Dynamic Light Scattering from Ternary Polymer Solutions: Influence of Polymer Incompatibility on the Translational Diffusion of Polyisobutylene Chains in Solutions of High Molecular Weight Polystyrene

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ABSTRACT: This paper describes dynamic light scattering results on the polyisobutylene (PIB)/polystyrene (PS)/chloroform system, the measurements having been made to examine the influence of mutual chain incompatibility on probe diffusion in a semidilute matrix. The systems were chosen so that the PIB probe chain is smaller than that of the PS matrix, while its radius of gyration exceeds the polymer-polymer correlation length defining the matrix. Comparison is made between PIB/PS and PIB/PIB systems. The self-diffusion coefficient of the PIB probe passes through a pronounced minimum with increasing PS concentration in contrast to the monotonic decrease for the same probe in the analogous PIB/PIB system. With different PS molecular weights, a universal curve is obtained when the matrix concentration is normalized with the corresponding entanglement concentration. It is concluded that the observed effect derives in great part from the inhibition of interchain entanglement in the PIB/PS system.

Introduction

The purpose of this paper is to illustrate the influence of limited polymer compatibility on the dynamical behavior in a ternary polymer$_1$/polymer$_2$/solvent system as reflected in the self-diffusion coefficient of the minor polymer component.

The measurements have been made by utilizing the theory originally put forward by Akcasu et al.[1] and further developed by Benmouna et al.[2] Borsali et al.[2b-d] found experimentally that, for a bidisperse mixture of homopolymers differing only in molecular size, the cooperative diffusion coefficient of the matrix chains and the interdiffusion coefficient may be isolated from the bimodal autocorrelation function. With a trace amount of the probe chain, the interdiffusion coefficient should approximate the self-diffusion coefficient of this component.[3] With this assumption, Brown and Zhou[4] examined the homopolymeric polyisobutylene (PIB) system PIB$_1$/PIB$_2$/chloroform using dynamic light scattering and pulsed-field-gradient NMR. It was confirmed through comparison with data on the binary PIB/solvent systems using these two methods that one may simultaneously isolate the cooperative diffusion coefficient of the semidilute matrix polymer and, with a trace concentration of the probe chain, the self-diffusion coefficient of this component. It should be noted that in these experiments the so-called "optical labeling" method has not been used; the contributions from the two polymeric components, differing in molecular size only, could be separated by Laplace inversion. However, the interpretation of the modes may not be straightforward, except in some limiting cases. Akcasu[5] has recently shown, for example, that whereas the two exponentially decaying modes represent the pure normal modes of the system, the interdiffusion and cooperative diffusion processes will correspond to mixed modes; i.e., the relaxation rates will be determined by the superposition of the pure modes. It may also be added that the transport mechanism for the probe has been shown[4d] to follow Rouse dynamics rather than reptation.

The ternary system chosen here is polyisobutylene (PIB)/polystyrene (PS)/chloroform, and comparisons are made with the earlier investigated homopolymeric PIB$_1$/PIB$_2$/chloroform system. In the latter[4b] we described the self-diffusion of large PS coils ($M = 8.42 \times 10^6$) in solutions of lower molecular weight PIB chains. It was found that, at a given reduced concentration (C/C^*) of PIB, the reduced diffusion coefficient (D/D_0) for polystyrene was substantially larger than the same quantity for a large PIB coil in the same PIB matrix. It was concluded that the difference might in part originate from a contraction of the PS coil in the presence of the PIB chains caused by limited compatibility.

The present paper is directed to experiments with an alternative geometry: small PIB chains diffusing in a matrix of high molecular weight PS chains. In particular, the dependence of the probe diffusion rate on matrix concentration and molecular weight has been examined as well as the influence of the molecular weight of the probe.

Experimental Section

Polyisobutylene samples were narrow distribution fractions from Polymer Standards Service, Mainz, FRG. Polydispersity indices, molecular weights, and intrinsic viscosities were summarized in ref 4c. Polystyrenes were from Toya Soda Ltd., Tokyo, Japan ($M = 8.42 \times 10^6$, $M_w/M_n = 1.05$; $M = 5 \times 10^6$, $M_w/M_n = 1.04$; $M = 3.42 \times 10^6$, $M_w/M_n = 1.03$; $M = 9.3 \times 10^5$, $M_w/M_n = 1.03$). Stock solutions of the probe chains (≈0.05%) were first prepared, and these were used as the solvent for making the semidilute solutions of the matrix polymer. All solutions were filtered through 0.45-μm Millipore Durapore filters.

Dynamic Light Scattering. Measurements were made as previously described.[4b] The autocorrelator was a multi-τ model (ALV-3000) from ALV, Langen, FRG, allowing 23 simultaneous sampling times and thus a monitoring of widely spaced decays in the same experiment. Laplace inversion was performed with a constrained regularization routine (REPES)[6] to obtain the distribution of decay times. This program directly minimizes the sum of squared differences between the experimental and calculated correlation functions ($g^2(t)$) using nonlinear programming and allows selection of the parameter P, the "probability to reject", which determines the degree of smoothing. The analysis of data, encompassing 191 exponentially spaced grid points and a grid density of 10 per decade, can be rapidly performed on an IBM-compatible desk top computer.

Static Light Scattering. Intensity light scattering measurements were made with a photon-counting apparatus supplied by Hamamatsu. The optical constant for vertically

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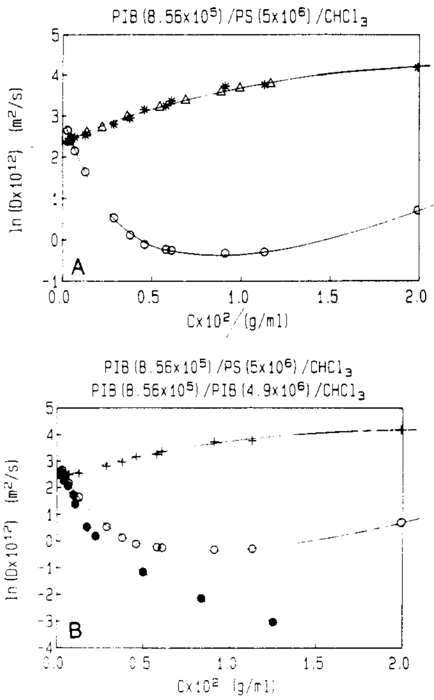

Figure 1. (A) Dynamic light scattering in the ternary PIB/PS/chloroform system. Plot of the translational diffusion of probe chain (PIB(8.56 × 10^5)) (open circles) in PS(5 × 10^6) where C refers to the matrix (PS) concentration. The stars indicate the cooperative diffusion of the PS matrix. The triangles are for the binary PS/chloroform system. (B) Comparison of the data in (A) (○) with data for the same PIB probe but using a PIB matrix (●) (M_w = 4.9 × 10^6).

polarized light is

$$K = 4\pi n_0^2(\mathrm{d}n/\mathrm{d}c)^2/N_A\lambda^4$$

where n_0 is the solvent refractive index, dn/dc is the refractive index increment = 0.095 mL·g^{-1} for PIB in $CHCl_3$ and 0.169 mL·g^{-1} for PS in $CHCl_3$,[6] and λ is the wavelength, here 633 nm. The Rayleigh ratio (R_θ) was obtained by calibration using benzene: R_{90} = 8.51 × 10^{-6} at 25 °C.[8] Zimm plots are shown in Figures 6 and 7.

Results and Discussion

Parts A and B of Figure 1 show typical data. The stars in Figure 1A and the open circles are, respectively, the fast and slow components of the bimodal autocorrelation function, corresponding to the PS(5 × 10^6) matrix and the PIB(8.56 × 10^5) probe chain. Separation of these components was obtained by Laplace inversion using REPES[6] (a modified form of CONTIN[9]), as described previously.[4b] The corresponding peaks are well-defined and do not overlap at any concentration. Also included in Figure 1A are points for the PS matrix chains in the binary system PS/chloroform. The intercepts (note 10) correspond to the D_0 values obtained by extrapolation of data in the dilute binary solutions and, in the case of PIB, with the extrapolated value derived from pulsed-field-gradient NMR measurements.

The self-diffusion coefficient of the probe is seen to pass through a minimum in the vicinity of C_{PS} = 0.8%. As shown in Figure 1B, this behavior contrasts with that when a PIB fraction of the same molecular weight is used as the matrix instead of PS, and the expected monotonic decrease in D is observed.

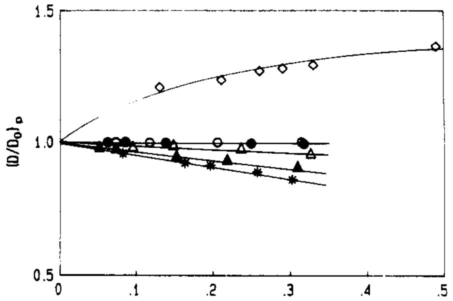

Figure 2. Dependence of the probe diffusion coefficient on probe (PIB) concentration in the system PIB(2.47 × 10^5)/PS(5 × 10^6)/chloroform where the matrix (PS) concentration is maintained constant at the following values: 0% (◇); 0.0126% (●); 0.092% (○); 0.19% (△); 0.42% (▲); 1.01% (*). Plot of the reduced probe concentration $(D/D_0)_{\text{probe}}$ versus C_{probe}.

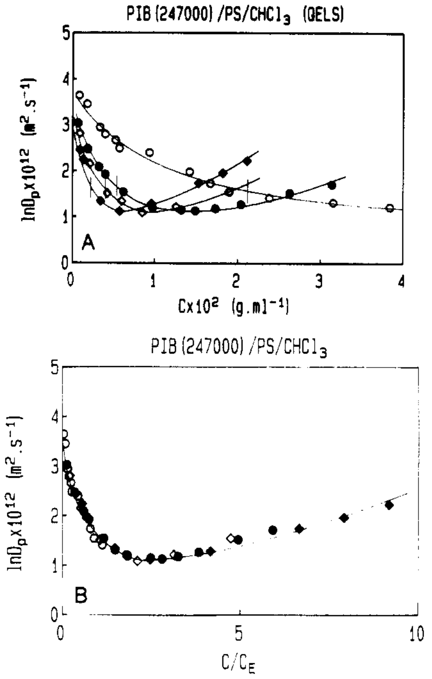

Figure 3. (A) Plots of translational diffusion for PIB(2.47 × 10^5) in PS matrix chains. PS M_w = 8.42 × 10^6 (◆), 5 × 10^6 (◇), 3.72 × 10^6 (●), and 9.3 × 10^5 (○). (B) Data as in (A) but with the PS matrix concentration normalized by its entanglement concentration, C_E (note 11).

Figure 2 shows the dependence of the reduced probe diffusion coefficient (D/D_0) on probe concentration where the concentration of the matrix (PS(5 × 10^6) is held constant at various values between zero and 1.01%. This latter concentration exceeds C_E for the matrix (≈0.4%). It is seen that, although the concentration dependence in the binary system (0% matrix) is substantial, the dependence of D_{probe} on its own concentration within the considered range is small in the ternary systems, first becoming perceptible when the matrix is entangled. The interactions between PIB probe chains are thus effectively screened by the PS chains. Importantly, the self-diffusion coefficient of the probe is effectively determined in these experiments when the concentration of probe chains is low. Here we use $C_{\text{probe}} \approx 0.05\%$, satisfying this requirement.

The present results differ significantly from those in the ternary system PS/poly(vinyl methyl ether), for which Chang et al.[11] found the concentration dependence for probe (PS) diffusion to change strongly and systematically from positive to negative with increasing matrix concentration. This difference may derive from the greater miscibility of the latter polymers compared with PS and PIB.

Figure 3A shows data obtained with different molecular weight PS matrix chains (ranging from M = 9.3 × 10^5 to

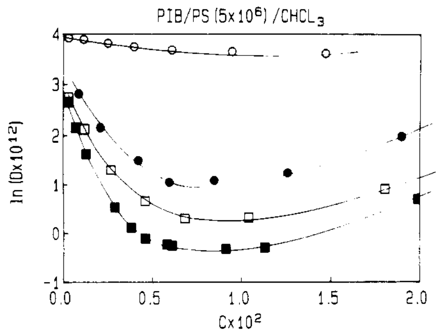

Figure 4. Plots of translational diffusion for PIB probes in PS matrix ($M_w = 5 \times 10^6$) of concentration C. PIB $M_w = 1.12 \times 10^5$ (○), 2.47×10^5 (●), 6.1×10^5 (□), and 8.56×10^5 (■).

Table I

PS			PIB		
M_{matrix}	C_E/%	R_g/Å	M_{probe}	R_g/Å	R_H/Å[a]
8.42×10^6	0.23	1600	1.12×10^5	175	90
5×10^6	0.40	1175	2.47×10^5	275	125
3.72×10^6	0.53	985	6.1×10^5	450	220
9.3×10^5	2.12	430	8.56×10^5	540	260

[a] Hydrodynamic radii determined from the diffusion coefficients at infinite dilution.

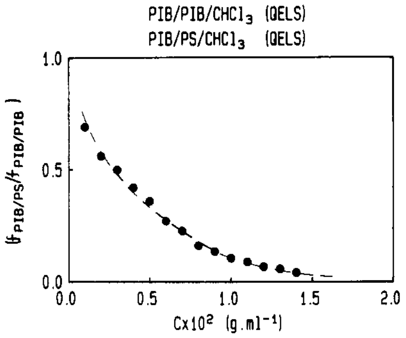

Figure 5. Ratio between the friction coefficient (defined by $D = kT/f$) for PIB(8.56×10^5) in, respectively, the polystyrene matrix and polyisobutylene matrix as a function of the matrix concentration. The data are interpolated values from Figure 1B.

$M = 8.42 \times 10^6$). It is noted that the upward trend in the self-diffusion coefficient for the PIB probe with increasing concentration of PS becomes more pronounced the higher the molecular weight of the PS matrix. The vertical lines indicate the entanglement concentration, C_E.[12]

Figure 3B shows that a universal curve is obtained from the data in Figure 3A when the matrix concentration is normalized using its entanglement concentration. Thus one may conclude that, while at concentrations smaller than C_E the PS and PIB chains mix relatively freely, they are unable to interpenetrate at $C > C_E$.

Figure 4 shows the dependence of PIB self-diffusion on its own molecular weight. At the lowest molecular weight ($M = 1.12 \times 10^5$), D_{PIB} is almost independent of C_{PS}. This was also observed in the homopolymeric PIB/PIB system with probe chains of this size or smaller. At $C = C_E$, the correlation length defining the PS matrix is $\xi \approx 195$ Å, and this is larger than the hydrodynamic diameter of the smallest probe (180 Å) (see dimensions in Table I). For the higher molecular weight probes, the coil hydrodynamic diameters well exceed the correlation length of the matrix and then there is a strong reduction in the self-diffusion rate of the probe.

One may argue that among possible factors influencing probe diffusion are (a) interchain friction and (b) a progressive contraction of the PIB probe coil with increasing PS concentration. Figure 5 shows a plot of the relative friction coefficient for the probe (PIB(8.56×10^5)), in, respectively, PS and PIB semidilute solutions, as a function of matrix concentration, where these data have been interpolated from the curves in Figure 1B. It is clear that the magnitude of the effect is much greater than can be accounted for in terms of coil contraction for the probe chain, which may maximally be about 55% in terms of the ratio between good and Θ solvent coil radii.

In order to obtain an estimation of the possible influence of one chain type on the radius of gyration of the other due to their limited compatibility, static light scattering measurements were made on large PS chains dissolved in PIB solutions of fractions of lower molecular weight. Here PS was used as the low-concentration component since its refractive index increment was larger, allowing very low concentrations to be employed. It was then assumed that practically all of the detected angular disymmetry derives from the large PS chain. A decrease in R_g could not be detected with PS(3.72×10^6) in PIB(2.47×10^5), where the concentration of the latter was changed over the range 0–1.85%. The Zimm plot for this system is shown in Figure 6A. The intercept on the vertical axis corresponds to the zero-angle value of KC/R_θ for PS in the binary solvent system at the concentration used (0.09%) in the ternary experiment. Figure 6B depicts the Zimm plot for the binary PS/chloroform system where the highest concentration (C_4) is that used for the PS probe in Figure 6A. If anything, the increase in the angular dependence at finite PIB concentrations suggests a small increase in $(R_g)_{\text{app}}$ for the PS coil with increasing PIB concentration. We note that there is a strong negative concentration dependence for $KC/R_{\theta=0} = 0$ up to a PIB concentration of 1.5%, which is close to C^*. This Zimm plot has an unusual form; plots of this type have been described previously by Benoit and Benmouna[13] and Kaddour.[14,15] The subsequent upswing in KC/R_θ apparently reflects the onset of multiple scattering. This observation is consistent with the early light scattering results of Kuhn et al.[17] for PS in PMMA matrix solutions of different molecular weight, who showed that the concentration of PMMA at which the second virial coefficient became zero was a linear function of the inverse intrinsic viscosity (i.e., $\approx C^*$ for PMMA).

Because of the pivotal importance of changes in coil dimensions for interpretation, we also endeavored to determine R_g for the probe chain in the presence of matrix chains by other routes: (a) plots of D versus q^2, where $D/D_0 = (1 + CR_g q^2)$ with $C = 0.173$ for coils;[18] (b) by plotting the relaxation rate for the probe versus q^2 and fitting the eventual deviation from linearity in terms of the form factor $P(q)$ as done by Borsali et al.[2c] In neither case could $(R_g)_{\text{app}}$ values be extracted since the relaxation rate was found to be linearly dependent on q^2 as would be anticipated since the relaxation rate for the probe component has been separated from the contributions of internal modes using REPES. A third possibility explored was to plot the ratio of the intensities ($A_{\text{fast}}/A_{\text{slow}}$) versus q^2. As shown by Sedlak et al.,[19] it should be possible to extract apparent R_g values, and this had been done in ref 19 for clusters in aqueous solutions of poly(methacrylic acid). In the present case, $A_{\text{fast}}/A_{\text{slow}}$ was found to be independent of angle to a first approximation.

In spite of the experimentally well-known limited compatibility of PS and PIB chains,[20-24] it appears that the polymer–polymer interaction parameter $\chi_{2,3}$ is very small for these polymers in various solvents. A number of detailed studies have been reported. Allen et al.[20] give a value $\chi_{2,3} = 0.01$ in the PS/PIB/carbon tetrachloride

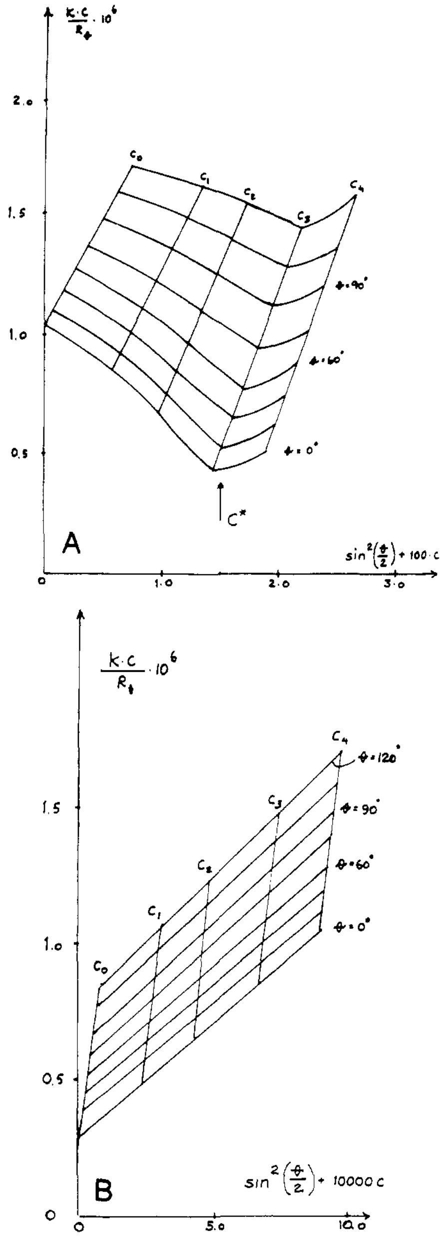

Figure 6. (A) Zimm plot for PS(3.72×10^6) in PIB(2.47×10^5)/chloroform where the concentration of PS is maintained at 0.09% and that of PIB varied. On the horizontal axis C is the total polymer concentration. (B) Zimm plot for the binary PS(3.72×10^6)/chloroform system where C_4 = 0.09% (equals the PS concentration used in (A).

system, Hyde et al.[21,22] also give $\chi_{2,3}$ = 0.01 for the PS/PIB/benzene system, and Van den Esker and Vrij[23] give values ranging from 0.029 to 0.008, depending on molecular weights and composition, for the PS/PIB/toluene system. Nagata et al.[24] give 0.0225–0.0386 in the dilute limit for the PS/PIB/bromobenzene system. Both Allen et al.[20] and Van den Esker and Vrij[23] discuss the (apparently) anomalously low values of $\chi_{2,3}$ at some length. Allen et al. considered that the two polymers do not really mix and that the number of 2–3 contacts is smaller than for random mixing. Van den Esker and Vrij, on the other hand, conclude from the interaction parameters, in common with Joanny et al.,[25] that polymer A cannot distinguish between polymer A and polymer B segments. The result from static light scattering measurements, which shows that there is no perceptible shrinkage of the coils of one polymer when adding the second, stands in contrast to the supposition of Allen et al.[20] that avoidance of overlapping (or entanglement) should necessarily lead to contraction of coil dimensions. This does not seem to be the case.

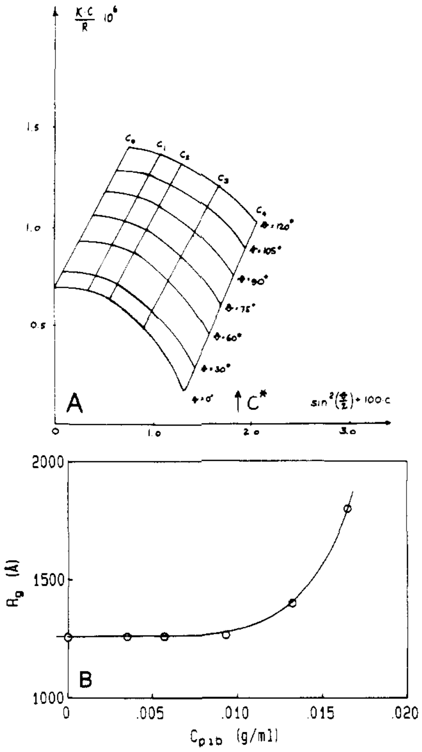

Figure 7. (A) Zimm plot for PS(5×10^6) in PIB(2.47×10^5)/benzene at 25 °C where benzene is isorefractive with PIB. PS concentration = 0.066%. Benzene is a Θ solvent for PIB at 24.5 °C. C is the total polymer concentration. (B) Dependence of the radius of gyration of PS(5×10^6) at a constant concentration of 0.066% on the concentration of PIB(2.47×10^5). System as in (A). C^*(PIB(2.47×10^5)) = 0.0188 g·mL^{-1}.

We also made static light scattering measurements for PS in PIB using benzene as solvent. The latter is isorefractive with PIB. Benzene is a Θ solvent for PIB at 24.5 °C but a good solvent for PS. The Zimm plot is depicted in Figure 7A and is very similar to the unusual diagram (Figure 6A) found in the solvent $CHCl_3$ (a good solvent for both polymers).

Figure 7B shows that $(R_g)_{app}$ is effectively constant up to about C_{PIB} = 1.2%, followed by a strong increase, presumably indicating the start of aggregation of PS chains prior to overlap (at C_{PIB} = 1.88% in this case). The approximate constancy of $(R_g)_{app}$ is similar to the result of Hyde and Tanner,[22] who found no change in R_g for large PS chains in PIB solutions in cyclohexane in dilute solution (C_{PIB} < 0.05%). This result is understandable since the PS probe chain is surrounded by PIB chains with which it cannot entangle and there will be no screening by other PS chains. These results contrast, on the other hand, with those of Kuhn and Cantow,[26] who found for the PS/PMMA/benzene system the $(R_g)_{app}$ for PS to decrease with increasing PMMA concentration, although the R_g value was 30–50% higher in the Θ solvent formed with PMMA than the dimension in a simple Θ solvent. It is possible that this difference is related to the higher compatibility of PS and PMMA, allowing a greater degree of coil interpenetration, compared with the PS/PIB pair. A different situation apparently prevails in the homopolymeric polystyrene system in which the chains can interpenetrate and entangle freely. Recent results from SANS determinations of the single-chain coil size of PS(9.3×10^5) dissolved in semidilute solutions of PS(9×10^4, deuterated) in benzene[27] show that the large coil decreases in size to approximately Θ dimensions at a PS matrix concentration of $C \approx C^*$ (corresponding to about $6C^*$ for the high-MW probe). This result is in approximate agreement with those of Daoud et al.,[28] who observed using SANS a monotonic decrease in R_g over the *whole* concentration range. R_g was observed to decrease from its infinite-dilution value throughout the dilute and semidilute regions. The pronounced decrease in R_g in the dilute range is not readily understood, however.

The observation that normalization of the matrix concentration with the entanglement concentration leads to a universal curve suggests that the greater part of the observed effect in, for example, Figure 1B is related to differences in the relative entanglement frequency of the two types of chain. In the homopolymeric PIB/PIB system, the entanglement concentration for the matrix with $M = 4.9 \times 10^6$ is $C_E \approx 0.24\%$. This means that the friction is determined over most of the concentration range by interchain entanglements. In the PS(5×10^6) matrix, at concentrations below C_E (=0.4%) the interchain friction may not be very dissimilar to that in the PIB matrix. Above C_E, on the other hand, mutual chain incompatibility will prevent entanglements forming between the two different types of chain, and thus the PIB/PS and PIB/PIB curves will diverge increasingly. It is concluded that the probe coils are effectively segregated in the matrix of the second polymer and to some extent become "trapped" as regards diffusional motion and consequently progressively adopt the dynamics of the matrix chains. Support for this view is provided by results of Hyde and Tanner,[22] who observed that PS solutions in cyclohexane containing PIB were stable even at 5 °C below the Θ temperature.

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