

A Study of Mass Transport of Linear Polystyrene in Polyethyl Methacrylate Gel by Dynamic Light Scattering

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ABSTRACT: Mass [i.e., linear polystyrene (PS) probe] transports in polyethyl methacrylate (PEMA) gels with ethylene dimethacrylate (EDMA) as crosslinker were studied by dynamic light scattering (DLS). For PEMA gels in toluene, we have established that it is a very well matched system, so that it is very convenient to study the mass transport of the PS macromolecule in such a system. Experiments show that the obstruction effects of PEMA gels for the mass transport of PS are obvious. Reasonably, the lower the gel obstruction for mass transport, the higher the diffu-

sion coefficient D_t of PS in gel. Moreover, the larger the molecular weight of PS, the greater the obstruction effect of the gel. Furthermore, we traced quantitatively the evolution of D_t of PS during the crosslinking copolymerization of PEMA. The results show that, after the reaction, the obstacle for mass transport in the gel develops gradually. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2062–2066, 2002

Key words: PEMA gel; probe; mass transport; dynamic behavior; DLS

INTRODUCTION

The diffusion of polymers in polymer solutions and gels has been the subject of increasing research interest in the past decade.^{1–5} The diffusion of polymers in gels is relevant to the diffusion of polymers in porous media and enhanced oil recovery.^{6–8} This topic is also important in solving a number of biological problems.⁹

The question of probe diffusion in gel is very complex and depends on several factors, such as the size of the probe compared to the characteristic mesh size of the network, concentration, and temperature. A central focus in such research has been whether the tracer chains move by reptation in these matrices. Numasawa et al.¹⁰ observed a crossover from Stokes–Einstein (S-E) to reptation and determined the crossover curve separating these two regions for polystyrene (PS) probes in poly(methyl methacrylate) (PMMA) solution in benzene (isorefractive with PMMA matrix). So far, however, only a few studies relate these to mass transport in gel.

In this study we present a novel approach that relates dynamic behaviors of gel to mass transport of probe from the vantage point of diffusion by use of a

new isorefractive system by dynamic light scattering (DLS). In other words, we investigate the obstacle problems in gel for mass transport by DLS, addressing such issues as: Where do obstacles originate? How is it affected? Is there S-E to reptation crossover for PS probes with different molecular weights (M_w)? Furthermore, we have also quantitatively tracked the evolution of obstacles during the formation of a gel to obtain information on the influence of the structure of the gel on the obstacle.

EXPERIMENTAL

Sample preparation

The samples used in these experiments were PEMA gels obtained by copolymerization of ethyl methacrylates (EMA) with small amounts of ethylene dimethacrylate (EDMA) as the crosslinking agent in toluene. The probe polymer, linear PS, dissolved in a dilute solution of toluene was added to the monomer mixture. To prevent the phase separation of PS from the gel, we maintained the total monomer concentration Φ [=12.5% (w/w)] with different degrees of crosslinking: $f_c = [\text{EDMA}]/(\text{EMA} + [\text{EDMA}])$ (w/w), varying between 0 (the linear polymer) and 5% (gel), and varied the weight-average molecular weight (M_w) of PS from 3.8×10^4 to 1.2×10^6 giving us five samples (Table I). The reaction was initiated with azobis(isobutyronitrile) (ABIN) (2×10^{-2} of total monomer) (w/w) and

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TABLE I
Characterization of PS Samples

Sample ^a	M_w	PI ^b	D^c (10^{-8} /cm ² /s)				
			15°C	20°C	25°C	35°C	45°C
1	3.83×10^4	1.29	1.45	2.65	4.68	4.12	7.39
2	6.32×10^4	1.11	1.06	2.52	4.42	5.43	6.31
3	1.85×10^5	1.09	1.29	2.12	3.52	4.53	5.75
4	5.80×10^5	1.20	1.02	1.56	1.76	2.50	2.28
5	1.24×10^6	1.18					

^a Nos. 1–5 denote PS1–PS5, respectively.

^b Polydispersity index.

^c Determined in toluene by DLS.

allowed to proceed for 5 days at 52.5°C in cylindrical light-scattering cells. By the end of this period, the gelation reaction was completed. Before reacting, all reactants were filtered using 0.22- μ m filters (Millipore, Bedford, MA) to remove dust.

Apparatus

Dynamic light-scattering measurement was performed by photon correlation spectroscopy (PCS) (BI-200SM spectrophotometer and BI-9000AT correlator; Brookhaven Co., USA). An argon ion laser was adopted, having single-line power 1 W, $\lambda = 514.5$ nm with power track (Innova 304, Coherent Co., USA).

Data analysis

The details of DLS can be found elsewhere.^{11–13} In DLS for a gaussian light field, a precise intensity–intensity time correlation function $G^{(2)}(\tau)$ in the self-beating mode can be measured, which has the following form:

$$G^{(2)}(\tau) = A(1 + \beta |g^{(1)}(\tau)|^2) \quad (1)$$

and for the monodisperse system,

$$g^{(1)}(\tau) = \exp(-\Gamma\tau) \quad (2)$$

where A , β , $g^{(1)}(\tau)$, Γ , and τ are baseline, instrument coherent factor, normalized electric field–electric field time correlation function, linewidth, and delay time, respectively.

For a small angle, approximately,

$$\Gamma = D_t q^2 \quad (3)$$

and through the Stokes–Einstein equation,

$$R_h = k_b / (6\pi\eta D_t) \quad (4)$$

where D_t , q , R_h , k_b , and η are translation diffusion coefficient, scattering vector ($=[4\pi/\lambda]\sin(\theta/2)$), hydrodynamic radius (i.e., correlation length or mesh size ξ

for gel), Boltzmann's constant, and the solvent viscosity, respectively. The parameter ξ characterizes the dynamic behavior of the gel.

For a polydisperse system,

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma) e^{-\gamma\tau} d\Gamma \quad (5)$$

where $G(\Gamma)$ is the linewidth distribution function, which is solved by Laplace transformation with the CONTIN program and, finally, the distribution function of ξ can be obtained.

RESULTS AND DISCUSSION

Process and system

Before this study, we defined a process for our work, which is as follows: the first, to establish a criterion by which to judge the degree of obstacle for mass transport in gel; the second, to reveal what is responsible for the obstacle and then to study the influence of both structure and environment on the obstacle. Here we chose the diffusion coefficient of the probe molecule in gel as a criterion by which to judge the obstacle of gel for mass transport. When the obstacle increases, the diffusion coefficient decreases.

For simplification, it is very important that the solvent is isorefractive with the gel matrix.⁷ Among several acrylate gels with PS, such as methacrylate (MA), methyl methacrylate (MMA), ethylacrylate (EA), and ethyl methacrylate (EMA), EMA is the best because it is a transparent gel without any phase separation. Furthermore, we also measured the intensity scattered at different temperatures and plotted the correlation curve. As is well known, the better the isorefractivity, the lower the intensity. Based on this principle, PEMA gels in toluene exhibit excellent isorefractivity at around 37°C, as determined from both intensity (Fig. 1) and correlation curves. In reality, there is no correlation curve on

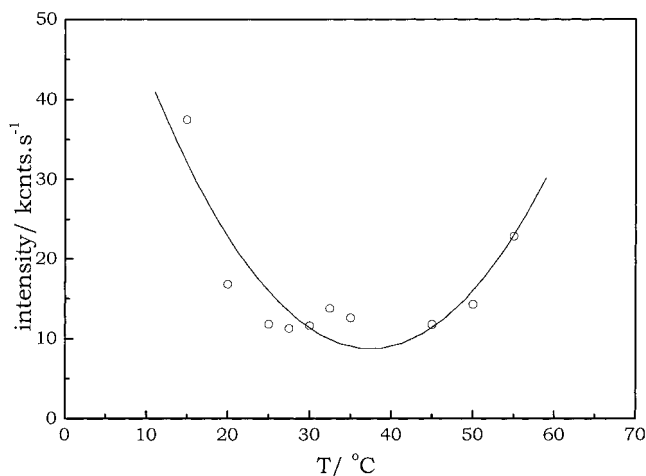


Figure 1 The scattered intensity of PEMA gel as a function of the temperature.

PEMA gels in toluene. Thus in this study we chose this system as the object.

Source and influence factors

Figure 2 shows various diffusion coefficients D_t of PS in PEMA gels with different values of f_c . The D_t decreases following the increase of f_c . Furthermore, the greater the influence of f_c on D_t , the lower the f_c . Figure 3 is the comparison of D_t for gels in toluene with different M_w values under different temperatures. In these figures, values of D_t are all increased after increasing temperature for both situations. However, in the case of toluene, the obstacle is much smaller than that in the case of gel; and the higher the temperature, the greater the difference. Furthermore, the higher the M_w , the smaller the influence. As a result, from Figures 2 and 3, the conclusion that the main origin of the obstacle comes from crosslinking can be discounted.

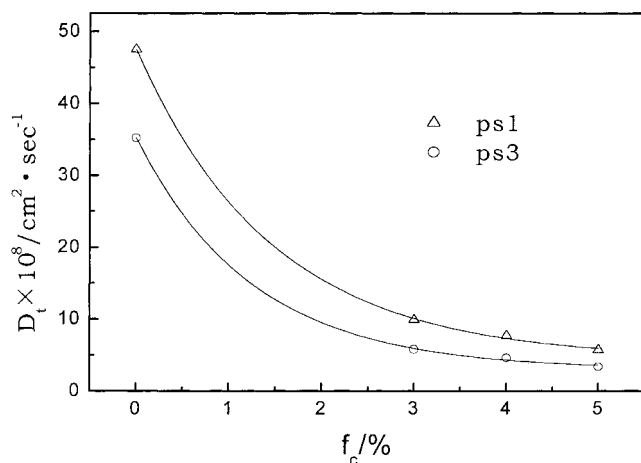


Figure 2 The plot of the D_t of PS versus the f_c in PEMA gels.

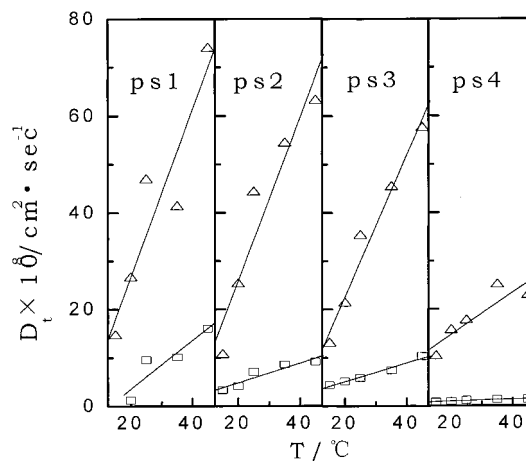


Figure 3 The plot of the D_t of PS versus temperatures: Δ in toluene; \square in gel.

In other words, the higher the f_c , the greater the obstacle, a finding that agrees well with our previous experiments.¹⁴

Although Figure 3 depicts the influence of temperature, the situation is more complicated. There seems to be some contradiction concerning the influence of temperature on the diffusion of PS in the gel. According to corresponding experimental results of polyacrylic acid gels, when the temperature increases, the mesh size ξ decreases (i.e., the obstacle increases), such that the value of D_t should decrease. However, the opposite scenario is depicted in Figure 3. To clarify it, more information is needed. Here we suggest a new approach, the *ratio method* to analyze these data, that is, normalized by the data of PS in toluene. The results are presented in Table II. If there is no difference, the corresponding ratio should be the same; however, if there is doubt, the result is opposite. After increasing the temperature, the ratios are smaller for the gel and the differences are increasingly greater for the kinds of ratios. These interesting results show us that, even though two opposite factors exert their effects on D_t at same time, the excess value still increases. Of the two

TABLE II
Influence of Temperature on the Diffusion Coefficient of PS in PEMA Gel

f_c /PS ^a	D_{20}/D_{15} ^b	D_{25}/D_{15}	D_{35}/D_{15}	D_{45}/D_{15}
PS2	2.3774	4.1698	5.1226	5.9528
3/PS2	1.2724	2.1806	2.6256	2.7924
PS3	1.1596	2.6370	3.1589	4.5697
3/PS3	1.1730	1.3275	1.6797	2.3543
PS4	1.4589	1.7943	2.3040	2.8016
3/PS4	1.0500	1.4372	1.5797	1.7005

^a PS in toluene; 3/PS in gel ($f_c = 3\%$).

^b D_{20}/D_{15} is the ratio of diffusion coefficient of PS and the subscripts denote the temperatures.

TABLE III
Slopes of Curves of D_t/D_{15} versus the Temperature for PS Samples

Sample	Slope	r
PS2	0.06229	0.93434
PS3	0.04328	0.98459
PS4	0.02451	0.94141
PS5	0.00972	0.80506

factors, temperature and the network frame (ξ), the former causes the D_t to increase and the latter causes it to decrease. Consequently, values of D_t increase at a slow rate, which indicates the influence that the crosslinking degree of gel has on the diffusion of PS in it.

If, when plotting D_t/D_{15} versus temperature, we obtain slopes of these curves (Table III) for different M_w values, we then draw a plot using these slopes. The curve falls gradually as the molecular weight of the PS probe increases. These results show quantitatively the influence of the network frame (ξ) and M_w on the diffusion (i.e., the mass transport). All data suggest that with decreasing both crosslinking degree of the gel and the molecular weight of the PS probe, the obstacle effect is more sensitive to temperature.

Figure 4 shows the experimental results of the influence of PS molecular weights on the diffusion in PEMA gels. There are two distinct scaling regimes in the plot of D_t/D_0 versus M_w . D_0 is the diffusion coefficient of PS in toluene. From Figure 4, for $M < M_c$ ($\cong 3 \times 10^5$), we find that it is very nearly independent of molecular weight, and thus in the low molecular weight region ($M < M_0$), $D_t \sim D_0 \sim M^{-0.6}$. This is in agreement with the known behavior of PS in a dilute solution in a good solvent. The dynamics demonstrated in this case are consistent with the probe poly-

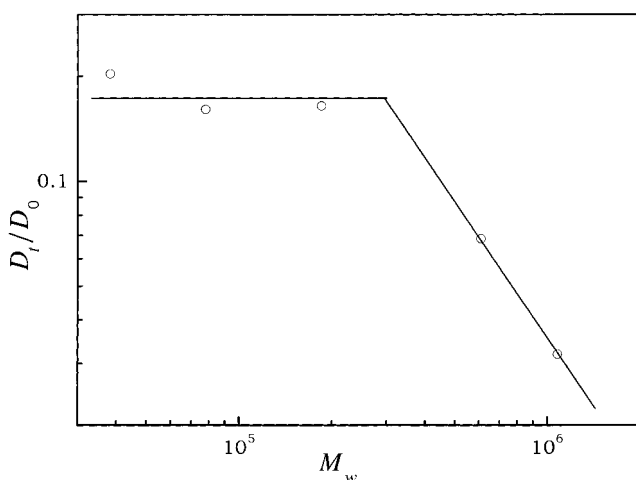


Figure 4 Log-log plot of D_t/D_0 versus the M_w of PS in PEMA gels.

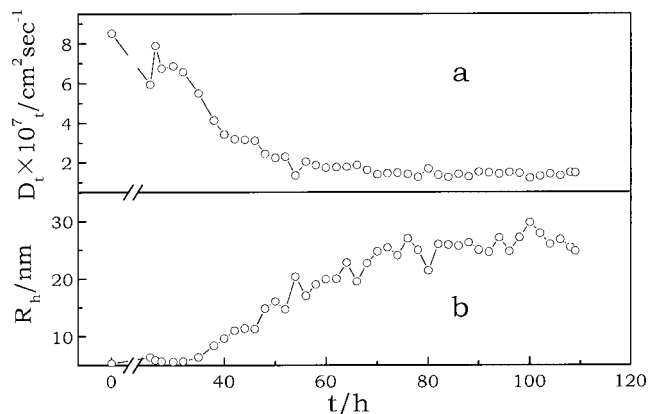


Figure 5 The plot of R_H and D_t of PS3 during the gelation of PEMA.

mer diffusion as a Stokes–Einstein particle of hydrodynamic radius $R_H \sim M^{-0.6}$ in a medium of effective viscosity η .^{7,15,16} For $M > M_c$, the diffusion coefficient decreases very rapidly with increasing molecular weight and $D_t/D_0 \sim M^{-1.3}$, which implies that $D \sim M^{-1.9}$. Thus, in this range of molecular weights, the dynamic behavior of the probe polymer is consistent with the reptation prediction.¹⁷ At this time, the mass transport in gel is exceedingly difficult.

Tracking experiment

Furthermore, for probing the relationship between structural evolution, linear-branch-crosslinking, during gelation, and the gel obstacle for probe diffusion at the molecular level, we designed a novel tracking experiment by DLS: during the gelation of PEMA, we determined both D ($2R_H$) and D_t on-line at desired time intervals. Abundant data show that (1) before the viscosity (observation by eye) of the reactant is essentially negligible, the dynamic behavior of PS exhibits no obvious change. However, (2) following the increased growth and complexity of the PEMA structure, its obstruction effect on probe diffusion (i.e., on mass transport of the probe molecules) becomes increasingly stronger, reaching a maximum at gelation point T_g (~ 109 h). Finally, (3) although there is some fluctuation, the obstruction effect tends to stabilize gradually (Fig. 5).

This instructive experiment, at a minimum, tells us that the diffusion of PS in PEMA gel is very sensitive to the structure of the gel so that any change, from either the internal or the external environment, will significantly affect the mass transport. In Figure 5, by the end of the reaction, the obstacle increases almost fourfold as much as that at the beginning, if using the change of R_H and D_t as a criterion.

The evolution on distributions of both R_H and D_t of PS during the gelation are also very informative and will be detailed in a future study.

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