A possible interpretation is that there is a progressive reduction of shielding of intramolecular electrostatic repulsions among charged side-chain amino groups on decreasing the H_2SO_4 concentration. In other words, it is possible that the large part of the polyelectrolyte effect is screened out at very low concentrations of H_2SO_4 but a residual effect persists at considerably higher H_2SO_4 concentrations. This hypothesis could explain the behavior of the curve in Figure 5, in the range of solvent composition between 0 and 50% H_2SO_4.

Conclusions

From the result presented in this paper we suggested that solvation effects and protonation of amide groups as well might account for the changes of the CD pattern of PLL in H_2SO_4–H_2O mixtures of different composition. Evidence for protonation of amide groups in the peptide backbone arises from the increased intrinsic viscosity of the polymer in concentrated H_2SO_4.

In drawing these conclusions the tacit assumption was made that the changes of the CD pattern are not a direct consequence of changes of the polymer conformation from an extended coil to a more compact one. In other words the variation of the CD spectrum of PLL on going from water to concentrated sulfuric acid solutions has been interpreted in terms of changes of protonation and solvation of the peptide groups in the different solvent media. According to our interpretation, these changes are directly responsible for the modifications of the CD pattern and not the conformational change from an extended coiled form to a more compact one. This assumption is equivalent to saying that different coiled forms in the same solvent medium should exhibit the same CD spectrum, since in the unordered state there is no possibility of coupling with the transition moments of the peptide chromophores.

In this connection we wish to comment on some recent data obtained by Tiffany and Krimm[21,22] on PLGA and PLL. According to these authors polypeptides with charged side chains are not satisfactory models for an unordered chain. They suggest that the CD spectra of charged PLGA in aqueous solutions, in the absence of added salts, indicate the presence of an "extended-helix structure with parameters close to those of the three-fold left-handed helix of polyproline II."[22] The truly unordered form of charged PLGA occurs, according to the authors, in 4.5 *M* $LiClO_4$ or in 3 *M* guanidine hydrochloride.[22] In our opinion, in these particular cases, caution must be exercised in the interpretation of changes of CD spectra in terms of changes of conformation. It is in fact quite clear that concentrated salt solutions are solvent media completely different from water in a number of features. For instance added salts might cause marked changes in the structural properties, and therefore in the solvation properties of water. It is possible that the different CD patterns of charged PLGA in water and in concentrated salt solutions reflect different solvation conditions of amidochromophores (with consequent effects on the electronic transitions) more than a conformational change of the polymer backbone. Furthermore, possible alteration of the optical rotatory properties could arise from specific binding of ions to the peptide groups.

Acknowledgment. We thank Dr. E. Scoffone for the continuous and stimulating discussions during this work. We are deeply indebted to Dr. F. A. Bovey for a critical reading of the manuscript.

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The Macrolattice of a Triblock Polymer

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ABSTRACT: A triblock polymer of polystyrene–polybutadiene–polystyrene, having molecular weights 21,100, 63,400, 21,100, respectively, 38.5 wt % polystyrene, was studied by small-angle X-ray scattering to determine its three-dimensional structure. A two-phase model was assumed, one phase being a pure polystyrene phase and the other phase a pure polybutadiene phase. Spherical polystyrene domains were shown to be 356 Å in diameter and assigned to an orthorhombic macrolattice of unit cell dimensions 676, 676, 566 Å. The implications of this type of macrolattice are discussed. The macrolattice is itself held in a regular array by forces due to the maximization of polymer chain entropy.

Triblock polymers, that is, polymers of $A_nB_mA_n$, where A is polystyrene and B is a diene polymer, are well known to be two-phase systems. Electron micrographs of polystyrene–polybutadiene–polystyrene do show a strong tendency to form ordered domains of styrene-rich phases imbedded in a diene-rich matrix.[2,3] Low angle X-ray studies[4] have shown the effects of

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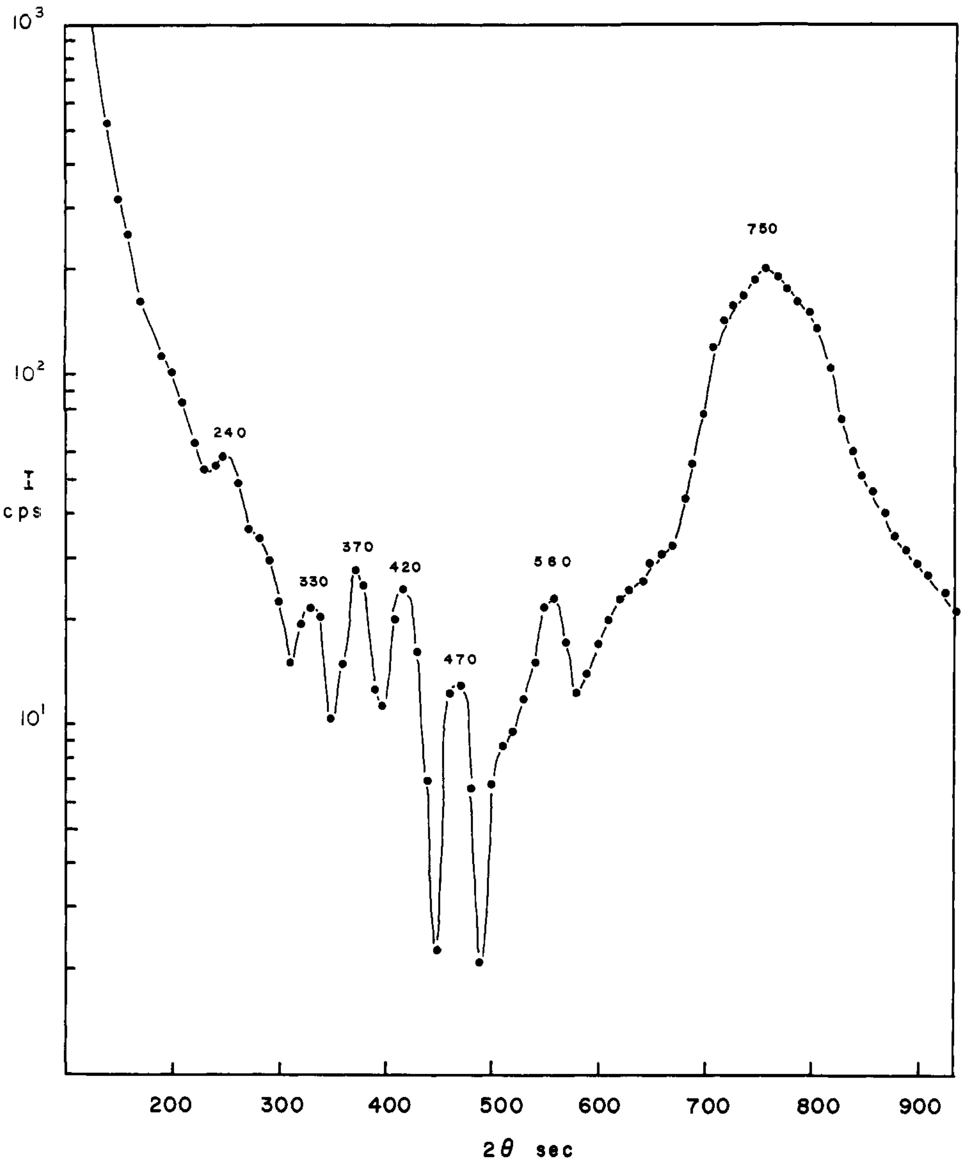

Figure 1. Intensity of scattering, corrected for infinite slits, against scattering angle (2θ) for a solvent-cast film of triblock polymer, styrene-butadiene-styrene, having mol wt 21,100, 63,400, 21,100.

solvents, molecular weights, and impurities on the sharpness of the domain formation. The present study illustrates how at least one triblock polymer phase separates into domains that are ordered in space in a very regular array. That such a triblock polymer should form such a lattice array of styrene-rich domains seems initially surprising. It is, to the authors' knowledge, the first time that large spherical domains (~360 Å), coupled to each other by covalent bonds, are shown to fit a lattice structure.

Experimental Section

Materials. The triblock copolymer used in this study was made by anionic polymerization. The structure is polystyrene-polybutadiene-polystyrene (S-B-S) having molecular weights, 21,100, 63,400, 21,100, respectively.[5] Films (2 mil) were cast from THF-MEK mixtures (90%/10%) and then dried under high vacuum at 95° for 6 days until the samples were at constant weight.

X-Ray Measurements. A Bonse-Hart[6] 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 counts/sec) was so low that counting times of 1.5 hr were used for each point. The diffractometer can routinely be aligned to measure scattering with 20 sec of the incident beam.

The scattering data were corrected for slit smearing by the technique of Schmidt,[7] using an infinite slit correction.[8]

Figure 1 shows the desmeared scattering diagram for the S-B-S samples from 140 sec of angle near the incident beam

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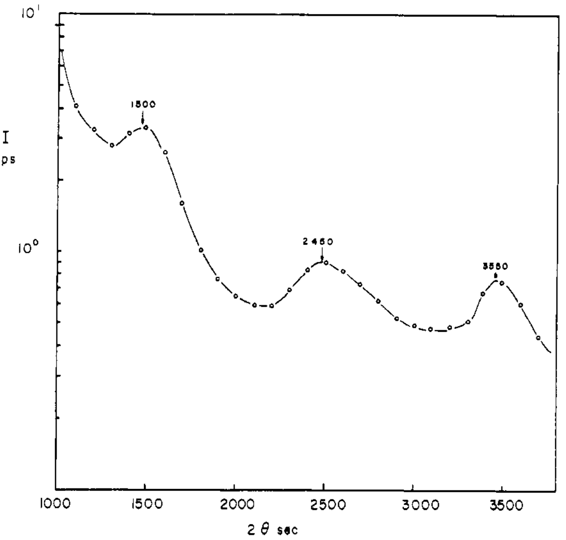

Figure 2. Intensity of scattering, corrected for infinite slits, against scattering angle (2θ) for a solvent-cast film of triblock polymer, having mol wt 21,100, 63,400, 21,100.

to the end of the first main peak at 790 sec. The vertical lines through the points indicate the 2σ error values of the measurements.

Figure 2 shows on a different intensity scale the scattering of the same S–B–S sample at much larger angles.

Discussion

Theory. The scattering of the spherical domains has both an intradomain interference and an interdomain interference because the domains are present at high concentration. (There appears to be no way in which the phase-separated triblock polymer can be reduced to a concentration of domains of extremely low concentration.) In consequence, the scattering equation which describes the combined intra- and interdomain interference is no longer simple.[9] The scattering intensity of isolated monodisperse spheres is given by the factor $F^2(s)$ in eq 1, where s is the scattering vector of magnitude $2 \sin \theta/\lambda$, a is the radius of the sphere, and $(\rho - \rho_0)$ is the difference in density between the sphere and the surrounding medium. The scattering intensity varies as a function of s in a series of maxima and minima of ever decreasing amplitude, from whose extrema the radius can easily be determined if the order of extrema can be assigned.

$$F^2(s) = \left[(\rho - \rho_0)\frac{4\pi a^3}{3}\right]^2 \times \frac{9\,(\sin 2\pi as - 2\pi as \cos 2\pi as)^2}{(2\pi as)^6} \qquad (1)$$

In a triblock structure it is also necessary to consider the effect of interparticle interference in the scattering equations. As the distance between centers of the scattering domains becomes smaller, that is, increasing domain concentration, the intensity begins to show an interference peak at small but easily measured angles. A correlation function, $P(x)$, describing the positions of the domain centers, x, allows the total scattering intensity $I(s)$, to be written simply, as shown in eq 2, where v_1 is the volume of the particle.

$$I(s) = F^2(s)\left\{1 + \frac{2}{sv_1}\int_0^\infty [P(x) - 1]x \sin (2\pi sx)\, dx\right\} \qquad (2)$$

Table I
Spherical Domain Scattering Analysis of Figure 2

Angle (2θ), sec	Order	$(2\pi sa)_A$(theor)	Radius, Å
0	0	0	
1500	1	5.31	179
2450	2	8.63	178
3550	3	11.85	169

Since the single domain scattering factor multiplies the interdomain interference factor, it is possible to determine the radius of spherical domain from eq 1, when the interdomain interference factor has become small and only slowly decreasing with angle. In these experiments, for example, the intensity at the main interdomain peak of 740 sec angle is 40 counts/sec, whereas 1000 sec of angle the intensity is diminished to 4 counts/sec. It is at this low level of interdomain interference that the single domain scattering becomes apparent.

Calculation of Domain Size. By choosing the maxima shown in Figure 2 by an arrow and assigning an order to each maximum listed in column 1 of Table I, it is possible to calculate the radius of spherical domains. Equation 1 can be evaluated for an infinite slit and can be shown to have maxima at the values of sa shown in column 3 of Table I. The values of the radius calculated from the spherical scattering equations are shown in column 4.

If the interdomain interference peak does not lie too close to the zero-angle region, the radius of gyration may be determined from a Guinier plot. The deduced radius of gyration would likely be inaccurate, since the influence of interparticle interference always remains at these concentrations; however, the radius was calculated to give a value of the correct order of magnitude. Figure 3 shows a Guinier plot of the data. The final points in Figure 3 have been taken from intensity measurements at angles between 150 and 300 sec. The radius of the sphere calculated from the final points is 220 Å. However, there can be no confidence in the exact radius reported, since the tangent is arbitrarily chosen. At extremely low angles below 200 sec the background scattering correction must be very carefully determined.

The radius of the particle determined from the Rayleigh scattering peaks is taken to be 178 Å for the purpose of this paper. It is felt that in later work, using different samples, the distribution of domain sizes can be determined from the same data. Additional scattering experiments are presently in progress to determine the sharpness of the phase separation in the triblock polymers.

Calculation of Interdomain Spacing. Figure 1 shows a main scattering peak at 790 sec. Closer inspection of Figure 1 and similar type curves of the block polymers reveals systematic variations in the curve on

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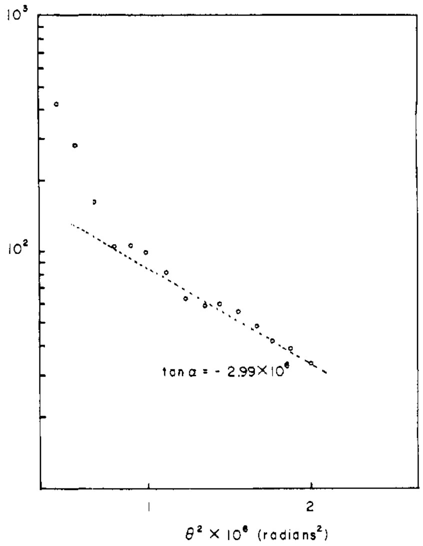

Figure 3. Guinier plot of scattering intensity against the square of the scattering angle θ^2, for the data of Figure 1.

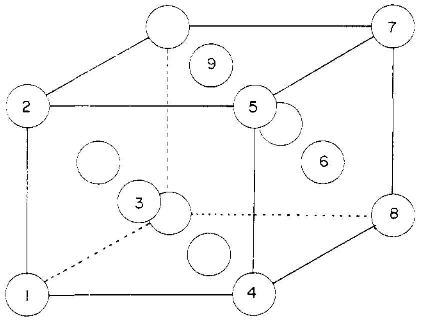

Figure 4. Schematic orthorhombic lattice.

both sides of the main peak. The small effect is heightened by longer counting times and repeated trials. The smaller peaks below the main peak are at 240, 330, 370, 410, 470, and 560 sec and are beyond experimental uncertainty. Later discussion will postulate that there may be another peak around 600 and 700 sec. The last peak occurs as a shoulder on the rapidly rising main peak and is not unambiguously demonstrable, but fortunately its existence is not essential to the structural model proposed in this paper. There also are suggestions of shoulders in the scattering curve below 300 sec, that is at 285 and 250 sec, the latter peaks can easily be accepted as multiples of the peaks at higher angles.

Proposed Structure for this Triblock Sample. All of the scattering peaks shown in Figure 1 can be mostly easily reconciled with the face centered orthorhombic lattice shown in Figure 4. Table II illustrates the agreement found when the main peak is assigned to the distance (Figures 1–3) in Figure 4, the nearest neighbor and most frequent distance. Column 1 of Table II is the peak angle taken from Figure 1, column 2 the Bragg spacing calculated from Bragg's relation, columns 3 and 4 are the assignments based on the orthorhombic model of Figure 4. Those peaks that cannot be assigned unambiguously and may not be readily apparent are labeled with a question mark. The frequency of the given distance is calculated from the model of Figure 4.

TABLE II
ASSIGNMENT OF SCATTERING PEAKS OF FIGURE 1 TO MODEL IN FIGURE 4

2θ, sec	Bragg spacing, Å	Distance (Figure 4)	Calcd frequency (Figure 4)
790	430	1–3	24
560	566	1–2	4
470	676	1–4	8
410	775	1–6	16
370	860	1–5 or $2x$ (1–3)	8
330	964	1–8	4
250		$3x$ (1–3)	
700(?)	480	2–9	12
600(?)		$\sqrt{3}/\sqrt{2}$ (1–3)	
285(?)		$2x$ (1–2)	

All of the scattering peaks can be accounted for on the basis of the simple model shown in Figure 4. There are two reasons for choosing such a simple model. (1) The highest type of symmetry would be expected for the placement of the styrene domains, since the chain forces connecting the domains are presumably isotropic. (2) The structure must also yield the stoichiometric volume per cent of styrene domains, if the domains are truly pure polystyrene. Earlier attempts in this work to correlate an even simpler close-packed lattice with the observed lines was unsuccessful in explaining all of the peaks and did not yield a reasonable value of the volume per cent of polystyrene. The orthorhombic lattice was chosen because all clear peaks can be accounted for and the volume of polystyrene is in good agreement with the stoichiometric value.

The calculation of the volume per cent of styrene in the domains arranged on a lattice has made assuming a density of polybutadiene of 0.89[10] and a density of glassy polystyrene of 1.036. (The extrapolated value of the liquid polystyrene is 1.054.[11]) The polybutadiene value is characteristic of a material that is 50% *trans*, 40% *cis*, and 10% 1–2 structure. The volume per cent of polystyrene in the sample based on the known chemical composition is 36.34 for glassy polystyrene at 25° and 35.94 for liquid polystyrene at 25°. The sample had been cast and annealed so as to enhance the most complete separation of the domains.[4]

The final proposed structure is shown to scale in Figure 5. The polystyrene domain radius has been chosen as 178 Å; the three-unit cell distances have been chosen as 676, 676, and 566 Å. The calculated volume per cent of glassy styrene from the orthorhombic lattice is 36.52 compared to a stoichiometric per cent based on chemical composition amount of 36.34. Within the experimental accuracy of the unit cell determinations, the known density of polybutadiene, and the assumption of complete chemical separation in the domains, the agreement is excellent. Since there might be an expectation of some phase blending near the interface an exact agreement would be fortuitous.

Other Possible Polymeric Structures. Since the

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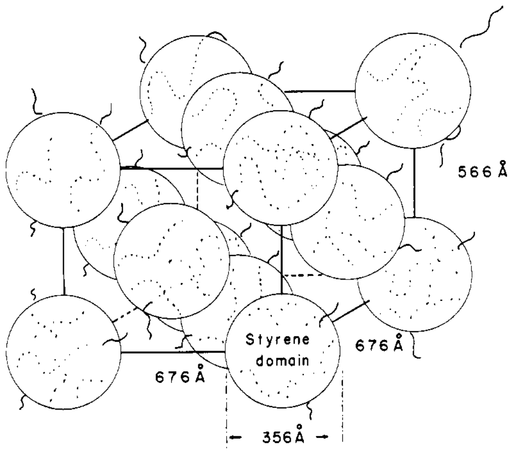

Figure 5. Scale model of proposed macrolattice of S–B–S, 38.5% styrene, mol wt 21,100, 63,400, 21,000.

tension in the diene chain is holding the domains at the distance needed to minimize the free energy, and since the chains and domains are *a priori* assumed isotropic in nature, it is surprising to find this particular macrolattice. The one possible unexplained line at 600 sec and the existence of rather subdued peaks indicate that this lattice for a 38.5 wt % polystyrene is not as isotropic as perhaps another triblock polymer of lower per cent styrene might develop. (The 600 sec peak, for example, is $\sqrt{3}/\sqrt{2}$ of the main peak—a strong characteristic distance in the face-centered cubic system.) It is the authors' belief that all of the triblock (S–B–S) polymers from 15% styrene to 40% styrene form macrolattices. Around 30% styrene the lattice is perhaps isotropic but below 15% styrene domains tend to become random, and about 40% styrene the domains tend to form a lamellar structure. Further work in progress appears to bear out these tentative proposals for styrene contents between 15 and 40%.

It is therefore presumed that the 30% styrene content (S–B–S) polymer will have a more isotropic macrolattice, perhaps a face-centered cubic lattice. Increasing the styrene content of the (S–B–S) triblock polymer may decrease one dimension of the cubic cell until the layers of the original (*lll*) planes of the face-centered cubic lattice become the alternating lamellar layers of pure polystyrene and pure polydiene. Further work on many samples between 40 and 50 vol % would have to be investigated to determine the exact structural changes. Perhaps the change in molding observed by Matsuo[2] can be accounted for by the deformation of the unit cells under stress at a particular point in the cell.

The length of the butadiene chain between nearest neighbors is the 1–3 distance minus twice the radius of the domains, or 54 Å. A polybutadiene of mol wt 63,400 would be expected to have an unperturbed end-to-end distance of ~250 Å, although the unperturbed end-to-end distance of a chain held at both ends could be expected to be much larger. At this time there would be many possible explanations of the unexpectedly small distance between domains. (1) The domains, particularly near the interface, are not pure polystyrene. (2) A polybutadiene chain is connected not only to its nearest neighbors but also to all other domains in the lattice with decreasing frequency. (3) The domains have several points at which there are surface contacts of a polybutadiene chain.

If the proposed macrolattice structure is accepted the phases must be composed primarily of demixed polymer except at the surface because the volume fraction of polystyrene agrees so well with the stoichiometry. Future work on the polydispersity of domain sizes should help clarify the latter point. It must be recalled that the lattice itself is not sharply defined like a crystal lattice. The forces holding the lattice at a given distance are entropic in nature, governed only by the kinetic energy of the diene chain. This type of force would not be expected to give an extremely sharp entropy maximum like other lattice forces. Consequently, the domain positions and monodispersity will always be an averaged quantity that may not agree with the simple weighting of the stoichiometric per cent.

It is conceivable that some of the diene chains are not connected at their ends to nearest neighbors. But any averaging with nearest neighbors should be on a statistical basis due to the solid angle subtended. Actually the next nearest distance of any frequency is the 1–2, or 1–4 distance, that is, 676 or 566 Å. These distances have a coordination number or contact frequency of 8 and 4, respectively. The distance allowed for the chains connected in this array is 320 ar 210 Å, respectively. These distances are, of course, much more reasonable. If the distances of these two additional neighbors are weighted by their contact frequency and added to the nearest neighbor distance weighted by its contact frequency, the diene chain end-to-end distance would become ~133 Å. This distance is much more reasonable than the 54 Å value for nearest neighbors only, but is still much too low to be easily understood. Other large distances in the lattice are available to the chain and may be expected to increase the average distance slightly. But certainly more important is the fact that the expected end-to-end distance of a chain held apart at both ends will always be much larger than any average distance calculated from the lattice. Consequently, another physical explanation of the small interdomain distance is needed.

Only a few surface contacts are required to reduce the interdomain chain size appreciably. And furthermore such contacts are physically feasible because the interfacial tensions are not extremely repulsive. Indeed there is likely to be a very large diffuse interface. A simple lattice model of 178 Å domains requires 700 chains of butadiene to exit from the surface of each domain. If the cross-sectional end area of a single chain is assumed to be 5–10 Å^2, there must be many regions on the surface of a domain that have no diene chains exiting from them so that additional butadiene has a high probability of being adjacent to the surface. If these adjacent contacts on the surface come from segments toward the middle of the diene chain, then the shortened diene distance can be easily understood. Those measurements are essentially equilibrium measurements so that it is surprising that in time the domains do not separate farther. They do not.[4] No doubt kinetic effects like chain entanglements or trapping of chains in phases have a role that is not easily explained at the present time. Preliminary X-ray studies of the triblock polymers under stress indicate very marked changes in all of the scattering peaks. However, the interpretation is no longer as simple as in the above experiments.

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The Association Behavior of Polystyryllithium, Polyisoprenyllithium, and Polybutadienyllithium in Hydrocarbon Solvents[1a]

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ABSTRACT: The states of association of the following polymer–lithium species were determined in various solvents: polystyryllithium in benzene; polyisoprenyllithium in benzene, *n*-hexane and cyclohexane; and polybutadienyllithium in benzene. Both concentrated solution viscosity and light-scattering measurements yielded convincing evidence that all of these polymeric molecules are associated *in pairs* in these hydrocarbon solvents. As indicated in previous studies, the effect of ethers, such a tetrahydrofuran, is to break up these dimeric associated species, presumably by means of a solvation equilibrium. These results appear to vitiate the postulate, which has been advanced at various times, that the isoprene and butadiene systems must have higher states of association in order to explain the low kinetic order of the propagation reaction in hydrocarbon media.

It has been long recognized on the basis of experimental evidence that organolithium compounds are associated to various extents in hydrocarbon media. Thus ethyllithium has been found to be a hexamer in both benzene[2] and cyclohexane[3] but a tetramer in the vapor state.[2] In these solvents *n*-butyllithium[4] also is a hexamer. This aggregation of organolithium species is the result of multicenter bonding, *i.e.*, the number of atomic orbitals available for bonding exceeds the number of electrons which are available to occupy them with the result that the available atomic orbitals are combined to form molecular orbitals which extend over more than two atoms but which can only accommodate one electron pair.

The variation in the degree of association between the straight and branched chain organolithiums has been discussed by Brown.[2] He noted that in any proposed structures for ethyllithium, the distance between adjacent alkyl groups was much greater in the tetramer than in the hexamer. Thus, in those instances in which there is little interaction between the alkyl groups, the hexamer would be the preferred structure. However, in *sec*-butyllithium and *t*-butyllithium the comparatively bulky branched chains will interact with its neighbors in the hexamer structure. Thus these organoliths would be expected to accept the next most favorable association state, the tetramer, and this has actually been found to be the case for *sec*-butyllithium on benzene[5] and for *t*-butyllithium in both benzene and hexane.[6]

On steric grounds, one might also anticipate low states of association for long chain organolithiums, *e.g.*, *n*-dodecyllithium is reported to be a tetramer in benzene.[7] The polymerization of styrene, butadiene, and isoprene by organolithium initiation in hydrocarbon solvents has brought to light the fact that these polymer–lithium species are also associated even at very low lithium concentration (10^{-3} to 10^{-4} *M*, as contrasted with 0.2–3 *M* for the alkyllithiums). The state of association of polystyryllithium and polyisoprenyllithium was actually first[8,9] determined by precise molecular weight measurements, using the concentrated solution viscosity method. These results showed that these polymeric species were associated *in pairs*, the degree of association being about 98–99% at 10^{-3} to 10^{-4} *M* concentrations of lithium. As might be expected, in such polymerization systems, the polymer–lithium species might cross-associate with any unreacted alkyllithium initiator, and evidence for this has also been found.[8]

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