V. Conclusions

We have evaluated the translational friction coefficient of wormlike cylinders by the Oseen-Burgers procedure. The final results may be written in terms of only the molecular dimensions. From the point of view of classical hydrodynamics, the Ullman theory is not correct; it is correct only when his parameter α (friction constant per unit length) is taken as infinity. The Hearst-Stockmayer theory is not unphysical, though its application leads to smaller estimates of the diameter of the cylinder than does the present theory in the case of typical stiff chains. An analysis of the intrinsic viscosity of wormlike cylinders will be given in the next paper.

Acknowledgment. The authors benefited from numerous discussions with Professor H. Fujita in the course of the present work and from his similar calculation for flexible bead models, for which the authors thank him.

Thermodynamic and Structural Properties of Polystyrene-Polybutadiene-Polystyrene Block Copolymers

E. Campos-Lopez,[1a] D. McIntyre,*[1b] and L. J. Fetters[1b]

Facultad de Quimica, Universidad Nacional de Mexico, Mexico 20 D.F., Mexico, and the Institute of Polymer Science, The University of Akron, Akron, Ohio 44325. *Received December 4, 1972*

ABSTRACT: Four polystyrene-polybutadiene-polystyrene (SBS) triblock polymers were anionically polymerized under controlled conditions so that (1) the polystyrene composition remained constant (~27%), (2) the diblock and homopolymer impurities were low (<1%), (3) the heterogeneity of molecular weight was low ($M_w/M_n < 1.1$), and (4) the overall molecular weight (M_n) varied over a large range; 4.9×10^4, 9.0×10^4, 1.4×10^5, and 9×10^5. The polymer films were cast from tetrahydrofuran-methyl ethyl ketone (90:10), dried under vacuum, and then examined by low-angle X-ray scattering. The placement of the spherical polystyrene domains was found to be a face-centered cubic array. From the cell dimensions and the sphere size, the end-to end distance of chains, the interfacial region, and the molecular weight dependence of domain size and spacing were deduced. The data are found to be in good agreement with the theory of Meier if the interfacial tension is assumed to be 1 dyn cm^{-1}; a value that is in good agreement with estimates made independently.

For some time the existence of phase separated domains in carefully prepared triblock (ABA) copolymers has been accepted. The most detailed theoretical description of thermodynamic and conformational features leading to microphase separations of pure A domains and pure B domains from an AB chain has been given by Meier.[2a] In all cases the sizes of the domains are related to the molecular sizes of the A or B part of the triblock copolymer as well as the ratio of A:B. Of course the compatibility of A and B with each other and the flexibility of the individual chains has a considerable influence on whether or not phase separation will indeed take place and what type of microphases can be expected to grow. For example, two segments, A and B, that are scarcely different chemically, are not likely to phase separate into pure A and pure B domains, if indeed at all. Similarly any tendency to crystallize will interfere with the separation because crystal growth kinetics will interfere with the separation.

The ideal study of the thermodynamic parameters involved in phase formation naturally would be concerned with polymers that are: (1) not too similar chemically, (2) are not readily crystallizable, (3) mobile throughout the whole phase separation process, and (4) available over a large range of molecular weight as well-prepared triblock copolymers having no homopolymer or diblock copolymer impurities. The polystyrene-polybutadiene-polystyrene (SBS) triblock copolymers have these desirable features and were chosen for this study, since: (1) the homopolymers are known to be incompatible and therefore are enough different chemically for phase separation;[2b] (2) neither polystyrene nor polybutadiene is a crystalline polymer when either is anionically polymerized; (3) the glass temperatures of butadiene (−100°) and polystyrene (~100°) are sufficiently low so that these materials will have considerable mobility during the casting of films from solution; and (4) the synthesis of these materials by anionic polymerization poses no problems in obtaining high molecular weights other than the rigorous exclusion of impurities during the polymerization. Earlier work in these laboratories had shown that this system could easily yield good triblock copolymers,[3,4] and that the morphological features could be studied by low-angle X-ray scattering.[5]

The study of the thermodynamic factors involved in the triblock domain morphology assumes that somehow an equilibrium state is attained. There is no sure way to determine if kinetic processes are so hindered as to prevent such an equilibrium state. However, it seems desirable to avoid the high viscosity of the bulk state for as long as possible. For this reason, this study of triblock copolymers has concentrated on the morphology of solvent-cast films. No attempt has been made to consider molded or extruded specimens. All samples were annealed under high vacuum at high temperatures in order to be certain that there was only a one-component polymer system free of solvent and that the final state of the cast film was as near as possible to an equilibrium state.

The choice of the ratio A/B was made to ensure spherical domains for the microphases. In particular, a 27 vol % of A was chosen. Other studies of the SBS triblocks at higher and lower volume per cents polystyrene will be reported later. The 27% polystyrene samples also had the de-

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(1) (a) Facultad de Quimica, Universidad Nacional de Mexico, Mexico 20, D.F., Mexico. (b) Institute of Polymer Science, The University of Akron, Akron, Ohio.

(2) (a) D. J. Meier, *J. Polym. Sci., Part C*, **26**, 81 (1969). (b) A. Droby and F. Bayer-Kawenoki, *J. Polym. Sci.*, **2**, 90 (1947).

(3) L. J. Fetters, *J. Elastoplast.*, **4**, 34 (1972).

(4) M. Morton, J. E. McGrath, and P. C. Juliano, *J. Polym. Sci., Part C*, **26**, 99 (1969).

(5) D. McIntyre and E. Campos-Lopez, *Macromolecules*, **3**, 322 (1970).

sirable features that the spherical packing was that of close-packed spheres—unlike the higher percentages of polystyrene.

The packing of a polymer chain inside a sphere such that one end must be on the spherical surface does demand in some way that the radius of the sphere be related to the end-to-end length of the flexible polymer chain. Meier[2a] has made an extensive calculation of the chain dimensions that exist in a diblock phase separated system. There will be an entropy loss due to the restricted volume in which the polymer lies, and, in particular, with the fact that one end is fixed at the boundary of the surface. The decrease in entropy due to loss of chain configurations is moderated by the surface and bulk free-energy change involved in becoming a two-phase rather than a single phase mixture.

By determining what chain expression would yield a constant polymer segment density throughout the whole spherical domain it is then possible to relate the radius of the domain (R_{dom}) to the unperturbed size of the end chain, $N_{\mathrm{a}}l^2$, where N_{a} is the number of elements in chain a and l is the step length of the element and the ratio of perturbed to unperturbed chain dimensions is represented by α. This relation is shown in eq 1 and can be tested by measuring R_{dom} as a function of molecular weight for a constant value of the interfacial tension, $\sigma_{\mathrm{A-B}}$. Also the equivalent test of the theory can be given as the relation of the chain expansion factor to the unperturbed size of the polymer chain at different values of the interfacial tension as shown in eq 2, where N is Avogadros number, k is Boltzmann's constant, T is the absolute temperature, M_{a} is molecular weight, and ρ is density.

$$R_{\mathrm{dom}} = (4/3)\alpha(N_{\mathrm{a}}l^2)^{1/2} \qquad (1)$$

$$\alpha^3 - \alpha = (3/4)\frac{M_{\mathrm{a}}^{1/2}\sigma}{Nk\rho T} \qquad (2)$$

Another somewhat simpler expression has been given by Bianchi,[6] in which he chooses to count only the simplest form of a placement entropy of the chains separated as islands of A in a matrix of B. This decrease in entropy which depends on the size of the domain is regulated by the surface energy required to form large or small domains. These two opposing effects of chain placement entropy and surface mixing free energy are balanced and depend on the interfacial tension. It is difficult to get specific relations between chain size and molecular weight, but a general relation between the free energy (ΔG) and the domain size can be obtained for different values of the interfacial tension. This relation is shown in eq 3 and can be

$$\Delta G = f'(R, \sigma_{\mathrm{A-B}})_{\mathrm{const\ comp}} = (4\pi)^{1/3}(3V_2)^{2/3}(2\nu)^{1/3}\,\sigma_{12}(\langle i\rangle - 1)^{-1/3} + RT\ln\langle i\rangle \qquad (3)$$

negative for several pairs of values of R and the interfacial tension. In the explicit eq 3, V_2 is the volume of polystyrene, ν is the number of copolymer molecules, and i is the number of A chains in an "A" domain.

There are other thermodynamic theories that discuss the free energy of mixing block copolymers,[7] but the latter theories are even less detailed from a structural point of view. However all theories require an estimate of either the volume mixing parameter of A and B segments or the interfacial tension between pure A and pure B. Separate thermodynamic studies, not morphological studies, must always be made to determine this parameter. All of the theories discuss only the random placement of islands of pure A and pure B. However, the triblock polymers have shown an amazingly regular array of islands.[5,8-10] This regularity is caused by the elastic, spring-like deformations of the rubbery polymer chains radiating isotropically from each plastic domain (A).

From a structural point of view it is important to determine the average size of the A domains to analyze the factors in the domain separation. Of course it is important also to understand the factors involved in the domain separation, particularly if they are regularly spaced. The arrangement of A domains depends on the character of the B chains and the method of making the ABA specimen. If the A domains are isotropically arranged in space, the interdomain distance is the only parameter that needs to be considered. However, there is no certainty that the domains are isotropically arranged in space.

The electron microscope can be used advantageously to determine the geometrical type of domains and their arrangement in space after suitable staining and specimen preparation techniques of microtoming or thin-film casting. However, the X-ray scattering technique does have a decided advantage by averaging over an entire specimen and determining the extent of regularity in a precise way if the array is truly ordered. If the domains are randomly placed, there is the possibility of determining the size of the domain and its average distance and in the most favorable situation its domain correlation function. The X-ray method is particularly advantageous in determining the changes in morphology in a sample upon the addition of impurities, mechanical stress, or change in casting conditions or temperatures. A combination of both electron microscopy and X-ray scattering investigations is by far superior to either one alone. Since the domains of the useful triblock copolymer systems are ≈200 Å and the interdomain spacings are of the same order of magnitude, it is essential to use small-angle X-ray scattering techniques rather than wide angle.

Cast films of triblock ABA polymers of ≈1-mil thickness have not shown different scattering patterns in different orientations when there is a low percentage of A present.[11,12] That is, there is no unique structural axis that is propagated throughout the film. Consequently the powder pattern equation or the scattering equation for liquid-like scattering may be used as shown in eq 4. That is,

$$I(\theta) \propto \int_0^\infty F^2(s)G(r)\,\frac{\sin(ksr)}{ksr}\,r^2\mathrm{d}r \qquad (4)$$

the intensity of scattering, I, at a scattering angle, θ, is related to the particle scattering factor, F, and the correlation function, $G(r)$ for a distance of r, where k is $2\pi/\lambda$, and s is the scattering vector $2\sin\theta/2$. If the scattering domains are present in small amounts, the equations can be solved[13] so that the initial slope is ⅓ of the radius of gyration shown in Figure 1 as region 1, the Guinier region. For the usual triblock copolymers the Guinier region is not applicable, as was shown in ref 5. Farther out in scattering angle, the dense particles begin to show detailed scattering if they are somewhat monodisperse. For spheres

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(6) U. Bianchi, E. Pedemonte, and A. Tuvturro, *J. Polym. Sci., Part B*, **7**, 785 (1969).

(7) S. Krause, *Macromolecules*, **3**, 84 (1970).

(8) M. Matsuo, S. Sagae, and H. Asai, *Polymer*, **10**, 79 (1969).

(9) J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *J. Polym. Sci., Part C*, **26**, 117 (1969).

(10) P. R. Lewis and C. Price, *Nature (London)*, **223**, 494 (1969); *Polymer*, **12**, 258 (1971).

(11) D. McIntyre and E. Campos-Lopez in "Block Polymers," S. L. Aggarwal, Ed., Plenum Press, New York, N. Y., 1970.

(12) E. Campos-Lopez, Doctoral Thesis, Universidad Nacional Autonoma de Mexico, 1970.

(13) A Guinier, "X-Ray Diffraction," W. H. Freeman and Co., San Francisco, Calif., 1963.

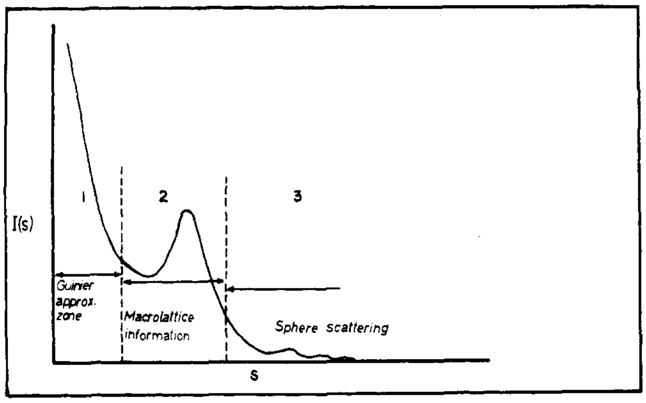

Figure 1. Schematic diagram of scattering curves and interpretation; s is scattering angle and $I(s)$ is intensity.

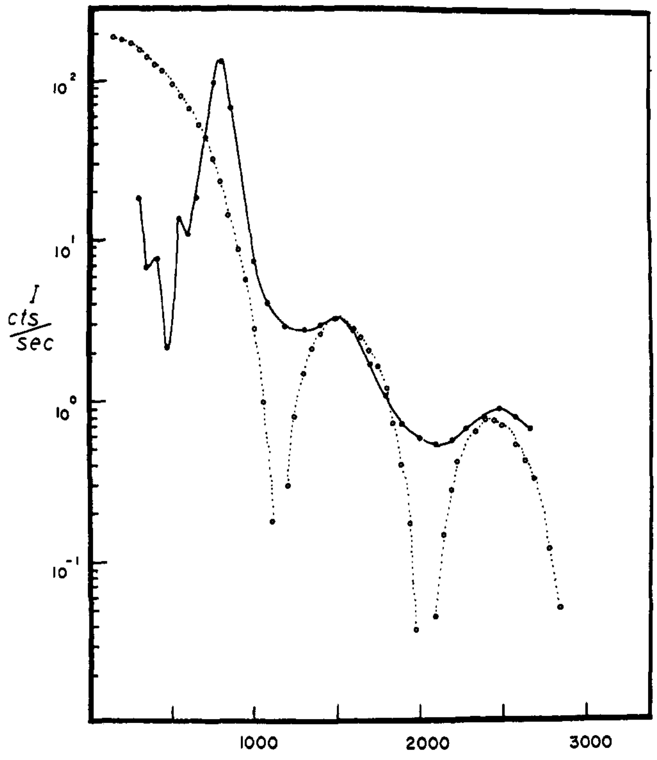

Figure 2. Comparison of single sphere scattering from X-ray measurements on SBS sample (ref 5) (solid curve) with theoretical expression for spheres; radius = 178 Å, dotted curve).

we get an oscillatory Bessel function, shown in Figure 1 as region 3, the Rayleigh region. If now the scattering domains are present in reasonable concentrations the interference between domains becomes noticeable and a strong average interdomain peak becomes permanent. If the interdomain distances become regularly spaced it is possible to have a macrolattice of the domains. The peaks of such a lattice will extend on both sides of the main interdomain distance peak. If a true macrolattice exists, there would be selection rules consistent with its extent in space and degree of perfection. Indeed if there were a perfect lattice and perfectly arranged spheres the transform of eq 4 would leave several sharp peaks only where the sphere scattering and lattice scattering were both zero. No X-ray patterns of triblock copolymers have shown any such sharp peaks; consequently, the existence of any extended perfectly ordered lattice is unlikely.

What is more likely is an ordered liquid-like structure where order extends with regularity over only a few neighboring sites. In such a case the lattice scattering will only modulate the particle scattering and the selection rules for crystals extended in space would not apply. Figure 2, from ref 5, represents the theoretical Rayleigh equation for spheres superposed on the scattering from a triblock copolymer. The fit is excellent and shows the possibility of using the Rayleigh region when it appears in a useful range as modulated by the lattice scattering. The most difficult analysis occurs when the domain scattering and interdomain scattering are of comparable size and fall in the same angular range as the main peak.

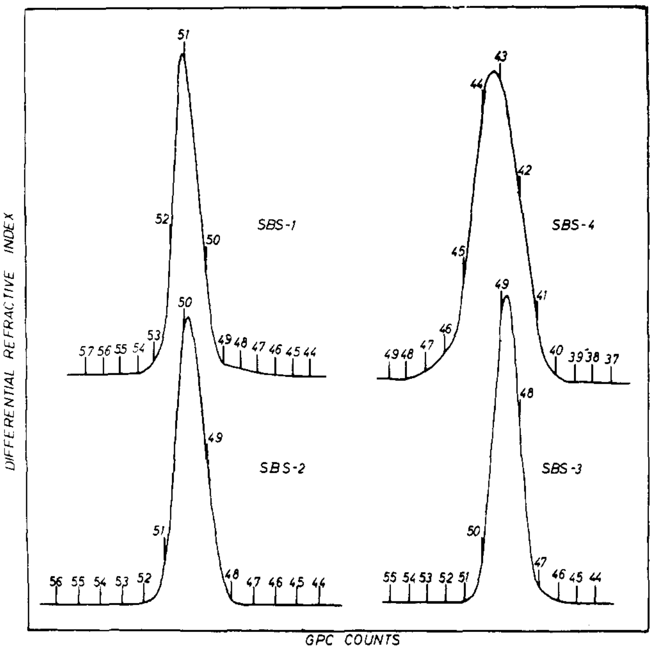

Figure 3. GPC curves for samples 1, 2, 3, and 4.

Exception has been taken[14] to the above interpretation of the scattering, although no alternative explanation of the experimental data was provided to fortify the claim of the author. However, if one avoids the semantic difficulty of considering a lattice to be only an infinite lattice, the selection rules for scattering at angles less than the main peak no longer need be obeyed. Also the lattice modulation of the single particle scattering cannot be too severe because the particle scattering has not been eliminated as can be seen by the fall of the intensity in Figure 2. However, all of the fine structure of the scattering patterns can be ignored and a plausible analysis made in the following manner. The main peak is considered to be an interdomain peak denoting a close packed isotropic lattice formed by spheres. Furthermore, the volume of the spheres must equal the volume fraction of polystyrene given by the stoichiometry of the original preparation. Such a model allows no detection of different arrangements and applies only to a completely clean two-phase separation. By analyzing the other structural details of the scattering pattern beside the main peak, much more can be said about the actual morphology of the triblock systems.

Experimental Section

Synthesis. The synthesis of the triblock polymers followed procedures outlined elsewhere.[4] The only modification involved the use of a mixture of di-*n*-butyl- and di-*sec*-butylmagnesium to purge the monomers. This organometallic serves to purge the monomers of impurities but does not cause the polymerization of either monomer. The polymerizations were terminated with methanol, precipitated in isopropyl alcohol, and dried.

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(14) A. Skoulios, *Macromolecules*, 4, 268 (1971).

Table I
Molecular Weights and Composition of SBS Block Copolymers

SBS Samples	$M_s{}^a \times 10^{-3}$ g mol^{-1}	$M_n \times 10^{-3}$ g mol^{-1}	Wt % Polystyrene	Vol % Polystyrene	GPC Peak Elution Count
1	7.0-35.0-7.0	49.0 (±3%)	28.5	24.6	51.3
2	13.7-63.4-13.7	94 (±3%)	30.0	26.6	49.7
3	21.2-97.9-21.2	142 (±5%)	30.0	26.6	48.7
4	120-660-120	900 (±10%)	27.0	23.5	43.3

[a] M_s denotes the stoichiometric molecular weights of the block polymer segments as determined from the ratio of monomer to *sec*-butyllithium initiator.

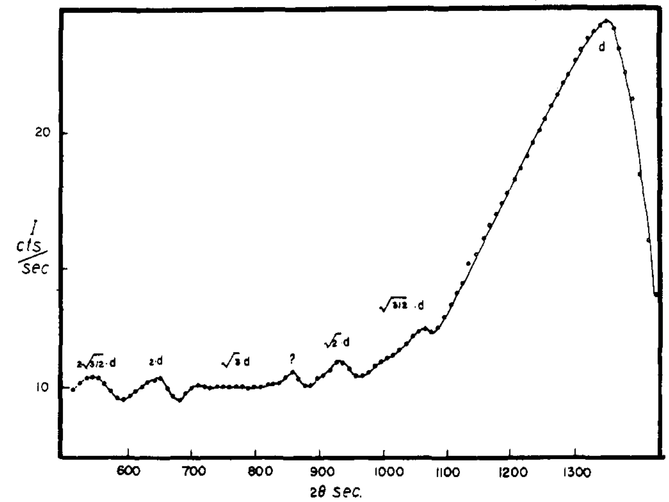

Figure 4. Lattice scattering curve for sample 1.

Characterization. The number-average molecular weights were determined with Hewlett-Packard 502 and 503 osmometers. The solvent used was toluene at 37°. The number-average molecular weights were ascertained from the usual $(\pi/c)^{0.5}$ *vs.* c plots. S and S-08 membranes were used.

A Waters Ana-Prep gel permeation chromatograph was used at a flow rate of 0.25 ml min^{-1} with 0.25 wt % solutions in tetrahydrofuran at a temperature of 45°. A differential refractive index detector was used with the following seven columns of polystyrene gel: 7-50 (10^5) Å, 1.5-7 (10^5) Å, 5-15 (10^4) Å, 1.5-5 (10^4) Å, two columns with 5-15 (10^3) Å, and 2-5 (10^3) Å. The GPC chromatograms for the four samples are shown in Figure 3. These chromatograms revealed the virtual lack of both polystyrene and diblock material. The absence of these polymeric impurities is crucial since it has been shown[15] that their presence can markedly influence the morphology of these triblock materials. It should also be noted that the plot of peak elution count against molecular weight (M_n) yields a linear plot. This further indicates that the samples all possess virtually identical molecular weight distributions.

Film Casting. The films of SBS were prepared from solutions containing 10% (w/v) SBS in a 90:10 mixture of tetrahydrofuran and methyl ethyl ketone. The films were cast with a Gardner knife set at 2 mils and drawn across glass. The films were then dried under high vacuum at 95° for 6 days until the samples were at constant weight. The high molecular weight sample was cast on mercury because a film that held together was desired and a film cast on glass was difficult to obtain in one whole piece.

X-Ray Measurements. A Bonse-Hart[16] small-angle X-ray diffractometer manufactured by Advanced Metals Research, Burlington, Mass., was used in these experiments. The sample thickness was approximately 1.8 mm and consisted of several layers of cast film. The transmission coefficient was approximately 0.5. The generator was the ultrastable Philips Model PW 1310. The exposure time for each angle varied as follows. (1) For scattering angles from 0 to 1000 sec the readings were taken every 10 sec of angle and the counting times were 100 sec for each point. (2) For scattering angles greater than 1000 sec the intensity of scattered radiation (~3 cps) was so low that counting times of 1.5 hr were used for each point. The diffractometer can routinely be aligned to measure scattering within 20 sec of the incident beam.

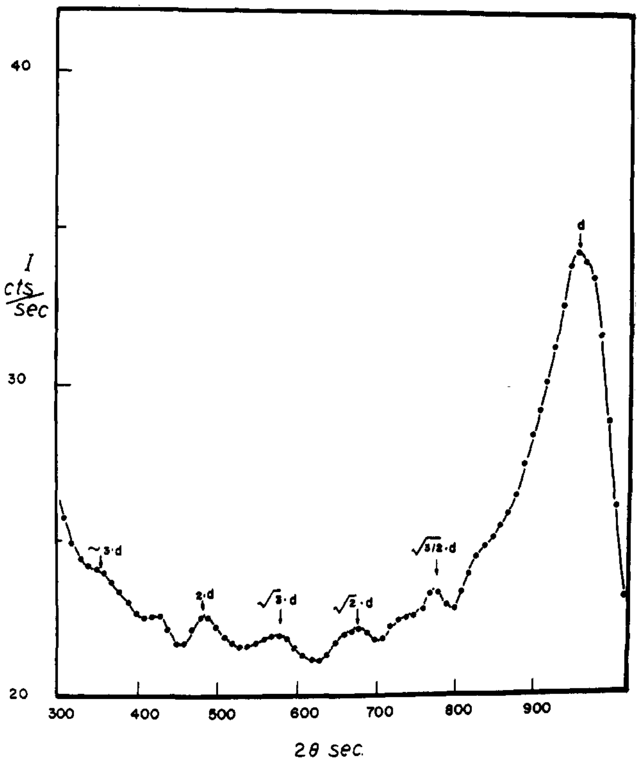

Figure 5. Lattice scattering curve for sample 2.

The scattering data were corrected for slit smearing by the technique of Schmidt,[17] using an infinite slit correction.[18]

Results

Characterization. Table I contains the number-average molecular weights, weight per cent polystyrene, and the stoichiometric molecular weights of the triblock copolymers.

X-Ray Scattering. Figures 4-7 show the X-ray scattering in the main peak and its surrounding macrolattice region. These figures and Figures 8-11 are presented in order of their increasing molecular weight. Figures 8-11 detail the scattering intensities in the region of single sphere scattering.

Table II lists in column 2 the main peak position as a Bragg spacing (Å), d. The width of the main peak at the half-height is listed in column 3. The base line was taken as a smooth descending curve and the half widths cannot be dealt with quantitatively. However, the line widths are large, covering intervals of 200-300 sec out of a peak position of ~700 sec. The half-width reported is the width at half-height and is normalized to the data for the main peak of sample 3. It should be added that the scattering of these films showed no difference when the films were rotated around the axis normal to the plane of the polymer films.

The radius of the domain is reported on the basis of the first maximum observed and the use of the Rayleigh equation for the scattering of spheres. The half-width is calculated on the basis of the width at half-height and is

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(15) L. J. Fetters, B. L. Meyer, and D. McIntyre, *J. Appl. Polym. Sci.*, **16**, 2079 (1972).

(16) U. Bonse and M. Hart, *Phys. Lett.*, **7**, 238 (1965).

(17) P. W. Schmidt, *Acta Crystallogr., Sect. A*, **19**, 938 (1965).

(18) C. C. Gravett and G. W. Brady, *J. Appl. Crystallog.*, **2**, 289 (1969).

Table II
Principal and Secondary Peaks for SBS Block Copolymers

Sample	Principal and Secondary Peaks: Main Peak (Å)	Half-Width	Domain Radius (Å)	Half-Width
1	240	4.04	93	1.48
2	338	1.68	116	1.20
3	473	1.00	170	1.00
4	498	2.02	207	1.12

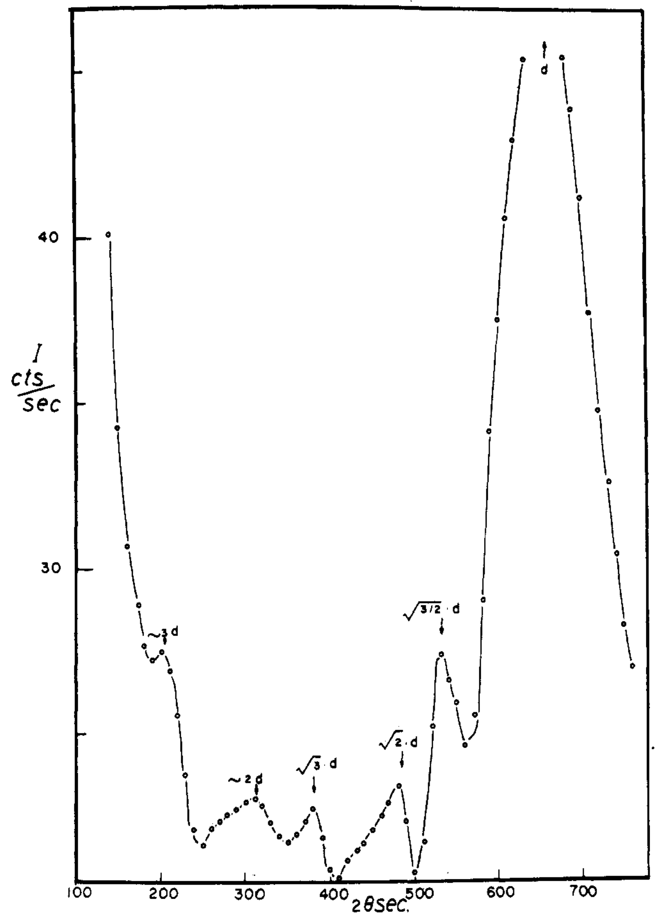

Figure 6. Lattice scattering curve for sample 3.

normalized to the width of the first sphere scattering peak for sample 3. In the case of sample 1 there is only one visible peak. For sample 2 there is also only one peak.

Discussion

The agreement of the stoichiometric number-average molecular weights and the measured number-average molecular weights is very good. The agreement shown in Table I is particularly pleasing at the high molecular weight of 9 × 10⁵ because it indicates that the reaction likely went as well as could be expected. The GPC peak in Figure 3 indicates that some coupling of chains may have taken place in sample 1. This is most likely due[19] to the accidental presence of carbon dioxide in the methanol terminator. Similar results have been observed when these anionic polymerizations were terminated by exposure to air. Except for the <5% pentablock impurity in the lowest sample, all samples appear to be good preparations with minimal contaminant.

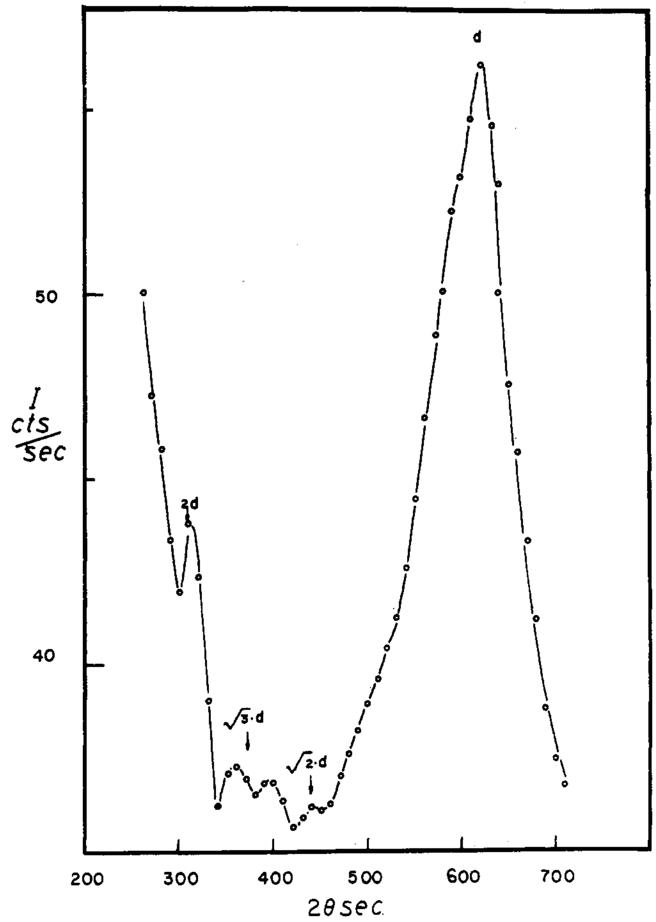

Figure 7. Lattice scattering curve for sample 4.

The scattering patterns are in many ways similar as might be expected with a homologous series of compounds. As the molecular weight increases the domain radius also increases. Likewise the main peak Bragg spacing increases with molecular weight, although the increase in spacing from samples 3 to 4 is so small as to signal a change in packing. The half-widths of both peaks of the various molecular weight samples show small changes from the narrowest sample, but the large increase for the smallest molecular weight sample, number 1, suggests that the phase separation is less sharp in this sample than in the others. This is reflected in the fact that samples with end segment molecular weights of less than 10^4 possess far inferior tensile strengths when compared to samples of higher end block molecular weights.[20]

Further consideration of Figures 8–11 shows that if the main peak is considered to be "*d*," the other peaks are in the ratio $(3/2)^{1/2}d$, $2d$, $3d$, and $2(3/2)^{1/2}d$.

Only sample 4 appears to be lacking in, or has weakly registered peaks at $(3/2)^{1/2}d$, $2d$, and $3d$ with a striking $2d$ peak. If the high-angle side of the main peak is observed there are no resolved peaks except the Rayleigh sphere peaks, although there is the suggestion of a shoulder in both samples 1 and 2 that could be another peak. The above subsidiary peaks suggest a face-centered cubic lattice, however, weakly developed. In the case of sample 4 the suppression of the $(3/2)^{1/2}d$ peak and the strength of the $2d$ peak suggests a different lattice.

If the lattice were diffracting like an extended crystal,

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(19) D. P. Wyman, V. R. Allen, and T. Altares, Jr., *J. Polym. Sci., Part A*, **2**, 4545 (1964).

(20) M. Morton, L. J. Fetters, F. C. Schwab, C. R. Strauss, and R. F. Kammereck, "4th Synthetic Rubber Symposium," Rubber and Technical Press, London, 1969, p 70.

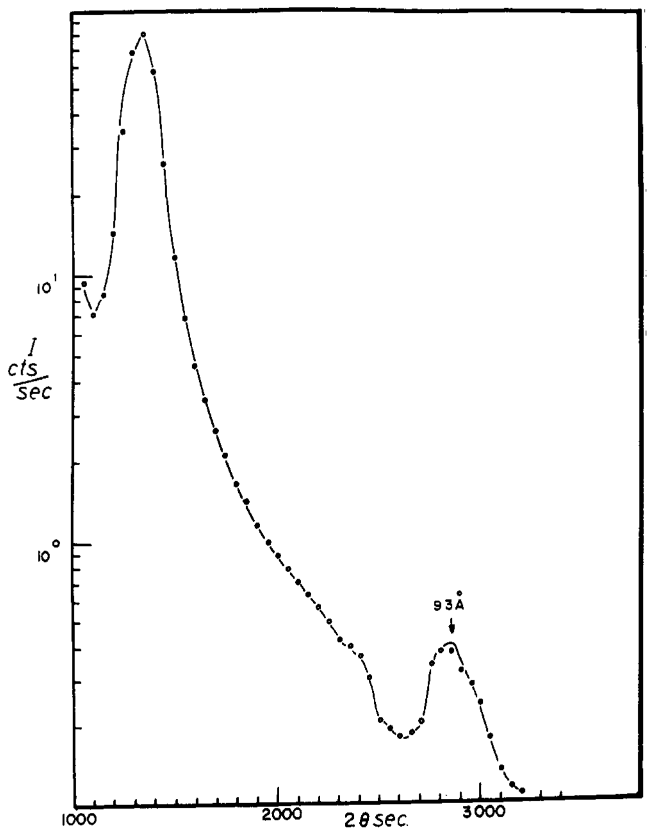

Figure 8. Particle scattering curve for sample 1.

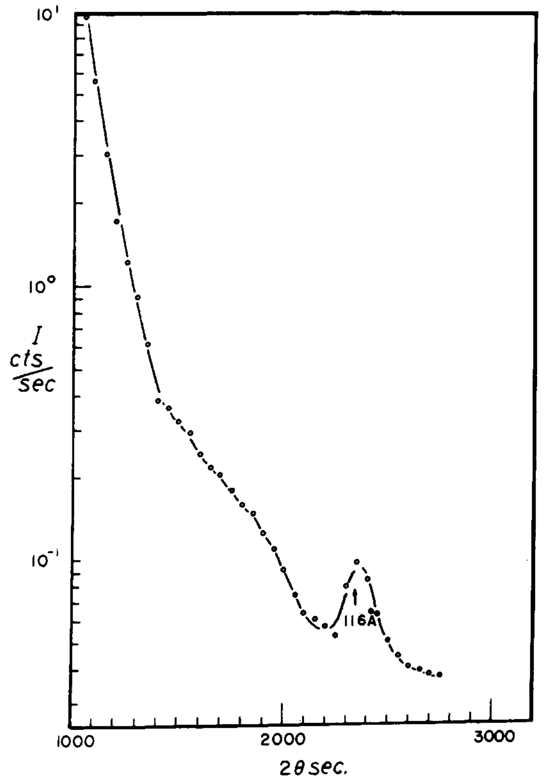

Figure 9. Particle scattering curve for sample 2.

the *d* spacing would represent the [1,1,1] plane for the cubic system while the [1,1,0] and [1,0,0] planes, appearing in the diagram as $(3/2)^{1/2}d$, and $3d$, would not appear due to the selection rules. Also the $2d$ and $3d$ distances would not appear. On the other hand, a good crystal would be expected to show [2,0,0], [2,1,0], [2,1,1], and higher Miller indices on the high-angle side of the main peak. None are clearly visible. Apparently the macrolattice is sufficiently blurred after a few neighbors so that the highest order planes are not in registration and the selection rules for the lower orders are not obeyed.

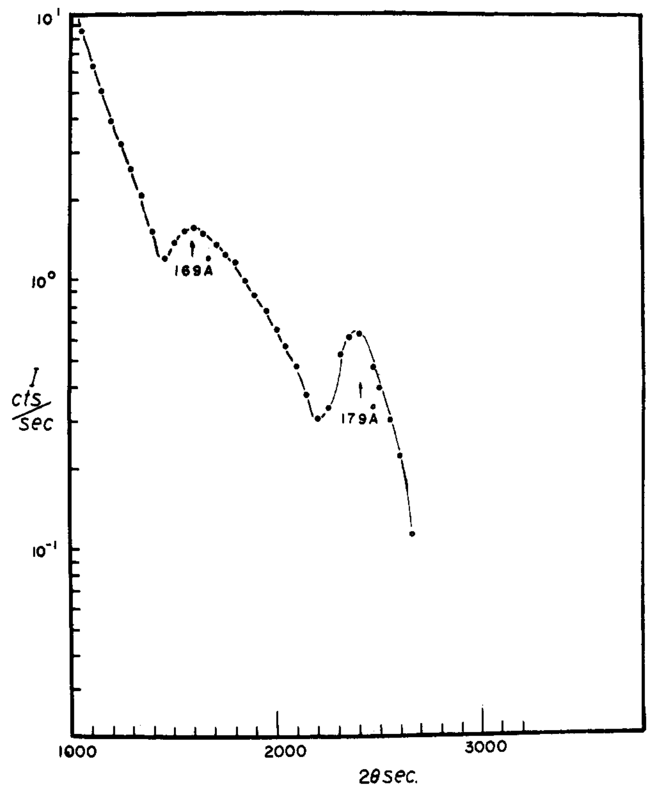

Figure 10. Particle scattering curve for sample 3.

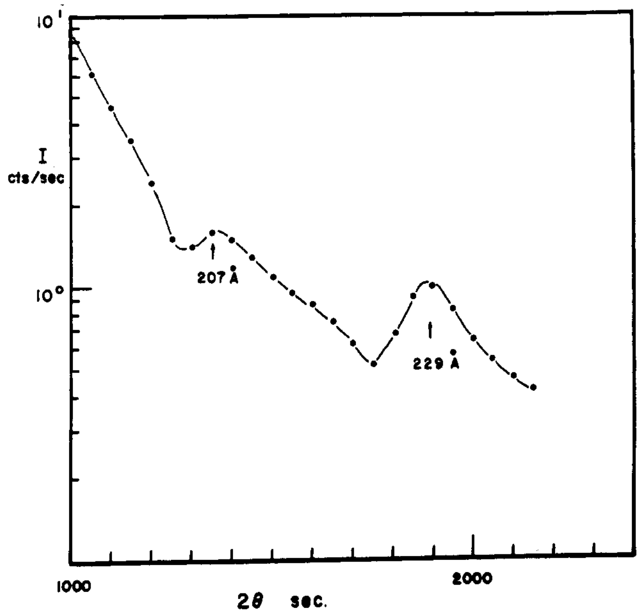

Figure 11. Particle scattering curve for sample 4.

It seems clear that the easiest description of the order in the triblock copolymer system is that of an ordered liquid or a not too well-ordered macrolattice. However, the above lattice interpretation does allow statistically valid determinations of chain parameters for use in assessing the influence of chain parameters on microphase separation.

If the main peak in Table II is considered to be the nearest-neighbor distance in a face-centered cubic system, and the sphere radius in Table II is used, the series of

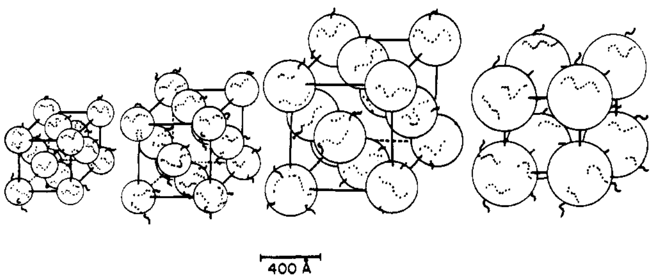

Figure 12. Scale models of lattice packings of polystyrene spheres determined only from X-ray scattering. From left to right: sample 1, 2, 3, and 4.

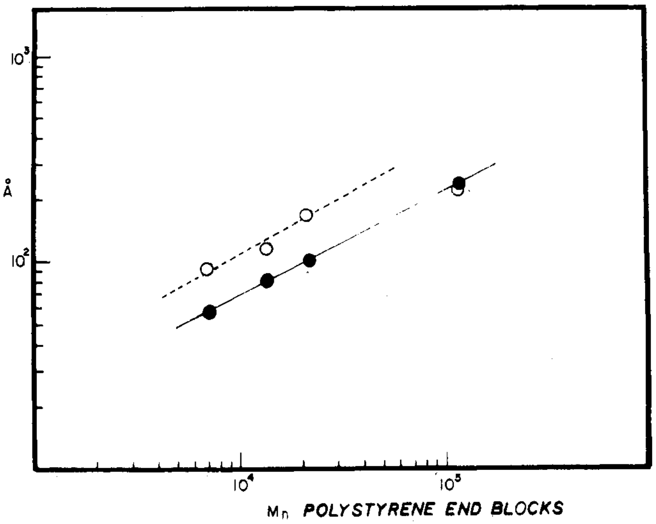

Figure 13. Plot of polystyrene domain radius (from SAXS measurements) against M_n (stoichiometry) of polystyrene end blocks (solid points, solid line). Theoretical unperturbed end-to-end distance of polystyrene (open circles, dotted line).

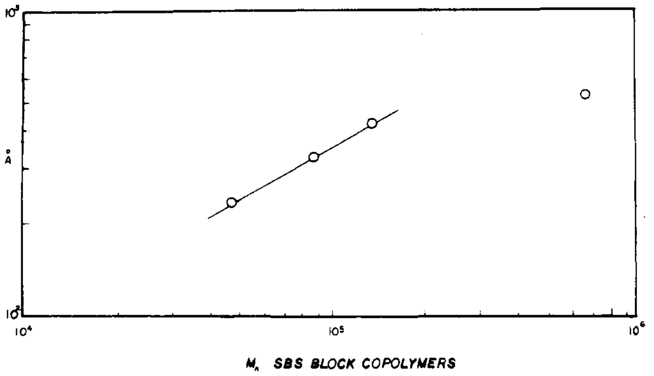

Figure 14. Plot of main peak distance (nearest-neighbor distances of polystyrene domains) against M_n of the block copolymers.

Table III
Stoichiometric and Scattering Volume Fractions of Polystyrene

Sample	ϕ Stoich	ϕ Lattice
1	0.27	0.34
2	0.266	0.246
3	0.266	0.27
4	0.235	0.295

Table IV
Lattice and Molecular Parameters of SBS Block Copolymers

	Polystyrene			Polybutadiene		
Sample	Domain Radius (Å)	$\langle R_0^2\rangle_\theta^{1/2}$	Ratio	$\langle R_0^2\rangle_\theta$	Distance	Ratio
1	93	57	0.61	164	133	1.23
2	116	79	0.68	225	215	1.05
3	170	98	0.58	286	295	0.97
4	207	230	1.11	716	233	3.08

packings shown to scale in Figure 12 can be drawn. The highest molecular weight is drawn with the main peak becoming the nearest distance of a neighbor in a simple cubic structure. The switch to simple cubic for this high molecular weight system is based upon the impossibility of reconciling the stoichiometric ratio of the volume of polystyrene with the macrolattice volume for a face-centered cubic as well as the absence of a $(3/2)^{1/2}d$ spacing and the strength of the $2d$ spacing. Columns 2 and 3 of Table III show the agreement between the stoichiometric volume fraction of polystyrene and the scattering calculation. The poor agreement of sample 1 is easily reconciled with the large half-widths of the scattering curves. It is reasonable to assume that the phase blending in this sample is greatest; a consequence of the low molecular weight of the end segments. A more complete discussion of the two-phase model will come back to this point later. The high molecular weight sample will not phase blend in a thermodynamic sense, but it may be the most difficult sample to kinetically phase separate. This polymer sample could not be cast on cellophane or glass and retain any mechanical integrity. It had to be cast on mercury in order to get a whole piece of film. The assumption of a face-centered cubic system would make the stoichiometric and lattice volume disagreement a factor of 2 greater. Unlike the low molecular weight sample the high molecular weight sample may have phase blending not by a large diffuse interface but rather by a polystyrene chain threading its way to other domains and unable to move back into just one domain. Unfortunately the intensities were not accurately enough normalized in thickness to allow a comparison of absolute scattering intensities.

It is, however, possible to calculate chain parameters based on these models. Table IV lists the domain radius from the scattering pattern and the end-to-end distance of the polystyrene chain estimated from the θ dimensions, as well as their ratio. The ratios near 0.6 are to be expected, since the domain size should be about twice the size of polymer end-to-end distance. However, the high molecular weight sample is again out of line, the end-to-end distance being greater than the domain. This result is again in accord with the notion that single chains do not enter only one domain but perhaps thread through several. Figure 13 is a plot of the domain size against the molecular weight of the polystyrene end blocks. Included on the plot is also the end-to-end distance of the unperturbed dimensions, having a slope of 0.50. The slope for the lower molecular weight, excluding the high molecular weight, is 0.55. The logarithm of the principal peak (nearest neighbor) also gives a linear fit with the molecular weight of the whole sample and is shown in Figure 14 with a slope of 0.56. In both cases the results are quite interesting. The latter slope of 0.56 would, under the ideal model, be the distance between the centers of domains and can be compared to an ideal chain that runs from the center of one domain to the center of another nearest neighbor. The chains do not of course only end up at nearest neighbors but also at next nearest neighbors. However, if the lattice does not change, this factor will be constant, and the total chain dimensions would appear to follow a $M^{0.56}$ relation.

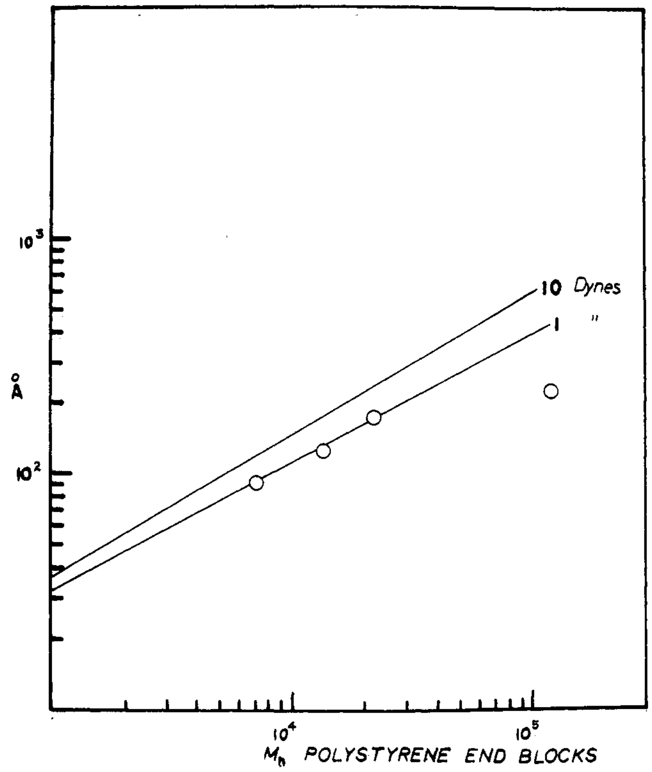

Figure 15. Plot of polystyrene domains radius against M_n of polystyrene end blocks as calculated from Meier's theory (ref 2a) for different values of the interfacial tension. Experimental points for samples 1 to 4 are open circles.

This is one of the few tests that have been made of the end-to-end distance of polymers in the bulk liquid state. Of course one does expect some chain expansion due to the mixing of the dissimilar end and middle blocks and the corresponding chain extensions. Unfortunately there are no direct dilute solution light scattering data on total theta solvent conditions for both chains. Meier[2a] has calculated that for a diblock copolymer the ratio of $\langle R_0^2 \rangle_{\mathrm{Sty}}$ to the styrene domain radius should be $0.75/\alpha$. The above data indicate that a value of 0.58–0.68 occurs when the system is well separated. An attempt to estimate the butadiene end-to-end length was made and the results are given in column 6 of Table IV. The difference between the lattice dimensions and the spherical domain size was attributed to butadiene. The interdomain distances were then weighted to take into account nearest and next nearest neighbors and are shown in column 6. The ratio of unperturbed butadiene end-to-end distances (taken from ref 21 and shown in column 5) is shown in column 7. The ratio is about 1.00 except at low and high molecular weights. The butadiene chains are apparently very close to their unperturbed dimensions.

The final tests of current theories using these new experimental results demand knowledge of the interaction parameter between polystyrene and polybutadiene. An estimate of σ has been taken from Rounds[22] who made phase diagrams and contact angle measurements. His estimate of the interfacial tension is about 1 dyn or less. Figure 15 shows the agreement of eq 2 from Meier[2a] with the assumption of 1 dyn as the interfacial tension. Figure 16 calculated from Bianchi's[6] calculation (eq 4) shows that any triblock copolymers in the usual range of molecular weights would have to have a critical interfacial tension of ~0.2 dyn/cm². Bianchi's theory, being less detailed, can say less about the molecular parameters. From Meier's theory using the lattice parameters found in this work, a chain expansion of 1.1–1.2 would be calculated for an interfacial tension of 1–2 dyn/cm². The measured chain expansions are in reasonable agreement.

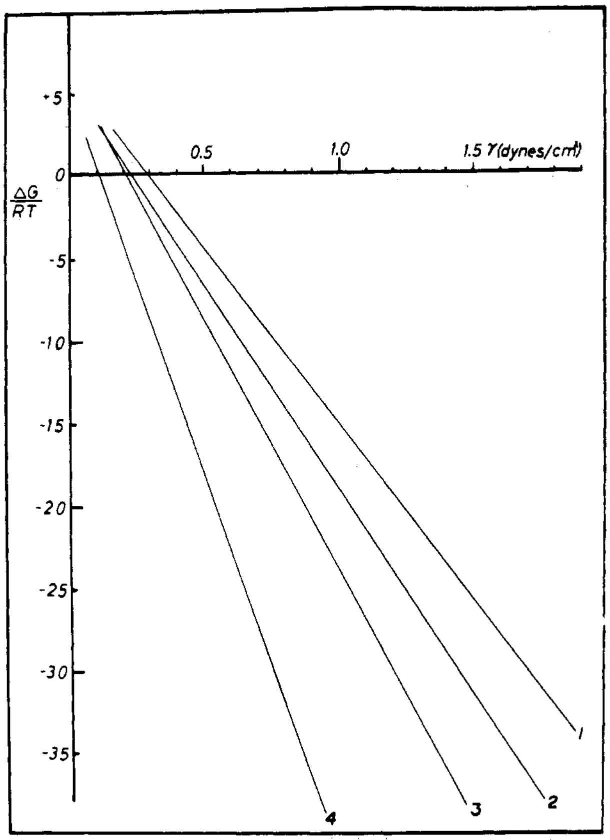

Figure 16. Plot of the free-energy function calculated from Bianchi (ref 6) as a function of interfacial tension using the domain sizes and number experimentally determined. Curves 1–4 represent samples 1–4.

The differences between the stoichiometric volume and the lattice volumes for polystyrene in samples 1 and 4 is undoubtedly a consequence of the scattering of the mixed phase. For the lowest molecular weight sample the interface would be less than 10 Å out of 93 Å for the measured radius. The close agreement of the lattice and stoichiometric volumes for the middle molecular weight polymers indicates that the X-ray technique may not be useful in detecting interfaces smaller than 5 Å. Even for the highest molecular weight samples these two volumes can be made to agree by only a 15-Å increase in the radius of the spheres.

Studies of the morphology of cast films of triblock polymers are presently confusing. That is, early electron microscopic studies and small-angle X-ray studies[5,9-11,23] seemed to imply a spherical domain structure. Later electron microscopy studies of Price[25] seem to favor rodlike domains. From only the straight-forward X-ray analysis the experimental average interdomain spacing always is unequivocal. But the surmise of a regularly arrayed domain structure is only verifiable when a very high-resolution diffractometer is used. The size of the domain in all cases can be deduced from volumes based on the chemical

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stoichiometry and a given domain packing. Most X-ray studies have used the latter method to estimate domain size.

The only way in which a direct X-ray analysis can yield the domain size at the level of several hundred ångstroms is to assume that a domain structure exists that has a known particle scattering factor. In practice, workers assume a simple shape factor like those of spheres or rods. Only a few extrema will appear in the experimental data. Consequently the difference between sphere and rodlike behavior is not easily differentiated when only the first two extrema are observable. Only spheres have scattering patterns that are independent of the degree of orientation of the domains. Consequently, the ambiguity in the interpretation of small-angle X-ray data can only be resolved by comparison of the assumed shape and packing (guided by an analysis of the experimental extrema) with the stoichiometric volume. In this paper the sphere-like assumption gives better agreement between the domain volume calculated from scattering and the stoichiometric volume known from the synthesis.

From electron microscopy measurements, the idea has been advanced[25] that rodlike domains dominate in solvent cast films of polystyrene–polyisoprene tri- and tetra-star block copolymers. However, it should be mentioned that the synthesis procedure used for these materials may influence the morphology. The initiator used was *n*-butyllithium in benzene, an organolithium compound that reacts quite slowly with styrene in hydrocarbon solvents.[26,27] Thus, the star block copolymers synthesized *via* *n*-butyllithium possess moderately polydisperse end segments as well as chains garnished with low molecular weight (<5000) polystyrene segments; blocks too low in molecular weight to form articulate, discrete domains.[2a] The polydispersity and low molecular weight content of these polystyrene blocks has been verified *via* GPC analysis of polystyrene prepared by *n*-butyllithium. Heterogeneity indices of about 1.3 were observed. Thus, any interpretation advanced on the morphology of block copolymers where some of the end blocks can blend with the center blocks should be considered with caution.

Acknowledgment. This work was supported in part by NSF Grant GP-18587.

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The Influence of Solvent on the Secondary Structures of Poly(L-alanine) and Poly(L-proline)

K. H. Forsythe and A. J. Hopfinger*

Division of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106.

Received January 15, 1973

ABSTRACT: The conformational properties of L-alanine chains and both *cis*- and *trans*-L-proline chains were calculated as a function of interaction with solvent and chain length. The solvents considered were water, methanol, ethanol, formic acid, and acetic acid. The hydration shell model was used to compute the macromolecule–solvent interactions. The conformational properties of the molecules *in vacuo* were also computed and used as references. Both the *size* and the *polarity* of the solvent molecule are important factors in dictating chain secondary structure. The conformational properties of L-alanine chains are more dependent upon both chain length and interaction with solvent than the L-proline chains. A very delicate balance between polymer–solvent interactions and formation of intrachain hydrogen bonds dictates whether an L-alanine chain will be extended or α helical. *trans*-Poly(L-proline) has a greater stabilizing interaction with polar solvents than *cis*-poly(L-proline). Rotation about the imide bond in both *cis*- and *trans*-L-proline chains is possible, in all solvents, up to $|\omega| = 10°$.

In a previous paper[1] we reported the solvent dependent conformational analysis of some homopolypeptides in an aqueous media. The polymer–solvent interactions were taken into account through a hydration shell.[2] In this report we consider the solvent-dependent behavior of two homopolypeptides, poly(L-alanine) ($(\mathrm{Ala})_n$) and poly(L-proline) ($(\mathrm{Pro})_n$), in five different solvents, and *in vacuo*. Polymer–solvent interactions are again described by the hydration shell model. The solvents are methanol, ethanol, water, formic acid, and acetic acid. This particular set of molecules provides a considerable range of solvent polarity while minimizing the internal conformational degrees of freedom of the solvent molecules which would drastically complicate our calculations. $(\mathrm{Ala})_n$ has been chosen in these calculations because the conformational properties of this polymer, as it precipitates and/or crystallizes from solution, have been studied in considerable detail,[3] and because there have been a number of recent studies[4-7] of the secondary structure of this polymer in a variety of solvents.

Solvent-dependent conformational energy calculations were carried out on $(\mathrm{Pro})_n$ because Krimm and Venkatachalam[8] have investigated, using their polymer–solvent model, the conformational properties of $(\mathrm{Pro})_n$ in aqueous solution. In their model, solvent molecules are explicitly brought into the vicinity of the polymer and the resulting free energy is minimized. In this paper we discuss and compare our solvent-dependent $(\mathrm{Pro})_n$ conformational

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