Hydrogen Bonding Effect on Probe Diffusion in Semidilute Polymer Solutions: Polymer Chain Structure Dependence

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ABSTRACT: The diffusivity of 4-[[4′-(dimethylamino)phenyl]azo]benzoic acid (p-MR) in poly(methyl methacrylate) (PMMA)/toluene solution was found to be much lower than in polystyrene solution due to the hydrogen bonding interaction between the diffusant and the polymer matrix. In order to study the effect of the H-bonding interaction in a quantitative manner, the content of MMA units in the polymer matrix capable of H-bonding with p-MR was varied using mixtures of polystyrene (PS) and PMMA as well as PS/PMMA random and diblock copolymers. In the mixture or diblock copolymer systems, the diffusion behavior of the probe could be well represented by a phenomenological model which assumes the additivity of the diffusional activation barriers due to hydrodynamic interaction and H-bonding interaction. On the other hand, we observed far more effective H-bonding in random copolymers than in mixtures or in block copolymers. The diffusivity of p-MR in a solution of random copolymers with MMA content of 40% or higher was found to be similar to pure PMMA. This peculiar behavior of p-MR diffusion in random copolymers may reflect the difference in binding efficiency of the copolymers and in the microscopic environment for the diffusion path of p-MR.

Introduction

The fact that diffusion of small molecules in polymer solutions or in gels is retarded relative to the diffusion in solvent constitutes the foundation of the separation mechanisms in many analytical methods such as gel electrophoresis and gel filtration. In the absence of specific interactions such as Coulombic or hydrogen bonding interactions, the diffusion of small molecules through a mesh of polymer chains is retarded mainly by the hydrodynamic interaction between the diffusant and the polymeric segment.[1−5] Therefore, the retardation of the diffusion in a polymer matrix can be represented as a function of the diffusant's size and the mesh size of the polymer matrix, a function of the polymer concentration. In fact, it has been well established for the small probe diffusion in a polymer matrix without specific interaction that the relative diffusivity follows a stretched exponential form,[6−22]

$$D/D_0 = \exp(-\alpha\phi^{\nu}) \qquad (1)$$

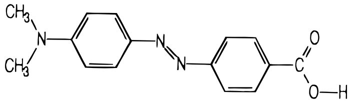
where D is the diffusivity in the presence of a polymer matrix at the concentration of ϕ, D_0 is the diffusivity in pure solvent, and α and ν are constants depending on the system of interest including the size of the diffusant.

Several years ago, Lee and Lodge reported that the diffusion of methyl red was retarded more in toluene solutions of poly(vinyl acetate) (PVAc) compared to polystyrene at the same polymer concentration.[23] They proposed that the further retardation resulted from the hydrogen bonding interaction between methyl red and PVAc. This proposal was supported by the fact that the retardation effect was reduced in ethyl acetate solution, where the H-bonding was mitigated by the presence of H-bonding solvents. Later Lee et al. confirmed that the further retardation in the PVAc matrix was due to H-bonding effect, by measuring the diffusion of two isomers of methyl red and their methyl ester derivatives.[24] The methyl esters of the dyes, which could not hydrogen bond to the PVAc, showed the same diffusivity in PS and PVAc matrices. In addition, they reported that the concentration dependence of the diffusivity followed the stretched exponential form (eq 1) even in the presence of H-bonding interactions.[24]

The next question that arises concerns the quantitative dependence of the probe diffusion on the density of H-bonding in, for example, copolymers or polymer mixtures of H-bonding and non-H-bonding monomeric units. In this paper, we report the results of the probe diffusion measurement and a phenomenological explanation of the probe diffusion behavior as a function of the H-bonding moiety fraction in the polymer matrix.

Experimental Section

The probe dye, 4-[[4′-dimethylamino)phenyl]azo]benzoic acid (p-MR), was acquired from TCI. The polymers employed are tabulated in Table 1. PMMA was chosen in place of the PVAc used in previous works, since the former can be easily copolymerized with PS while the latter cannot. PS/PMMA random copolymers were prepared in this laboratory by a typical bulk polymerization procedure using AIBN as the initiator. In order to avoid composition drift, copolymerization was stopped before the conversion reached 10% by precipitating the polymer in an excess amount of methanol. The composition of the copolymers was determined by ^{1}H NMR spectroscopy. PS/PMMA diblock copolymers were generously provided by Professor Stadler at the University of Mainz, Germany.



p-MR

Toluene solutions of the polymer and p-MR were prepared gravimetrically. The solutions were filtered through 0.2 μm pore PTFE membrane filters (Gelman) directly to 5 mm path length spectroscopic quartz cuvettes for the forced Rayleigh scattering (FRS) measurements.

The FRS apparatus used in this study was described in detail elsewhere.[25] The 488 nm line of an Ar ion laser (Coherent, Model 90-3) was used for the writing beam and the 632.8 nm line of a He/Ne laser (Melles Griot, 5 mW) was employed for the reading beam. The temperature of the cell was controlled at 25.0 ± 0.1 °C. The concentration of probe

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Table 1. Characterization of Polymers Used

polymers	M_w ($\times10^3$)	M_w/ M_n	MMA (%)	source
homopolymer				
PS (narrow)	170	1.06		Pressure Chemical
PS (broad)	237	2.26		Miwon Petrochemical
PMMA (narrow)	160	1.15		Pressure Chemical
PMMA (broad)	136	2.02		Aldrich
random copolymer				
SMR1	36.6	2.07	7.4	homemade
SMR2	155	2.11	13.6	homemade
SMR3	189	2.46	26.3	homemade
SMR4	34	3.42	37.5	homemade
SMR5	77	2.58	43.0	homemade
SMR6	276	2.15	58.7	homemade
block copolymer				
SMB1	53		56.5	University of Mainz
SMB2	95		67.9	University of Mainz

dye was kept below 0.1 mg/mL so as to avoid the dye concentration dependence in diffusivity. In all the systems examined in this study, we obtained single exponential FRS decay profiles. Thus, the decay time constant, τ, of the diffraction intensity was determined by nonlinear regression fit to the following four-parameter model function:

$$I_d(t) = [A \exp(-t/\tau) + B_{coh}]^2 + B_{incoh}^2 \qquad (2)$$

where B_{coh} and B_{incoh} denote the coherent and incoherent background optical field, respectively. Diffusion coefficients are obtained from the slope of $1/\tau$ vs q^2 plots, where $q = 2\pi/d$ and d is the spacing of the optical fringe created by crossing the writing beam.

Results and Discussion

Figure 1 shows D/D_0 of p-MR in toluene solution of polystyrene (PS) and poly(methyl methacrylate) (PMMA) as a function of the polymer weight fraction. We tested for possible molecular weight dependence by using PS and PMMA with both narrow and broad molecular weight distributions. The tests clearly show that the molecular weight distribution does not significantly affect the diffusion of p-MR. This is not surprising, since it has been shown that the diffusivity of small molecules is practically independent of the polymer molecular weight.[23,26] The solid lines represent the best fit of the data to eq 1, where the polymer weight fraction was used for ϕ. The relation evidently fits the data very well. From the fit, the parameters α and ν are found as $3._6 \pm 1.1$ and 1.03 ± 0.05 for PS and $5._7 \pm 1.1$ and 0.73 ± 0.02 for PMMA, respectively. As reported earlier, the further retardation of diffusion in PMMA compared to PS is due to H-bonding between the diffusant and the PMMA segments, which does not exist in the PS matrix. The retardation efficiency of PMMA is nearly equivalent to that of PVAc.

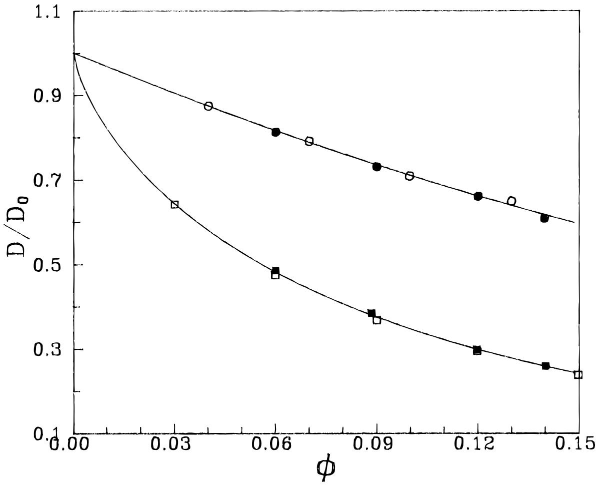

Figure 1. Plot of D/D_0 of p-MR in toluene solution of PS (circles) and PMMA (squares) vs the polymer weight fraction, ϕ. $D_0 = 1.2 \times 10^{-5}$ cm^2/s. Filled symbols: Narrow molecular weight distribution. Open symbols: Broad molecular weight distribution. The solid lines represent best fits to eq 1.

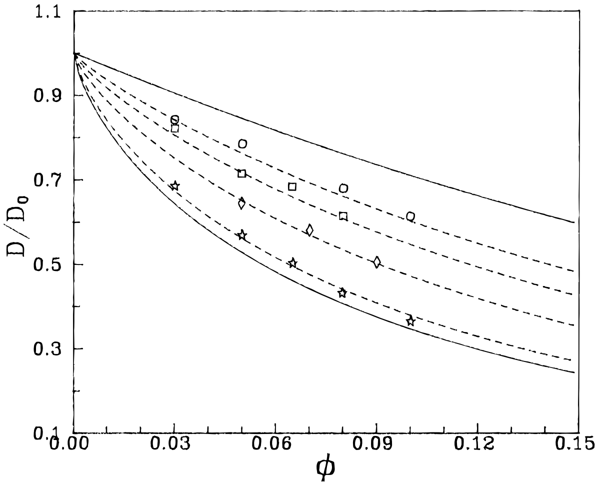

Figure 2. Plot of D/D_0 of p-MR in PS/PMMA/toluene ternary solution vs total polymer weight fraction, ϕ. PMMA content, f: ○, 10%; □, 20%; ◇, 40%; ☆, 80%. The upper and lower solid lines represent D/D_0 of 100% PS and PMMA matrix, respectively. The dashed lines are drawn according to eq 4 for f = 0.1, 0.2, 0.4, and 0.8; the quality of the fits appears quite reasonable.

Polymer Mixture. Turning to the question how the probe diffusion is affected by the density of H-bonding moiety, the p-MR diffusivity in PS/PMMA/toluene ternary solution was measured. The result is shown in Figure 2. The D/D_0 of p-MR in PS/PMMA mixtures falls in between those of pure PS and PMMA matrix, which represent two model matrices without H-bonding and with full H-bonding interaction, respectively. Therefore, it is clear that the retardation of diffusion of small molecules depends on the density of the H-bonding moieties in the polymer matrix. Is it then possible to predict the extent of retardation from the content of the H-bonding moiety (i.e., MMA unit) in the intermediate region between pure PS and pure PMMA? Here we wish to propose a scheme to predict the diffusivity in the intermediate region, which, as shown in Figure 2, describes the composition dependence in the PS/PMMA mixture very well.

A Phenomenological Equation. We have shown earlier that the H-bonding between the diffusant and polymer matrix retards the diffusion of the probes and increases the activation energy of diffusion.[27] If we assume that the diffusional activation barrier due to the simple sieving process (retardation due to the hydrodynamic interaction only, as in a pure PS matrix) and that due to the H-bonding interaction are additive (i.e., two retardation mechanisms are independent each other), we can postulate the following relationship:

$$D/D_0 = D(\mathrm{S{+}H})/D_0 = D(\mathrm{S})/D_0 \times D(\mathrm{H})/D_0 \qquad (3)$$

D(S), D(H), and D(S+H) represent the diffusivities of the probe retarded by sieving process only, by H-bonding interaction only, and by both effects, respectively. Among these, D(S+H) is the experimentally measured quantity in a PS/PMMA mixture. In addition, we can take D/D_0 in a matrix which does not exhibit H-bonding with the diffusant such as a PS matrix for p-MR, as

$D(\mathrm{S})/D_0$. Under this postulate, we can then extract the retardation effect solely due to H-bonding interaction, $D(\mathrm{H})/D_0$, from the experimental values of $D(\mathrm{S})/D_0$ and $D(\mathrm{S+H})/D_0$. $D(\mathrm{H})/D_0$ is not experimentally measurable, but convenient to describe the retardation effect due to H-bonding interaction.

From the data discussed earlier, we can assign $D(\mathrm{S})/D_0$ and $D(\mathrm{S+H})/D_0$ as follows:

$$D(\mathrm{S})/D_0 = D/D_0 \text{ (for PS matrix)} = \exp(-3.6\phi^{1.03})$$

and

$$\begin{aligned} D(\mathrm{S+H})_{\mathrm{PM}}/D_0 &= D/D_0 \text{ (for PMMA matrix)} \\ &= \exp(-5.7\phi^{0.73}) \end{aligned}$$

From the above two equations we can extract the $D(\mathrm{H})_{\mathrm{PM}}$ (for PMMA matrix) as follows:

$$\begin{aligned} D(\mathrm{H})_{\mathrm{PM}}/D_0 &= [D(\mathrm{S+H})_{\mathrm{PM}}/D_0]/[D(\mathrm{S})/D_0] \\ &= \exp(-5.7\phi^{0.73} + 3.6\phi^{1.03}) \end{aligned}$$

For the intermediate cases such as a PS/PMMA/toluene ternary solutions,

$$D(\mathrm{H})/D_0 = \exp[-5.7(f\,\phi)^{0.73} + 3.6(f\,\phi)^{1.03}]$$

where f is the weight fraction of PMMA in the PS/PMMA mixture, i.e., $\phi_{\mathrm{PMMA}}/\phi$. Then the relative diffusivity in ternary solution is

$$\begin{aligned} D/D_0 &= D(\mathrm{S+H})/D_0 = D(\mathrm{S})/D_0 \times D(\mathrm{H})/D_0 \\ &= \exp[-3.6\phi^{1.03} - 5.7(f\,\phi)^{0.73} + 3.6\,(f\,\phi)^{1.03}] \quad (4) \end{aligned}$$

The dashed lines in Figure 2 are drawn according to eq 4, and the quality of the fit appears to be quite reasonable. It is apparent that the simple phenomenological model depicts the composition dependence of D/D_0 very well.

Random Copolymer. On the other hand, we found that, as shown in Figure 3, the model fails completely for the random copolymer system. In the figure, D/D_0 is shown for p-MR in toluene solutions of 6 PS/PMMA random copolymers having different MMA content. The three dashed lines were drawn according to eq 4 for 7.4% and 13.6%, and 26.3% MMA content, while the two solid lines again represent the pure PS and PMMA matrices. At 7.4% MMA content, the model fits the data well. However, the experimental data start to deviate from the model prediction as the MMA content of copolymers is increased. The retardation effect on p-MR diffusion in the random copolymer solution approaches that of pure PMMA when the MMA content of the copolymer exceeds 40%. This clearly indicates that the effect of the H-bonding interaction on the diffusivity of p-MR is influenced not only by the density of the MMA moiety, but also by the microstructure of the polymer chain.

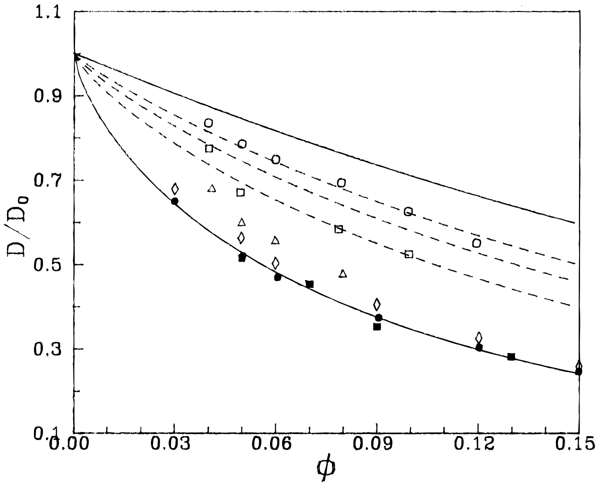

Figure 3. ϕ dependence of D/D_0 of p-MR in the toluene solutions of six PS/PMMA random copolymers having different MMA content. Different symbols stand for different MMA content in the copolymers: ○, 7.4%; □, 13.6%; △, 26.3%; ◇, 37.5%; ●, 43.0%; ■, 58.7%. The three dashed lines were drawn according to eq 4 for 7.4%, 13.6%, and 26.3% MMA content while the upper and lower solid lines represent the pure PS and PMMA matrix, respectively. At 7.4% MMA content the model fits the data well; however, the experimental data start to deviate from the model prediction as the MMA content of copolymers is increased. The retardation of p-MR diffusion in the random copolymer solution approaches that of pure PMMA when the MMA content in the copolymer exceeds ca. 40%.

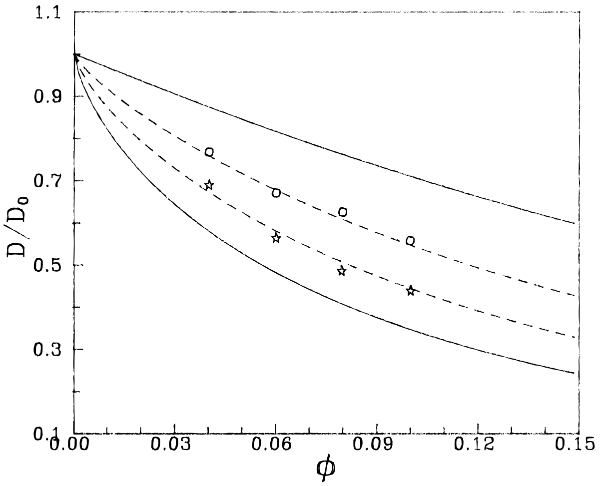

Figure 4. Plot of D/D_0 vs. ϕ in the ternary systems of PS, PS/PMMA random copolymer of 58.7% MMA content, and toluene. The copolymer contents of the ternary solutions are 20% (○) and 50% (☆), which contains MMA units of only 11.7% and 29.4%, respectively. The upper and lower solid lines are the reference lines of D/D_0 in the matrix of PS and the random copolymer of 58.7% MMA content, respectively. The lower line is practically indistinguishable from $D(\mathrm{S+H})_{\mathrm{PM}}/D_0$. Two dashed lines are drawn according to eq 4 with f of 0.2 and 0.5. The good fit indicates that the random copolymer behaves just like pure PMMA in terms of its capability to retard p-MR diffusion.

In order to confirm the elevated efficiency of the H-bonding effect in the random copolymers, we investigated the mixture of random copolymers with PS. Figure 4 shows a plot of D/D_0 vs polymer concentration in a ternary system of PS, PS/PMMA random copolymer of 58.7% MMA content, and toluene. The solid lines are again the reference lines of $D(\mathrm{S})/D_0$ and $D(\mathrm{S+H})_{\mathrm{copolymer}}/D_0$. The line representing $D(\mathrm{S+H})_{\mathrm{copolymer}}/D_0$ is practically identical to the $D(\mathrm{S+H})_{\mathrm{PM}}/D_0$ shown in Figure 3. The two dashed lines are drawn according to eq 4, and the model also appears applicable for the ternary solutions. It is thus clear that the copolymer of 58.7% MMA content behaves just like the pure PMMA in terms of its capability to retard p-MR diffusion.

Block Copolymers. The effect of microstructure on the diffusivity of p-MR was further investigated in toluene solutions of PS/PMMA diblock copolymer. Figure 5 shows the result obtained with two different diblock copolymers whose MMA contents are 56.5% and 67.9%. The two solid lines again indicate the D/D_0 in pure PS and PMMA solutions. The D/D_0 values of p-MR in the block copolymer solutions follow the model

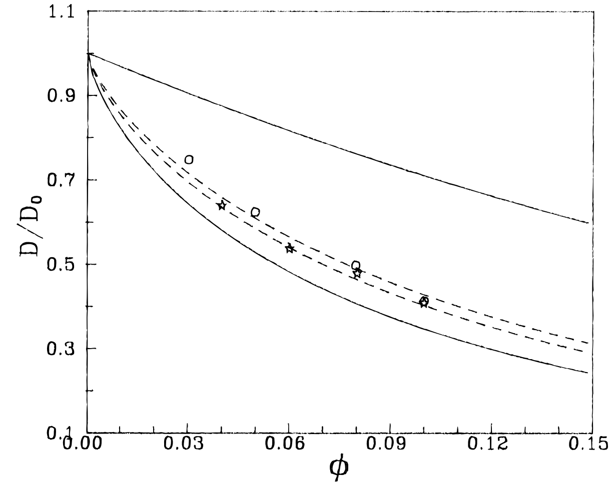

Figure 5. ϕ dependence of D/D_0 of p-MR in toluene solutions of two PS/PMMA diblock copolymers having MMA contents of 56.5% (○) and 67.9% (☆). The two solid lines represent D/D_0 in pure PS and PMMA solutions. The D/D_0 values of p-MR in the diblock copolymer solutions follow the model prediction (dashed lines, $f = 0.565$ and 0.679 in eq 4) very well, as observed for the polymer mixture.

prediction very well. In other words, the block copolymers behave just like the polymer mixtures. This result unambiguously confirms that the retardation efficiency is strongly influenced by the microstructure of the polymer chains. In addition, it appears that the frequency of MMA units in the polymer chain is an important parameter for the diffusion of small molecules capable of H-bonding to polymer segments.

In order to explain the above observation, we may propose the following mechanisms for the diffusant to differentiate the microstructure of polymer chains. First, the binding efficiency of p-MR to an MMA unit could depend on the frequency of MMA units in the chain. In other words, an MMA unit adjacent to the MMA unit bound to p-MR is not as effective as free MMA units (with unbound adjacent units) in binding to p-MR. This is a reasonable postulate since the hydrodynamic size of the p-MR molecule is 6.4 Å, while the distance between the adjacent carbonyl group on a PMMA chain is 2.5 Å (assuming a trans zig-zag conformation). Therefore, steric effect should favor p-MR binding to a free MMA unit. This difference in binding constant should in turn affect the extent of retardation of p-MR diffusion. Although it would prove surprising, a random copolymer having 40% MMA content could exhibit a comparable binding efficiency to that of pure PMMA. Johnson and co-workers[28] and Lee and Lodge[23] have previously attempted to analyze the retarded diffusivity in a H-bonding system in terms of binding equilibrium. To our knowledge, however, there is no experimental proof on the relation between the retarded diffusivity and the binding constant. The measurement of quantitative change in binding efficiency with MMA content requires a careful experiment on equilibrium binding, which is being carried out in this laboratory.

In addition, we would like to suggest a possibility of the difference in the microscopic diffusion path of p-MR. Since the fringe spacing in the FRS measurement is much larger (10–20 μm) than the mesh size of the polymer matrix, the overall population of polymer chain segments averaged over the fringe spacing is identical for all three systems—polymer mixture, random copolymer, and block copolymer matrix. Along the diffusion path, however, p-MR molecules should experience a different local environment. Since the H-bonding interaction is more short-ranged relative to the hydrodynamic interaction, a more uniform environment (as in random copolymer matrix) could exert a more efficient H-bonding interaction along the diffusion path.

In summary, we have found that in mixed or diblock copolymer solutions, the tracer diffusion of the probe could be well represented by a phenomenological model which assumes the additivity of the diffusional activation barriers due to hydrodynamic and H-bonding interactions. On the other hand, we observed a far more effective H-bonding interaction in random copolymers than in mixtures or in block copolymers. This peculiar behavior of tracer diffusion in random copolymers could reflect the difference in binding efficiency of copolymers and/or in the microscopic environment for the diffusion path of the probe. All of these qualitative arguments, however, need to be further elaborated through experiments on equilibrium binding and additional theoretical investigations.

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