The carrier migration closely correlates with the segmental motion of the PPO backbone. Substituting eq 7 to eq 6, one obtains

$$\frac{T}{T_{\mathrm{g}}}\,\frac{\sigma(T)/\sigma(T_{\mathrm{g}})}{1/a_{\mathrm{T}}} = A'\exp\left(-\frac{U/2\epsilon}{kT}\right) \quad (8)$$

where A' is a constant. The activation energies (E_{a}) for the dependences of Figure 8 were calculated from the slopes of the linear lines, as shown in the figure. The E_{a} values were compared with the calculated $U/2\epsilon$ values. In the strict sense, the term U should be the effective dissociation energy of the ion pair (U') in the ionic atmosphere. However, the assumption that $U \simeq U'$ greatly simplifies the analysis. The U of $\mathrm{LiClO_4}$ calculated from Kapunstinskii's equation[22] was 7.43 eV. The ϵ values, which could be estimated from the complex impedance measurements, were 7–12. Thus, we could calculate that the $U/2\epsilon$ values were roughly 0.3–0.5 eV. The calculated $U/2\epsilon$ values approximately corresponded to the experimentally obtained E_{a} values. This might imply that the E_{a} values shown in Figure 7 are the activation energy for carrier generation. $\mathrm{LiClO_4}$ incorporated in PEUU does not completely dissociate, and the carrier generation in the PEUU·$\mathrm{LiClO_4}$ complexes obeys the Arrhenius activation process. However, the calculated $U/2\epsilon$ values did not clearly increase with $\mathrm{LiClO_4}$ concentration. Thus, it is still not clear that the activation energy for carrier generation is expressed simply by the term $U/2\epsilon$. A higher activation energy for the PEUU·$\mathrm{LiClO_4}$ complex with [$\mathrm{LiClO_4}$]/[PO unit] = 0.062 may be caused by a stronger ion–ion interaction energy for the carrier generation.

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Sedimentation Behavior of Block and Random Copolymers in the Semidilute Regime

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Received July 15, 1985

ABSTRACT: Sedimentation velocity measurements have been carried out on 1,2-dibromoethane semidilute solutions of styrene–isoprene diblock and random copolymers of various molecular weights in the range $2 \times 10^5 < M_{\mathrm{w}} < 1 \times 10^6$, all having a styrene content of about 50% by weight. The concentration dependence of the sedimentation coefficient s has been examined for both the copolymers and the corresponding homopolymers over the concentration range $0.015 < c < 0.07$ g/cm^3, for which the data were molecular weight independent. The results show that s decreases as $c^{-0.79\pm0.01}$ for both the copolymers and the homopolymers. Though 1,2-dibromoethane is a solvent with moderate affinity for homo-PS and homo-PI, the present behavior is very similar to that observed previously for flexible homopolymers in good solvent conditions. The sedimentation data were analyzed in terms of the permeability coefficient defined by Mijnlieff and Jaspers and the screening effect described by Brochard and de Gennes. The results show that the permeability data for the block polymers are superimposable on the data for homo-PS and homo-PI, the latter being fortuitously identical. They also show that permeability of random copolymers is less than that of block polymers because of the larger number of repulsive heterocontacts inherent in their random structure.

Introduction

The sedimentation behavior of flexible polymer chains in the semidilute regime, that is, above the critical concentration c^* at which chains begin to overlap, has received much attention in recent years.[1-8] At $c > c^*$ the sedimentation process is no longer governed by the hydrodynamic properties of the individual chains as evidenced by the independence of the sedimentation coefficient, s, on molecular weight. The flexible chains form a transient network, and it is the permeability of this network to solvent that governs the sedimentation velocity at a given concentration. Mijnlieff and Jaspers[1] were the first to

0024-9297/86/2219-0819$01.50/0

develop a general theory of polymer sedimentation based on the permeability concept. An important result of this theory is that a permeability coefficient, k, can be evaluated from the sedimentation coefficient by the simple relation

$$k = \frac{\eta_0 s}{c(1 - \bar{v}_2/\bar{v}_1)} \qquad (1)$$

where η_0 is the solvent viscosity and $\bar{v}_2$ and $\bar{v}_1$ are the partial specific volumes of the solute and solvent, respectively, at the concentration c. More recently, Brochard and de Gennes[2] derived for the concentration dependence of k at $c > c^*$ a scaling law of the form

$$k \propto c^{-2\nu/(3\nu-1)} \qquad (2)$$

where ν is the exponent in the relation between the radius of gyration and molecular weight for a single chain

$$R_g \propto M^{\nu} \qquad (3)$$

When applied to eq 1, relation 2 yields a corresponding scaling law for s of the form

$$s \propto c^{(1-\nu)(3\nu-1)} \qquad (4)$$

According to the physical model proposed by Brochard and de Gennes,[2] the transient network can be viewed as an assembly of impenetrable coils (blobs) of hydrodynamic radius ξ_h, the latter being the correlation length above which the hydrodynamic interactions between a segment pair in a given subchain are screened out by the segments of the other subchains in the network. As shown by these authors, the permeability k of such an assembly of blobs should vary as ξ_h^2. It is by assuming that ξ_h displays the same concentration dependence as the correlation length ξ_s derived previously by Daoud and Jannink[9] for the static interactions between segment pairs

$$\xi_s \propto c^{-\nu/(3\nu-1)} \qquad (5)$$

that they arrived at relation 2. Theoretically, relation 5, as well as relations 2 and 4 derived from it, is restricted to two limiting behaviors: that based on a tricritical approach at the Θ conditions for which $\nu = 0.50$, and that based on the excluded volume effect in good solvent conditions for which $\nu = 0.60$.[9] There is no theoretical basis for generalizing relation 5 to systems between Θ and good solvent conditions. For these latter systems, the Daoud and Jannink theory[9] predicts a crossover from good solvent behavior ($\nu = 0.60$) to Θ behavior ($\nu = 0.50$) at another critical concentration c^{**} lying above c^*. Nevertheless, because the screening effect produced by the surrounding subchains is greater for large repulsive interactions than for small repulsive interactions, it is expected that, at a given concentration between c^* and c^{**}, ξ_h and consequently k should decrease with increasing polymer–solvent affinity.

A large body of experimental data has now been published concerning the concentration dependence of s for various homopolymers in the semidilute regime. In these works there was no specific need to extract k from s since both are simply related together by eq 1. The main concern was to test the relevance of a scaling law of the form $s \propto c^{-\alpha}$ and the validity of relation 4 for predicting the value of the exponent α for Θ and good solvent conditions. For Θ systems, the prediction based on the Brochard and de Gennes theory is remarkable.[3,7,8] A simple power relationship is observed between s and c and the experimental values of α are close to the predicted value of 1.0. Unfortunately, the case of good solvent systems is more complex. For these latter systems, a simple power relationship is not observed.[6,7] In other words, the exponent α is not a constant but a variable that slowly increases with concentration. Its values range from 0.6 to 0.8 depending on the concentration range investigated. Only the lowest value, $\alpha = 0.6$, observed at low concentrations for very high molecular weight polystyrene fractions,[5,7] compares favorably with the predicted value of 0.5.

The present paper is concerned with the sedimentation behavior of block and random copolymers in the semidilute regime. In dilute solution, block polymer flexible chains differ from random copolymers by their smaller number of heterocontacts, that is, contacts between unlike monomer units.[10] Increasing the concentration should give rise to a peculiar situation where the unlike chains in block polymer solutions undergo a microphase separation because of their repulsive interactions.[11] Such a situation is not expected for random copolymer solutions. Although, as indicated in a recent work by Hashimoto et al.,[12] the critical concentration at which microphase separation occurs in block polymer solutions might be well above the semidilute regime, the sequential distribution of the unlike monomer units in the latter might affect their sedimentation behavior compared to random copolymers. In order to clarify these points, and more particularly how the permeability coefficients of block and random copolymers compare to those of the corresponding homopolymers in the semidilute regime, sedimentation velocity measurements have been carried out on 1,2-dibromoethane solutions of polystyrenes (PS), polyisoprenes (PI), and styrene–isoprene diblock polymers (SI) having a styrene weight fraction close to 0.5. Also studied was a styrene–isoprene random copolymer of about the same microstructure and the same composition as the block polymers. 1,2-Dibromoethane was chosen as solvent because of its moderate affinity for both homo-PS and homo-PI at 25 °C. In such a solvent, it is expected that the contribution of the repulsive heterocontacts to the excluded volume effect will not be masked by that due to solvent perturbation, as might be the case in a good solvent.[10] Since this solvent is intermediate, thermodynamically, between a Θ and a good solvent, it was also interesting to investigate the concentration dependence of s for PS and PI in that particular situation not explored previously for homopolymers. Another feature of the present solvent is a small refractive index increment, dn/dc, that is positive for PS and the copolymers and negative for PI. This allowed the use of conventional schlieren optics as a monitoring system for the displacement of the sedimentation boundary in solutions of concentrations as high as 0.07 g/cm^3 without undesirable saturation of the patterns.

Experimental Section

Materials. The molecular characteristics of the polymer samples used for the sedimentation study are reported in Table I. The polystyrenes were narrow distribution samples supplied by Waters Assoc. The polyisoprenes and the styrene–isoprene diblock polymers were narrow distribution samples prepared by anionic polymerization using benzene as solvent and *sec*-butyllithium as initiator. Their characterization has been made according to standard procedures described in an earlier work.[13] The random copolymer was also prepared by anionic polymerization in benzene. The details concerning its preparation and its characterization have been published elsewhere.[10] The microstructure of the isoprene units in the PI and SI samples was 71% 1,4-cis, 22% 1,4-trans, and 7% 3,4.[13] The microstructure of the random copolymer was 66% 1,4-cis, 27% 1,4-trans, and 7% 3,4.[10] The solutions were all prepared on a weight basis in reagent-grade 1,2-dibromoethane containing 0.02% of the antioxidant 2,6-di-*tert*-butyl-*p*-cresol. The concentrations (in g/cm^3) were calculated from the density of the solutions measured at 25

Table I
Weight-Average Molecular Weight, M_w, Styrene Weight Fraction, w_s, and Partial Specific Volume, $\bar{v}_2$, of the Sample Materials

sample	$M_w \times 10^{-5}$	w_s	$\bar{v}_2$, g/cm^3
PS-a	1.11	1.00	0.928
PS-b	4.1		
PS-c	6.7		
PI-a	1.60	0	1.10
PI-b	4.35		
PI-c	9.15		
SI-a	1.93	0.48	1.01
SI-b	5.75	0.45	1.02
SI-c	10.5	0.49	1.01
SI-random	2.13	0.46	1.02

°C with a Sodev Model 03D vibrating densimeter. The density measurements were also used for calculating the partial specific volumes, $\bar{v}_2$, of the polymers in the concentration range of the present study ($0.015 < c < 0.07$ g/cm^3). The values of $\bar{v}_2$ thus obtained were concentration-independent in the limit of the experimental error (±0.5%). They are listed in the last column of Table I.

Sedimentation Velocity Measurements. The sedimentation experiments were carried out at 25 °C in a Spinco Model E analytical ultracentrifuge. All runs were performed at 48000 rpm in a 4° single sector cell having an optical path length of 3 mm. The cell was filled at the same level for each run. The displacement of the sedimentation boundary (flotation boundary in the present case) was monitored by means of the schlieren optics. The radial distance r of the solvent–solution boundary was measured as a function of the time at the peak position on photographs of the schlieren patterns. The sedimentation coefficient was determined by a least-squares analysis of the data based on the quadratic relation[8,14]

$$\ln r = \ln r_b + s\omega^2 t + Bt^2 \tag{6}$$

where r_b is the radial position of the bottom of the cell, ω is the angular velocity, and B is a parameter that takes into account both the effect of the hydrostatic pressure gradient in the cell and the effect of the concentration change due to the sector shape of the cell. For solutions with c less than 0.03 g/cm^3, the quadratic term in eq 6 was small and negative. For larger c it was negligible. Note that the value of r at the bottom of the cell, r_b, is used as the origin in eq 6 because of the flotation situation. For the same reason, the values of s obtained by using eq 6 are negative. They correspond to the pressure at the bottom of the cell, that is, approximatively 420 atm in the present case. At this pressure, the concentrations of the solutions are increased by a small factor that depends on their compressibility. It was assumed that this factor should be the same for all the solutions, and no attempt was made to correct the concentration data for this effect.

Results and Discussion

Homopolymers Study. At 25 °C, 1,2-dibromoethane is a solvent with moderate affinity for both PS and PI homopolymers. This can be inferred from the close to 0.6 values of the exponents in the following Mark–Houwink relationships obtained for a series of PS and PI samples of narrow molecular weight distributions in the range $5 \times 10^4 < M_w < 1 \times 10^6$:

$$[\eta]_{PS} = 4.29 \times 10^{-2} M_w^{0.60} \qquad (\mathrm{cm^3/g})$$

$$[\eta]_{PI} = 6.30 \times 10^{-2} M_w^{0.58} \qquad (\mathrm{cm^3/g})$$

Figure 1 shows log s vs. log c plots of the sedimentation coefficients measured on the three PS and the three PI samples of different molecular weights. The range of concentration studied ($0.015 < c < 0.07$ g/cm^3) corresponds to the semidilute regime as indicated by the independence of s on molecular weight in either case. Linear least-squares analysis of the data points in Figure 1 gives the following concentration dependences of s for the two homopolymers:

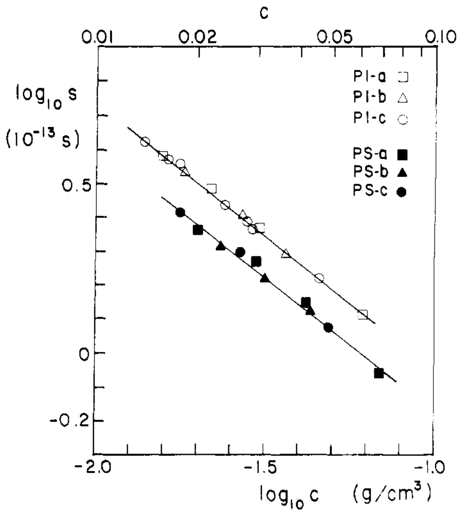

Figure 1. Bilogarithmic plots of the sedimentation coefficient as a function of concentration for polyisoprenes (PI) and polystyrenes (PS) of various molecular weights in 1,2-dibromoethane at 25 °C. For molecular weights, see Table I.

$$s_{PS} = 0.113c^{-0.78} \qquad (10^{-13}\ \mathrm{s})$$

$$s_{PI} = 0.145c^{-0.79} \qquad (10^{-13}\ \mathrm{s})$$

The values of the exponents α in these $s \propto c^{-\alpha}$ relationships are very close to those reported by Pouyet and Dayantis[4] for the good solvent systems PS–bromobenzene and PMMA–benzene in the same range of concentration. They are also in good agreement with the α values one can predict by means of relation 4 derived from the Brochard and de Gennes theory. Indeed, if one applies to relation 4 the values of ν (close to 0.53) deduced from the above Mark–Houwink relationships by means of the well-known relation

$$[\eta] \propto R_g^3/M \propto M^{3\nu-1} \tag{7}$$

one can predict α values of 0.78 and 0.82 for the PS and PI systems, respectively. Nevertheless, this agreement might be fortuitous, particularly if one considers that similar predictions were not proved to be satisfactory for good solvent systems in the concentration range of the present study. For instance, in the case of PS–bromobenzene for which[15] $[\eta] = 1.19 \times 10^{-2} M^{0.72}$, relation 7 yields a ν value of 0.57 from which relation 4 predicts an α value of 0.59, that is, well below the experimental value of 0.82 reported by Pouyet and Dayantis[4] for the concentration range $0.01 < c < 0.07$ g/cm^3. An explanation for this discrepancy has been proposed by Pouyet et al.[6] Essentially, they showed that for non-Θ systems there must be a critical size for the hydrodynamic screening length ξ_h below which the assumption that ξ_h should behave like ξ_s, the static screening length given by relation 5, is no longer valid. They argued that for good solvent systems such as PS–bromobenzene and PMMA–benzene, the actual value of ξ_h, which is a decreasing function of the concentration, reaches this critical size at concentrations well below 0.01 g/cm^3. Their argument was made by applying to ξ_h a theory of chain statistics in good solvent derived by Weill and des Cloizeaux[16] in which it is shown that the hydrodynamic radius R_h of a chain comprising N segments converges much more slowly to its asymptotic limit $R_h \propto N^\nu$ ($\nu = 0.60$ for $N \rightarrow \infty$) than the static radius of gyration of the same chain. Their argument strongly suggests that for non-Θ systems, unless one deals with very high mo-

Table II
Values of Permeability Coefficients, *k*, for PS in Various Solvents Calculated by means of Eq 1 from Sedimentation Data in the Semidilute Regime

solvent	$k \times 10^{14}$, cm^2 c = 0.02 g/cm^3	 c = 0.05 g/cm^3	ref
cyclohexane (35 °C)	64	11.6	8
cyclopentane (20 °C)	65	10.6	7
toluene (25 °C)	20	4.1	7
bromobenzene (25 °C)	16.1	3.1	6
1,2-dibromoethane (25 °C)	18.7	3.7	present work

lecular weight samples, there should be no simple scaling law for describing the concentration dependence of ξ_h and consequently of any property related to ξ_h, such as the permeability coefficient k or the sedimentation coefficient s.

On the basis of the present sedimentation data, it is clear that the excluded volume effect still plays an important role on the sedimentation behavior of systems intermediate between Θ and good solvent systems. As judged from the values of the exponent α alone, this effect appears to be as important as for good solvent systems. In either case, in the concentration range of the present study, the values of α are close to 0.80, that is, well below the values close to 1.0 observed for Θ systems.[3,7,8] A more direct comparison of this effect can be made on the basis of the values of the permeability coefficient k calculated from s at a given concentration by means of eq 1. Because this property is independent of the buoyancy force, it provides a rational basis for comparing the present PS data to PS data reported in the literature for good and Θ solvents. Such a comparison is made in Table II, where values of k calculated from the existing data of s for PS in five different solvents, including the present solvent 1,2-dibromoethane, are given at two concentrations (0.02 and 0.05 g/cm^3) in the semidilute regime. All calculations have been made by using solvent density and viscosity data, at P = 1 atm, reported by Timmermans[17] together with the value $\bar{v}_2$ = 0.928 cm^3/g measured in the present work for PS in 1,2-dibromoethane. Inspection of the data in Table II shows that about the same values of k are obtained for the Θ solvents cyclohexane at 35 °C and cyclopentane at 20 °C. Also remarkable is the small difference between the values of k obtained for the good solvents toluene and bromobenzene at 25 °C. At the two concentrations, the permeability of PS for Θ conditions appears to be about 3 times greater than for good solvent conditions. Interestingly, this behavior for PS is very similar to that previously reported by Mijnlieff and Jaspers[1] for poly(α-methylstyrene) in various Θ and good solvents. On the other hand, as judged by the values of k in Table II for PS in 1,2-dibromoethane, which fall between those for the good solvents toluene and bromobenzene, it appears that there is no important effect associated with the lesser affinity of 1,2-dibromoethane for this polymer. In fact, if the latter comparison were restricted to bromobenzene, in which s was measured in flotation conditions at a pressure ($P \simeq$ 400 atm)[4] close to that of the present study, one would quantify to 15% only the increase in permeability associated with the lesser affinity of 1,2-dibromoethane. This suggests that the crossover between the Θ and good solvent regime for permeability occurs in the vicinity of the Θ conditions, that is, for ν values less than 0.53. Such behavior is also substantiated by the data of Mijnlieff and Jaspers,[1] which show that the poly(α-methylstyrene) permeability measured in cyclohexane drops sharply with increasing temperature in the range $T = \Theta$ to $T = \Theta + 30$ °C and remains unchanged for higher temperatures.

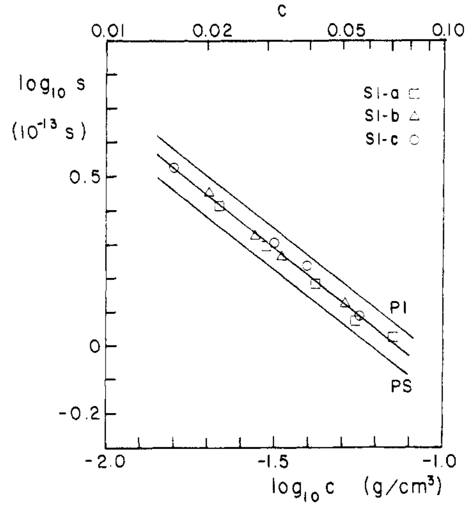

Figure 2. Bilogarithmic plot of the sedimentation coefficient as a function of concentration for styrene–isoprene diblock polymers (SI) of various molecular weights in 1,2-dibromoethane at 25 °C. For molecular weights and styrene contents, see Table I. Also shown for comparison are the linear relationships for polyisoprene (PI) and polystyrene (PS).

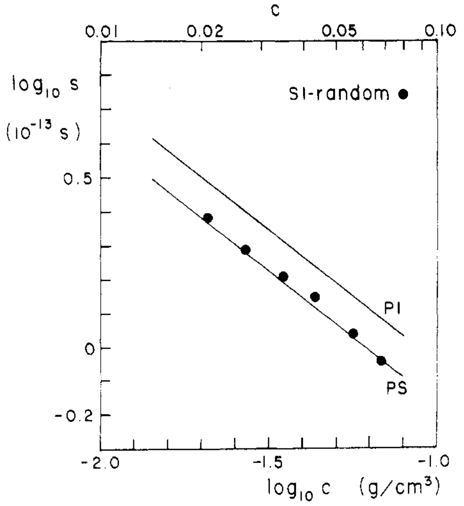

Figure 3. Bilogarithmic plot of the sedimentation coefficient as a function of concentration for the styrene–isoprene random copolymer (M_w = 2.13 × 10^5, w_s = 0.46) in 1,2-dibromoethane at 25 °C. Also shown for comparison are the linear relationships for polyisoprene (PI) and polystyrene (PS).

Block and Random Copolymers Study. Figure 2 shows log s vs. log c plots of the sedimentation coefficients measured on the three SI diblock polymer samples of different molecular weights. Also shown in Figure 2 are the linear curves describing the sedimentation behavior of the PS and PI homopolymers. From Figure 2 it may be seen that the sedimentation coefficients of the diblock polymers are also molecular weight independent in the concentration range 0.015 < c < 0.07 g/cm^3. Linear least-squares analysis of the data points yields the following power relationship:

$$s_{\mathrm{SI}} = 0.126c^{-0.79}$$

which exhibits an exponent value close to those obtained for the PS and PI homopolymers. Quantitative analysis of the data in Figure 2 shows that the values of s measured for the diblock polymers are close (±5%) to the weight average of those of the two homopolymers measured at the same concentration. This behavior contrasts with that of

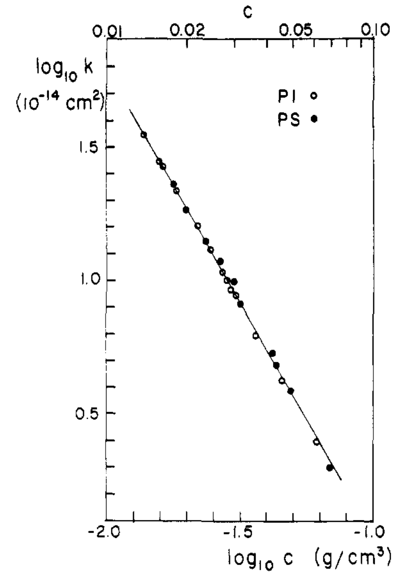

Figure 4. Bilogarithmic plots of the permeability coefficient as a function of concentration for polyisoprene (PI) and polystyrene (PS) in 1,2-dibromoethane at 25 °C.

the random copolymer, which, as shown in Figure 3, exhibits sedimentation coefficient values shifted toward the PS data, that is, about 10% lower than those of the diblock polymers.

Since the relative values of *s* measured at a given concentration for the present homopolymers and copolymers first depend upon the different values of their partial specific volumes, $\bar{v}_2$, it is evident that a comparison based directly on the *s* values is inadequate. A better approach is to consider again the permeability coefficient *k* defined by eq 1.

log *k* vs. log *c* plots of the permeability coefficients calculated by means of eq 1 for the PS and PI homopolymers are shown in Figure 4. It may be seen that the two homopolymers exhibit the same permeability in the concentration range of the present study. Linear least-squares analysis of the whole of the data points in Figure 4 gives the following concentration dependence of *k*:

$$k_{\mathrm{PS}} = k_{\mathrm{PI}} = 1.84 \times 10^{-16} c^{-1.77} \qquad (\mathrm{cm}^2)$$

The permeability data of the SI diblock polymers are plotted in Figure 5 together with the data of the random copolymer. For comparison, the straight line that corresponds to the above relation for the homopolymers is also shown in Figure 5. As expected from the preceding analysis of the sedimentation data in Figure 2, permeability of the diblock polymers can be fitted by the straight line of the homopolymers. On the other hand, permeability of the random copolymer appears to be systematically less than that of the diblock polymers. The difference is small (10%) but appears to be real. It cannot be attributed to a systematic error in the $\bar{v}_2$ data given in Table I. In fact such a difference would correspond to an inadmissible error of 5% on $\bar{v}_2$.

The smaller permeability of the random copolymer compared to the diblock polymers can be rationalized by considering that the hydrodynamic screening length ξ_h of the former is reduced because of the additional excluded volume effect associated with the larger number of heterocontacts inherent in its random structure. This interpretation is based on the simplified views proposed by Brochard and de Gennes[2] that ξ_h should decrease with increasing excluded volume effect and that permeability should increase with ξ_h. In the preceding section where a comparison was made of PS permeabilities measured in various solvents, it appeared that a change in the excluded volume associated with a change in the solvent affinity, in conditions remote from Θ conditions, does not produce an important effect upon ξ_h. This effect, if present, was difficult to quantify because some of the measurements were made at high pressure in flotation conditions and others at atmospheric pressure in normal sedimentation conditions. Since the present comparison between permeabilities of random and block polymers of styrene and isoprene is based upon measurements made under identical experimental conditions, there are good reasons to believe that one deals with a small but a real effect related to a difference in the excluded volume.

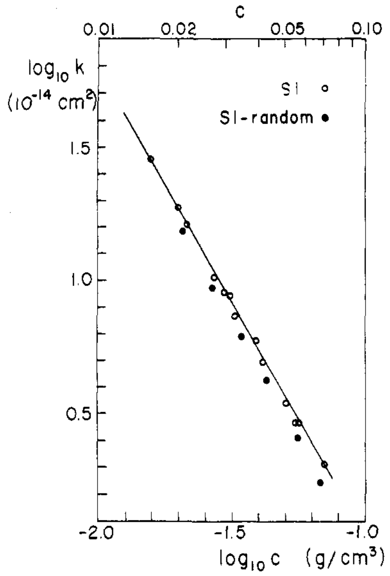

Figure 5. Bilogarithmic plots of permeability coefficient as a function of concentration for the styrene–isoprene diblock polymers (SI) and the random copolymer (SI-random) in 1,2-dibromoethane at 25 °C. Also shown for comparison is the linear relationship (full line) for polyisoprene and polystyrene.

The fact that the permeability of the block polymers appears to be about the same as that of the corresponding homopolymers PS and PI suggests that each subchain of a given type in the block polymer semidilute solutions experiences a hydrodynamic screening effect similar to that it would experience in the absence of heterocontact repulsions. However, in view of the small effect observed for the random copolymer, this does not mean that microphase separation already exists in the concentration range of the present study. In fact, according to a recent small-angle X-ray scattering study made by Hashimoto et al.[12] for concentrated solutions of SI diblock polymers in toluene and dioctyl phthalate similar to those studied in the present work, a transition between a disordered structure and a lamellar periodic structure occurs at a molecular weight dependent critical concentration that lies well above the concentration range of the present study. Though a scattering peak was observed for the disordered structure, Hashimoto et al. did not attribute this peak to phase separation. They rather assigned it to the correlation hole effect described previously by de Gennes[18] and Leibler[19] for scattering by homogeneous block polymer melts. This effect arises from local fluctuations in segment concentration related to the blocky nature of the polymer chains. In other words, for statistical reasons only, the local concentration in styrene (or isoprene) segments must be greater near the center of gravity of the PS (or PI) blocks. The same argument shows that there should be a smaller average number of heterocontacts for block polymers

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compared to random copolymers of the same composition.

Conclusion

As suggested by Brochard and de Gennes,[2] the use of permeability coefficient derived from sedimentation data by means of the Mijnlieff and Jaspers relation provides a very useful parameter for probing the hydrodynamic screening effect in semidilute solutions of flexible polymer chains. A comparison of permeability data for polystyrene in various solvents, based on the existing sedimentation data in the literature, shows that the values of this parameter are solvent-independent in both the limits of Θ and good solvent conditions. In Θ solvents its values are about 3 times greater than in good solvents, indicating an important hydrodynamic screening effect associated with the excluded volume effect present in the good solvent systems. The present data for 1,2-dibromoethane, a solvent with moderate affinity for PS, are close to the good solvent data, indicating that the crossover between the Θ and good solvent regime should occur in the vicinity of the Θ conditions. Therefore, it is not surprising that the extra excluded volume effect arising from heterocontact repulsive interactions in either homogenous block polymer solutions or random copolymer solutions scarcely affects their permeability behavior in solvent conditions remote from Θ conditions. Such behavior has been observed in the present study. The permeability data for styrene–isoprene diblock polymers in 1,2-dibromoethane are superimposable on the data obtained for homo-PS and homo-PI, the latter being fortuitously identical, while those for a random copolymer having about the same composition as the block polymers appear to be slightly displaced toward lower values. The smaller permeability for the random copolymer is consistent with the larger number of heterocontacts inherent in its random structure.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada and the Quebec Ministry of Education.

Registry No. (Styrene)·(isoprene) (copolymer), 25038-32-8.

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Kinetics of the Degradation of Electrical Conductivity in Polypyrrole

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Received August 21, 1985

ABSTRACT: A kinetic study of the degradation of the electrical conductivity of polypyrrole is reported. Polypyrrole was synthesized with a variety of anions including the *p*-toluenesulfonate, perchlorate, and tetrafluoroborate anions. Two different kinetic processes were found depending on the choice of anion. One process followed first-order reaction kinetics and the other was multiorder. The degradation of the conductivity of polypyrrole/toluenesulfonate was found to obey first-order reaction kinetics, while the other dopants investigated followed multiorder kinetics.

Introduction

The development of conducting polymers can be traced to the mid-1970's when researchers at the University of Pennsylvania reported that films of polyacetylene could be rendered conducting by reaction (doping) with a suitable electron-withdrawing group or electron-donating group.[1] Since that time, several other conducting polymers have been discovered.[2] One class of these conducting polymers is the polyheterocycles such as polypyrrole and its chalcogen analogues. Polypyrrole is normally synthesized electrochemically,[3] and as a result of the simultaneous oxidation and polymerization of the pyrrole monomer, the conducting form of the polymer is actually an oxidized backbone (see Figure 1) with a delocalized positive charge on the π electron system. Electrical conduction is thought to occur by conduction of these "holes".[4] In order to maintain charge neutrality an anion from the electrolyte is incorporated into the polymer. Typical anions that are incorporated are perchlorate (ClO_4^-), tetrafluoroborate (BF_4^-), and *p*-toluenesulfonate (PTS).

Polyacetylene is the most investigated of the conducting polymers, and it is considered the prototypical conducting polymer. It has been the basis for many possible applications, ranging from Schottky-barrier-type devices to rechargeable batteries.[5] Although polyacetylene (undoped, p-doped, and n-doped) reacts with oxygen and water leading to a decrease in conductivity,[6] it still possesses potential utility if used in an inert atmosphere. This is because n-type polyacetylene (i.e., alkali metal doped) is thermally stable.[7] Many researchers have investigated the

0024-9297/86/2219-0824$01.50/0