \ldots + t_{N-2} \\ t_2 + t_1 + t_0 + \ldots + t_{N-3} \\ \cdot \qquad\qquad\qquad \cdot \\ \cdot \qquad\qquad\qquad \cdot \\ \cdot \qquad\qquad\qquad \cdot \\ \cdot \qquad\qquad\qquad \cdot \\ t_{N-1} + \ldots\ldots + t_0 \end{array} \right| \tag{6}$$

for a homopolymer chain containing N segments of scattering power f.

For an ABA copolymer, containing m segments of type A per block and n segments of type B, the intensity of scattering is shown in eq 7. This array illustrates the different types of terms which contribute to the total intensity of scattering. If entire blocks rather than individual monomers are numbered, a more concise representation is seen in eq 8. Terms along the diagonal are a result of scattering within the various blocks; the first terms off the diagonal arise from interactions between adjacent blocks (first-order neighbors); the second terms off the diagonal are the result of interactions between blocks separated by an intervening block (second-order neighbors); etc. All such arrays are symmetric about the diagonal.

$$I = \left[\begin{array}{lll} \text{1–1 interactions} & \text{+ 1–2 interactions} & \text{+ 1–3 interactions} \\ \text{+ 1–2 interactions} & \text{+ 2–2 interactions} & \text{+ 2–3 interactions} \\ \text{+ 1–3 interactions} & \text{+2–3 interactions} & \text{+3–3 interactions} \end{array} \right] \tag{8}$$

The intensity of scattering for a block copolymer containing p blocks of type A and $p - 1$ blocks of type B is

$$\begin{aligned} I = {} & p f_a^2 \left[m + 2 \sum_{z=1}^{m-1} (m-z) t_z \right] \\ & + (p-1) f_b^2 \left[n + 2 \sum_{z=1}^{n-1} (n-z) t_z \right] + 4 f_a f_b \sum_{i=1}^{p-1} (p-i) I_{1,2i} \\ & + 2 f_a^2 \sum_{i=1}^{p-1} (p-i) I_{1,2i+1} + 2 f_b^2 \sum_{i=1}^{p-2} (p-i-1) I_{2,2i+2} \end{aligned} \tag{9}$$

where for a copolymer consisting of random coils,

$$t_z = e^{-bz} \tag{10}$$

$$I_{1,2i} = \exp\langle -\{(i-1)(n+m)\} b \rangle \sum_{x=0}^{n-1} \sum_{y=1}^{m} e^{-b(x+y)} \tag{11}$$

$$I_{1,2i+1} = \exp\langle -\{in + (i-1)m\} b \rangle \sum_{x=0}^{m-1} \sum_{y=1}^{m} e^{-b(x+y)} \tag{12}$$

$$I_{2,2i+2} = \exp\langle -\{im + (i-1)n\} b \rangle \sum_{x=0}^{n-1} \sum_{y=1}^{n} e^{-b(x+y)} \tag{13}$$

Similar expressions are given in Appendix A for a rigid rod copolymer molecule and for one consisting of alternating sequences of coils and rods. It should be noted that the equations for the last case are based on the assumption that the junction point between coil and rod sections is a molecular swivel joint.[13,14] This assumption allows the joint probability correlation between these species to be uncoupled. Mathematically, this means that

$$P_{ijh}(r_{ih}) \equiv P_{ij}(r_{ij}) \cdot P_{jh}(r_{jh}) \tag{14}$$

For copolymers containing an even number of blocks, p of each type, eq 9 becomes

$$\begin{aligned} I = {} & p \left[f_a^2 \left\{ m + 2 \sum_{z=1}^{m-1} (m-z) t_z \right\} \right. \\ & \left. + f_b^2 \left\{ n + 2 \sum_{z=1}^{n-1} (n-z) t_z \right\} \right] + 2 f_a f_b \sum_{i=1}^{p} (2p - 2i + 1) I_{1,2i} \\ & + 2 \sum_{i=1}^{p-1} (p-i)(f_a^2 I_{1,2i+1} + f_b^2 I_{2,2i+2}) \end{aligned} \tag{15}$$

with the same expressions for t_z, $I_{1,2i}$, $I_{1,2i+1}$, and $I_{2,2i+2}$.

$$I = \left[\begin{array}{l} f_a^2(t_0 + t_1 + \ldots + t_{m-1}) + f_a f_b (t_m + t_{m+1} + \ldots + t_{m+n-1}) + f_a^2(t_{m+n} + t_{m+n+1} + \ldots + t_{2m+n-1}) \\ + f_a^2(t_1 + t_0 + \ldots + t_{m-2}) + f_a f_b (t_{m-1} + t_m + \ldots + t_{m+n-2}) + f_a^2(t_{m+n-1} + t_{m+n} + \ldots + t_{2m+n-2}) \\ \cdot \\ \cdot \\ \cdot \\ + f_a^2(t_{m-1} + t_{m-2} + \ldots + t_0) + f_a f_b (t_1 + t_2 + \ldots + t_n) + f_a^2(t_{n+1} + t_{n+2} + \ldots + t_{m+n}) \\ + f_a f_b (t_m + t_{m-1} + \ldots + t_1) + f_b^2(t_0 + t_1 + \ldots + t_{n-1}) + f_a f_b (t_n + t_{n+1} + \ldots + t_{m+n-1}) \\ \cdot \\ \cdot \\ \cdot \\ + f_a f_b (t_{m+n-1} + t_{m+n-2} + \ldots + t_n) + f_b^2(t_{n-1} + t_{n-2} + \ldots + t_0) + f_a f_b (t_1 + t_2 + \ldots + t_m) \\ + f_a^2(t_{m+n} + t_{m+n-1} + \ldots + t_{n+1}) + f_a f_b (t_n + t_{n-1} + \ldots + t_1) + f_a^2(t_0 + t_1 + \ldots + t_{m-1}) \\ \cdot \\ \cdot \\ \cdot \\ + f_a^2(t_{2m+n-1} + t_{2m+n-2} + \ldots + t_{m+n}) + f_a f_b (t_{m+n-1} + t_{m+n-2} + \ldots + t_m) + f_a^2(t_{m-1} + t_{m-2} + \ldots + t_0) \end{array} \right] \tag{7}$$

Table I

$a = 2$ Å $q = \frac{1}{3}$ $\lambda = 1.54$ Å $f_a = 1.0$ $f_b = 1.1$

	Block sizes	
	m	n
A–B–A case	46	75
A–B–A–B–A case	30	38
A–B–A–B–A–B–A case	23	25

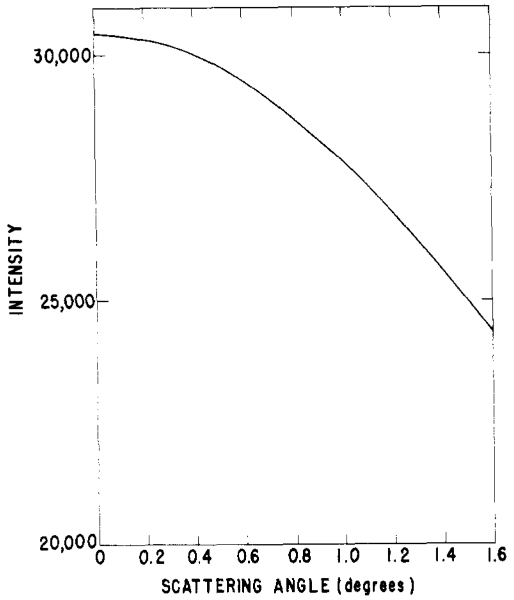

Figure 1. Scattering curve for three copolymer coils of different structures. Curves are superimposable since chain length and composition are constant.

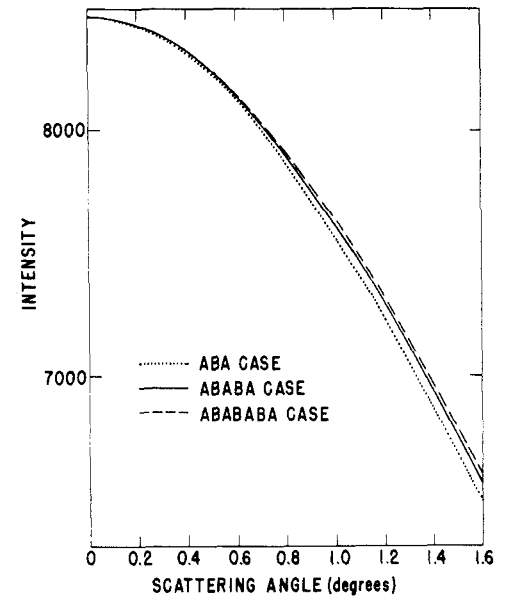

Figure 2. Scattering curves for three copolymer coils where the solvent's electron density matches that of the B segments.

Results

Random Coils. In Figure 1, we plot the total intensity of scattering vs. scattering angle for three block copolymer coils of nearly identical length and composition but different structures. Table I shows the molecular parameters for each molecule. The curves are exactly superimposable because the distances between segments have been assumed to obey a Gaussian distribution, which is not affected by block size.

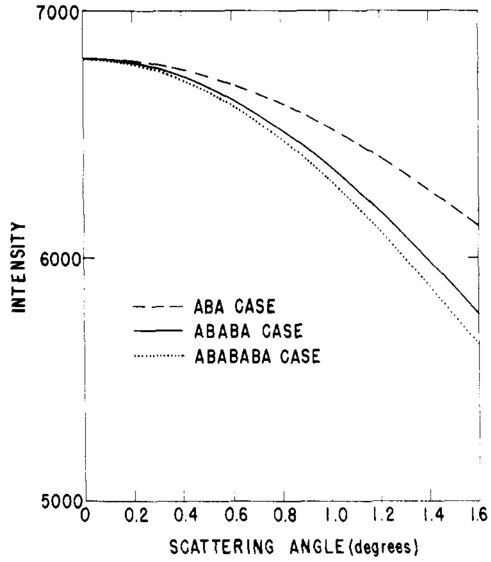

Figure 3. Scattering curves for copolymer coils in a solvent whose electron density matches that of the A blocks.

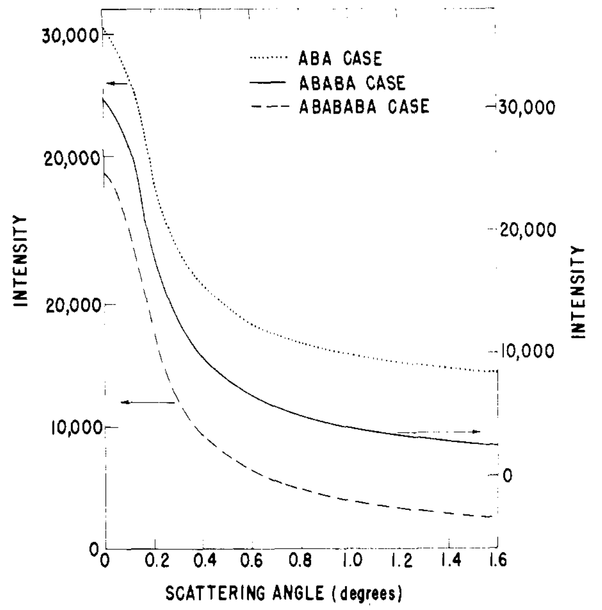

Figure 4. Intensity vs. scattering angle for copolymer rods, shifted to different scales for clarity. Curves are not superimposable.

If these same block copolymers are dissolved in a solvent whose electron density is the same as that of the B segments, the intensity of scattering changes to that shown in Figure 2. In this case, there is a small but significant difference between the curves, with the larger blocks giving the more steeply decaying curves.

When the copolymers are dissolved in a solvent whose electron density is the same as that of the A blocks, the intensity of scattering varies as shown in Figure 3. In contrast to Figure 2, the results in Figure 3 indicate that this scattering is more sensitive to block size but in the opposite direction. That is, the longer blocks have more intense scattering at larger angles than the shorter ones. This reversal occurs because the apparent size of the chain is shortened when the scattering from the terminal group is masked by the solvent; and the longer the blocks the greater the "chain-shortening" effect.

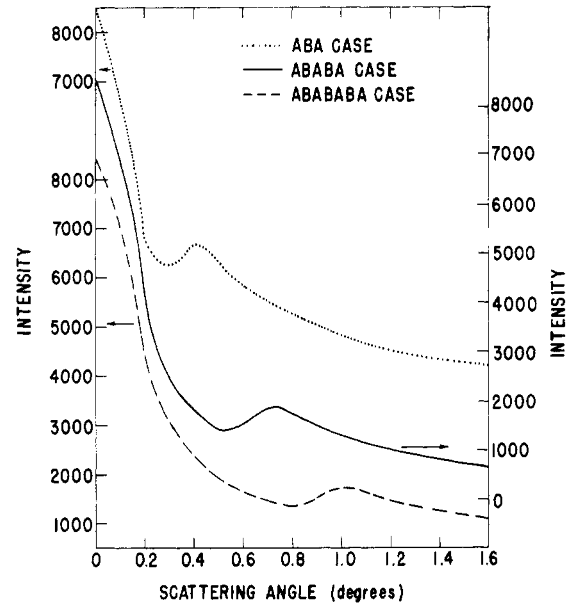

Figure 5. Scattering curves for rods dissolved in a solvent of the same electron density as that of the B segments.

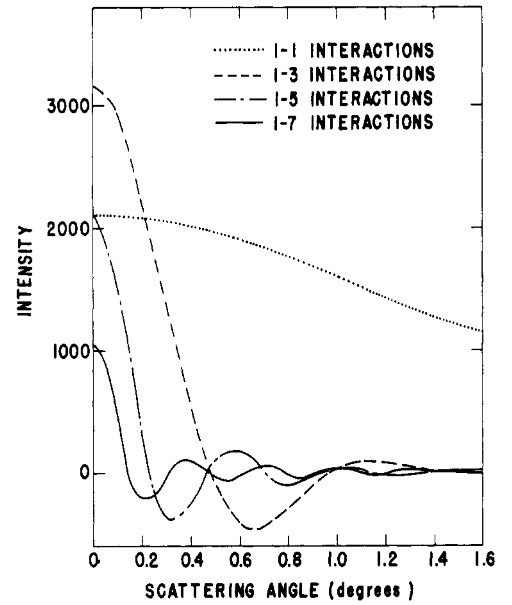

Figure 6. Components of the A-block scattering for the seven-segment rigid rod molecule.

Rigid Rods. In Figure 4, we plot the total intensity of scattering vs. scattering angle for the same three block copolymers but now assumed to be rigid rods. In contrast to the results presented in Figure 1, the curves are not superimposable since the distribution of the various intersegment distances is no longer Gaussian but is governed by the structure of the molecule.

When these molecules are dissolved in a solvent whose electron density matches that of the B segments, the scattering changes to that shown in Figure 5. Close examination of the curves reveals that the initial slope is steeper for larger blocks. The secondary maxima move to larger angles as the block sizes are decreased. The intensity of the secondary maximum decreases as more complicated interactions become possible. To demonstrate how these secondary maxima arise, we plot in Figure 6 the various contributions for the seven-block molecule. These curves clearly show that the overall secondary maximum occurs at the angle where each interaction but the 1–1 is near one of its own secondary maxima.

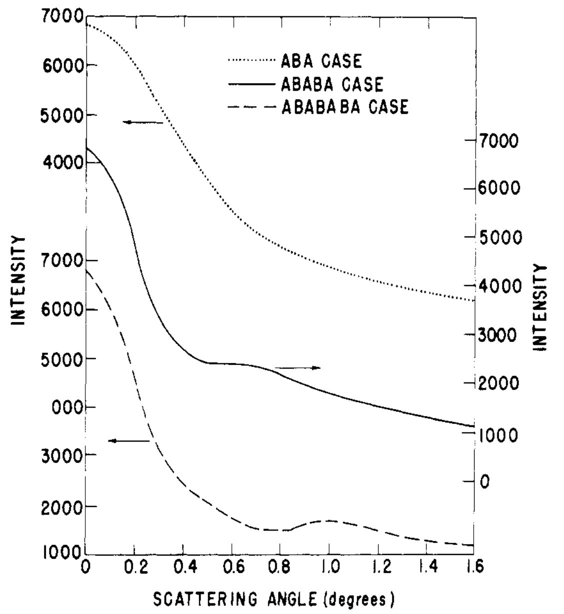

Figure 7. Angular distribution of scattering for copolymer rods where the solvent's electron density matches that of the A blocks.

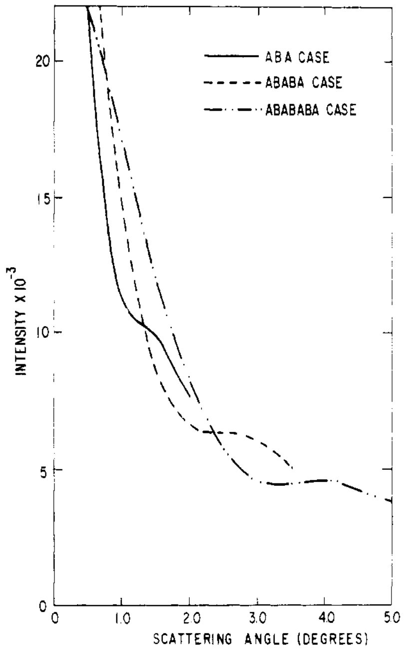

Figure 8. Total intensity of scattering for coil–rod hybrid molecules.

When the copolymers are dissolved in a solvent whose electron density is equivalent to that of the A segments, the results shown in Figure 7 are found. The curve for the ABA case clearly indicates that in the absence of a 1–3 interaction term no maximum will be observed. For the five- and seven-block cases, the trend in the secondary maxima is the same as in Figure 6. In contrast, the initial slope is less steep for the longer blocks than for the shorter ones. This difference in slope is due to the same "chain-shortening" effect as in the case of polymer coils.

Coil–Rod Hybrid Molecules. In Figure 8, we plot the total intensity of scattering for the three copolymer molecules where the A segments are random coils and the B segments are rigid rods. The secondary maxima occur at larger angles for the smaller blocks and are less intense, just as they were

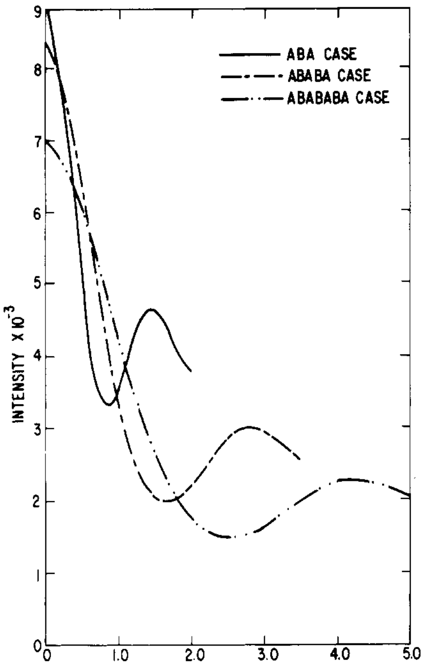

Figure 9. Scattering curve of the three hybrid copolymer molecules in a solvent of the same electron density as the B blocks.

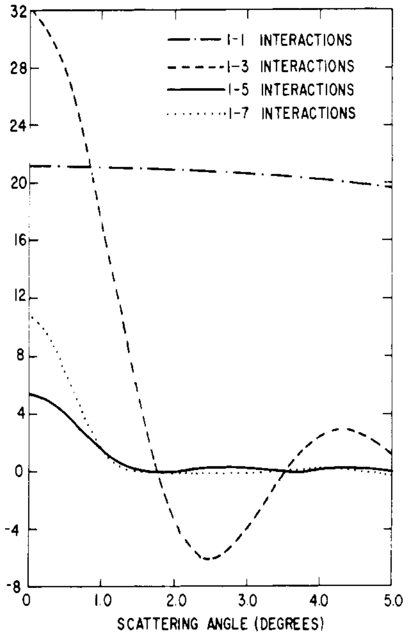

Figure 10. Components of the A-block scattering from the seven-segment hybrid molecule.

for the rigid rods. But Figure 9, which is a plot of the scattering which would occur if the solvent electron density matched that of the B segments, shows that the maxima are due to maxima from coil scattering. The alternate plot, the scattering when the A segments were masked by solvent, shows no secondary maximum. Evidently, the rods cause the maxima by imposing a separation between flexible segments rather than allowing them to be located randomly. If we decompose the coil scattering of the seven-block molecule into its components, as shown in Figure 10, it is clear that the maxima in the A-block scattering are mostly due to the 1–3 interactions.

From these calculations it is obvious that small-angle x-ray scattering probes not only the shape of the molecule in solution but also its internal structure. Experimentally, it would be difficult to find solvents which are theta solvents for the molecules and at the same time possess electron densities equivalent to the polymer segments. However, the chain expansion or contraction in a solvent of appropriate electron density may be evaluated by gathering light-scattering data on the respective homopolymers in the same solvent and comparing the observed dimensions with those obtained in theta solvents.

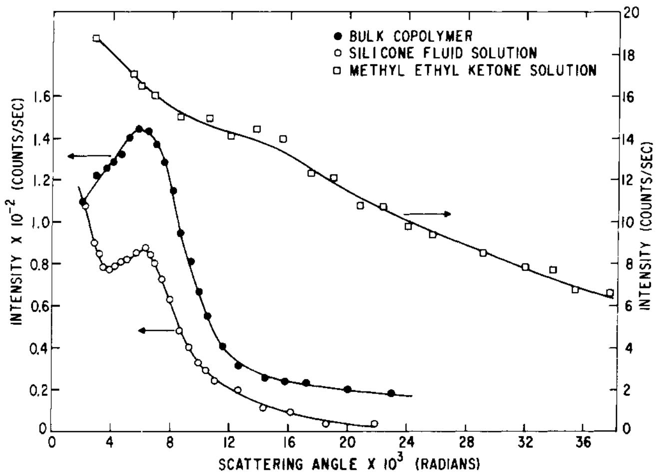

Figure 11. Experimental scattering curve of a bisphenol-A polycarbonate–polydimethylsiloxane block copolymer in the bulk state and in two different solvents.

These calculations are obviously only a beginning in interpreting the small-angle x-ray curves of block copolymers since each calculation treats only a single molecule with a certain composition, molecular weight, and structure. Later work will extend the method to more realistic systems which are polydisperse in all these characteristics. We hope also to treat more concentrated solutions, since concentrations low enough to ensure isolated single molecules may cause experimental difficulties.

As an example of the type of scattering which is observed experimentally, Figure 11 shows small-angle x-ray scattering data from a block copolymer of polydimethylsiloxane and bisphenol-A polycarbonate. Three curves are shown: one from the bulk material and two from 1% solutions of the polymer in hexamethyldisiloxane and in methyl ethyl ketone. Qualitatively, this material is similar to a coil–rod hybrid since it is composed of relatively stiff polycarbonate blocks interspersed with softer silicone segments. And its scattering curve exhibits a secondary maximum just as the calculated curves for such a molecule do. However, these very preliminary data also indicate that both the flexibility and configurational behavior of the copolymer in solution are very dependent on the solvents used.

This work does show that scattering is sensitive to copolymer structure, which has been the least experimentally accessible element of copolymer characterization. Scattering curves also give an indication of the copolymer's conformation in solution, especially when solvents to match each type of polymer block can be used. When used in conjunction with other techniques, small-angle x-ray scattering can provide unique information about block copolymer molecules.

Appendix

For a rigid rod copolymer molecule composed of p A segments and $(p - 1)$ B segments, the scattering intensity is expressed by eq 9 where

$$t_z = \frac{\sin (ksaz)}{ksaz}$$

$$I_{1,2i} = \sum_{x=0}^{n-1} \sum_{y=1}^{m} \frac{\sin \{ksa[x + y + (i - 1)(n + m)]\}}{ksa[x + y + (i - 1)(n + m)]}$$

$$I_{1,2i+1} = \sum_{x=0}^{m-1} \sum_{y=1}^{m} \frac{\sin \{ksa[x + y + in + (i - 1)m]\}}{ksa[x + y + in + (i - 1)m]\}}$$

and

$$I_{2,2i+2} = \sum_{x=0}^{n-1} \sum_{y=1}^{n} \frac{\sin \{ksa[x + y + im + (i - 1)n]\}}{ksa[x + y + im + (i - 1)n]}$$

For the asymmetric rodlike molecule with p blocks of type A and p blocks of type B, the master intensity equation is (15) with t_z, $I_{1,2i}$, $I_{1,2i+1}$, and $I_{2,2i+2}$ as above.

The coil–rod hybrid molecule is treated by the techniques of Adelman and Deutch. For the symmetric case involving p units of A coils and $(p - 1)$ units of B rods, the intensity is given by

$$\begin{aligned} I = {} & pf_a^2\left\{m + 2\sum_{z=1}^{m-1} (m - z)t_z^{\mathrm{A}}\right\} + (p - 1)f_b^2 \\ & \times \left\{n + 2\sum_{z=1}^{n-1} (n - z)t_z^{\mathrm{B}}\right\} + 4f_af_b \sum_{i=1}^{p-1} (p - i)I_{1,2i} \\ & + 2\left\{f_a^2 \sum_{i=1}^{p-1} (p - i)I_{1,2i+1} + f_b^2 \sum_{i=1}^{p-2} (p - 1 - i)I_{2,2i+2}\right\} \end{aligned}$$

where

$$t_z^{\mathrm{A}} = e^{-bz}$$

$$t_z^{\mathrm{B}} = \frac{\sin (ksaz)}{(ksaz)}$$

$$I_{1,2i} = \frac{m(1 - e^{-\mu})}{\mu} \left[\sum_{i=1}^{n} \frac{\sin (ksai)}{ksai}\right] \left[e^{-\mu} \frac{\sin (nksa)}{nksa}\right]^{i-1}$$

$$I_{1,2i+1} = m^2 \left[\frac{1 - e^{-\mu}}{\mu}\right]^2 \left[\frac{\sin (nksa)}{nksa}\right]^i (e^{-\mu})^{i-1}$$

$$I_{2,2i+2} = \left[\sum_{i=1}^{n} \frac{\sin (ksai)}{ksai}\right]^2 (e^{-\mu})^i \left[\frac{\sin (nksa)}{nksa}\right]^{i-1}$$

$$\mu = bm$$

For a molecule of p A blocks in a coil configuration and p B blocks in a rod configuration the master intensity equation changes to

$$\begin{aligned} I = {} & pf_a^2 \left\{m + 2\sum_{z=1}^{m-1} (m - z)t_z^{\mathrm{A}}\right\} + pf_b^2 \\ & \times \left\{n + 2\sum_{z=1}^{n-1} (n - z)t_z^{\mathrm{B}}\right\} + 2f_af_b \sum_{i=1}^{p} (2p - 2i + 1)I_{1,2i} \\ & + 2\sum_{i=1}^{p-1} (p - i)(f_a^2I_{1,2i+1} + f_b^2I_{2,2i+2}) \end{aligned}$$

where the t_z's, $I_{1,2i}$, $I_{1,2i+1}$, and $I_{2,2i+2}$ are the same as for the symmetric case.

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Surface Modification of Polyethylene by Radiation-Induced Grafting for Adhesive Bonding. 2. Relationship between Adhesive Bond Strength and Surface Structure

Shinzo Yamakawa,* Fumio Yamamoto, and Yoshinori Kato

Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki 319-11, Japan.

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ABSTRACT: Mutual irradiation of polyethylene (PE) sheets in methyl acrylate (MA) vapor has been found to form an optically isotropic surface layer on an anisotropic graft copolymer layer consisting of PE and MA components. This isotropic layer, which can extend to a thickness of 70 μm, consists of poly(methyl acrylate) (PMA) homopolymer except in the boundary region (6–9 μm) adjacent to the inner anisotropic copolymer layer. The high stability of the former layer to solvent treatments indicates that this homopolymer is not only cross-linked but is also linked by chemical bonds to the PE and grafted PMA chains in the contiguous copolymer layer. In the adhesive joints of the saponified grafts with epoxy adhesives, the peel strength increases abruptly with the formation of the isotropic layer and without exception reaches PE adherend failure at a thickness of more than 10 μm. It is thus proposed that the thickness can be used as a criterion for estimating the resulting bond strength in advance of bonding.

Surface modification of PE is a prerequisite for its strong structural adhesive bonding at temperatures below the softening point. Among many surface pretreatments proposed, the most effective techniques are[1,2] CASING (cross-linking with activated species of inert cases),[3] ablative oxidative treatments using atomic oxygen,[4,5] and chromic acid.[6] Although the increased bond strengths are thought to result from the removal of weak boundary layers or from an increase