Notes

A Phenomenological Approach to Separating the Effects of Obstruction and Binding for the Diffusion of Small Molecules in Polymer Solutions

J. A. Davies and P. C. Griffiths*

Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, United Kingdom

Received March 11, 2002
Revised Manuscript Received November 11, 2002

Introduction

The diffusion of small molecules within a swollen polymer environment is influenced by a host of factors, including those specific to the diffusant (molecular size and shape) and those specific to the matrix (polymer molecular weight, flexibility, and concentration). Significant changes in diffusivity can occur due to specific interactions such as hydrogen bonding.

A number of different approaches have been proposed to describe small molecule diffusion in polymer solutions. Of most note are the theories of Mackie and Meares,[1] Johansson et al.,[2] Fujita,[3] Vrentas and Duda,[4] and Phillies.[5,6] Each of these models molecular diffusion in polymer solutions from a quite different origin—free volume, obstruction, or hydrodynamics. None of these models attempt to account for any reduction in mobility arising as a result of specific interactions between the constituent components.

The basis of free volume theories centers on a diffusive flux created by the transfer of penetrant from one element of this free volume to the next while the integrity of the polymer chains remains intact.[3] Consequently, the diffusion coefficient of a small solute molecule becomes a function of the probability of encountering a volume commensurate in size with the cross section of the diffusing molecule

$$\frac{D}{D_0} = \exp\left[\frac{B_g}{f_w}\left(1 - \frac{1}{1-\varphi_p}\right)\right] \qquad (1)$$

where B_g is a measure of the size of the diffusing molecule, f_w is the free volume contributed by the solvent, D is the self-diffusion coefficient of the probe at a polymer weight fraction, φ_p, and D_0 is the free probe self-diffusion coefficient, i.e., when $\varphi_p = 0$.

The phenomenological stretched exponential formalism proposed by Phillies[5,6] has also been extensively used to describe the diffusion of probes in polymer solutions.[7−9]

$$\frac{D}{D_0} = \exp(-\alpha\phi^{\nu}) \qquad (2)$$

The constants α and ν are thought to be dependent on the system of interest, yet there is still no definitive agreement on their physical significance.[10] Phillies suggests that α varies according to R/a_0, where a_0 is the distance of closest approach between a solute probe and a polymer bead.[11] Cukier[12] also presents evidence for a relationship between α and R_H, the radius of a diffusing probe within a polymeric solution. These results seem to suggest that, within a given probe/polymer/solvent system, there may be a correlation between the scaling parameter α and the physical obstruction experienced by the probe due to the polymer matrix. When specific interactions are present, the probe diffusion can be affected significantly. For example, Lee et al.[10] reported that the diffusion of methyl red (MR) was substantially slower in a poly(vinyl acetate) (PVAc)/toluene solution than in a polystyrene (PS)/toluene solution. The slower diffusion of MR in the presence of a PVAc matrix was ascribed to the hydrogen bonding present between the probe and polymer, and an equilibrium binding constant was extracted from these data. There is a possible correlation between ν and the strength of any specific interaction between the probe molecule and the polymer segment. Park et al.[13] found that by systematically increasing the amount of hydrogen-bonding capable moieties within a random copolymer, a systematic decrease in the diffusivity of a hydrogen-bonding capable probe was achieved. They found that the stretched exponential relation described their data very well, and with an increase in hydrogen-bonding capable units, ν decreased from 1.03 ± 0.05 to 0.73 ± 0.02. This suggests that ν is a measure of the strength of the specific interaction. However, in that study, the mole fraction of hydrogen-bonding capable polymer was increased within the copolymer, and therefore the obstructing nature of the matrix was not kept constant; obstruction and specific interaction were not decoupled.

Here, we describe PGSE-NMR measurements of the diffusion of three probe molecules, toluene, aniline, and phenol in polymer solutions. A purely phenomenological approach is adopted that decouples specific binding and obstruction and therefore lends some further credence to the use of the stretched exponential formulism.

Experimental Section

Materials. All materials were used as received; *d*-methanol (methyl-d_3 99.8% D, Sigma), poly(vinyl acetate) (PVAc), $M_w = 190\,000$ (Aldrich); poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) [PEG_{76}-*b*-PPG_{29}-*b*-PEG_{76}], $M_n = 8400$ (Aldrich), aniline (Aldrich), toluene (Fischer Scientific UK), and phenol (Aldrich).

Sample Preparation. Stock polymer/diffusant/solvent samples were sealed, turned end-over-end until dissolution, and then left for 12 h to equilibrate. 0.600 g aliquots of these were then pipetted into 5 mm NMR and diluted in the NMR tube with 1.0% w/w solutions of diffusant.

10.1021/ma0203748 CCC: $25.00
Published on Web 01/04/2003

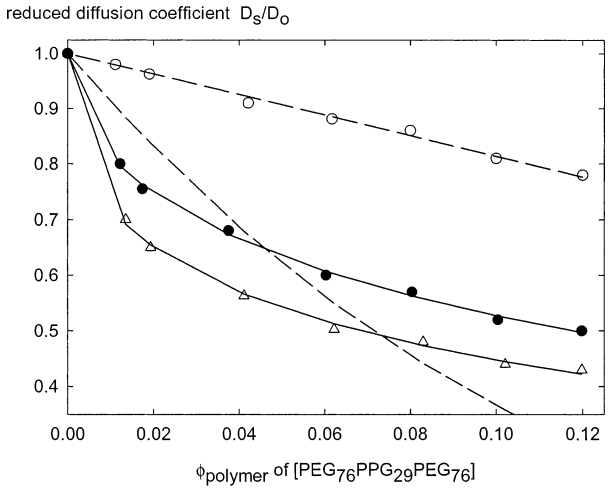

Figure 1. Plot of reduced diffusion coefficient D/D_0 for toluene (open circles), aniline (solid circles), and phenol (triangles) against $\phi_{polymer}$ of [PEG_{76}-*b*-PPG_{29}-*b*-PEG_{76}]. The lines represent the fit to the models of Phillies **(**solid**)** and free volume **(**dashed**)**.

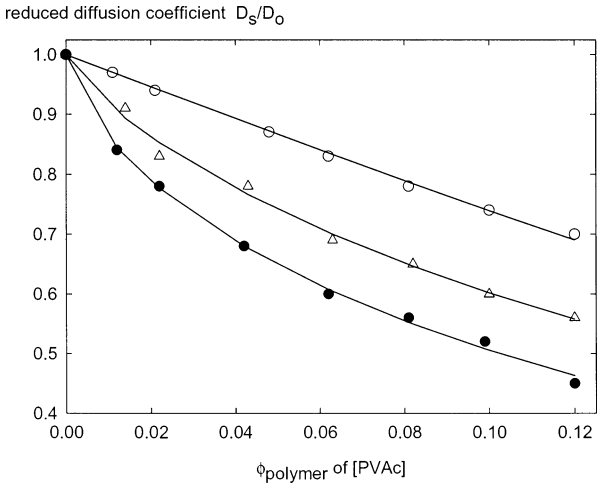

Figure 2. Plot of reduced diffusion coefficient D/D_0 for toluene (open circles), aniline (solid circles), and phenol (triangles) against $\phi_{polymer}$ of [PVAc]. The (solid) lines represent the fit to the model of Phillies.[5,6]

Pulsed-Gradient Spin-Echo NMR (PGSE-NMR) Diffusion Measurements. The self-diffusion measurements were performed on a Bruker AMX360 high-resolution NMR spectrometer employing a stimulated echo sequence. Briefly, a constant current gradient amplifier (Bruker) delivers pairs of read and write gradients matched to better than 10 ppm. These gradients are ramped up to the maximum value and down again over a time σ, typically 250 μs, which in conjunction with three prepulses before every scan minimizes distortions due to coil heating and eddy currents.

The self-diffusion coefficient, D_s, is extracted by fitting to eq 3 the measured peak integral, $A(G,\delta)$, as a function of field gradient duration δ, ramp time σ, intensity G, and separation Δ:

$$A(G,\delta) = A_0 \times \exp\left[-\gamma^2 G^2\left(\frac{30\Delta(\delta+\sigma)^2 - (10\delta^3 + 30\sigma\delta^2 + 35\sigma^2\delta + 14\sigma^3)}{30}\right)D_s\right] \quad (3)$$

where γ is the magnetogyric ratio of the nucleus under observation, in this case protons. The A_0 term is determined by the number of protons in the sample. All experiments were performed at 21 °C.

Results

The proton signals for all the probe molecule are well-resolved, and accordingly, only single-exponential decays were observed in these systems. Figure 1 shows the reduced diffusion coefficients D/D_0 of the three diffusant molecules as a function of the polymer weight fraction φ_p for the copolymer. It is evident that the self-diffusion coefficients of the diffusant molecules decrease with increasing polymer concentration and are quite evidently a function of interaction strength between the diffusant and the polymer. Note that the effective molecular size of the diffusant molecule must include a shell of d-MeOH molecules but by employing the reduced diffusion coefficient eliminates the effects of diffusant/diffusant and diffusant/solvent interactions. Hence, the reduced diffusion coefficient reflects primarily the polymer−diffusant interactions. Both the free volume (eq 1) and Phillies (eq 2) treatments fit the toluene data, but only that of Phillies describes the aniline and phenol data. The failure of the free volume theory to describe the aniline and phenol data is attributed to the presence of specific interactions between the polymer and the probe molecules.

α is constant ($\alpha = 2.0 \pm 0.1$) for each of the diffusant molecules; α is dominated by obstruction effects.[11,12] ν decreases from $\nu \approx 1.0$ for a system where there is no hydrogen bonding (toluene) to $\nu \approx 0.49$ (aniline) and $\nu \approx 0.35$ for a system where the hydrogen bonding is strong (phenol).

Analogous data for the PVAc system are shown in Figure 2; as found previously, the reduced diffusion coefficients of toluene are higher than those of both aniline and phenol. However, the order is now slightly different; the diffusion of aniline is less than that of phenol. Similar trends in α and ν are observed as in the copolymer system; $\alpha = 3.0 \pm 0.1$ for each of the diffusant molecules studied and ν decreased from $\nu \approx 1.0$ (toluene) to $\nu \approx 0.77$ (phenol) and $\nu \approx 0.66$ (aniline).

Discussion

In the toluene systems, the only retarding force experienced by the probe molecule with increasing polymer concentration is due to obstruction. The toluene data may therefore be interpreted as the effect due to obstruction alone. Once the decrease in diffusion arising through obstruction effects have been removed, any further retardation is due only to specific interactions between the probe molecule and the polymer.

Figures 3 and 4 show the retardation component to aniline and phenol data for the two polymer systems, i.e., the diffusion correct for the obstruction effect described by the free volume fit to the toluene data. The greater retardation of the diffusion of phenol compared to aniline within the PEG-*b*-PPG-*b*-PEG system is a manifestation of the fact that phenol forms a stronger hydrogen bond with the polymer than aniline due to the greater electronegativity of oxygen compared to that of nitrogen.

The relative strengths of the hydrogen bonds formed by these two probe molecules can be estimated by calculating the ratio of the obstruction-corrected relative diffusion coefficients over the approximately linear part of the polymer concentration range, i.e., $0.05 < \varphi_p < 0.13$. This analysis yields a value of 0.77 ± 0.02 for the

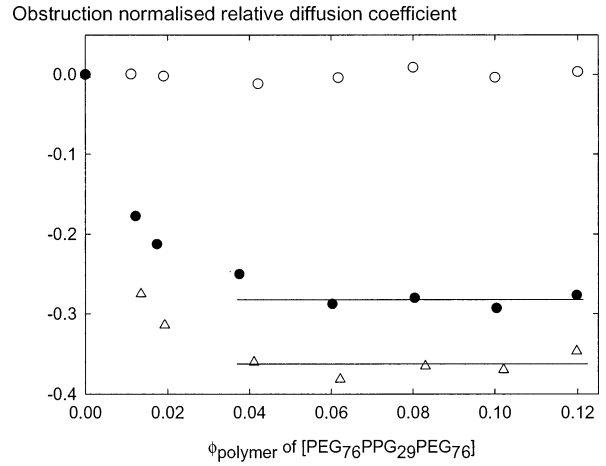

Figure 3. Obstruction normalized relative diffusion coefficient for toluene (open circles), aniline (solid circles), and phenol (triangles) against $\phi_{polymer}$ of [PEG_{76}-*b*-PPG_{29}-*b*-PEG_{76}].

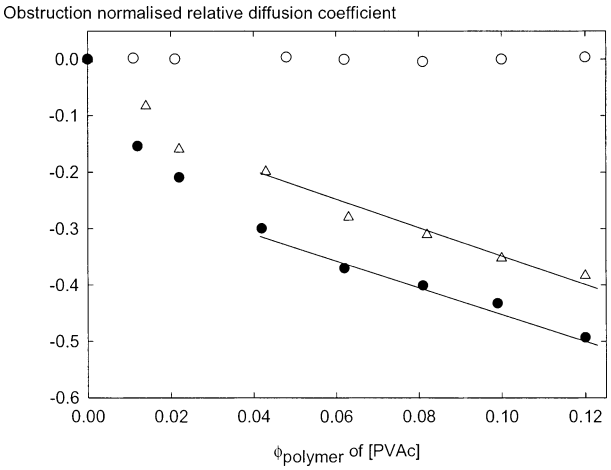

Figure 4. Obstruction normalized relative diffusion coefficient for toluene (open circles), aniline (solid circles), and phenol (triangles) against $\phi_{polymer}$ of PVAc.

relative strength of the hydrogen bond formed by aniline, relative to phenol. Repeating this analysis for the PVAc system yields the ratio 1.68 ± 0.06, but noting that aniline can form two hydrogen bonds but phenol only one; i.e., this ratio should be halved. Thus, the PVAc-derived relative hydrogen-bonding strength is 0.84 ± 0.03, in excellent agreement with the copolymer estimate.

Conclusions

In the systems studied, the stretched exponential approach of Phillies[5,6] can account for both obstruction and specific binding effects, whereas the free volume theory fails when there is any hydrogen bonding present. Having removed the retardation due to obstruction using the toluene data, the retardation in the probe diffusion due to hydrogen bonding alone can be estimated. It is shown that the strength of the hydrogen bond formed by aniline is ≈80% that of the hydrogen bond formed with phenol.

Acknowledgment. This work was supported in part by ICI Imagedata, Brantham, Essex.

References and Notes

(1) Mackie, J. S.; Meares, P. *Proc. R. Soc. London, A* **1955**, *232*, 498.
(2) Johansson, L.; Elvington, C.; Lofroth, J. E. *Macromolecules* **1991**, *24*, 6024.
(3) Fujita, H. *Adv. Polym. Sci.* **1961**, *3*, 1.
(4) Vrenta, J. S.; Duda, J. L.; Ling, H. C.; Hou, A. C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 289.
(5) Phillies, G. D. J. *Macromolecules* **1987**, *20*, 558.
(6) Phillies, G. D. J. *J. Phys. Chem.* **1989**, *93*, 5029.
(7) Chang, T.; Kim, H.; Yu, H. *Macromolecules* **1987**, *20*, 2629.
(8) Furukawa, R.; Arauz-Lara, J. L.; Ware, R. R. *Macromolecules* **1991**, *24*, 599.
(9) Park, I. H.; Johnson, C. S., Jr.; Gabriel, D. A. *Macromolecules* **1990**, *23*, 1548.
(10) Lee, J.; Park, K.; Chang, T.; Jung, J. C. *Macromolecules* **1992**, *25*, 6977.
(11) Phillies, G. D. J. *Macromolecules* **1988**, *19*, 875.
(12) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
(13) Park, H. S.; Sung, J.; Chang, T. *Macromolecules* **1996**, *29*, 3216.

MA0203748