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Conformation of Styrene-Isoprene Block Copolymers in Dilute Solution†

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Viscosity, gel permeation chromatography and light scattering data for two- and three-block copolymers of styrene and isoprene of various compositions and molecular weights have been determined in methylisobutyl ketone at 35°, a near theta solvent for both polystyrene and polyisoprene. The three techniques show that the molecular dimensions of the copolymers are only slightly larger than the sum of the unperturbed dimensions of individual sequences. Such results are interpreted in favour of a nearly segregated conformation with a limited number of heterocontacts.

1 INTRODUCTION

Dissimilar homopolymers are generally incompatible as evidenced by a general phenomenon of phase separation in ternary systems consisting of two polymeric species and a common solvent.^{1,2} The structural feature of block or graft copolymers is that long sequences of dissimilar polymers are chemically connected together inside the same molecules. If interactions of a repulsive nature exist between the dissimilar sequences, an intramolecular phase separation can be expected. This kind of intramolecular segregation is universally recognized to occur in the solid state, in the melt or in the concentrated solutions, where it leads to the formation of microscopic domains.^{3,4} However, the situation with regard to dilute solutions is still not clear. In order to solve this problem, solution properties of a number of block copolymer systems, principally those of styrene-methyl methacrylate,^{5–7} styrene-isoprene^{8–10} and

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styrene-butadiene,¹¹ have received much attention in the recent years. For solvents which dissolve both types of chains, the general behavior of block copolymers can be summarized as follows. Intrinsic viscosities and both short-range and long-range intramolecular interaction parameters are generally intermediate of those of the corresponding homopolymers of equal molecular weight. This behavior contrasts with that of random copolymers which show larger hydrodynamic volumes and larger interaction parameters.⁵⁻⁷ There are two different interpretations for these solution properties of block copolymers. One interpretation suggests a segregated structure in which the chemically different units do not interpenetrate,^{5,6,9,10} while another postulates a more interpenetrating "pseudogaussian" structure.^{7,8,11} The first hypothesis was advanced in order to explain the apparent negligible influence of the polymer-polymer interaction parameter χ_{ab} on the solution properties. It was rendered still more valid by the recent observations of discontinuities when measuring the intrinsic viscosities, second virial coefficients and apparent radii of gyration as a function of temperature.^{8,12-15} Unfortunately, this phenomenon has not been observed by all experimenters who examined apparently identical systems.¹⁰

In a series of previous papers,^{9,10,16} we successively applied viscometry and gel permeation chromatography to the study of solution properties of two- and three-block copolymers of styrene and isoprene in various solvents. The properties of these copolymers conform to the general behavior mentioned above. Moreover, it was shown that intrinsic viscosities as well as K_θ and B parameters obtained from the Stockmayer-Fixman plots are very nearly equal to the weighted average of those of homopolymers of the same molecular weight. The GPC study was performed with toluene, a good solvent for both polystyrene (PS) and polyisoprene (PI). The data obtained obey well the universal calibration, $\log [\eta]M$ vs. elution volume, as proposed by Benoit *et al.*^{17,18} This implies that such a plot could have been used to determine the molecular weight of the copolymers under consideration. On the other hand, from the molecular weight calibration procedure, it was observed that the copolymer data points were near the polyisoprene curve in the range where data were obtained for this homopolymer. This discrepancy from a weighted average of hydrodynamic volumes was interpreted as small expansion due to hetero-contact interactions.

In the present paper, viscosity, GPC as well as light scattering data obtained in methylisobutyl ketone will be discussed. In such a poor solvent for both homopolymers, it is expected that the effect of interactions between unlike segments will be more easily detectable because of the smaller expansion due to solvent-polymer interactions. In order to make a more accurate comparison with the parent homopolymers, a series of polyisoprenes of wider molecular weight range was examined.

2 EXPERIMENTAL

The anionic synthesis and the characterization of the block copolymers have been described elsewhere.^{9,10} The reactions were carried out at 25° in benzene using *sec*-butyllithium as initiator. For the two-block copolymers, designated as SI, styrene was polymerized first and isoprene was added slowly by distillation. The same sequential procedure was followed for the three-block copolymers, designated as SIS, except that one per cent of THF was introduced before the last addition of styrene. This accelerates the otherwise slow reaction of polyisoprenyllithium with styrene and reduces the heterogeneity of the final styrene sequence. The polyisoprene samples were prepared under the same conditions. Their microstructure is 71% *cis*, 22% *trans* and 7% 3,4. Both block copolymers and polyisoprenes were stored under vacuum at -15°. The polystyrenes used were narrow distribution samples supplied by Waters Associates. As indicated in Table I, the ratios M_w/M_n for both the homopolymers and the block copolymers are lower than 1.1 for M_w lower than 5×10^5 and lower than 1.2 for the samples of higher molecular weight.

Number average molecular weights were determined in toluene using a Mechrolab 503 rapid membrane osmometer, with Schleicher and Schuell 08 grade membrane filters. Weight average molecular weights were determined in cyclohexane at 35° using a Sofica light scattering apparatus, with unpolarized light of wavelength 4358 Å. Benzene was used as standard with Raleigh ratio of $51 \times 10^{-6} \text{cm}^{-1}$. In the aforesaid conditions, the refractive index increments, dn/dc , of PS and PI are 0,180 and 0,117 cm^3/g , respectively.¹⁹ The values of dn/dc for the block copolymers have been observed to be close to the weight averages of those of the homopolymers. Intrinsic viscosities were determined using Cannon-Ubbelohde semi-micro dilution viscometers checked to have negligible kinetic energy corrections. The reagent-grade methylisobutyl ketone used for light scattering and viscosity measurements was purified according to the method previously described.⁹ Antioxidant (0.02% of 2, 6-di-*t*-butyl-4-methoxyphenol) was added to the solutions.

GPC measurements were carried out on Waters Associates Model 200 instrument. A series arrangement of three Waters columns containing porous silica beads (Porasil) with upper porosity designation 10^6 , 10^5 and 5×10^4 Å was used. The flow rate was 1 cm^3/min and 2 cm^3 of solution at a concentration of 0.005 g/cm^3 were injected. The solvent, 99.5%-grade methylisobutyl ketone supplied by Aldrich Chemical Company, was used as received. Solutions were prepared with 0.02% of the aforesaid antioxidant. This was found to be necessary with MIBK which gave evidence of extensive breakdown of polyisoprene chains in absence of antioxidant. As checked with the polystyrene standards, the presence of this low molecular weight material is not affecting the results in the range of molecular weights studied in the present work.

3 RESULTS AND DISCUSSION

Molecular characteristics, intrinsic viscosities and peak elution volumes are summarized in Table I. The molecular weights obtained from light scattering are apparent values in the case of the copolymers. Nevertheless, in the case of sufficiently homogeneous block copolymers, the results computed from the equations valid for homopolymers are expected to approximate the true M_w , particularly when the refractive index increments are high for both parent homopolymers. Such is the case for cyclohexane which was the solvent used for M_w determinations. In view of the small difference between M_w and M_n for all the samples studied here and in view of the averages being normally found nearer to M_w than to M_n when deduced from intrinsic viscosities and from peak elution volumes, the weight average was used throughout this investigation.

TABLE I

Molecular characteristics, intrinsic viscosities and peak elution volumes in methylisobutyl ketone at 35°

Sample	w_{PS}^a	$10^{-5}M_n$	$10^{-5}M_w$	$[\eta]$ dl/g	V_e ml
PS-1 ^b	1.00	7.73	8.67	0.843	98.5
PS-2		3.92	4.11	0.590	106.9
PS-3		1.93	2.00	0.406	116.4
PS-4		1.11	1.11	0.304	121.9
PS-5		0.33	0.36	0.159	131.7
PS-6		0.200	0.208	0.123	134.5
PI-3	0	3.19	3.39	0.899	105.5
PI-6		1.49	1.60	0.585	114.5
PI-7		1.77	1.93	0.633	112.8
PI-8		0.573	0.653	0.353	123.5
PI-9		4.20	4.35	1.04	102.7
PI-10		—	9.15	1.59	94.5
SI-a-2	0.48	0.947	1.04	0.383	121.5
SI-a-5	0.50	2.21	2.40	0.601	111.5
SI-a-6	0.48	—	10.5	1.39	95.2
SI-b-1	0.76	0.31	0.355	0.179	131.2
SI-b-2	0.75	1.275	1.36	0.376	119.2
SI-b-6	0.75	2.74	2.94	0.575	110.9
SI-b-7	0.74	4.8	5.25	0.792	103.9
SI-c-1	0.24	5.3	6.47	1.26	98.5
SI-c-2	0.25	0.58	0.616	0.330	124.8
SIS-1	0.65	1.54	1.83	0.473	115.0
SIS-4	0.63	5.1	6.32	1.01	100.0
SIS-5	0.40	1.96	2.25	0.606	111.5

^a Calculated from the polymerization data.

^b Values of M_n and M_w for the PS standards are those reported by Waters Associates, Inc.

At 35°, methylisobutyl ketone is a poor solvent for both polystyrene and polyisoprene. Although no direct determinations of the theta temperatures have been done for these two systems, this assertion is evident from plots of $\log [\eta]$ vs. $\log M_w$ where the Mark-Houwink K and a parameters obtained are 6.19×10^{-4} and 0.53 for PS and 6.07×10^{-4} and 0.57 for PI. When binary copolymers are dissolved in such a near theta solvent and providing that a sufficient number of heterocontacts exists, it is expected that the repulsive interactions between unlike units would result in a positive coil expansion.²⁰ According to Froelich and Benoit,²⁸ the expansion factor of a "pseudo-gaussian" copolymer coil can be related to the three parameters z_{aa} , z_{bb} and z_{ab} which characterize the interactions between the similar and unlike units as follows

$$\langle R^2 \rangle / \langle R^2 \rangle_0 = 1 + (134/105) (C_{aa} z_{aa} + C_{bb} z_{bb} + C_{ab} z_{ab}) + \dots \quad (1)$$

where $\langle R^2 \rangle$ and $\langle R^2 \rangle_0$ are the actual and the unperturbed mean square radius of gyration and C_{ij} are the appropriate probabilities for i - j contacts along the chain contour. When both z_{aa} and z_{bb} vanish (*i.e.*, when both homopolymers are under theta conditions), it can be shown⁵ that z_{ab} becomes proportional to χ_{ab} , the difference in interaction free energy in forming a - b contact from a - a and b - b contacts. Under such conditions, $\langle R^2 \rangle / \langle R^2 \rangle_0$ is governed solely by the magnitude of χ_{ab} . If this parameter becomes negligible, the dimension of the copolymer is the unperturbed one given by

$$\langle R^2 \rangle_{0,\text{copol}} = \langle R^2 \rangle_{0,a} + \langle R^2 \rangle_{0,b} \quad (2)$$

where $\langle R^2 \rangle_{0,a}$ and $\langle R^2 \rangle_{0,b}$ are the unperturbed radii of gyration of homopolymers A and B of the same molecular weight as parts A and B of the copolymer. If we assume as a first approximation that in methylisobutyl ketone one obtains unperturbed coil dimensions for both homopolymers, Eq. (2) can be used to check the contribution of heterocontact effects on the dimensions of the block copolymers.

3.1 Viscometry

For homopolymers, the theoretical dependence of $[\eta]$ on chain dimensions has been calculated by several authors. In the limit of negligible draining effect, these results all reduce to the form

$$[\eta] = \Phi_0' \langle R^2 \rangle_\eta^{3/2} / M \quad (3)$$

where Φ_0' is supposed to be a universal constant. Using the value of Φ_0' evaluated by Pyun and Fixman²¹ ($\Phi_0' = 39.4 \times 10^{21}$ when $[\eta]$ is given in deciliters per gram), we have computed $\langle R^2 \rangle_\eta$ for both homopolymers and block copolymers. The results are shown in Figure 1 as well as the theoretical dimensions calculated from Eq. (2) and data for homopolymers. As mentioned

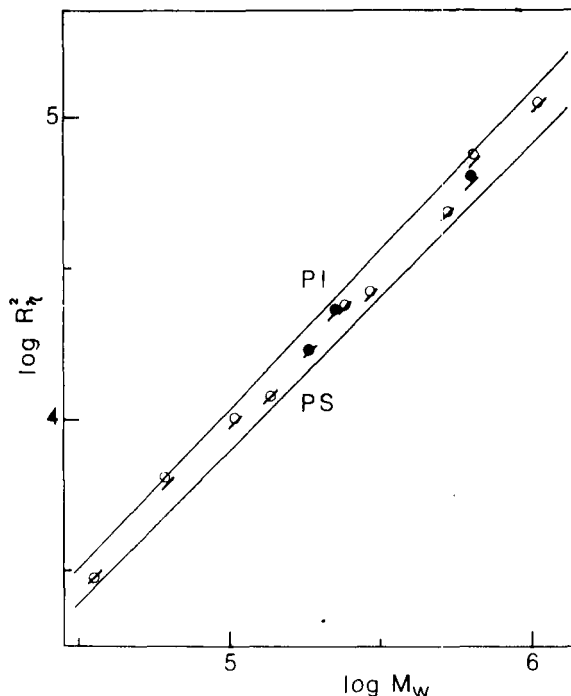


FIGURE 1 Plot of $\log \langle R^2 \rangle_\eta$ vs. $\log M_w$. (○) two-block copolymers, (●) three-block copolymers, (—) calculated from Eq. (2). Solid curves for parent homopolymers.

above, Eq. (2) is strictly valid under the assumptions that the two homopolymers are under theta conditions and that the heterocontact effects are negligible. In the case of our block copolymers, it can be seen quite clearly that their actual dimensions are only slightly larger than the theoretical dimensions, which means that the heterocontact effects are very small. In fact, $\langle R^2 \rangle / \langle R^2 \rangle_0$ shows an average value of 1.04 ± 0.03 for all the samples studied.

3.2 Gel permeation chromatography

Figure 2 shows the plot of $\log [\eta]M_w$ vs. peak elution volume for all data. The smoothed curve is the calibration curve drawn through the data points (not shown) for the polystyrene standards. As observed previously in toluene, the polyisoprene and the block copolymer data points fit well the calibration curve. Only small disagreements occur for the block copolymers of high molecular weight, but a close examination shows that in that range, the molecular weights evaluated from the calibration curve are correct within a margin of 20%. Therefore, the results of this investigation are consistent with those of our previous

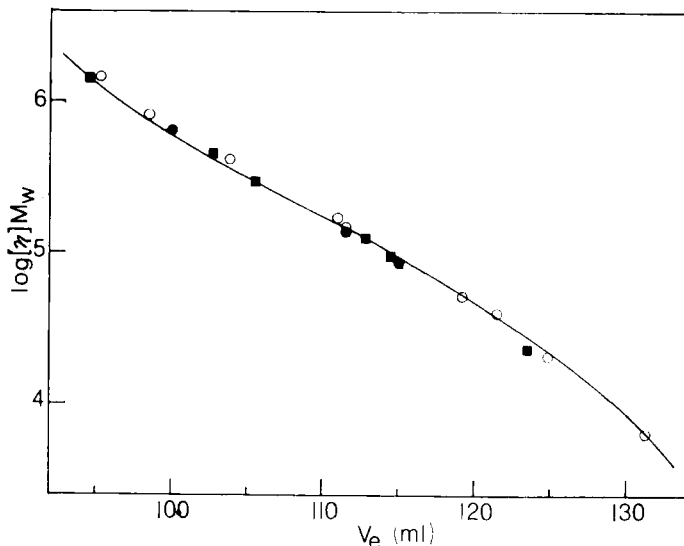


FIGURE 2 Plot of $\log [\eta]M_w$ vs. elution volume. Solid curve for polystyrene, (■) polyisoprene, (○) two-block copolymers, (●) three-block copolymers.

investigation using toluene and confirm the correctness of the universal calibration based on $[\eta]M$. In fact, if one excludes specific interactions between the polymers and the stationary phase, retention time in GPC can be considered to depend on the depth to which each species is able to diffuse into the pores. According to that, the hydrodynamic volume of the polymer seems to be the appropriate parameter governing GPC separation. That $[\eta]M$ is a measure of hydrodynamic volume can be shown from Einstein's law for the viscosity of a dilute suspension of spherical particles. On the other hand, as shown by Rudin and Hoegy,²² the fact that $[\eta]$ is obtained at infinite dilution while peak elution volumes are measured at finite but low concentrations is likely to be of weak consequence on the adequacy of the method as long as the chemically different polymers show similar solvating powers. This is nearly the case for PS and PI in both toluene and methylisobutyl ketone.

To investigate the matter further, we should now attempt to estimate the hydrodynamic volumes from the peak elution volumes and compare the results to the unperturbed hydrodynamic volumes calculated from Eq. (2) and (3):

$$V_{h,\text{copol}}^{2/3} = V_{h,a}^{2/3} + V_{h,b}^{2/3} \quad (4)$$

in which $V_{h,a}$ and $V_{h,b}$ are the unperturbed hydrodynamic volumes of parts A and B in the block copolymers. Figure 3 shows the molecular weight calibration plots (*i.e.*, $\log M_w$ vs. peak elution volume) for both polystyrene and polyisoprene. It can be seen that these calibration curves are neither linear nor

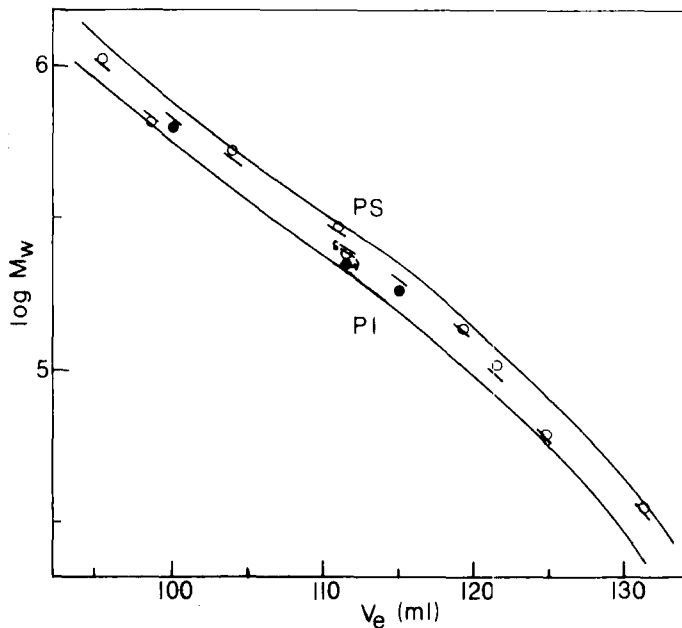


FIGURE 3 Plot of $\log M_w$ vs. elution volume. (○) two-block copolymers, (●) three-block copolymers, (—) calculated from Eq. (5). Solid curves for parent homopolymers.

perfectly parallel to each other. Therefore, it is not easy to evaluate directly V_h from the peak elution volumes and applied Eq. (4). Nevertheless, as suggested by Cramond *et al.*²³ and Runyon *et al.*,²⁴ one can suppose that if there were no heterocontact effects, the molecular sizes of block copolymers expressed as $\log M_{\text{copol}}$ should be given by the weighted average

$$\log M_{\text{copol}} = w_a \log M_a + w_b \log M_b \quad (5)$$

in which w_a and w_b are the weight fractions of constituents A and B, and M_a and M_b are the molecular sizes of the corresponding homopolymers at the same peak elution volume as the copolymer. Such an approximation is debatable but, at least, it provides a simple and new way to study the conformation of block copolymers. Both experimental and theoretical data are shown in Figure 3. It can be seen that the values of M_{copol} computed by means of Eq. (5) are relatively close to the actual molecular weights M_w . In fact they are slightly lower for the two-block samples and systematically higher for the three-block samples. In the case of the two-block copolymers, the magnitude of the differences is such that there is no way of deciding whether the apparent coil contraction observed reflects experimental inaccuracies or inadequacy of Eq. (5). In contrast, the three-block copolymers show a systematically small

expansion which might be explained by the larger number of heterocontacts favoured by their architecture.

3.3 Light scattering

Radii of gyration determined according to the method of Zimm (*i.e.*, from the initial slope of the angular envelope at zero concentration) are reported in Table II for a group of samples selected for their high molecular weight. As demonstrated by Benoit *et al.*,^{25,26} when this method is applied to block

TABLE II
Light scattering data

Sample	dn/dc	$10^{-4}\langle R^2 \rangle_{LS}(\text{\AA}^2)$	$10^{-4}\langle R^2 \rangle_{0,b}(\text{\AA}^2)$
PS-1	0.214 ^a	8.30	
PS-2		3.32	
PS-3		1.38	
PI-3	0.157 ^a	5.77	
PI-9		7.34	
PI-10		17.2	
SI-a-6	0.183	14.7	13.7
SI-b-7	0.198	5.11	4.65
SI-c-1	0.170	10.6	10.5
SIS-4	0.191	10.6	7.93

^a Estimated from a plot of dn/dc against solvent refractive index.

^b Theoretical values computed by means of Eqs. (7) or (8).

copolymers it leads to an apparent mean square radius of gyration $\langle R^2 \rangle_{LS}$ given by

$$\langle R^2 \rangle_{LS} = \alpha \langle R^2 \rangle_A + \beta \langle R^2 \rangle_B + \alpha\beta \langle r^2 \rangle \quad (6)$$

where α and β are quantities equal to $w_a\nu_a/\nu$ and $w_b\nu_b/\nu$, and ν_a , ν_b and ν are the refractive index increments of homopolymer A, homopolymer B and copolymer. $\langle R^2 \rangle_A$ and $\langle R^2 \rangle_B$ are the mean square radii of gyration about the centers of gravity G_a and G_b of parts A and B, and $\langle r^2 \rangle$ is the mean square distance of the centers of gravity G_a and G_b . Moreover, using normal gaussian coil statistics, the same authors²⁶ have calculated $\langle R^2 \rangle_A$, $\langle R^2 \rangle_B$ and $\langle r^2 \rangle$ for different types of block copolymers. In the case of AB architecture their formulae lead to

$$\langle R^2 \rangle_{0,LS} = \alpha(1 + 2\beta)\langle R^2 \rangle_{0,a} + \beta(1 + 2\alpha)\langle R^2 \rangle_{0,b} \quad (7)$$

and for the symmetrical ABA architecture to

$$\langle R^2 \rangle_{0,LS} = \alpha(2 + \beta)\langle R^2 \rangle_{0,a} + (\beta + \frac{1}{2}\alpha\beta + \frac{3}{2}\alpha)\langle R^2 \rangle_{0,b} \quad (8)$$

in which $\langle R^2 \rangle_{0,a}$ and $\langle R^2 \rangle_{0,b}$ are the unperturbed mean square radii of gyration

of the individual sequences A and B. Since these equations are strictly valid under theta conditions involving no heterocontact effects, they provide a new point of comparison to check the behavior of our block copolymers. Last column of Table II shows the values of $\langle R^2 \rangle_{0,LS}$ computed by means of Eqs. (7) and (8) using the refractive index increments also reported in the table. The appropriate values for $\langle R^2 \rangle_{0,a}$ and $\langle R^2 \rangle_{0,b}$ were evaluated by means of the log $\langle R^2 \rangle_{LS}$ vs. log M_w plots drawn from the data on the two homopolymers. It is interesting to note that here again the expansion factor of the only three-block sample studied contrasts with those of the two-block samples. For the two-block copolymers SI-a-6, SI-b-7 and SI-c-1, $\langle R^2 \rangle / \langle R^2 \rangle_0$ is equal to 1.07, 1.09 and 1.01, respectively, when $\langle R^2 \rangle / \langle R^2 \rangle_0$ of sample SIS-4 reaches the larger value of 1.25.

4 CONCLUSION

From the above results we may conclude that the product $C_{ab}z_{ab}$ which characterizes the effect of intramolecular *a-b* interactions on styrene-isoprene block copolymers is very small, particularly for the AB architecture. As pointed out previously, when solvent is theta for both homopolymers (*i.e.*, $\chi_{as} = \chi_{bs} = 0.5$), the parameter z_{ab} is proportional to χ_{ab}

$$z_{ab} = (3/2\pi)^{3/2} l^{-3} M^{1/2} (\bar{v}^2/V_1 N_A) \chi_{ab} \quad (9)$$

where l is the unperturbed effective segmental length $(6\langle R^2 \rangle_0/M)^{1/2}$, \bar{v} is the specific volume of the polymer, V_1 is the molar volume of the solvent and N_A is the Avogadro number. Therefore, from the present data alone, distinction between interpenetrated conformation ($C_{ab} > 0$) and segregated conformation ($C_{ab} \simeq 0$) (for which Eqs. (1)–(3) are no longer valid), would depend largely on the estimated value for χ_{ab} . This term is strongly solvent dependent as shown by Dondos and Benoit²⁷ from a study of styrene-methyl methacrylate random copolymers. In fact, χ_{ab} increases when solvent power decreases. Although such a study has not been done yet for styrene-isoprene random copolymers, a rough estimation of the magnitude of χ_{ab} obtained from cohesive energy densities predicts a value close to 0.2 for this parameter. For a block copolymer such as sample SI-a-6 ($M = 10^6$ and $w_{PS} = 0.5$), this figure used in Eq. (9) leads to a predicted z_{ab} of close to 1.2. By using this value of z_{ab} and the value of $\langle R^2 \rangle / \langle R^2 \rangle_0$ (1.07) obtained by both viscosity and light scattering for this sample, the frequency factor C_{ab} can be calculated from Eq. (1). The result, $C_{ab} = 0.05$, is considerably lower than the value of 0.31 predicted independently by Froelich and Benoit²⁸ and Pouchly *et al.*²⁹ for a gaussian equimolar AB block copolymer in which polymer A and polymer B have the same unperturbed effective segmental length.

On these grounds it is clear that styrene-isoprene two- and three-block

copolymers exhibit a nearly segregated conformation. On the other hand it is interesting to note that the theoretical treatment of Pouchlý *et al.* predicted a sharp decrease of C_{ab} from 0.31 to 0.06 for long chains when χ_{ab} increases from 0 to 0.2 in theta solvent for both homopolymers. But according to these authors, complete segregation ($C_{ab} = 0$) would occur only for a solvent acting as a precipitant for one of the blocks. Our results seem to confirm this view, namely that although there is no complete segregation for our block copolymers, their degree of segregation is such that the heterocontact effect on the global coil dimension is almost negligible.

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DISCUSSION

Prof. S. Krause (*Rensselaer Polytechnic Institute, Troy, New York*): Would you expect GPC calibration curves in selective solvents to be as good as those you observed for the block copolymers in non-selective solvents?

Prof. J. Prud'homme: In selective solvents, the effect of concentration upon the peak elution volumes might be quite different for the two homopolymers and hence result in some inadequacy for the universal calibration procedure.

Dr. G. Thomas Wells (*Dow Chemical Company, Midland, Michigan*): In reference to your slide of intrinsic viscosity *vs.* temperature, what is the effect of changing the ratio of block size on the position and shape of these curves?

Prof. J. Prud'homme: Urwin and Girolamo have reported that plots of intrinsic viscosities *vs.* temperature for two-block copolymers of styrene and isoprene exhibit a discontinuity in cyclohexane and other poor solvents for polystyrene. The slide you are referring to is a reproduction of a figure published by these authors where the discontinuities are seen to depend upon both composition and molecular weight. As we have shown on a second slide, this behavior was not observed for our samples, among which some present the same molecular weights and compositions as those investigated by Urwin and Girolamo.