

## **The Behavior of the Tracer Diffusion Coefficient of Polystyrene in Isorefractive "Solvents" Composed of Poly(Vinyl Methyl Ether) and *o*-Fluorotoluene**

**Brian Hanley<sup>1</sup>, Matthew Tirrell<sup>1</sup>, and Timothy Lodge<sup>2</sup>**

<sup>1</sup> Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA

<sup>2</sup> Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

### Summary

In this paper, we describe and use a relatively new technique - dynamic light scattering from refractive index-matched ternary solutions- to study a quantity very closely related to the self-diffusion coefficient in binary systems. We refer to this quantity as the tracer diffusion coefficient. This tracer diffusion coefficient is expected to behave in much the same way as the self-diffusion coefficient, in terms of its concentration and molecular weight dependencies. In this study, we use two compatible polymers, polystyrene and poly(vinyl methyl ether), and a solvent, *o*-fluorotoluene, chosen specifically because its refractive index matches that of the poly(vinyl methyl ether). The technique is advantageous in that it allows the experimenter to vary independently the molecular weight of both the probe and "invisible" matrix polymers, their individual molecular topologies, and the overall polymer concentration with relative ease. No special chemical tagging is required, although it must be borne in mind that we are not measuring self-diffusion but the diffusion of a dissimilar tracer. Our experiments probe the diffusion of linear polystyrenes in matrices composed of linear poly(vinyl methyl ether)/*o*-fluorotoluene. Our results show a crossover from non-free draining (Zimm) to free draining (Rouse) hydrodynamic behavior of polystyrene as the concentration of the invisible poly(vinyl methyl ether) making up the matrix is increased.

### Introduction

We report here further dynamic light scattering results on the tracer diffusion coefficient of polystyrene in refractive index-matched solutions containing an "invisible" background of poly(vinyl methyl ether) and a suitable solvent (1, 2, 3). The solvent is chosen to preserve the compatibility of polystyrene with poly(vinyl methyl ether). In addition, the solvent must have optical characteristics which give rise to little or no excess scattering with the addition of poly(vinyl methyl ether). The polystyrene must be present in only very dilute solution so as to minimize chemical potential driving forces and cross-diffusional effects. Under these conditions, we observe a "tracer" polystyrene diffusion coefficient, which is expected to mimic self-diffusion

behavior.

## Experimental

The detailed interpretation of light scattering spectra from index-matched ternary systems has been described previously (1). The system o-fluorotoluene(1) - polystyrene(2) - poly(vinyl methyl ether)(3) is one in which the two polymer components remain compatible and in which the condition of index-matching is nearly met at room temperature. In this study, all experiments were performed at  $30^{\circ}\text{C} \pm 0.1^{\circ}$ . The refractive index increment for the pair o-fluorotoluene/polystyrene at this temperature is approximately 0.10 ml/gm while for o-fluorotoluene/poly(vinyl methyl ether) the refractive index increment is less than 0.001 ml/gm. Our previous analysis of light scattering from index-matched ternary solutions (1) leads us to believe that this small shift away from the temperature of complete index matching will have no effect. Experiments performed on a binary solution containing 6% by weight of poly(vinyl methyl ether) yielded no detectable correlation function from  $17^{\circ}\text{C}$  to  $45^{\circ}\text{C}$  for delay times of 1 microsecond to  $10^4$  microseconds. Polystyrene standards with molecular weights of 50,000 and 1,800,000 were obtained from the Pressure Chemical Co. In addition, NBS standard reference polystyrenes with molecular weights of 179,000 and 1,050,000 were used. The concentration of polystyrene tracer used in these experiments was held at 10% of the polystyrene overlap concentration or less. The poly(vinyl methyl ether) sample was obtained from Polysciences, Inc. The weight-average molecular weight was determined to be 60,000 using a Chromatix KMX-6 low angle light scattering photometer. Subsequent GPC analysis showed the sample to be of fairly broad molecular weight distribution, with polydispersity of order 3. The intrinsic viscosity of the poly(vinyl methyl ether) was found to be 45 ml/gm. The overlap concentration for this sample is therefore estimated to be  $c^* \sim 0.07$  gm/ml, using  $c^* = 3/[\eta]$ . We estimate the zero-shear viscosity critical molecular weight for poly(vinyl methyl ether) melts to be approximately 30,000 (4). The o-fluorotoluene was obtained from the Aldrich Chemical Co. and was used without further purification. Samples were prepared in either of two ways. If the overall polymer concentration was low enough, the solutions were made up directly and filtered through  $0.2 \mu\text{m}$  filters into the scattering cuvettes. However, if the concentration of polymer was too high to allow direct filtration, the solutions were prepared by filtering dilute stock solutions into the scattering cuvettes and allowing these solutions to evaporate in a dust free environment until the desired final concentrations were reached.

The dynamic light scattering photometer has been described elsewhere (2, 5). All experiments were performed in the homodyne mode. Most data analysis was performed by subtracting the experimental baseline (the average of the last 16 channels, which were delayed by 1096 channels) and fitting the resulting data to the cumulant expansion:

$$1/2 \ln g(t) = \ln \beta - \Gamma t(1 + u_2/2 t + \dots) \quad (1)$$

where  $\Gamma = D_{tr} q^2$  is the first cumulant. It is important to remember that, in these experiments, the excess scattering arises from the dilute polystyrene tracer and not from the invisible poly(vinyl methyl ether) matrix. The experimental results are thus readily interpreted in terms of dilute solution models of correlation function behavior.

## Results and Discussion

Figure 1 presents results for the concentration dependence of the tracer diffusion coefficient for the four molecular weights of polystyrene mentioned earlier. Note that in all cases the molecular weight of the polystyrene tracer is approximately equal to or greater than the molecular weight of the poly(vinyl methyl ether). The qualitative features of this concentration dependence are in agreement with those exhibited by the concentration dependence of binary self-diffusion coefficients - a relatively mild concentration effect below  $c^*$  ( $c^* \sim 0.07$  gm/ml) which becomes much stronger for concentrations above  $c^*$  (6, 7, 8). Even at moderate concentrations of poly(vinyl methyl ether), the instantaneous power-law exponents exceed in absolute magnitude the reptation/scaling predictions of  $D \propto c^{-1.75}$  for monodisperse polymers in good solvents and  $D \propto c^{-3}$  for theta solvents. This is interesting since we do not expect to see reptation behavior for the molecular weights and concentrations used in this study. It has been argued (9) that the steep downturn in the observed

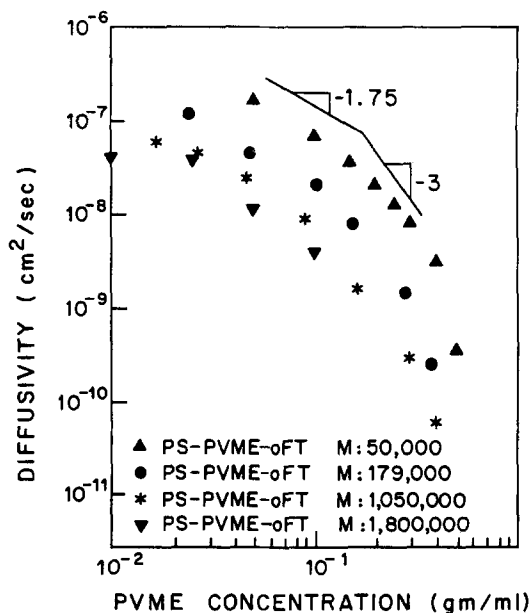


Figure 1. Behavior of the polystyrene tracer diffusion coefficient with poly(vinyl methyl ether) concentration. Note the strong concentration dependence above  $c^*$  ( $\sim 0.07$  gm/ml). Lines with concentration power law exponents of -1.75 and -3 (obtained from reptation/scaling arguments) added as a guide to the strength of the concentration dependence.

concentration dependence of the self-diffusion coefficient in semidilute solution is due to the fact that the monomeric friction coefficient undergoes tremendous changes as polymer concentration is increased; the reptation/scaling predictions account only for the influence of topological constraints and do not consider the variation of the monomeric friction coefficient with concentration (10). By analogy we expect the very strong concentration dependence of the tracer diffusion coefficient to include a component which is due to the concentration dependence of the monomeric friction coefficient. This particular concentration effect is operative in our samples whether reptation occurs or not and would be expected to dominate at higher concentrations.

In order to investigate the effect of the molecular weight of the polystyrene,  $M_2$ , upon the value of the tracer diffusion coefficient, we make a scaling postulate. We assume that the function relating the tracer diffusion coefficient to both tracer molecular weight and to concentration,  $D_{tr}(c, M_2)$ , can be reduced to a function of a single variable, the concentration, with the appropriate choice of molecular weight scaling:

$$[D/M_2^{\mu(c)}] = W(c) \quad (2)$$

We have made the power law exponent,  $\mu$ , concentration dependent also to account for transitions in the molecular weight dependence due to changes in the mechanisms of center-of-mass motion with concentration. The molecular weight power law exponents that we investigate are  $\mu = 0.5, 1.0, 2.0$ , which are the predictions for the non-free draining, free draining, and reptation models, hereafter referred to as the Zimm, Rouse, and reptation models (we expect the power law exponent,  $\mu$ , to vary smoothly with concentration, but we only investigate these three distinct possibilities). The non-free draining, or Zimm, model accounts for intramolecular hydrodynamic interaction via the Kirkwood-Riseman formalism. This effect would be most likely to occur in dilute solutions (11). With increasing polymer concentration, intramolecular hydrodynamic interaction is considerably weakened by the presence of segments from other chains in the domain of a given polymer molecule. For this reason, the free draining, or Rouse, model is often chosen to describe this screening effect, which increases the local friction each chain subunit experiences, thus producing a more pronounced molecular weight dependence. Rouse-like behavior is observed in viscoelastic experiments at intermediate polymer concentrations where "entanglement" effects are not important (12, 13, 14). Finally, we examine the predictions of the reptation model, which take into account the effects of topological constraints upon the diffusion of polymer chains. Reptation behavior is expected in binary solutions sufficiently high in polymer content and in molecular weight to bring about extensive overlapping of individual coils and thus lead to the formation of what might be called a temporary network. As long as the relaxation time of this network is very much longer than the reptation time of an individual chain, then individual chains will be forced to diffuse along paths defined by their contour lengths. In cases where

there are two different polymeric species present, with differing molecular weights, in addition to a solvent, it is not clear what combination of parameters will lead to reptation of one of the polymeric components (15). We still investigate its possible occurrence in this system, even though the ratio of the tracer molecular weight to the matrix molecular weight is large.

Figures 2, 3, and 4 are plots of "scaled" diffusion coefficients versus polymer concentration for the three cases above. Figure 2 demonstrates that non-free draining behavior is observed in dilute solutions, while figure 3 shows that free draining-like behavior is observed at more elevated concentrations, in agreement with expectations. There is a trend toward a more pronounced molecular weight dependence than that of the free draining model, which can be observed in figure 4. Because the molecular weight of the poly(vinyl methyl ether) is not greatly above its critical molecular weight and because of the fact that the molecular weights of the polystyrene tracers are equal to or greater than that of the poly(vinyl methyl ether), we do not expect to see any clear manifestation of reptation in these experiments. Preliminary studies using a poly(vinyl methyl ether) with a molecular weight of 1,300,000 and some of the polystyrenes mentioned above have yielded results which are in keeping with the reptation model.

In short, dynamic light scattering from ternary systems composed of a visible "tracer" polymer and a "solvent" composed of an "invisible" polymer and a small molecule species can be used to simulate self-diffusion in binary systems. The tracer diffusion coefficient obtained from these systems behaves,

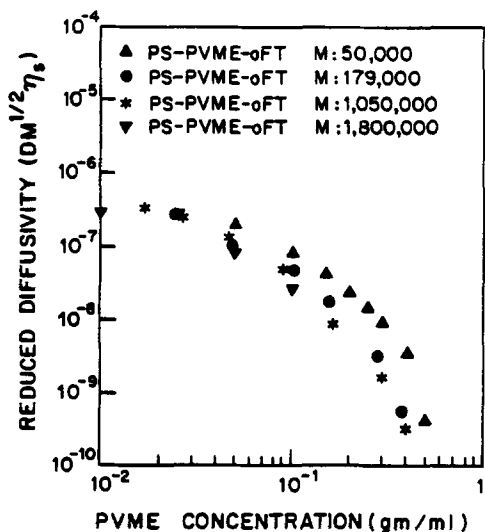


Figure 2. Reduced polystyrene tracer diffusion coefficient for Zimm-like behavior,  $D \sim M^{-1/2}$ . Note that the data collapse to a common locus at low concentration. Data also scaled by the solvent viscosity.

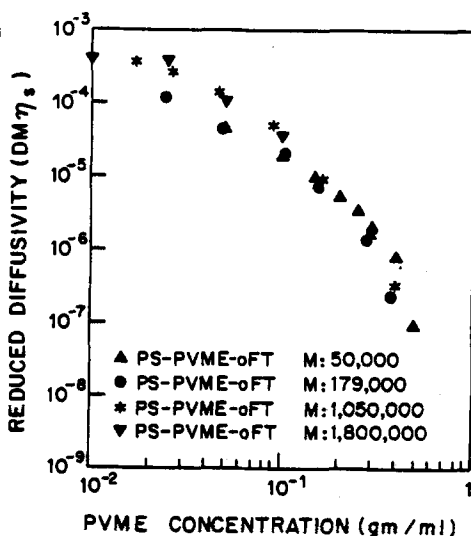


Figure 3. Reduced polystyrene tracer diffusion coefficient for Rouse-like behavior,  $D \sim M^{-1}$ . Note that the data collapse to a common locus at intermediate concentration. Data also scaled by the solvent viscosity.

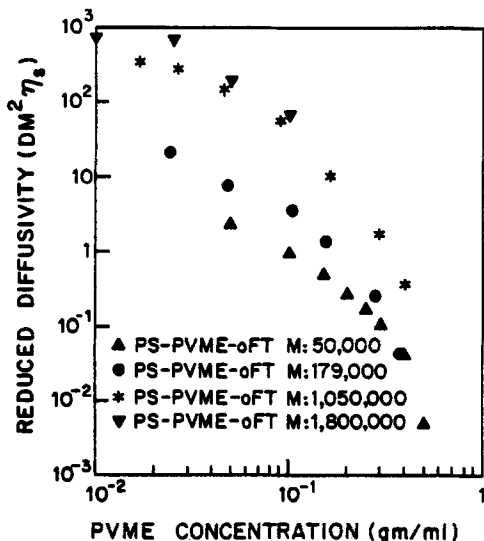


Figure 4. Reduced polystyrene tracer diffusion coefficient for the reptation model. Note that there is a trend toward a molecular weight dependence greater than  $D \sim M^{-1}$  as in figure 3. Data also scaled by the solvent viscosity.

in most respects, in the same manner as the self-diffusion coefficient does. The concentration dependence of the tracer diffusivity is mild below  $c^*$ , but increases dramatically as the overall polymer concentration is increased. The dependence of the tracer coefficient on the molecular weight of the tracer species exhibits a transition from Zimm-like to Rouse-like behavior with increasing concentration. At the highest concentrations investigated, it appears as though reptation might be a possible mechanism of transport for the lower molecular weight tracer species.

## References

1. B. Hanley, S. Balloge, and M. Tirrell, *Chem. Eng. Commun.* **24**, 93 (1983).
2. T. Lodge, *Macromolecules* **16**, 1393 (1983).
3. J. Martin, *Macromolecules* **17**, 1279 (1984).
4. D.W. van Krevelin and P.J. Hoftyzer, "Properties of Polymers" Elsevier Amsterdam, Oxford, New York, 338 (1976).
5. S. Balloge and M. Tirrell, *Macromolecules* **18**, 817 (1985).
6. H. Hervet, L. Léger, and F. Rondelez, *Phys. Rev. Lett.* **42**, 168 (1979).
7. L. Léger, H. Hervet, and F. Rondelez, *Macromolecules* **14**, 1732 (1981).
8. P.T. Callaghan and D.T. Pinder, *Macromolecules* **14**, 1334 (1981).
9. N. Nemoto, M.R. Landry, I. Noh, T. Kitano, J.A. Wesson, and H. Yu, *Macromolecules* **17**, (1984).
10. M. Tirrell, *Rubber Chem. and Tech.* **57**, 523 (1984).
11. J.G. Kirkwood and J. Riseman, *J. Chem. Phys.* **16**, 565 (1948).
12. R.B. DeMallie, M.H. Birnboim, J.E. Frederick, N.W. Tschoegl, and J.D. Ferry, *J. Phys. Chem.* **66**, 536 (1962).
13. J.E. Frederick, N.W. Tschoegl, and J.D. Ferry, *J. Phys. Chem.* **68**, 1974 (1964).
14. L.A. Holmes and J.D. Ferry, *J. Polym. Sci.* **C23**, 291 (1968).
15. M. Daoud and P.G. deGennes, *J. Polym. Sci. - Phys.* **17**, 1971 (1979).