Diffusion and Equilibrium Binding of Methyl Red in Toluene Solutions of Polystyrene/ Poly(methyl methacrylate): Mixture vs Random Copolymer

Hyunjung Lee and Taihyun Chang*

Department of Chemistry and Polymer Research Institute, POSTECH, Pohang, 790-784, Korea

Received December 21, 1998
Revised Manuscript Received March 30, 1999

Introduction

Diffusion of small diffusants in semidilute polymer solution is greatly affected if there exists a specific interaction such as hydrogen bonding between the diffusant and the polymer matrix.[1−8] A good example is the diffusion of methyl red (MR) in a toluene solution of poly(vinyl acetate) (PVAc) or poly(methyl methacrylate) (PMMA).[2,3,6−8] Diffusion of MR is far more retarded in PVAc or in PMMA solutions than in a polystyrene (PS) solution at an equivalent concentration due to the hydrogen bonding between the carbonyl group of the polymer chain and the carboxylic hydrogen of MR. Lee and Lodge, the first to observe the retarded diffusion of MR in a semidilute PVAc/toluene solution relative to a PS/toluene solution, interpreted the retarded diffusion in terms of the binding equilibrium.[2] In that approach, the exchange rate of MR between the bound and free states was assumed to be much faster than the experimental time scale to monitor the diffusion process by forced Rayleigh scattering (FRS). Then they proposed that the measured diffusivity in PVAc solution represented the average value of the bound and free dyes (diffusivity of the bound dye was assumed to be zero) weighted by their mole fractions.

Further studies in this laboratory on the diffusion behavior of MR in solutions of PS/PMMA mixture as well as in PS−PMMA random and diblock copolymer solutions with respect to the polymer concentration and composition reveal an intriguing behavior.[9] In polymer mixtures or block copolymers, diffusivity of MR could be predicted reasonably well from the diffusivity in a homo-PS and a homo-PMMA solution based on the additivity of the activation energy of diffusion in PS and PMMA solutions. On the other hand, we found that the diffusion of MR is far more retarded in PS−PMMA random copolymer solution than in mixtures or block copolymers at the same polymer concentration and composition. For instance, diffusivity of 4-(4′-(dimethylamino)phenylazo)benzoic acid (p-MR), a structural isomer of methyl red, in a toluene solution of random copolymers with about a half or higher methyl methacrylate (MMA) contents was nearly the same as that in homo-PMMA solution at the same polymer concentration. This rather unexpected behavior was tentatively ascribed to the difference in binding efficiency of p-MR depending on the microstructure of polymers and/or the difference in the microscopic environment of the diffusion path of p-MR. In a length scale of the mesh size in a semidilute polymer solution, the microscopic environment felt by a small molecule diffusant would be different for random copolymer vs polymer mixture although the overall composition of the monomers is identical. It remains to be verified, however, that the effect would persist over the diffusion length scale monitored by FRS, which is much longer than the mesh size of the polymer matrix.

To explain the difference observed between random copolymer and polymer mixture system, it is necessary to study how the equilibrium binding of p-MR is affected by the structure of the polymer chains. Recently, a modified size exclusion chromatography (SEC) method has been successfully applied to study the association phenomena in polymer solutions such as micellization of block copolymers,[10,11] complexation of polyelectrolytes,[12] ligands binding to polymers,[13−15] and complexation of macromolecules with solvent molecule.[16] In a chromatographic technique called eluent SEC in the study of micellization of block copolymers[10,11] or in a technique called differential SEC in the study of complexation of polyelectrolyte and gelatin,[12] a dilute solution of the components forming association complex instead of a pure solvent in ordinary SEC is used for the eluent. When a sample solution of different concentration is injected, the excess (or depleted) amount of the component elutes out with positive (or negative) peak area. In the other applications as in the study of the ligands binding to polymers or preferential sorption of a solvent component to polymers,[13−16] one of the components forming association complex with the polymer of interest is premixed with the eluting solvent. When the polymer sample is injected into the SEC system, a negative peak appears in addition to a positive elution peak for the complex. The negative peak indicates the depletion of the component forming association complex with the polymers. We employed the latter method to study the equilibrium binding of p-MR in polymer solutions. Using a toluene solution of p-MR as the SEC eluent, we were able to extract the information on equilibrium binding of p-MR onto PS/PMMA mixtures and PS−PMMA random copolymers from the SEC experiments, which is difficult to obtain by other conventional equilibrium binding methods.

Experimental Section

4-(4′-(Dimethylamino)phenylazo)benzoic acid (p-MR) was used as a probe molecule for the study of diffusion and equilibrium binding in various polymer/toluene solutions. p-MR was acquired from Tokyo Chemical Inc. (TCI) and purified by recrystallization in methanol. Toluene was the solvent for both FRS and SEC experiments and used as received from Aldrich (HPLC grade). PS and PMMA were acquired from Miwon Petrochemical and Aldrich, respectively. PS−PMMA random copolymers were homemade by typical bulk copolymerization of styrene and methyl methacrylate using AIBN as an initiator. To avoid a significant composition drift of the copolymers, polymerization was quenched at about 10% monomer conversion by precipitating the polymer in methanol. The composition of the random copolymers was determined by ^{1}H NMR. The average molecular weight and the molecular weight distribution were estimated by SEC relative to PS standards. Molecular characteristics of polymers used in this study are summarized in Table 1.

Forced Rayleigh scattering (FRS) apparatus used in this study has been described previously.[6] All FRS experiments were performed at 25 ± 0.1 °C, and the experimental procedure

* To whom correspondence should be addressed. TEL +82-562-279-2109; e-mail tc@postech.ac.kr.

10.1021/ma981971q CCC: $18.00
Published on Web 05/21/1999

Table 1. Characteristics of Polymers Used

polymers	$10^{-3}M_w$[a]	M_w/M_n	MMA (%)[b]	source
PS	276	2.43		Miwon Petrochemical
PMMA	77.6	2.01	100	Aldrich
RC01	36.6	2.07	7.42	homemade
RC02	155	2.11	13.6	homemade
RC03	192	2.00	27.9	homemade
RC04	34	3.42	37.5	homemade
RC05	77	2.58	43.0	homemade
RC06	70	2.00	58.7	homemade
RC07	47	2.10	73.8	homemade

[a] GPC characterization result. [b] NMR spectrum result.

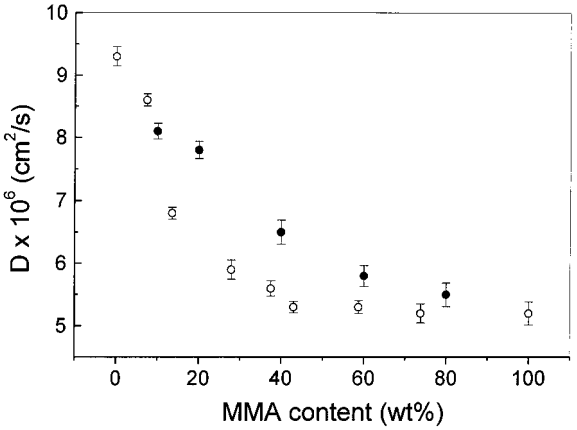

Figure 1. Diffusivity (D) of p-MR in toluene solution of PS/PMMA mixtures (●) and of random copolymers (○) as a function of the MMA fraction in the polymers. The measurement temperature was 25 °C.

was identical to our previous report.[9] The SEC system for the equilibrium binding study consists of an HPLC pump (LDC, ConstaMetrix 3200), a Rheodyne 7125 injector, a UV/vis absorption detector (TSP, Spectra 100), a refractive index detector (LDC, RefractoMonitor IV), and two PS gel columns (Shodex KF-8025). The temperature of the column was maintained at 25 °C using a homemade water jacket connected to a bath/circulator (NESLAB, RTE-111). Eluent was the toluene solution of p-MR, and the concentration of the p-MR was 0.01 mg/mL, which was a typical concentration of p-MR used in FRS study.

p-MR is a photochromic dye to change its absorption spectrum depending on its photochemical state, and the quantitative analysis of p-MR by the absorption spectroscopic method requires some caution. The most reproducible result was obtained when the wavelength of UV/vis detector was set at 382 nm, an isosbestic point of p-MR in toluene. It was confirmed by separate spectrophotometric measurements that the isosbestic point and absorptivity of p-MR at the isosbestic point remain unchanged in the experimental precision at the low concentration of PS or PMMA in toluene solution relevant to the concentration of the elution peak of the SEC experiments. Another advantage of selecting the wavelength at 382 nm is that neither the polymers nor toluene shows measurable absorption at that wavelength. Injection samples were prepared by dissolving the polymer in a small portion of the eluent and injected to a 100 μL loop of the injector. Under our experimental condition, the binding characteristics was independent of flow rate up to 1.0 mL/min, and the SEC measurements were carried out at the flow rate of 0.5 or 1.0 mL/min.

Results and Discussion

Figure 1 shows diffusivities of p-MR in toluene solution of PS/PMMA mixtures (filled circles) and PS−PMMA random copolymers (open circles) as a function of the MMA composition. Total concentration of the polymer solutions is fixed at 7% (w/w) for the FRS

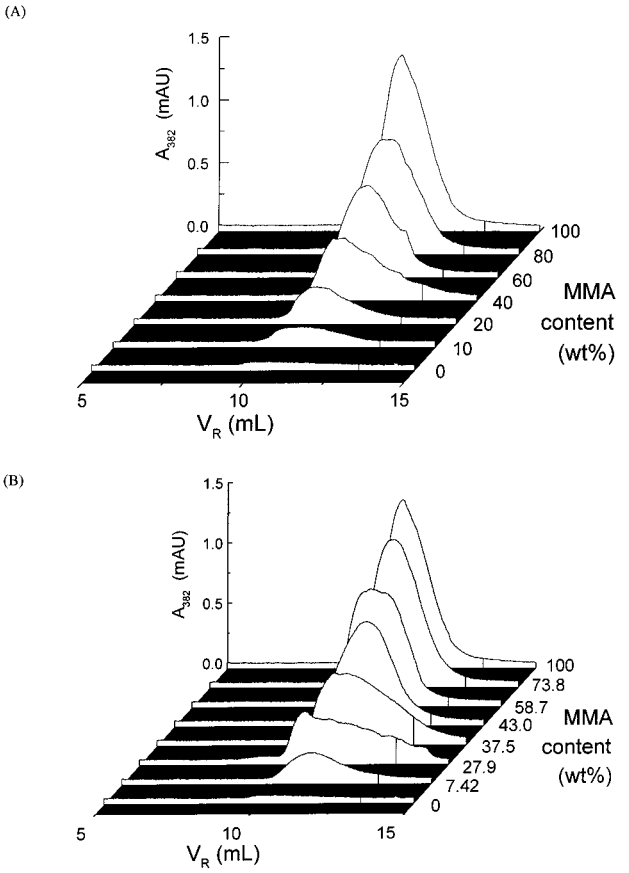

Figure 2. GPC chromatograms of (A) PS/PMMA mixtures and (B) random copolymers detected by UV/vis absorption detector at the wavelength of 382 nm. Polymers are eluted around 10 mL of V_R. The polymers are detected due to the excess p-MR sorbed to polymer chains.

measurements. The error bars represent one standard deviation in q^2 dependency of $1/\tau$. Without MMA, i.e., in 7% homo-PS solution, diffusion of the probe is influenced dominantly by the hydrodynamic effect. As the MMA content increases, diffusion of p-MR is further retarded due to the increasing hydrogen-bonding interaction. The random copolymer system shows a more effective interaction to retard the diffusion of p-MR more than the mixture system at the same MMA composition. Diffusivity of p-MR in a 50/50 PS−PMMA random copolymer solution almost reaches the value of pure PMMA solution, which is in good agreement with the previous report.[9]

Two sets of SEC chromatograms at different MMA contents for PS/PMMA mixtures (A) and PS−PMMA random copolymers (B) are shown in Figure 2. A 100 μL aliquot of PS/PMMA mixture solutions or random copolymers at the total polymer concentration of 7% (w/w) was injected, respectively. Since p-MR is the only species in the system absorbing light at 382 nm wavelength, the peaks appearing around 10−15 mL of the retention volume (V_R) in the chromatograms are the contribution of the excess dye molecules bound to polymer molecules. Since we only need to separate polymers from other small molecules for the equilibrium binding study, the pore size of the column is chosen to be small enough for all the polymers employed in this study to be eluted far apart from the injection solvent peak, of which V_R appears around 20 mL. No measurable negative peak (indicating the depletion of the dye due to binding to polymers) was found at the position

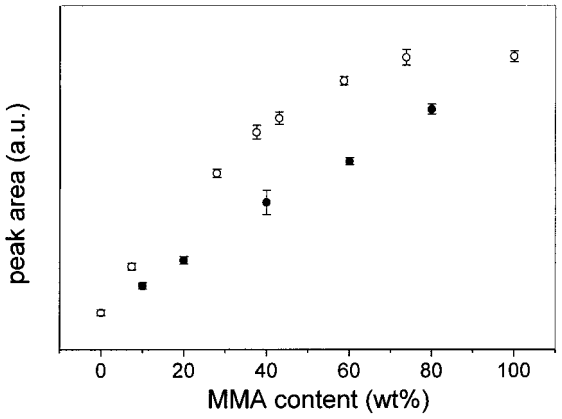

Figure 3. Plot of peak area of excess p-MR bound to polymers vs MMA content of the polymers in the PS/PMMA mixtures (●) and PS−PMMA random copolymers (○). Peak areas are integrated from the peaks in the chromatograms shown in Figure 2.

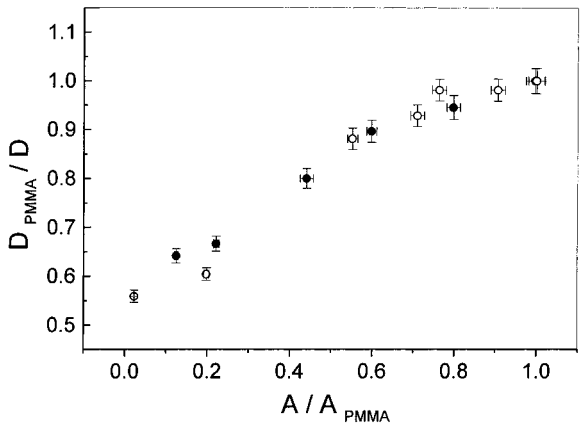

Figure 4. Plot of D_{PMMA}/D vs A/A_{PMMA}. The subscript PMMA indicates the diffusivity or peak area in the homo-PMMA system. D and A stand for the diffusivity and peak area in PS/PMMA mixtures (●) or PS−PMMA random copolymers (○), respectively. These values are already shown in Figures 1 and 3, respectively.

where the injection solvent was eluted. A possible reason for this observation will be given later.

In Figure 2A, the peaks of PS/PMMA mixtures grow with the PMMA content, showing that p-MR preferentially binds to PMMA. It is interesting to note that homo-PS shows a very small but finite peak area, indicating an excess amount of bound p-MR. It indicates that PS interacts with p-MR to a small extent. In fact, a fair amount of p-MR was adsorbed to the styrene gel packing material of the GPC column, so that preequilibrium of the column with the dye solution was necessary before the injection of the polymer in order to obtain reproducible results. This is likely the reason a negative peak was not observable at the injection solvent peak position. The dyes adsorbed in the packing material seemed to reequilibrate to compensate for the depletion of the dye in the injection solvent. We also found that the shape and the area of the polymer elution peaks (i.e., the excess amount of the bound dye) are independent of the dye concentration of the injected solution. The peak area remains unchanged within experimental error even when a sample solution without p-MR (polymer solution in pure toluene) was injected. Therefore, it appears that the dye in the injection solvent is fully equilibrated with the eluent during the elution period. Nonetheless, all the data reported in this paper were obtained from the injection of the polymer samples dissolved in the p-MR/toluene solution at the same dye concentration as that of eluent. It was experimentally confirmed that the absorption peak area due to excess bound dye is proportional to the polymer concentration in the injected solution as well as the dye concentration in the eluent. We also confirmed that the peak shape is independent of the polymer as well as dye concentration. In Figure 2B, for PS−PMMA random copolymer solutions, the peak area increases much more rapidly with MMA content than in Figure 2A and reaches the asymptotic value of pure PMMA at a relatively lower MMA contents.

In Figure 3, the integrated areas of the elution peaks in Figure 2 are plotted against the MMA content, which shows the general trend of the binding behavior of p-MR with the polymers of interest. For the solutions of a similar content of MMA, the random copolymer system (open circles) always shows a larger peak area, i.e., more effective binding efficiency, than the mixture system (filled circles). The uncertainty of the peak area is one standard deviation calculated from three independent measurements. The small standard deviation demonstrates that this chromatographic method provides an excellent reproducibility. In addition, the mixture system shows a good linearity between the peak area and the MMA contents, which is another evidence of simple additivity working well for the mixture system.

For the diffusion of a small molecule in dilute polymer solutions, the diffusivity is independent of polymer molecular weight and distribution.[2,9] For the copolymer system, we have not done a systematic study on the molecular weight dependence. However, the copolymers used in this study span a wide molecular weight range, 34K−192K, and no molecular weight dependence was observed in diffusivity and binding behavior of MR as shown in Figures 1 and 3. To correlate the diffusivity with the binding efficiency of dye to polymer chains, we made a plot, D_{PMMA}/D vs A/A_{PMMA} as shown in Figure 4 using the values plotted in Figures 1 and 3. The diffusivity and peak area in each system were normalized by the corresponding values of homo-PMMA. All the data points of both mixture and random copolymer systems fall on a single curve within experimental precision. Therefore, it is clear that the difference in the diffusion behavior in mixtures and random copolymers can be fully explained by the difference in binding efficiency in the two systems. Of course, this result does not provide information how equilibrium binding affects the diffusion in a quantitative manner. It only confirms that the retarded diffusion of p-MR is fully correlated with its binding behavior to the polymer chains, and it still remains to be answered how to make the quantitative relationship between the binding constant and the diffusivity.

Acknowledgment. This work is in part supported by the grants from the Korea Ministry of Education (the New Materials Research Fund and BSRI-98-3438). We thank Mr. Wonmok Lee for his help in the chromatography experiments.

References and Notes

(1) Rhee, K. W.; Gabriel, D. A.; Johnson, C. S., Jr. *J. Phys. Chem.* **1985**, *89*, 3193.

(2) Lee, J. A.; Lodge, T. P. *J. Phys. Chem.* **1987**, *91*, 5546.
(3) Huang, W. J.; Frick, T. S.; Landry, M. R.; Lee, J. A.; Lodge, T. P.; Tirrell, M. *AIChE J.* **1987**, *33*, 573.
(4) Xia, J. L.; Gong, S. S.; Wang, C. H. *J. Phys. Chem.* **1987**, *91*, 5805.
(5) Xia, J. L.; Wang, C. H. *J. Chem. Phys.* **1988**, *88*, 5211.
(6) Lee, J.; Park, T.; Sung, J.; Park, S.; Chang, T. *Bull. Korean Chem. Soc.* **1991**, *12*, 569.
(7) Lee, J.; Park, K.; Chang, T.; Jung, J. *Macromolecules* **1992**, *25*, 6977.
(8) Spiegel, D. R.; Marshall, A. H.; Jukam, N. T.; Park, H. S.; Chang, T. *J. Chem. Phys.* **1998**, *96*, 190.
(9) Park, H. S.; Sung, J.; Chang, T. *Macromolecules* **1996**, *29*, 3216.
(10) Wang, Q.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1437.
(11) Yu, G. E.; Altinok, H.; Nixon, S. K.; Booth, C.; Alexandridis, P.; Hatton, T. A. *Eur. Polym. J.* **1997**, *33*, 673.
(12) Tan, J. S.; Harrison, C. A.; Li, J. T.; Caldwell, K. D. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 537.
(13) Sebille, B.; Thuaud, N.; Tillement, J. P. *J. Chromatogr.* **1978**, *167*, 159.
(14) Barberousse, V.; Sacco, D.; Dellacherie, E. *J. Chromatogr.* **1986**, *369*, 244.
(15) Xia, J.; Dubin, P. L. *J. Chromatogr. A* **1994**, *667*, 311.
(16) Fischer, C.-H.; Berek, D.; Macko, T. *Polym. Bull.* **1994**, *33*, 339.

MA981971Q