polymer review

Self-diffusion: an experimental demonstration of the non-applicability of the reptation model to semidilute polymer solutions*

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The translational diffusion of probe chains in ternary systems has been measured in the homopolymeric polyisobutylene (PIB) system: PIB_1/PIB_2/chloroform. In the crossover region, dilute/semidilute, a universal curve is found with logarithmic $(D/D_0)_{probe}$ *versus* $(C/C^*)_{matrix}$ plots. Data for $M_{probe} \gg M_{matrix}$ and $M_{matrix} \gg M_{probe}$ follow the same relationship as those for hard spheres in the same systems. In semidilute solutions, a universal curve is found with logarithmic plots of $(DM)_{probe}$ *versus* $(C/C^*)_{matrix}$. These data establish that the reptation/scaling model is inapplicable in semidilute solutions even though the scaling predictions are fulfilled over the concentration interval employed. Recent theories for cooperative chain motion are seen to be the most promising means of describing the dynamics in congested solutions.

(Keywords: self-diffusion; reptation model; semidilute solutions)

INTRODUCTION

Translational diffusion in semidilute polymer solutions has been the subject of numerous experimental and theoretical investigations. Self-diffusion in polymer systems has been reviewed in its experimental aspects by Tirrell[1] and more recent summaries of current viewpoints pertinent to ternary systems have also been given by, for example, Nemoto *et al.*[2] and Wheeler and Lodge[3].

Much of the literature data refers to semidilute solutions in which the chains are unentangled or have a low entanglement density since the range of concentration which is readily accessible to measurement with fractions of high molecular weight imposes severe experimental curtailments. While there seems to be a general consensus that the reptation/scaling model[4] is valid for very strongly entangled systems such as the melt, the picture has been much less clear in the case of semidilute solutions which are less well entangled. The seat of the ambiguity would appear to stem from the early observations that the predicted exponents: $D \sim M^{-2}C^{-1.75}$ in good solvents[5–9] apply, at least over a restricted concentration interval, and yet much evidence has since accumulated that there is a significant dependence on the matrix molecular weight which does not fit with the model. The latter observation has led to modifications of the original theory to take account of the cooperative movement of chains surrounding the probe chain (so-called 'constraint release')[10–13]. In addition, both the molecular weight and concentration exponents exceed the predicted values as the concentration is further increased.

This has also led to interpretations based on the effect of decreasing solvent quality (i.e. contraction of coil dimensions down to the *theta* dimension at higher concentrations) and also corrections for the influence of monomer friction when concentration exceeds about 10%[14]. A strong argument against reptation in solutions however, derives from the simulation studies of Kolinski *et al.*[15] which find no evidence for the presence of the predicted 'tube' which is the underlying feature of the model. The central role of entanglements for the applicability of reptation theory is made clear in recent papers of Kavassalis and Noolandi[16,17]. Techniques such as forced Rayleigh scattering (FRS), pulsed field gradient nuclear magnetic resonance (n.m.r.) and dynamic light scattering in ternary ($polymer_1/polymer_2$/solvent) solutions in which one polymer is isorefractive with the solvent, have been the main methods applied in endeavours to establish the influence of the molecular weights of 'probe' and 'matrix' chains and of the concentration of the matrix chain on the diffusion of probe. Since what is required is to study the movement of a probe chain which is identical in all respects to those surrounding it except molecular size, it is clear that all of these methods have inherent drawbacks, the most severe of which is most likely the use of chemically different polymers in the optical labelling method. Instead, we use here an alternative approach recently described by Benmouna *et al.*[18,19] whereby $polymer_1$ is chemically identical to $polymer_2$, differing only in molecular size, thus approximating the ideal experiment. One of the polymers is maintained semidilute (matrix) and the other present in trace concentration (probe). The utility of the approach in determining self-diffusion coefficients of the probe chain was demonstrated in references 20 and 21. Pulsed-field-gradient n.m.r. was used to confirm the identity of the self-diffusion coefficients determined by dynamic light scattering. Over broad ranges of relative molecular size, precise determinations of the respective cooperative diffusion and self-diffusion coefficients may be made. The

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* Dedicated to Professor Walther Burchard on the occasion of his 60th birthday

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purpose of this paper is two-fold: first, to demonstrate the limitations to the possible applicability of the reptation/scaling model; second, to elucidate the parameters which are fundamental to self-diffusion in semidilute solution.

Nemoto *et al.*[2] considered that self-diffusion and sedimentation in concentrated systems (solutions and melts) could be expressed as the product of two separate contributions, one being the topological interaction between the probe chain and the surrounding matrix chains (m) and the other the hydrodynamic interactions pertaining to the probe chain (p). This combination constrains the motion of a flexible polymer chain, for example, in a semidilute matrix. Such an approach appears to be a fruitful one. It is convenient here to formulate in terms of the general ternary system, with the binary system with $M_p = M_m$ as a special case, since much of the literature data refer to ternary systems.

An approach leading to a 'universal' curve is a favoured means of attempting to establish the role of key parameters. Nemoto *et al.* found a master curve through plotting a reciprocal 'topological function' (ψ^{-1}) against M/M_e, where M_e is the molecular weight between entanglements. The term ψ^{-1} is considered to describe the screening effect of the hydrodynamic interactions while M/M_e represents the strength of topological restrictions on the mobility of the test chain.

Wheeler and Lodge[3] on the other hand, employed an arbitrary shift factor (C') to collapse their data to a double logarithmic master curve: (D/D_0) *versus* (C/C'). When $M_p \gg M_m$, C' was found to scale as C^*_m. When $M_m \gg M_p$, $C' \sim C^*_p$. In the intermediate range $C' \sim (C^*_m C^*_p)^{1/2}$. In detail, neither approach seems completely satisfactory. Nemoto's data reduction did not function for Wheeler's data, while, on the other hand, Wheeler *et al.* use an empirical shift. It will be shown in the present paper, on the other hand, that for the two extremes: $M_p \gg M_m$ and $M_m \gg M_p$, the data can be described in terms of a universal curve. Moreover, these data superimpose on those for the translational diffusion of hard spheres in solutions of the same matrix polymer. This is achieved by describing the topological effect of the matrix using the reduced concentration $(C/C^*)_m$, where $C^* \approx 1/[\eta]$ and $[\eta]$ is the intrinsic viscosity.

The hydrodynamic screening effect for overlapped coils ($C > C^*$) is given by ${M_p}^{-1}$. Thus double logarithmic plots of (DM_p) *versus* $(C/C^*)_m$ form a curve which is universal for $M_p \gg M_m$ and for $M_m \gg M_p$.

The experimental data which form the basis for the treatment described are for the homopolymeric polyisobutylene (PIB)/chloroform system and were obtained using dynamic light scattering. The presentation brings together the previously reported data[20,21] with those from new experiments and indicates a possible coherent interpretation.

EXPERIMENTAL

Polyisobutylene samples were mostly narrow distribution fractions from Polymer Standards Service Ltd, Mainz, FRG. A description of these materials was given in reference 25. The sterically stabilized silica particles were kindly donated by Dr K. de Kruif, University of Utrecht, The Netherlands. The stabilizing layer was terminally grafted $C_{18}H_{37}OSi$. The hydrodynamic radii were 1595 and 318 Å. Chloroform was spectroscopic grade from Merck, Darmstadt, FRG.

Dynamic light scattering measurements were made as previously described in reference 21. We have used a broad-band multi-tau, multi-bit autocorrelator enabling 23 simultaneous sampling times and with 191 exponentially spaced channels. A newly developed method (REPES)[22] for Laplace inversion was used, yielding the decay time distribution over wide spans in delay time, covering typically up to eight decades. The algorithm differs from CONTIN[23] in that the program directly minimizes the sum of squared differences between the experimental and calculated $g^2(t)$ function using nonlinear programming. The *a priori* chosen parameter P (probability to reject) was put equal to 0.5. Applying the method recently described[20,21], it was found possible to determine with good precision the self-diffusion coefficient for the probe over a wide range of relative molecular weights of probe and matrix when using a concentration of probe $\approx 0.1\%$, since at this concentration, D_{probe} has been shown to have a negligible dependence on its own concentration[21]. There will always be however, a range of relative molecular sizes where the probe and matrix components cannot be separated owing to the noise inherent in the data.

RESULTS

The data are presented below for the two extreme limits discussed above.

$M_p \gg M_m$

Experiments having this geometry are summarized in *Figure 1*. The same curve has been drawn through the data in *Figures 1a* and *b* and this serves to illustrate that the data for large PIB coils diffusing in PIB matrix chains of lower molecular weight superimpose exactly on those for both large and small silica spheres in the same PIB matrices. These data span a wide range of matrix polymer concentration, above and below C^*. Normalization of the matrix concentration with the relevant C^* value thus consistently describes the topological influence of the matrix. We have used throughout the definition of $C^* = 1/[\eta]$, since it was established experimentally[24] to provide a reliable index of overlap. Since $C^* \sim M^{-0.55}$, this means that $D_p \sim M^{-0.55}$ in accordance with non-draining Zimm behaviour. The probe diffusion has been normalized using the infinite dilution value, D_0. Similar plots were used earlier[25] to describe the data for silica spheres and polystyrene coils diffusing in PMMA matrix chains.

Figure 2 collects the data in *Figure 1* coupled with the solution viscosity characterizing the matrix solutions, and demonstrates the approximate applicability of the Stokes–Einstein equation in the concentration range used; i.e. large probes, independent of character, move in a medium characterized by the macroscopic viscosity, η. At the higher concentrations the SiO_2 spheres show a clear tendency to interact with the matrix chains.

$M_m \gg M_p$

Data for the reverse case to that above, i.e. with probes smaller than those of the matrix, but with radius of gyration (R_g) greater than the correlation length (ξ) defining the matrix component in the relevant concentration range, are shown in *Figure 3a*. Here the molecular weight of the matrix is varied. Probe diffusion is now observed to depend strongly on M_m even when $M_m/M_p >$

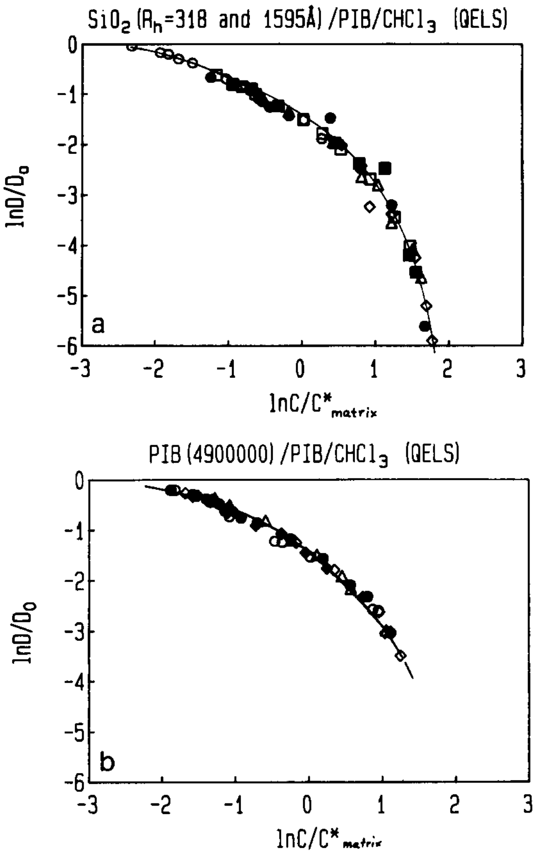

Figure 1 (a) Logarithmic plot of D/D_0 for silica spheres (radii 1595 and 318 Å) with D_0 the infinite dilution values *versus* PIB concentration, normalized with the overlap concentration C^*. PIB molecular weights: 5.4×10^4 (○); 1.82×10^5 (□); 6.1×10^5 (△); 1.1×10^6 (◇) with SiO_2 (1595 Å). 1.1×10^6 (●); 1.9×10^6 (□) with SiO_2 (318 Å). (b) Analogous data to those in (a) but for a high molecular weight PIB chain (4.9×10^6) as probe in PIB matrix chains with molecular weights: 8.04×10^4 (○); 1.82×10^5 (●); 2.47×10^5 (◇); 6.1×10^5 (◆); 1.1×10^6 (△)

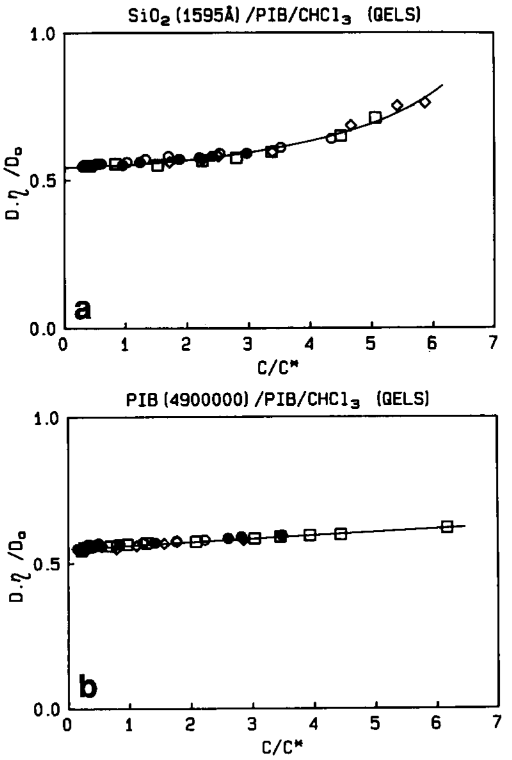

Figure 2 (a) Plot of $D\eta/D_0$ *versus* C/C^* for large SiO_2 spheres in PIB matrix fractions: 1.82×10^5 (○); 2.47×10^5 (●); 6.1×10^5 (□); 1.9×10^6 (◇). (b) Analogous plot to (a), but for the large PIB probe ($M=4.9\times10^6$) in the same PIB fractions

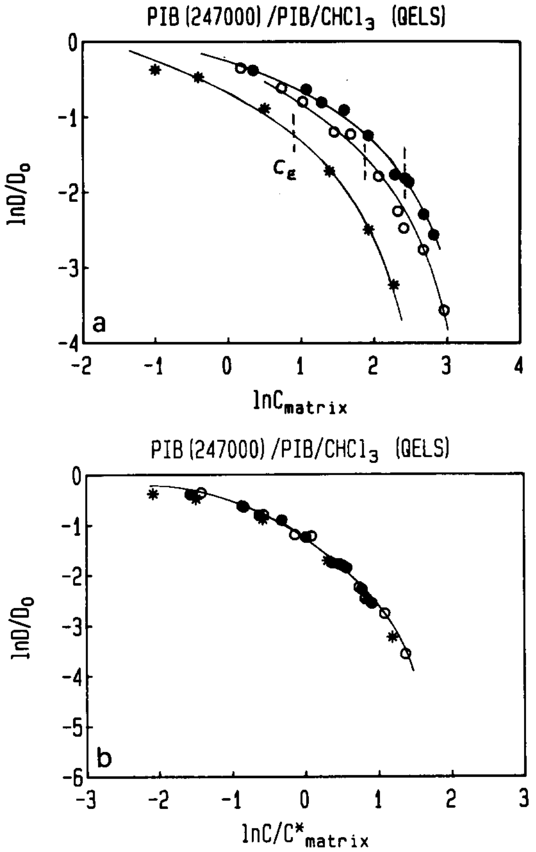

Figure 3 (a) Logarithmic plots (D/D_0) *versus* C for a low molecular weight PIB chain ($M=2.47\times10^5$) in high molecular weight PIB matrix chains: $M=1.1\times10^6$ (●); 1.9×10^6 (○); 4.9×10^6 (✱). The matrix entanglement concentration is indicated. (b) Diagram as in (a), but with matrix concentration normalized with C^*

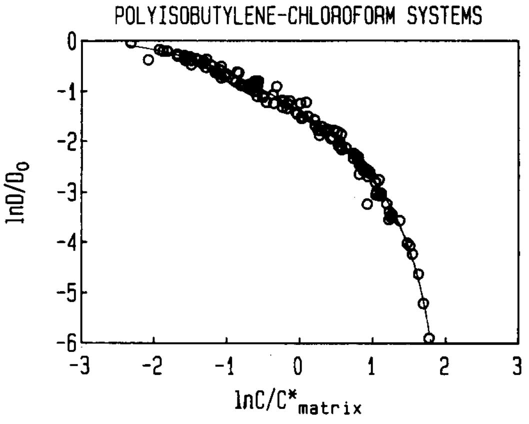

Figure 4 Master logarithmic curve of D/D_0 *versus* C/C^* for the collected data in *Figures 1* and *3*

10. However, even here normalization of the matrix concentration with its C^* (*Figure 3b*) leads to superposition of the curves shown in *Figure 3a*. It is important to note that *Figures 1a,b* and *3b* also superimpose, as demonstrated in *Figure 4* which is a master curve for the collected data from *Figures 1* and *3*.

Figure 5a shows the influence of varying the probe chain size, but still with $M_m > M_p$. (It may be noted that for very small probes when $R_g < \xi$ for the matrix, probe diffusion is essentially independent of the matrix concentration.) A strong residual dependence of the probe diffusion rate on M_p is seen if normalization with D_0 is used. For semidilute solutions (i.e. for $C > C^*$), this

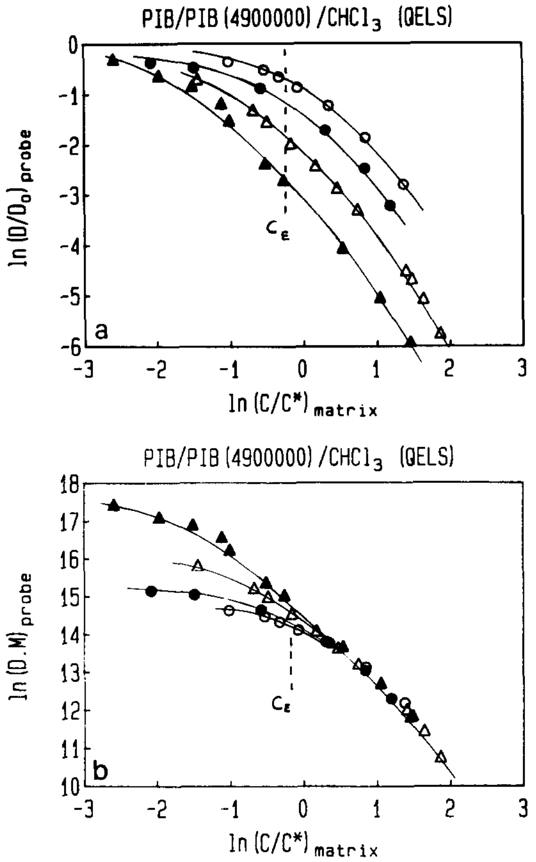

Figure 5 (a) Logarithmic plots (D/D_0 *versus* C/C^*) for PIB probe chains with molecular weights: 1.82×10^5 (○); 2.47×10^5 (●); 6.1×10^5 (△); 8.56×10^5 (▲) in PIB matrix chains ($M=4.9\times10^6$). The matrix entanglement concentration is shown. (b) Logarithmic plots of $(DM)_{\text{probe}}$ *versus* $(C/C^*)_{\text{matrix}}$ for the data in (a)

dependence disappears as shown in *Figure 5b* when (DM_p) is plotted logarithmically against $(C/C^*)_m$. The reasoning behind this is that, above the matrix overlap concentration, screening of the hydrodynamic interactions follows the Rouse model for freely draining coils with no entanglements: $D_p \sim M_p^{-1}$.

Concentrating now only on semidilute solutions, *Figure 6* summarizes the data for:

(a) the small probe in different matrix molecular weights;
(b) different probe molecular weights in a high molecular weight matrix;
(c) the large probe chain in matrix solutions of lower molecular weight.

It is important to note here that with the matrix of 4.9×10^6, $C_E \approx C^*$ and thus throughout the semidilute regime the chains are entangled.

It is shown in *Figure 7* that all the data in *Figure 6* (i.e. for both $M_p \gg M_m$ and $M_m \gg M_p$) fall on a master curve when plotted as $(DM)_{\text{probe}}$ *versus* $(C/C^*)_{\text{matrix}}$. Thus the probe molecular weight factor accounts adequately for the hydrodynamic screening while normalization of the matrix concentration with C^* describes its topological effect on the probe diffusion.

A set of new experiments has been performed with an intermediate system in order to show the crossover from $M_p > M_m$ to $M_m > M_p$ with a common matrix: ($M = 1.1\times10^6$). Probes both larger and smaller than that of the matrix were used and the results are shown in *Figure 8*. The line drawn through the points is the same as that used in the master curve (*Figure 7*).

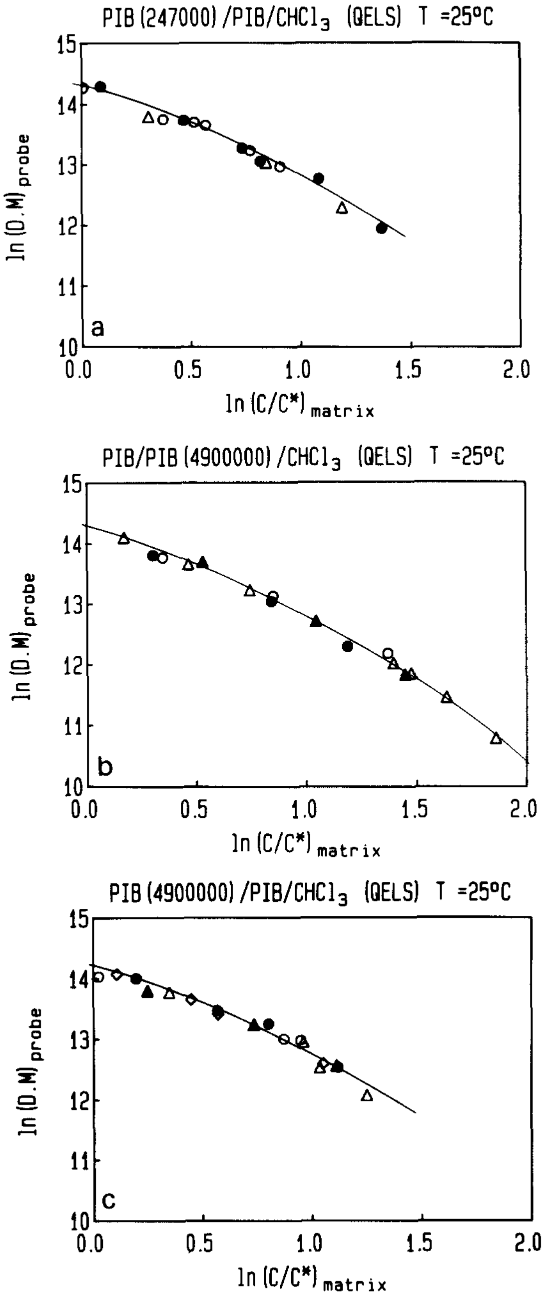

Figure 6 Logarithmic plots for semidilute solution data: $(DM)_{\text{probe}}$ *versus* $(C/C^*)_{\text{matrix}}$. (a) PIB (2.47×10^5) as probe in PIB with $M=1.1\times10^6$ (○); 1.9×10^6 (●); 4.9×10^6 (△) as matrix polymer. (b) PIB probes with $M=1.82\times10^5$ (○); 2.47×10^5 (●); 6.1×10^5 (△); 8.56×10^5 (▲) in PIB ($M=4.9\times10^6$) as matrix polymer. (c) PIB probe (4.9×10^6) in PIB with $M=8.04\times10^4$ (◇); 1.82×10^5 (○); 2.47×10^5 (●); 6.1×10^5 (▲); 1.1×10^6 (△) as the matrix polymer

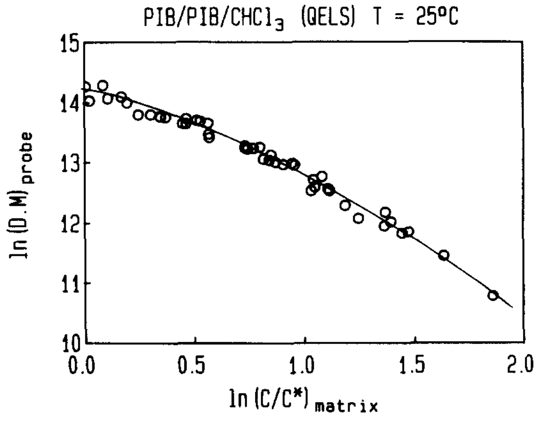

Figure 7 Master curve for the data in *Figure 6a,b,c*

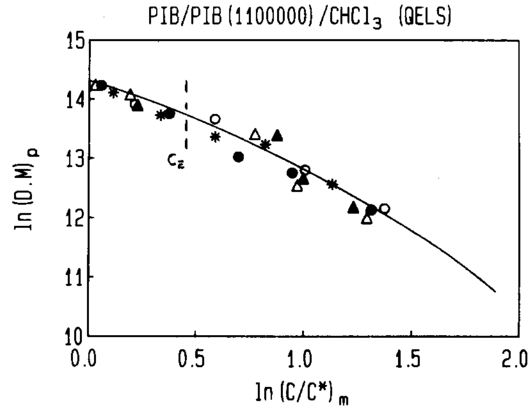

Figure 8 Logarithmic plots: $(DM)_{\text{probe}}$ *versus* (C/C^*) for various probe molecular weights: 8.04×10^4 (○); 1.82×10^5 (●); 2.47×10^5 (△); 1.9×10^6 (▲); 3.6×10^6 (✱) in PIB 1.1×10^6 as the matrix polymer. The matrix entanglement concentration is shown

DISCUSSION

A number of conclusions can be drawn from the data presented above.

Crossover regime: dilute/semidilute

Figures 1 and *2* show that flexible coils and hard spheres whose size is substantially greater than that of the matrix polymer (and thus whose characteristic relaxation time exceeds the lifetime of transient entanglements in the network), diffuse according to the Stokes–Einstein mechanism; i.e. the reduced diffusion coefficient D/D_0 is determined by the macroscopic viscosity of the medium. A master curve for (D/D_0) *versus* (C/C^*) thus exists over a wide range of matrix molecular weights and concentration from dilute to semidilute. Only as the matrix concentration becomes high ($C>3C^*$) does there appear to be a weak interaction between the silica spheres and the PIB chains. In the concentration region in which this occurs, the solutions are entangled with all molecular weights. With large PIB chains as probes, there is only a slight change in $(D\eta/D_0)$ with matrix concentration, which does not support a significant contraction of the probe chain over the concentration interval employed.

There is a strong dependence of probe chain diffusion on the molecular weight of the matrix in contrast to predictions of scaling/reptation. This extends in the present system up to $M_m/M_p=20$, although others[6,9] have reported that above $M_m/M_p=3$–5, matrix independence is observed. This dependence (the topological effect) is eliminated, however, when the matrix concentration is normalized with its overlap concentration. The modified reptation model of Hess[13,26] takes into account 'constraint release' with a gradual transition to 'pure reptation' with increasing concentration. This is found to be reflected in a transition from: $D\sim M_p^{-2}M_m^{-1}$ (constraint release) to $D\sim M_p^{-2}M_m^0$ (reptation). The present data correspond to an intermediate exponent: $M_m^{-0.55}$.

Semidilute solutions

With probe chains of different size and when the matrix concentration exceeds overlap, it is necessary to take into account the influence of hydrodynamic screening. Thus plots of $(DM)_{\text{probe}}$ *versus* $(C/C^*)_{\text{matrix}}$ form a master curve (i.e. there is a common relationship for probes both much smaller and much larger than the matrix). The molecular weight exponent increases smoothly with increasing concentration from about 0.6 in dilute solution to the previously established value of -2 which is approximately valid when $C>C^*$ although only over a limited range of concentration. *Figure 9* shows how the molecular weight dependence of the probe increases from $M^{-0.6}$ at infinite dilution via M^{-1} at about C^*, to $M^{-1.9}$ at $3C^*$. Above C^*, the concentration exceeds the entanglement concentration, C_E (ref. 27) for the matrix ($M=4.9\times10^6$).

Taken together, the data for semidilute concentrations establish (at least for the ranges of relative molecular weights and with the concentrations used in the present system) that a common mechanism is valid for probe diffusion. In the limit $M_p \gg M_m$, where the matrix chains are unentangled for the low molecular weights and entangled for the high, this is clearly the Stokes–Einstein mechanism. However, for probes smaller than the matrix $M_p<M_m$ but still having a R_g larger than the correlation length of the latter, diffusion is no longer simply related to the macroscopic viscosity of the medium. The translational diffusion is then, on the one hand, dependent on the matrix molecular weight and, on the other, it is necessary to take into account the influence of hydrodynamic screening. When this is done, a universal relationship is established for probe diffusion in systems differing widely in relative molecular weights of probe and matrix.

The latter means that it is not necessary to postulate a distinctly different mechanism for translation of the probe (such as reptation) when the probe size is smaller than that of the semidilute matrix. It may be objected here that the present data do not extend to sufficiently high concentration/molecular weight ranges to provide a test for the reptation/scaling model[4,30] in solution. Against this we would point out that the theoretical exponents predicted in good solvents ($D\sim M^{-2}C^{-1.75}$) are observed[21] in the presently used concentration range. One interpretation is that these exponents typify dynamical behaviour in semidilute solutions but are not sufficient criteria for reptation/scaling.

This paper is not a critique of the tube model. In the reptation model of de Gennes and Edwards, the probe chain diffuses in a dense network of entanglements formed by the neighbouring chains which are essentially *frozen* on the time scale of the probe chain motions; thus

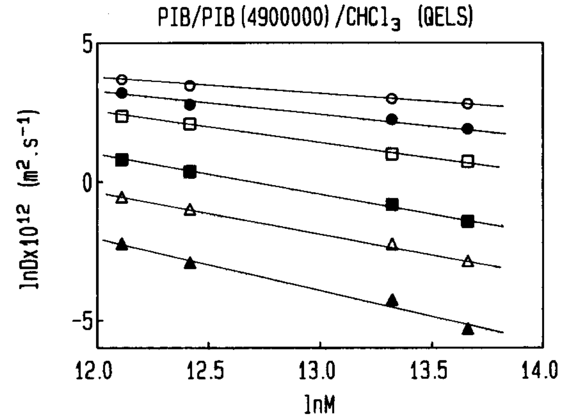

Figure 9 Logarithmic plots of D *versus* molecular weight for the probe at various concentrations of matrix: infinite dilution (○) 0.18%; $0.6C^*$ (●), 0.298%; C^* (□), 0.486%; $1.6C^*$ (■), 0.602%; $2C^*$ (△), 0.894%; $3C^*$ (▲). The slopes are, respectively, from top to bottom: -0.6; -0.85; -1.15; -1.44; -1.47; -1.92

one can understand the success of the model in describing the dynamics of polymer melts with long chains. The suitability of applying this model to data for semidilute solutions is less than clear. This remark is addressed to the bulk of the literature data on semidilute solutions.

The observed variation in the molecular weight dependence for probe diffusion and the progression in the exponent to a limiting value ($D \sim M^{-2}$) may be seen, instead, to be a general consequence of diffusion in congested systems and derives from the combined effects of hydrodynamic screening and the topological restrictions imposed by the matrix polymer. It thus becomes straightforward to understand the observed variation in the concentration exponent, which is well known to exceed the predicted reptation/scaling value of -1.75 (good solvents) and to increase towards a value of -3 or even higher[7]. It should be mentioned that the present concentration ranges are sufficiently low ($<3\%$) that it is unnecessary to correct for the influence of the monomeric friction coefficient on the concentration exponent. This should become significant for concentrations in excess of about 10%[14]. As pointed out, there has been considerable ambiguity with interpretation in terms of scaling since there will always be concentration/molecular weight ranges where an exponential model provides a plausible fit to the data. The work of both Skolnick and coworkers[15] and Phillies[31] have provided alternative theoretical viewpoints to reptation/scaling for self-diffusion in congested systems.

CONCLUSIONS

Probe self-diffusion coefficients have been estimated for PIB chains in matrix chains of the same polymer, such that probe chains much smaller than, and also much larger than, the matrix chains have been used.

In the crossover range from dilute to semidilute concentration of the matrix, the data form a universal curve when plotted logarithmically as (D/D_0) *versus* (C/C^*). Data for the translational diffusion of silica spheres of different sizes in the same PIB matrix chains fall on the same curve.

In the semidilute regime, hydrodynamic screening must also be taken into account. Then logarithmic plots of $(DM)_{\text{probe}}$ *versus* $(C/C^*)_{\text{matrix}}$ form a universal curve. Thus D_{probe} is determined by both hydrodynamic and topological contributions in congested solutions.

Taken together, the data demonstrate that the reptation/scaling model is inapplicable in semidilute solutions. Instead models that consider cooperative chain motions, such as those of Rendell *et al.*[29] and Skolnick and coworkers[15] are seen to be the most promising. The representation of Phillies[31] also provides an alternative and excellent phenomenological description of self-diffusion data in such solutions.

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