residues now extend into water and bind water (to lower their frequency). The 1661-cm^{-1} band (appearing in aqueous poly(L-lysine)[5] and in copolymer samples A, B, C, and D) may be attributed to random-coil poly(D,L-lysine); hence, the 1653-cm^{-1} band must arise from α-helical poly(L-alanine). The Raman scattering of pure water produces only one (weak) band in the region of the spectra of Figure 1. Unfortunately, this band occurs at 1640 cm^{-1} and could cast doubts on our assignments of the amide I band. However, the consistency in amide I frequencies of poly(L-lysine)[5,6] and of samples A, B, C, and D in salt-free water gives us confidence in the above assignments. In the amide III region, the 1322-cm^{-1} band [from α-helical poly(D,L-lysine)] disappears and that at 1391 cm^{-1} [from random-coil poly(D,L-lysine)] increases in intensity in water. The band at 1313 cm^{-1}, which persists in water, and other bands in the intermediate and low-frequency range indicate the presence of α-helical poly(L-alanine) residues. The existence of a complete random-coil conformation of poly(D,L-lysine) is indicated[5] by a shift of the 1215-cm^{-1} band to 1246 cm^{-1}; the appearance of two new bands at 250 cm^{-1} and 345 cm^{-1} is also probably attributable to random-coil poly(D,L-lysine).

In salt solution, the charges on the poly(D,L-lysine) blocks are partially shielded; as a result of the reduced electrostatic repulsions, the poly(L-alanine) block is thought[10] to fold into a hairpin-like structure with interhelical side-chain to side-chain hydrophobic bonds. The laser Raman spectrum of Figure 1C tends to support this view; *i.e.*, the vibrational frequencies of poly(L-alanine) [but not of poly(D,L-lysine)] are spread out into considerably broader bands. It was shown earlier[16] that formation of a hydrophobic bond leads to changes in the force constants (for torsional oscillations about carbon–carbon single bonds) which depend on the strength of the hydrophobic bond. Presumably, the broad peaks arise from a distribution of hydrophobic bonds of variable strength (arising from variable locations of the hairpin bends) mixed in with a certain amount of nonbonded methyl side chains; this variable degree of bonding would be expected to influence all of the poly(L-alanine) frequencies, not only those of the side-chain methyl groups. While one might have argued that the change in the nature of the environment (*i.e.*, addition of salt) would have a similar broadening effect on the spectrum, this argument is not valid since the effect is quite discrete, *i.e.*, only the alanine bands are broadened. In addition, other poly(amino acids) in salt solutions studied by us[17] and others[18] show no comparable broadening effects.

In conclusion, the laser Raman spectra of the copolymers studied here indicate that both the poly(D,L-lysine) and poly(L-alanine) blocks consist of mixtures of α helix and random coil in the solid state. In aqueous solution, the poly(D,L-lysine) is exclusively in the random-coil form, but the poly(L-alanine) remains as a mixture of helical and coil conformations. In the presence of salt, the spreading of the vibrational frequencies indicates the presence of alanine–alanine hydrophobic bonds (postulated earlier[10] as a feature of hairpinlike structures to account for the melting behavior in salt solutions). Since the Raman spectra are in agreement with the earlier ORD studies, we may use the laser Raman technique (which provides detailed information about vibrational modes in these biopolymers) as a probe of internal interactions.

Acknowledgment. We are very grateful to Professor D. B. Fitchen for the generous use of his laser Raman spectrometer.

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Light-Scattering Studies on Polystyrene–Polyisoprene Block Copolymers

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ABSTRACT: Two-block (AB) copolymers of styrene and isoprene have been prepared by an anionic method. Three samples were studied by light-scattering techniques in a number of solvents. With solvents having a refractive index far removed from those of polystyrene or polyisoprene, normal Zimm plots are obtained. Where the solvent refractive index approaches that of either component, the Zimm plots become distorted as expected if intermolecular interference is an important phenomenon. Under these conditions, the intermolecular excluded volume is a function of the size of the whole molecule, whereas only a smaller part of the molecule actually scatters light. It is shown that this can produce the results observed. Some separation of the two types of segments is implied.

Theoretical predictions[2] and experimental observations[3] show that chemically dissimilar polymers are generally incompatible as evidenced by a general phenomenon of phase separation in ternary systems consisting of two polymeric species and a common solvent. The exceptions to this incompatibility rule occur only in a limited number of cases, principally among pairs of polar molecules which interact favorably, *i.e.*, with negative heat of mixing. A peculiar situation arises, however, when dissimilar and incompatible homopolymers are combined in a block or graft copolymer. The repulsions between unlike segments of chain are expected to give rise to unusual structures, and this has been shown to be so for the structures of block copolymers of styrene and

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TABLE I
CHARACTERISTICS OF BLOCK COPOLYMER SAMPLES

Sample	$W_{\mathrm{ps}}{}^{a,b}$	$M_{\mathrm{calcd}}{}^{b} \times 10^{-5}$	$M_{\mathrm{n}}{}^{c} \times 10^{-5}$	d*n*/d*c* (4358 Å, 35°)			
				MIBK	c-C_6H_{12}	C_6H_6	C_6H_5Cl
SI-a-6	0.48	8.84		0.183	0.147	0.069	0.040
SI-a-7	0.50	1.54	1.52				
SI-b-7	0.76	4.99	4.80	0.198	0.163	0.089^{d}	0.066
PS	1.00			0.214^{d}	0.180	0.112	0.083
PI	0.00			0.157^{d}	0.117	0.020	−0.004

[a] Weight fraction of PS in the samples. [b] Calculated from the polymerization data. [c] Determined by osmometry (Mechrolab rapid membrane osmometer). [d] Estimated from a plot of d*n*/d*c* against solvent refractive index.

butadiene or isoprene in the solid state[4-8] and in concentrated solutions.[9] In the solid state, micrographs of solvent-cast films have revealed a variety of regularly organized structures involving intramolecular phase separation and agglomeration of chains of colloidal scale. The same phenomenon was observed in concentrated solutions where small-angle X-ray diffraction patterns have shown[9] the existence of liquid-crystal structures analogous to those occurring in concentrated soap solutions.

While intramolecular phase separation was confirmed experimentally for concentrated solutions, the molecular conformation of block copolymers in dilute solutions is still ambiguous. There appear to be two different conformations possible for the isolated block copolymer molecule in solution, one in which the dissimilar chains are interpenetrating, giving rise to a large number of heterocontacts, and one in which unlike segment separation occurs, with a limited number of heterocontacts. According to a large number of studies[10-20] mainly devoted to intrinsic viscosities of styrene–methyl methacrylate, styrene–butadiene, and styrene–isoprene copolymers, the experimenters have not been able to argue definitely in favor of one of the plausible conformations. The weakness of the viscosity approach is obviously due to the lack of a genuine theory for block copolymers predicting the change in viscosity when one passes from one structure to the other.

Another approach consists of considering individual chains in a block copolymer. For that purpose let us consider a two-block copolymer molecule AB and imagine the change in the dimensions of one of the two blocks, say A, during the transition from the interpenetrating to the segregated structure. According to the incompatibility of the parent homopolymers, one can anticipate that the large number of heterocontacts in the interpenetrating structure will make the radius of gyration of block A larger than that corresponding to the same block A in a pure homopolymer. On the other hand, the radius of gyration of the same block A in a segregated structure will be similar in value to that found in a homopolymer of the same molecular weight. This approach lends itself well to light-scattering studies where, by a suitable choice of a solvent which masks block B, one can obtain directly the radius of gyration of block A. The necessary condition for that purpose is the availability of a solvent giving a very low value of refractive index increment (d*n*/d*c*) for polymer B compared to polymer A.

Such a study carried out for AB block copolymers of styrene and isoprene is described in this paper. For comparison purposes, a number of solvents were used, methyl isobutyl ketone, tetrahydrofuran, cyclohexane, benzene, chlorobenzene, and bromoform (in order of decreasing refractive index). In this way the effect of variations in the amount of light scattered from the individual styrene and isoprene segments could be investigated.

Experimental Section

Samples of AB block copolymers of styrene and isoprene were prepared anionically according to a polymerization procedure described previously.[21] The high-vacuum apparatus used was a modification of that described for kinetic studies, scaled up for use with large solution volumes.[22] The reactions were carried out at 25° in benzene using *sec*-butyllithium as the initiator. Styrene was added first, since the interchange from polystyryllithium to polyisoprenyllithium occurs more rapidly than the inverse reaction. After the completion of styrene polymerization, isoprene was added slowly by distillation from a break-seal ampoule, and the reaction was terminated under vacuum by addition of a small amount of *tert*-butyl alcohol. The stability of the "living ends" during the reaction was checked by spectrophotometry. The presence of homopolystyrene was detected by density-gradient ultracentrifugation in carbon tetrachloride–cyclohexane mixtures. As shown previously,[21] this technique is very convenient for high molecular weight copolymers, facilitating the determination of the homopolymer contents as low as 1%. The microstructure of polyisoprene samples prepared under the same conditions was determined by nmr analysis in benzene solutions. These results obtained for homopolyisoprene should apply to the polyisoprene blocks in the copolymers studied. The amount of 1:2 was unnoticeable and the amounts of cis 1:4 and trans 1:4 and 3:4 were respectively 71, 22, and 7%. Samples so far investigated, SI-a-6, SI-a-7, and SI-b-7, were selected for their very low content in homopolystyrene (<1%). They are described in Table I.

Light-scattering measurements were made at 35° in a Sofica PGD instrument with unpolarized incident blue light (λ 4358 Å).

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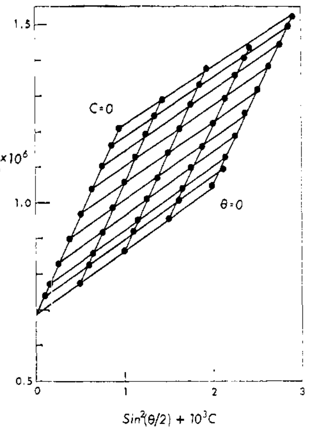

Figure 1. Zimm plot for the block copolymer SI-a-6 in methyl isobutyl ketone.

Solutions were clarified by filtration as described previously.[23] Pure benzene was used as standard with Rayleigh ratio of 51 × 10^{-6} cm^{-1} [24] (corrected to 35°). Scattering intensities were measured over the angular range 30–150°, for which the intensities scattered by benzene using a vertically polarized incident beam are constant to 1% after multiplying by the sin θ volume correction. The refractive index increments, dn/dc, were determined at 35° and 4358 Å with a Brice Phoenix differential refractometer. The values for the block copolymers agree within experimental error with the weight averages of those of the homopolymers (Table I).

Molecular weights were calculated from

$$M_w^{-1} = (2\pi^2/\lambda^4 N_a R_b) n_b^2 (dn/dc)^2 I_b (C/I_\theta)_{\substack{c=0\\ \theta=0}} \quad (1)$$

where I_b and R_b are respectively the scattering intensity and the Rayleigh ratio of the standard benzene and n_b is its refractive index.

Results

(1) Systems with High Refractive Index Increments for Both Blocks. Three solvents were chosen for this preliminary study, tetrahydrofuran (THF), which is a good solvent for both polystyrene and polyisoprene; cyclohexane, which is a Θ solvent for polystyrene and a good solvent for polyisoprene; and methyl isobutyl ketone (MIBK), which is a near-Θ solvent for both polymers. The Zimm plot obtained for sample SI-a-6 in MIBK is presented in Figure 1. Sample SI-a-7 studied in cyclohexane, sample SI-a-6 studied in THF, and sample SI-b-7 studied in cyclohexane and MIBK gave similar quite normal results. Sample SI-a-6 in cyclohexane showed an abnormally large decrease in dissymmetry with concentration. The combination of high molecular weight and lower dn/dc of cyclohexane compared with tetrahydrofuran or methyl isobutyl ketone produced the first symptoms of the abnormal behavior described later.

According to the Bushuk and Benoit equation for light scattering by copolymer solutions, the molecular weights calculated from eq 1 are apparent values given by the relation[25]

$$M_{ap} = M_w + 2P[(\nu_a - \nu_b)/\nu_0] + Q[(\nu_a - \nu_b)/\nu_0]^2 \quad (2)$$

in which M_w is the true weight-average molecular weight; ν_a, ν_b, and ν_0 are respectively the refractive index increments of homopolymer A, homopolymer B, and copolymer; and P and Q are parameters related to the heterogeneity in composition of the sample. Nevertheless, in sufficiently homogeneous copolymer samples, the calculated molecular weight M_{ap} is expected to be very close to M_w, particularly when dn/dc is high. This assertion is confirmed by the results presented in Table II, where M_{ap} values obtained for samples SI-a-6, SI-a-7, and SI-b-7 are in good agreement with the measured number-average molecular weight or that calculated from the synthesis data (Table I).

TABLE II
APPARENT MOLECULAR WEIGHT AND APPARENT RADIUS OF GYRATION DETERMINED BY LIGHT SCATTERING IN CYCLOHEXANE, METHYL ISOBUTYL KETONE, AND TETRAHYDROFURAN

	$M_{ap} \times 10^{-5}$			$(R_{ap}^2)^{1/2}$, Å		
Sample	c-C_6H_{12}	MIBK	THF	c-C_6H_{12}	MIBK	THF
SI-a-6	10.5	10.7	11.0	450	383	500
SI-a-7	1.60	1.59				
SI-b-7	5.25	5.15		244	226	

Corresponding radii of gyration determined according to the method of Zimm, *i.e.*, from the initial slope of the angular light-scattering envelope at zero concentration, are also reported in Table II. According to the Benoit and Wippler theory for angular distribution of light scattered by copolymer solutions, the values so obtained are again apparent ones given by the relation[26]

$$R_{ap}^2 = \alpha^2 R_a^2 + \beta^2 R_b^2 + 2\alpha\beta R_{ab}^2 \quad (3)$$

where α and β are equal to $x_a\nu_a/\nu_0$, and $x_b\nu_b/\nu_0$, respectively, x_i being the weight fraction of polymer i in the copolymer. R_a^2 and R_b^2 are the mean-square radii of gyration about the centers of gravity of blocks A and B, respectively, and R_{ab}^2 is given by the relation

$$R_{ab}^2 = 1/2(R_a^2 + R_b^2 + \overline{G_aG_b^2}) \quad (4)$$

in which $\overline{G_aG_b^2}$ is the mean-square distance of the centers of gravity of blocks A and B. Thus, it follows that R_{ap}^2 values such as those found in Table II must be interpreted with caution whenever the refractive index increments for the component chains differ.

(2) Systems with Very Low Refractive Index Increments for One of the Two Blocks. As pointed out previously, such systems should provide a way to study the conformation of the copolymer part for which the refractive index increment is still important. Equation 3 shows that R_{ap}^2 is equal to R_a^2 when ν_b is very low compared to ν_a. Chlorobenzene, selected for this purpose, is a good solvent for both polystyrene and polyisoprene and gives a very small negative dn/dc for polyisoprene (Table I). Measurements were also made in benzene and in bromoform, good solvents for which dn/dc is low for polyisoprene and polystyrene, respectively. A typical Zimm plot obtained for copolymer SI-a-6 in chlorobenzene is presented in Figure 2. Similar Zimm plots were obtained for samples SI-a-7 (Figure 3) and SI-b-7. They show a very peculiar behavior in that the observed angular light-scattering envelopes, although linear at zero concentrations, present an upward curvature at low angles which becomes more and more significant as the concentration and molecular weight increase. A similar effect was observed in bromoform, although because of the difficulties in working in this solvent, a complete Zimm plot was not constructed.

This kind of perturbation of the Zimm plots is very unusual and has been so far observed only in a few cases: for poly-

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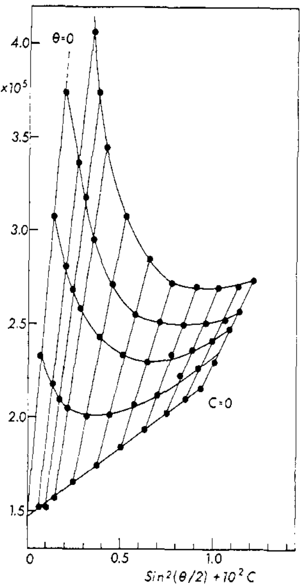

Figure 2. Zimm plot for the block copolymer SI-a-6 in chlorobenzene.

electrolytes in low ionic strength media, as reported by Doty, *et al.*;[27,28] for poly(vinyl carbanilates) in ketone solvents;[29] and for poly(4-vinylpyridine) in nitromethane.[30] The former authors explain this phenomenon in terms of external intermolecular interferences. Although the reasons for such intermolecular interferences are clear for charged polyelectrolytes with a very large abnormal excluded volume due to the strong electric potential of the macroions, the case for poly(vinyl carbanilate) is more problematic.[29] Similarly, the Zimm plots of the type presented in Figure 2 will be explained in terms of external interferences which are due to very large abnormal excluded volumes for the unmasked part of the copolymer molecules.

As pointed out by Doty and Steiner[27] and later by Burchard,[29] Fournet's theory,[31] which was derived in order to evaluate the loss in scattering power caused by external interferences for small-angle X-ray scattering from dense groups of particles, may be extended to such systems. This theory is valid for spherically symmetric particles and gives for the apparent particle scattering factor

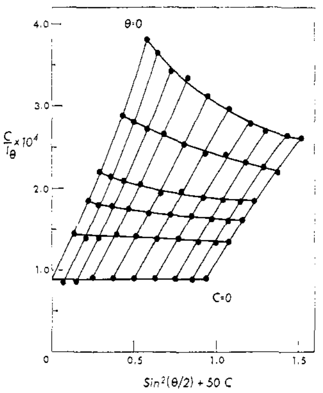

Figure 3. Zimm plot for the block copolymer SI-a-7 in chlorobenzene.

$$P'(\theta) = P(\theta)\left[1 + \frac{4\pi C N_a}{M}\int_0^\infty (1 - e^{-U(r)/kT})r^2\frac{\sin hr}{hr}\mathrm{d}r\right]^{-1} \qquad (5)$$

In this equation, $P(\theta)$ is the well-known particle-scattering factor characterizing the internal or intramolecular interferences and the terms in brackets describe the external or intermolecular interferences. M is the molecular weight of the scattering particles, C the concentration in grams per cubic centimeter, N_a Avogadro's number, and $U(r)$ the interaction potential between the particles. h is written for $[(4\pi/\lambda)\cdot\sin\theta/2]$ where λ is the wavelength of light in the medium and θ is the scattering angle.

Burchard[29] has shown that the integral in eq 5 may be expressed in terms of the excluded volume of the macromolecules and a continuously decreasing function $\Phi(\theta)$ similar to the scattering factor $P(\theta)$. Equation 5 then takes the form

$$P'(\theta) = P(\theta)\left[1 + \frac{C}{M}N_aV_{\text{excl}}\Phi(\theta)\right]^{-1} \qquad (6)$$

with

$$V_{\text{excl}} = \int_0^\infty (1 - e^{-U(r)/kT})4\pi r^2\mathrm{d}r \qquad (7)$$

and

$$\Phi(\theta) = (1 - h^2\overline{r^2}/6 + \ldots) \qquad (8)$$

defined as

$$\overline{r^2} = \frac{\int_0^\infty r^2(1 - e^{-U(r)/kT})4\pi r^2\mathrm{d}r}{\int_0^\infty (1 - e^{-U(r)/kT})4\pi r^2\mathrm{d}r} \qquad (9)$$

The form taken by the function $\Phi(\theta)$ for a given value of $\overline{r^2}$ will depend on the form of the interaction potential $U(r)$. Nevertheless, as observed for the $P(\theta)$ function, the first two terms of the $\Phi(\theta)$ function are perfectly general and, according to eq 6 and 8, a plot $\{[P(\theta)/P'(\theta)] - 1\}$ against $\sin^2\theta/2$ should yield a curve with a linear initial part, the intercept and the slope of which being a measure of V_{excl} and $\overline{r^2}$, respectively. Unfortunately, this linear initial region is not always accessible to experiment. In such a case, correct interpretation of experimental data needs the knowledge of the exact expression for $\Phi(\theta)$. Nevertheless, as suggested by Burchard,[29] one can hope to have a better approximation of the initial behavior of $\Phi(\theta)$ by plotting ln $\{[P(\theta)/P'(\theta)] - 1\}$ against $\sin^2\theta/2$. This is justified by the similarity of the function $\Phi(\theta)$ with the normal particle-scattering factor $P(\theta)$ for which Guinier's law is a better approximation of the exact power series than the two first terms.

Relation 6 leads to the following equation for the reciprocal of the scattered intensity

$$\frac{KC}{I_\theta} = \frac{1}{MP'(\theta)} = \frac{1}{MP(\theta)} + 2A_2\frac{\Phi(\theta)}{P(\theta)}C \qquad (10)$$

where K is an optical constant and A_2 is the second virial coefficient equal to^2 $N_aV_{\text{excl}}/2M^2$.

Equation 10 differs from the classical relationship of Zimm[32] by the ratio $\Phi(\theta)/P(\theta)$ appearing in the second virial term. Since $P(\theta)$ and $\Phi(\theta)$ both approach unity as θ approaches

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Table III

Apparent Molecular Weight, Apparent Radius of Gyration, Excluded Volume, and Radius of Gyration of the Excluded Volume Determined by Light Scattering in Chlorobenzene

Sample	$M_{ap} \times 10^{-5}$	$(R_{ap}^2)^{1/2}$, Å	$V_{excl} \times 10^{-8}$, Å^3	$(r^2)^{1/2}$,^{a} Å
SI-a-6	10.4	279	13	1010
SI-a-7	1.70		0.7	350
SI-b-7	5.53	257	5.6	550
M-11	4.80	285	3.3	

^{a} Average value.

zero, A_2 and V_{excl} can still be evaluated from the initial slope of the zero-angle curve in the Zimm plot. On the other hand, the ratio $P(\theta)/P'(\theta)$ can be estimated from the experimental ratio $[C/I_\theta]/[C/I_\theta]_{C=0}$.

These methods were applied to the data obtained for samples SI-a-6, SI-a-7, and SI-b-7 in chlorobenzene. Typical curves of ln $\{[P(\theta)/P'(\theta)] - 1\}$ against $\sin^2 \theta/2$ are given in Figure 4. For the three systems studied, the initial slopes of these curves are nearly independent of concentration in the fourfold range investigated, which means that $\overline{r^2}$ is approximately independent of concentration. Values obtained for V_{excl} and $\overline{r^2}$ are summarized in Table III. To facilitate a comparison, measurements were also performed in chlorobenzene for a polystyrene sample (M-11) of narrow distribution and of approximately the same molecular weight as the calculated molecular weight of polystyrene blocks of copolymers SI-a-6 and SI-b-7, which are approximately equal to 5 × 10^5 and 4 × 10^5, respectively. Results obtained for this sample are shown at the bottom of Table III. According to these results, the excluded volume of polystyrene blocks in the copolymers is considerably larger than that of the homopolystyrene of the same molecular weight, twice as large for sample SI-b-7 which contains 25% of polyisoprene and four times as large for sample SI-a-6 which contains 50% of polyisoprene. On the other hand, the values reported in Table III appear to correspond satisfactorily to the excluded volumes expected for the whole molecules.

In Table III we have also listed values for R_{ap}^2 and M_{ap} calculated from the same data, *via* the extrapolated angular envelopes at $C = 0$. According to the previous discussion, R_{ap}^2 so obtained may be interpreted as the radius of gyration of the polystyrene part of the copolymer and M_{ap} as the apparent molecular weight of the whole copolymer. With respect to molecular weights, the comparison with calculated values given in Table I shows a reasonable agreement. On the other hand, values obtained for R_{ap}^2 are very significant. Results are shown for samples SI-a-6 and SI-b-7. SI-a-7 is not shown since its coil dimension for the polystyrene part is too small for accurate determination. One observes that the three samples SI-a-6, SI-b-7, and M-11 exhibit roughly the same values for the radii of gyration of the polystyrene coils. For these two copolymers, the radius of gyration of the excluded volume $(\overline{r^2})^{1/2}$ is respectively three times and twice as large as the radius of gyration of the polystyrene coil.

Discussion

In solvents in which the whole polymer molecule scatters light, the Zimm plots are normal and show, in good solvents, only a small decrease in dissymmetry with increased concentration as expected for weak intermolecular interference effects. In solvents such as benzene and particularly chlorobenzene, where the isoprene units provide only a small or negligible contribution to the scattered light, intermolecular interference effects are very important. This latter effect depends on both types of unit being on the same chain and presumably in block form, for no such effects have been reported for random copolymers. An artificial mixture of homopolystyrene and homopolyisoprene (equal weights of each, $M \sim 250{,}000$) in chlorobenzene does not show the abnormal angular dependence shown in Figures 2 and 3, at least in the concentration range up to 1%. The effect is not restricted to styrene–isoprene block copolymers, since abnormal Zimm plots of this type have been observed in a styrene–methyl methacrylate A–B-type copolymer ($M \sim 300{,}000$) in benzene solution. This solvent has a refractive index close to that of poly(methyl methacrylate).

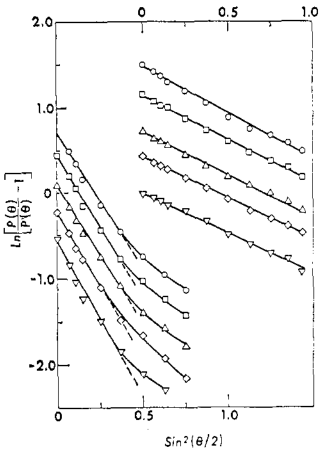

Figure 4. Plots of ln $\{[P(\theta)/P'(\theta)] - 1\}$ against $\sin^2 \theta/2$ for the block copolymers SI-a-6 (left) and SI-b-7 (right) in chlorobenzene.

For the styrene–isoprene block copolymers in chlorobenzene, the intermolecular excluded volume is comparable to that in THF. P_θ is, however, much closer to unity than in the latter solvent, so P_θ' depends more strongly than normal on intermolecular interference effects. Normally, inter- and intramolecular interference effects tend to cancel each other's action on the angular dependence of scattering. In fact, it can be shown approximately that if the P_θ function in chlorobenzene had reflected the size of the whole macromolecule rather than that of the smaller styrene part, then the observed maxima in scattered intensity would disappear, at least in the observable angular range. There would still be a pronounced variation of dissymmetry with concentration according to this calculation, but whether this is the result of inaccuracy in estimation of the P_θ function for the whole molecule in chlorobenzene or reflects some additional ordering of styrene parts of the molecules is not clear. In any case, to a large extent, the abnormal plots are the direct result of the application of normal light-scattering laws to a system in which the observable part of the macromolecule is smaller than the whole.

That this is so is clear from the results in Table III. In chlorobenzene there is a small negative contribution for polymer SI-a-6 of the isoprene segments to the measured radius of gyration, but this is completely negligible for polymer SI-b-7. The experimental values correspond essentially to the radius of gyration of the styrene segments, which is within experimental error unchanged from its value in a homopolystyrene of the same molecular weight. The total radius of gyration of the macromolecule is obviously larger.

In other solvents there are variable positive contributions to the measured radius of gyration from the rest of the molecule. If it is assumed that the segment distribution is normal and is at least approximately gaussian, then in solvents such as MIBK or THF, of refractive index far from either polymer component, for polymer SI-a-6, R_{ap}^2 will be close to the true value.

$$R_{ap}^2(\text{MIBK}) = 1.07R_a^2 + 0.92R_b^2 \qquad (11)$$

The actual radius of gyration on these assumptions is simply $R_a^2 + R_b^2$, with $\overline{G_aG_b}^2 = 2(R_a^2 + R_b^2)$.[33] If it is assumed that, as in chlorobenzene, R_a^2 and R_b^2 are unchanged from their values in the corresponding homopolymers, these can be calculated from data on polymer M-11 and estimated for isoprene from viscosity data.[34] The value calculated ($R_{ap}^2 = 10.5 \times 10^4$ Å^2) is appreciably lower than that observed (14.7×10^4 Å^2) in MIBK. This difference becomes smaller in good solvents such as benzene. Unfortunately, it is not possible to decide if the discrepancy in MIBK is caused by individual coil expansions caused by the presence of the other component in this poor solvent or by the formation of a more separated structure. In any case, it is clear that even gaussian statistics naturally provide some separation of the two polymer components. The mean-square distance between their centers of mass is twice the total radius of gyration. The results in chlorobenzene obviously require some separation of the two types of monomer unit, but whether this is produced by normal sequence distributions or is in a more exaggerated form cannot be decided by the present data.

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Block Copolymerization. III. Syntheses of Multiblock Copolymers of Polytetrahydrofuran and Polystyrene by Ion Coupling

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ABSTRACT: Multiblock copolymers of an (AB)$_n$ type were prepared by ion coupling of the polytetrahydrofuran (THF) dication and the polystyrene (St) dianion. The poly-THF dication was prepared by the polymerization of THF with 2,2′-octamethylene bis-1,3-dioxolenium perchlorate as a bifunctional initiator. The poly-St dianion was prepared by carboxylating the living polymer of St in THF initiated with α-methylstyrene tetramer dianion. The formation of multiblock elastomers such as (THF$_{110}$–St$_{53}$)$_{30}$ by ion coupling is a good indication of the high purity of the poly-THF dication and the poly-St carboxylate dianion.

Since the discovery of the cationic living polymer of tetrahydrofuran (THF), a unique method for forming a block copolymer by linking cationic living polymer with anionic living polymer has been suggested.[1] The present investigation aims at the synthesis of a multiblock copolymer of an (AB)$_n$ type by ion coupling of the poly-THF dication and the polystyrene (poly-St) dianion. Such an approach can prove the formation of the living polymer of THF, and is also useful for the syntheses of novel block copolymers. Although some multiblock copolymers have been prepared by condensation, a block copolymer consisting of long and well-characterized sequences is expected to present some information about structure–property relationships.

Although previous work suggested the possibility of ion coupling, it was still insufficient to prove the absence of homopolymers. Berger, Levy, and Vofsi[1] and, independently, Asami and Chikazawa[2] treated poly-THF cations with poly-St anions, and the partial formation of THF–St or THF–St–THF block copolymers was characterized by fractional precipitation. Although the poly-St dianion can be prepared easily by using the α-methylstyrene tetarmer dianion, a new bifunctional initiator is necessary to prepare the poly-THF dication. In previous papers,[3] we reported the formation of poly-THF dication by using bisdioxolenium perchlorate initiator. To obtain a multiblock copolymer, ion coupling must proceed without any side reactions, and some modification of the poly-St dianion was studied. The preparation of the initiator, the polymerization, and the ion coupling reaction were carried out in a high-vacuum system (10^{-6} mm).

Experimental Section

Materials. α-Methylstyrene (MS) and styrene (St) were purified in the usual manner, dried with calcium hydride in a high-vacuum system, and distilled into a small ampoule. Tetrahydrofuran (THF) was refluxed over sodium metal and sealed in an ampoule after distillation from a green-colored solution of sodium naphthalene in a high vacuum system. Ethylene oxide (EO) was dried over calcium hydride and distilled into a small ampoule in a high-vacuum system. Carbon dioxide gas was purified by passing through a silica gel–calcium chloride packed column in a high-vacuum system, and sealed in an ampoule.

Preparation of Cationic Initiator. 2,2′-Octamethylenebis-1,3-dioxolenium perchlorate (OMDO-ClO$_4$) was prepared by the addition of bis-2-bromoethyl sebacate to the dry nitromethane solution of silver perchlorate as described in a previous paper.[3]

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