Diffusion of Pyrene End-Capped Polystyrene Prepared via Atom Transfer Radical Polymerization into Polystyrene Gels in the Presence of Toluene†

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In-situ steady-state fluorescence (SSF) measurements were performed for studying diffusion processes of pyrene end-capped polystyrene (Py-PSt) in gels formed by free radical cross-linking copolymerization (FCC) of styrene (St) and ethylene glycol dimethacrylate (EGDM) in toluene solutions. The pyrene end-capped polystyrene was prepared by atom transfer radical polymerization (ATRP). The process involves the synthesis of 1-pyrenylmethyl 2-bromopropanoate (PMBP) and further use in the ATRP of St in conjunction with CuBr/2,2′-bipyridine (bpy) as the catalyst. Pyrene end-capped polymers with low polydispersities (PDI < 1.2) were obtained and characterized by GPC, ^{1}H NMR, and fluorescence spectroscopy. Gels were prepared at 70 ± 2 °C for various EGDM contents. After the drying of these gels, diffusion experiments were performed in toluene solution of Py-PSt in various molecular weights at room temperature in real time by monitoring of pyrene fluorescence intensity. During these experiments, it was observed that pyrene emission intensities increased due to trapping of Py-PSt chains into the gel as the diffusion time is increased. The Li−Tanaka equation was employed to produce the diffusion parameters. Diffusion time constants, τ_c, of Py-PSt chains were found to be increased as the cross-linker density of the gels and molecular weight of Py-PSt chains increased. It was observed that collective diffusion coefficient, D_c, decreased by increasing molecular weight M_n by obeying the $D_c \approx M^{-1}$ law.

Introduction

Polymers containing appropriate fluoresent or phosphorescent group such as anthracene[1−6] and pyrene[7−9] have been prepared and investigated by many authors. The interest in these polymers is mainly due to the expectations to create fluoresent probes and photoresponsive materials using the photosensitivity of anthracene and pyrene.

The control of polymerization is extremely crucial from the synthetic point of view. During the past five decades, the use of living polymerization processes has revolutionized the synthesis of polymers with well-defined structures, i.e., controlled composition, molecular weight distribution, and functionality. The controlled/living polymerization techniques in anionic, cationic, metathesis, and group transfer have been developed. However, besides high-purity requirements these techniques are limited to certain monomers and exclude monomers that polymerize by other mechanisms. Conventional free radical polymerization on the other hand is applicable to most vinyl monomers and less sensitive to the reaction conditions. However, conventional radical polymerization suffers from some defects, i.e., the control of the reactivity of the polymerizing monomers and in turn the control of the structure of the resultant polymer. Controlled radical polymerization has recently become an established method to obtain various polymer architectures such as block, graft, and star and gradient/statistical copolymers, hyperbranched polymers, and inorganic/organic hybrids. Nitroxide-mediated polymerization[10−12] (or stable radical mediated polymerization) (NMP), atom transfer radical polymerization[13−15] (ATPR), and reversible addition fragmentation transfer[16−18] (RAFT) processes are well-known techniques in this field. Among them ATRP has been proven to be effective for a wide range of monomers and appears to be a powerful tool for polymer chemists, providing new possibilities in structural and architectural design and also allowing polymers with desired fuctional groups. It involves reversible homolytic cleavage of a carbon−halogen bond by a redox reaction between an organic halide (R−X) and a transition metal. The synthesis of polymers with pyrene chromophoric groups with various polymerization techniques has been described. However, to the best of our knowledge, preparation of such polymers by ATRP has not yet been reported.

Polymer networks or gels are known to exist generally in two forms, swollen and shrunken. Volume transitions occur between these forms either continuously or in sudden jumps.[19,20] The equilibrium swelling and shrinking of gels in solvent has been extensively studied.[21−23] On the other hand, investigation of phase equilibrium in ternary systems involving cross-linked gel, a linear polymer, and a solvent has been of interests for many years. In general, swelling of a cross-linked polymer network by mobile polymer chains in solvent can be interpreted by the Flory−Rehner theory.[24] It has been found that the Flory−Huggins interaction parameter for the pure swollen network is usually much larger than in the corresponding un-cross-linked system. A swollen polymeric gel immersed in the solution of a linear polymer shrinks as the concentration of the linear polymer increases because of reduction in effective solvent quality of the polymer solution.[25] In other words the chemical potential of the solvent can be changed because of the osmotic contribu-

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tion of the polymer in the continuos medium. Bastide et al. studied volume change of polystyrene gel in a toluene solution of mobile polystyrene at high and low concentrations and interpreted the shrinking behavior of the gels on the basis of scaling concepts.[26] An equation of state for ternary systems was derived[27] by means of which the interaction parameter can be deduced. Partitioning of the mobile polymer chains between the solution and the gel was studied to understand the effect of the molecular mass on the partition coefficient.[28] Concentration-dependent collapse of single chains in the semidilute solution of incompatible polymer was studied theoretically[29] and experimentally.[30] More recently diffusion of liquid polystyrene into a glassy poly(phenylene oxide) was reported.[31] A simple physical model is proposed to correlate and predict diffusion rates assuming a relatively rapid dissolution of the high T_g polymer at the liquid−solid interphase. For a long time, the common belief has been that the mobile chains do not penetrate into gel, even if they are compatible with the cross-linked chains. Experimentally it is hard to discriminate between a thermodynamic and a kinetic behavior. However in all cases, the chains reptate only slowly inside the gel. Brochard studied the partition phenomenon on the basis of the extended Flory model and the scaling theory where three different regimes were distiguished.[32]

The swelling kinetics of chemically cross-linked gels can be understood by considering the osmotic pressure versus the restraining force.[33−37] The total free energy of a chemical gel consists of bulk and shear energies. In fact, in a swollen gel bulk energy can be characterized by the osmotic bulk modulus *K*, which is defined in terms of the swelling pressure and the volume fraction of polymer at a given temperature. On the other hand, the shear energy which keeps the gel in shape can be characterized by shear modulus *G*. Here shear energy minimizes the nonisotropic deformations in gel. A theory of the swelling of gel networks was first derived from the theory of elasticity by Tanaka, Hocker, and Benedek (THB).[38] Tanaka and Fillmore[39] employed that theory to describe the swelling kinetics of spherical gels, assuming that the shear modulus of the gel is negligible compared with the osmotic bulk modulus. Their model led to a relaxation time proportional to the square of the linear size of the gel and inversely proportional to the collective diffusion constant of the network. Later, Peters and Candau[40,41] extended Tanaka and Fillmore's model to long cylindrical and large disk gels for which the shear modulus cannot be neglected. Li and Tanaka[33] developed a model where the shear modulus plays an important role, which keeps the gel in shape due to coupling of any change in different direction. This model predicts that the geometry of the gel is an important factor and swelling is not a pure diffusion process.

Several experimental techniques have been employed to study the kinetics of swelling, shrinking, and drying of chemical and physical gels among which are neutron scattering,[42] quasielastic light-scattering,[41] and in-situ interferometric[43] measurements. The steady-state fluorescence (SSF) technique has been applied for studying swelling and drying kinetics in disk-shape gels.[44−46] Fast transient fluorescence[47,48] and optical transmission[49] techniques were also used in our laboratory to study swelling kinetics in pure solutions. Recently the molecular weight effect on swelling of poly(methyl methacrylate) gels in homopolymer solutions was studied using the SSF technique.[50]

In this work diffusion of pyrene end-capped polystyrene Py-PSt homopolymers into polystyrene gels were studied. Here, the synthesis of well-defined pyrene end-capped polystyrene via ATRP using 1-pyrenylmethyl 2-bromopropanoate (PMBP) as the initiator and CuBr/2,2′-bipyridine (bpy) as the catalyst was reported. Additionally, their diffusion into a polymeric gel with the emphasize on the molecular weight dependence has been investigated to understand the nature of the diffusion mechanism in swollen gels. Therefore, chain diffusion processes into gels with various cross-linker content formed by free radical cross-linking copolymerization (FCC) of styrene and ethylene glycol dimethacrylate (EGDM) were studied in polymer solutions. Polymer solution was prepared using Py-PSt chains in various molecular weights in toluene. In-situ steady-state fluorescence (SSF) experiments were performed by monitoring of Py fluorescence intensity during diffusion of chains into the gels. The diffusion time constant, τ_c, and collective diffusion coefficients, D_c, were measured by employing the Li−Tanaka model.

Theoretical Considerations

It is known that the kinetics of swelling of a polymer network or gel should obey the following relation:[33]

$$\frac{W(t)}{W_\infty} = 1 - \sum_{n=1}^{\infty} B_n e^{-t/\tau n} \tag{1}$$

Here $W(t)$ and W_∞ are the swelling or solvent uptake at time t and at equilibrium, respectively. $W(t)$ can also be considered as a volume difference of the gel between the time t and zero. Each component of the displacement vector of a point in the network from its final equilibrium location after the gel is fully swollen decays exponentially with a time constant τ_n which is independent of time t. Here B_n is given by the following relation:[33]

$$B_n = \frac{2(3-4R)}{\alpha_n^{\,2} - (4R-1)(3-4R)} \tag{2}$$

Here R is defined as the ratio of the shear and the longitudinal osmotic modulus, $R = G/M$. The longitudinal osmotic modulus, M, is a combination of shear, G, and osmotic bulk moduli, K, $M = K + 4G/3$, and α_n is given as a function of R as follows:

$$R = \left[1 + \frac{\alpha_n J_0(\alpha_n)}{J_1(\alpha_n)}\right] \tag{3}$$

Here J_0 and J_1 are the Bessel functions. In eq 1, τ_n is inversely proportional to the collective diffusion coefficient D_c of a gel disk and is given by the relation:[34]

$$\tau_n = \frac{3a^2}{D_c \alpha_n^{\,2}} \tag{4}$$

Here the diffusion coefficient, D_c, is given by $D_c = M/f = (K + 4G/3)/f$, f is the friction coefficient describing the viscous interaction between the polymer and the solvent, and α represents half of the disk thickness in the final infinite equilibrium which can be experimentally determined. The series given by eq 1 is convergent. The first term of the series expansion is dominant at large t, which corresponds to the last stage of the swelling. As seen from eq 4, τ_n is inversely proportional to the square of α_n, where α_n's are the roots of the Bessel functions. If $n > 1$, α_n increases and τ_n decreases very rapidly. Therefore, kinetics of swelling in the limit of large t or if τ_c is much larger than the rest of τ_n[33] all high-order terms ($n \geq 2$) in eq 1 can be dropped so that the swelling and shrinking

TABLE 1: Synthesis of Polystyrenes[a] with Pyrene End Groups by ATRP

polymer	react ratio[b]	conversion (%)	$M_{n,th}$	$M_{n,GPC}$ (PDI)[c]	$M_{n,NMR}$[d]
Py-PSt1	130/1/1/3	30	4495	4980 (1.18)	4925
Py-PSt2	100/1/1/3	67	7345	7540 (1,19)	6365
Py-PSt3	200/1/1/3	40	8760	9654 (1.15)	8520

[a] Temperature 110 °C; reaction time 4 h; bulk. [b] $[PSt]_0/[PMBP]_0/[CuBr]_0/[bpy]_0$. [c] Determined by GPC relative to polystyrene standards. [d] $M_{n,NMR}$ is calculated by assuming that only one pyrene group is incorporated into each polymer chain.

can be represented by the first-order kinetics.[43] In this case eq 1 can be written as

$$\frac{W(t_s)}{W_\infty} = 1 - B_1 e^{-t/\tau_c} \quad (5)$$

Equation 5 allows us to determine the parameters B_1 and τ_c from the experimental data.

Experimental Section

Materials. 1-Pyrenealdehyde, $NaBH_4$, 2-bromopropanoyl bromide (Aldrich), pyridine (py) (Lab-scan), CuBr (Aldrich), 2,2′-bipyridine (Aldrich), and EGDM (Merck) were used as received. Styrene were purified by the usual methods and distilled in vacuo over CaH_2. 2,2′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. Dichloromethane (CH_2Cl_2) (Lab-scan) was distilled over CaH_2 prior to use.

Synthesis of 1-Pyrenylmethanol (1). 1-Pyrenemethanol was synthesized by the reduction[51] of 1-pyrenealdehyde in the presence of $NaBH_4$. Mp: 126−127 °C. Yield: 92%.

^{1}H NMR (CDC_3) (δ, ppm): 8.27−7.93 (m, 9H, pyrenyl), 5.29 (s, 2H, CH_2), 2.21 (s, broad, 1H, OH).

Synthesis of 1-Pyrenylmethyl 2-Bromopropanoate (3). A 1.63 g (7 mmol) amount of 1-pyrenylmethanol (**1**) and 0.8 mL (770 mmol) of py were dissolved by heating in 20 mL of dry CH_2Cl_2. Then the reaction mixture was allowed to arrive at room temperature and 1 mL (0.01 mol) of 2-bromopropanoyl bromide (**2**) in 5 mL of CH_2Cl_2 was added under nitrogen, during 0.5 h. The reaction was maintained with stirring at room temperature for 8 h. After that period, the insoluble formed salt was filtered off and the solution was washed with a mixture of water/HCl (80/20 v/v) and several times with water. The solvent was removed by rotaevaporatory, and the crude product was redisolved in benzene and passed through a silca gel column. The first, white fraction was retained, and after evaporation of the solvent, a white powder was obtained.

^{1}H NMR ($CDCl_3$) (δ, ppm): 8.27−7.99 (m, 9H, pyrenyl), 5.907 (s, 2H, CH_2), 4.46−4.38 (q, 1H, CH), 1.84−1.81 (d, 3H, CH_3).

IR (cm^{-1}): 3200−3600 (broad) (OH), 1005 (C−OH). These peaks were absent in the spectrum of 1-pyrenealdehyde.

Synthesis of Pyrene End-Capped Polystyrene (4). A three-neck round-bottom flask equipped with a magnetic stirrer was used. The system was heated under vacuum and back-filled with dry nitrogen three times.

CuBr (0.0285 g, 0.2 mmol), bpy (0.0927 g, 0.6 mmol), and initiator PMBP (**3**) (0.0726 g, 0.2 mmol) were added to bulk styrene (3 mL, 26 mmol) in a three-neck round-bottom flask under nitrogen atmosphere. The flask was then immersed in a thermostated oil bath at 110 °C and stirred. After a given time, the mixture was diluted with THF and was passed through a column of basic aluminum oxide to remove the catalyst, part of the solvent was evaporated, and the rest was precipitated into methanol. The product filtered off and dried in vacuo. Reaction conditions and the results are given in Table 1.

Analysis of the Polymers. ^{1}H NMR spectra were recorded on a Bruker 250-MHz spectrometer with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) analyses were performed with a Polymer Laboratories Agilent model 1100 instrument consisting of pump, RI, and UV detector and four Waters styragel columns HR5E, 5E, 3, and 2. THF was used as an eluent at a flow rate of 0.3 mL/min at 30 °C.

Preparation of Polystyrene Gel. The radical copolymerization of St and EGDM was performed at 70 ± 2 °C in the presence of 2,2′-azobis(isobutyrronitrile) (AIBN) (0.26 wt %) as an initiator. Samples were deoxygenated by bubbling nitrogen for 10 min, and then radical copolymerization of St and EGDM was performed at 70 ± 2 °C. After gelations were completed, the gel samples were dried under vacuum and cut into disk-shaped gels for the swelling experiments. Here two different gels with the two different EGDM contents (0.5 and 1.0 vol %) were used for the diffusion experiments.

Fluorescence Measurements for Diffusion. Steady-state fluorescence (SSF) measurements were carried out using Perkin-Elmer model LS-50 spectrofluorometer. All measurements were made at the 90° position, and slit widths were kept between 4 and 10 nm. In-situ swelling experiments were performed in a 1 × 1 cm quartz cell at room temperature. Gel samples were attached to one side of the quartz cell by pressing the disk with thin steel wire. Initially the quartz cell was filled with a toluene solution of Py-PSt. This cell was placed in the spectrofluorometer. Gels were left in the cell, and then polymer solution was removed by a pipet for fluorescence measurements. These snapshot diffusion experiments were repeated during the penetration of Py-PSt into the PSt gels. Figure 1a,b presents the diffusion process and fluorescence measurements, respectively. The initial thicknesses of these disk-shaped gels were around 0.21 cm. The initial (d_i, m_i) thicknesses and weights are listed against EGDM contents in Table 2 for there different molecular weights of Py-PSt polymer chains.

TABLE 2: Experimentaly Measured Parameters for the Diffusion of Py-PSt Chains into the Poly Styrene Gels[a]

polymer	m_i (g)	m_f (g)	d_i (cm)	d_f (cm)	τ_c (min)	$10^{-5}D_C$ ($cm^2\,s^{-1}$)
			0.5 vol % EGDM			
Py-PSt1	0.06	0.31	0.21	0.30	83	0.48
Py-PSt2	0.06	0.33	0.21	0.36	138	0.25
Py-PSt3	0.06	0.33	0.21	0.37	98	0.33
			1.0 vol % EGDM			
Py-PSt1	0.06	0.32	0.21	0.36	90	0.34
Py-PSt2	0.06	0.29	0.21	0.35	155	0.19
Py-PSt3	0.06	0.24	0.21	0.33	109	0.24

[a] m_i, d_i: initial weight and thickness. m_f, d_f: final weight and thickness. M_n: average molecular weight of Py-PSt chains. τ_c, D_C; time constant and collective diffusion coefficient. EGDM: cross-linker.

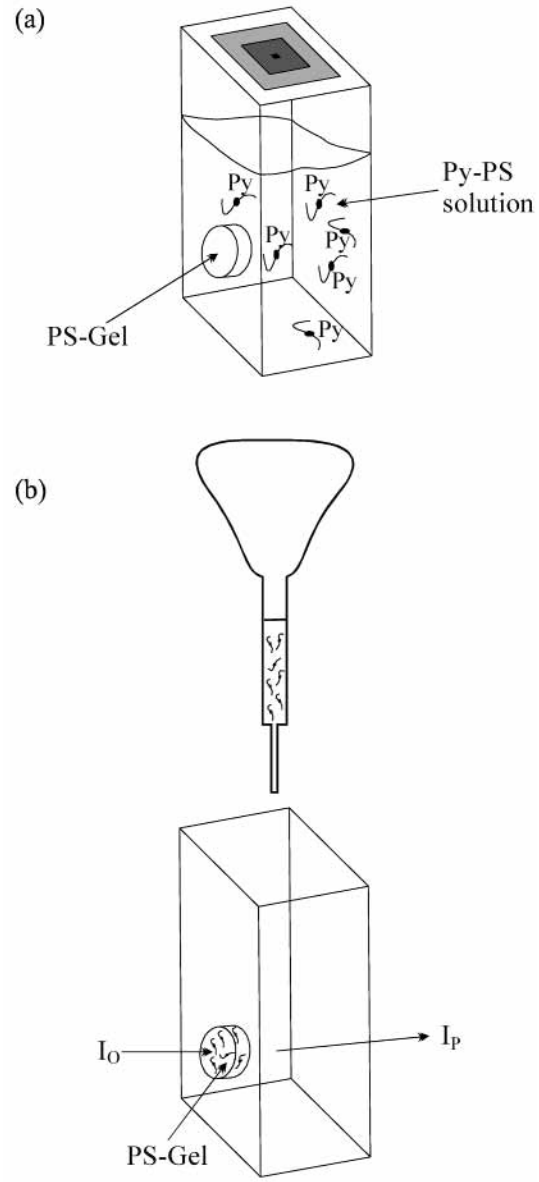


Figure 1. Fluorescence cell in a spectrofluorometer for the monitoring of gel: (a) gel in the polymer solution; (b) polymer solution removed by pipet for fluorescence measurements.

During the fluorescence measurements the wavelength of the excitation light was kept at 345 nm and pyrene spectra were monitored at each diffusion step. The Py spectra from Py-PSt1 and Py-PSt2 in 0.5% EGDM content gels are shown in Figure 2a,b at various diffusion steps, respectively. To quantify the fluorescence data the maximum intensity, I_p, at 395 nm was used during diffusion experiments. No shift was observed in the wavelength of maximum intensity, I_p, of Py. Gel samples were kept their transparencies during the diffusion experiments.

Results and Discussion

Synthesis of Pyrene End-Capped Polystyrene. This paper describes the synthesis of pyrene end-capped polystyrene (**4**) with low polydispersities. In the synthesis, the new pyrene-containing initiator, PMBP (**3**) (Scheme 1), was synthesized by reacting 1-pyrenylmethanol (**1**) with 2-bromopropanoyl bromide (**2**). It is purity and structure were confirmed by ^{1}H NMR and IR.

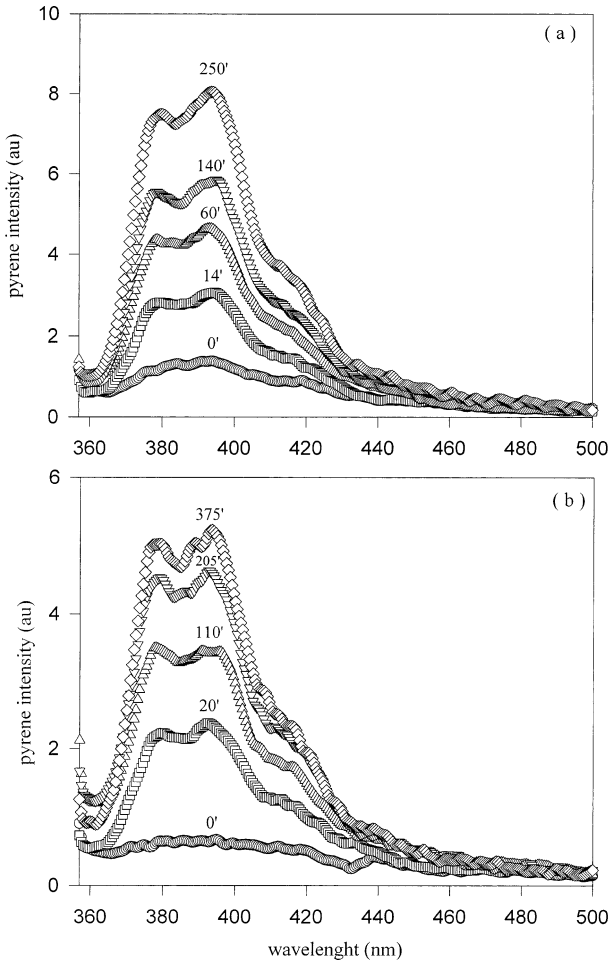
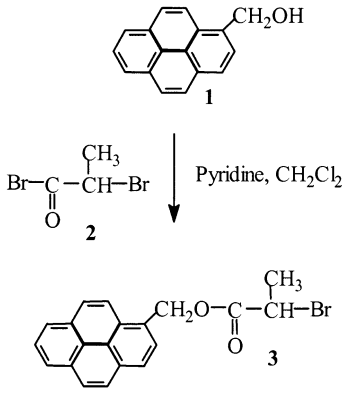


Figure 2. Pyrene emission spectra produced from (a) Py-PSt1 and (b) Py-PSt2 in 0.5% EGDM content gel at various diffusion steps. The number on each curve presents the time of diffusion in minutes.

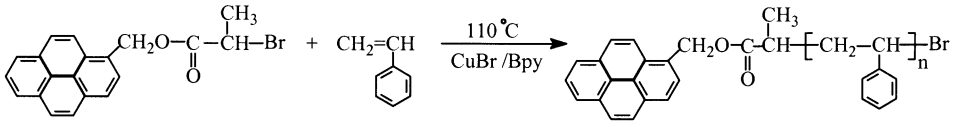
SCHEME 1



St was polymerized in bulk at 110 °C via ATRP using PMBP (**3**) and CuBr/bpy as the catalayst (Scheme 2). The volume of styrene was the same in each ATRP system, and the molar ratio of PMBP to CuBr to bpy was always 1/1/3.

Figure 3 shows the GPC−UV and RI chromatograms of the polymer I. The labeling of PSt by pyrene is assessed by GPC analysis with a double dedection. Signals recorded by the UV dedector at 345 nm are due to the absorption of pyrene end groups. Superimposition of the traces recorded by both methods clearly indicates that the pyrene moiety has been chemically incorporated in to the polymers.

SCHEME 2



3 **4**

The $M_{n,GCP}$ and PDI for polymers are listed in Table 1. Table 1 shows a relatively good correlation between the GPC and ^{1}H NMR data regarding the molecular weight of the polymers. The molecular weights determined by GPC and NMR are close to those calculated from the ratio of monomer to initiator. This confirms that the polymer chains are quantitatively functionalized to generate the desired pyrene-end capped polystyrenes. Polydispersities of the polymers are also low as a result of the ATRP mechanism. Figure 4 (parts a and b) shows the ^{1}H NMR spectra of PMBP and Py-PSt1. The typical proton signals of the pyrene moiety in Figure 4a are also seen in the spectrum of the polymer at 7.9−8.2 ppm (Figure 4b) indicating that pyrene units have been successfully attached to the polymer chain. Moreover, Figure 5a,b shows the fluorescence emission spectra of the initiator, PMBP, and PSt obtained therefrom in toluene at room temperature, respectively. Both spectra show the vibrational structures of the pyrene chromophore. These spectroscopic investigations suggest that pyrene groups were conserved under the polymerization conditions.

Diffusion of Pyrene End-Capped Polystyrene. The pyrene emission intensities, I_p (395 nm), from the Py-PSt1 and Py-PSt2 in 0.5% EGDM content gel against diffusion time are plotted in Figure 6a,b, respectively. The points in Figure 6 were obtained during in-situ fluorescence experiments described in Figure 1b, where Py-PSt chains were trapped in the swollen gel. As seen in Figure 6, trapping of Py-PSt chains in the swollen gel increases as the diffusion time, t, is increased. Since pyrene intensity, I_p, is proportional to the number of Py-PSt chains trapped in gel, solvent uptakes W and W_∞ can be considered to be proportional to I_p and $I_{p\infty}$, respectively, during the diffusion process. Here $I_{p\infty}$ represents the pyrene intensity at the equilibrium state of diffusion where solvent uptake by swollen gel is W_∞. The relation between solvent uptake and fluorescence intensity from the gel is given by the following relation:

$$\frac{W}{W_\infty} \approx \frac{I_p}{I_{p\infty}} \tag{6}$$

With the combination of eqs 5 and eq 6, the following useful relationship can be obtained:

$$\ln\left(1 - \frac{I_p}{I_{p\infty}}\right) = \ln B_1 - \frac{t}{\tau_c} \tag{7}$$

The data in Figure 6 are plotted in Figure 7a,b according to eq 7 for Py-PSt1 and Py-PSt2 in 0.5% EGDM content gels, respectively. The linear regression of the curves in Figure 7 provides us with B_1 and τ_c values. Taking into account the dependency of B_1 and R, one obtains R values, and from α_1-R dependence, α_1 values were produced.[33] Then using eq 4 for $n = 1$, collective diffusion coefficients, D_c, were determined. Here the time constant, τ_c, is the measure of diffusion (penetration) time of Py-PSt chains into the swollen gel. The produced τ_c and D_c values are listed in Table 2 for Py-PSt chains. Figure 8a,b presents the τ_c and D_c values versus molecular weight, M_n, respectively. It is seen in Figure 8a that high molecular weight Py-PSt2 chains penetrate (diffuse) into the PSt gel much slower

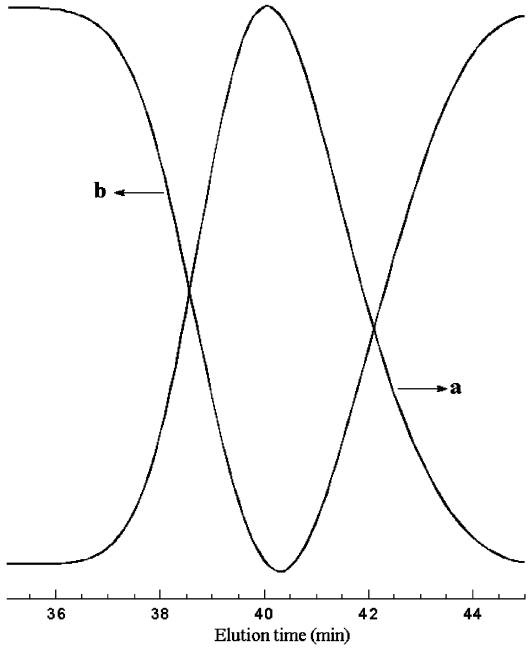


Figure 3. GPC trace for Py-PSt1, with $M_n = 4980$ and $M_w/M_n = 1.18$. Detectors: (a) RI; (b) UV absorption at 345 nm.

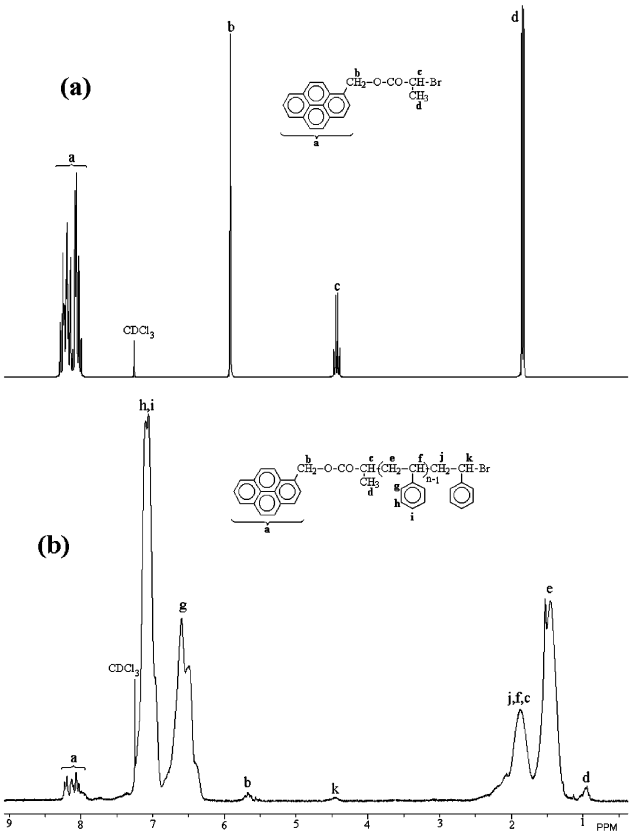


Figure 4. ^{1}H NMR spectra of initiator (a) PMBP and (b) Py-Pst1 in $CDCl_3$.

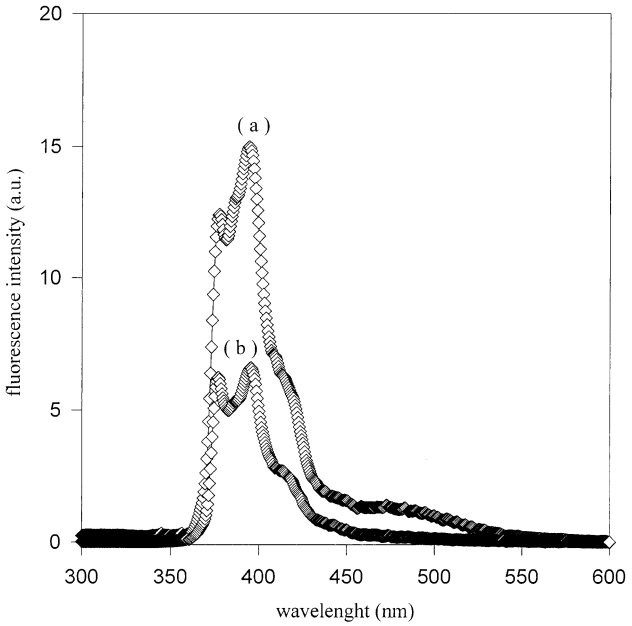


Figure 5. Plot of the fluorescence emission spectra of (a) the initiator, PMBP, and (b) Py-PSt1, respectively (λ_{ex} = 345 nm).

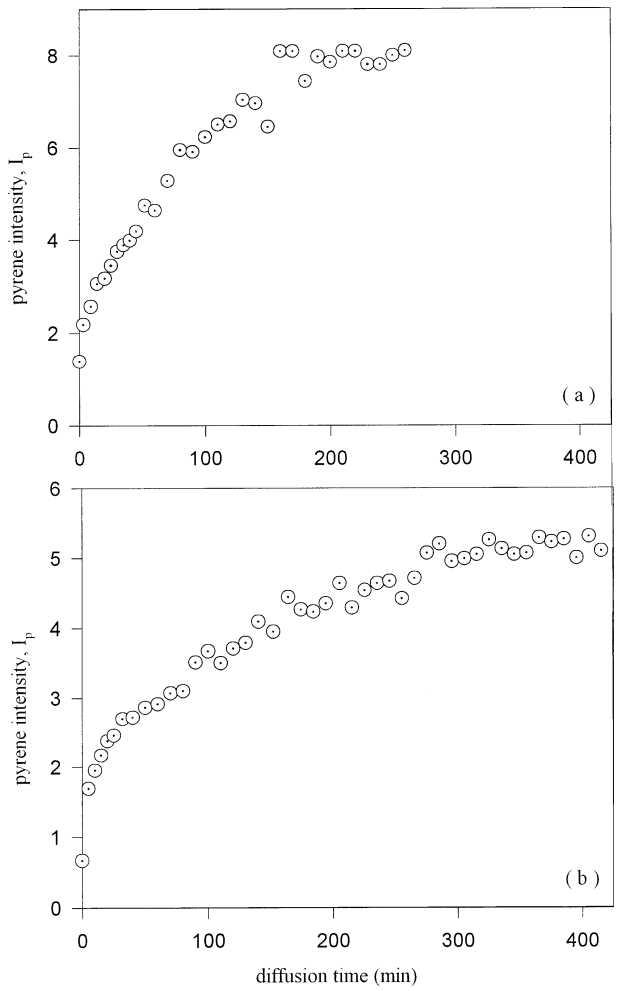


Figure 6. Plots of the pyrene emission intensities from (a) Py-PSt1 and (b) Py-PSt2 in 0.5% EGDM content against the diffusion time.

than low molecular weight Py-PSt1 chains as expected. On the other hand penetration of Py-PSt chains into the dense gels (1% EGDM) takes much longer than they do into loose gels (0.5% EGDM) for all molecular weight chains. The behavior of D_c

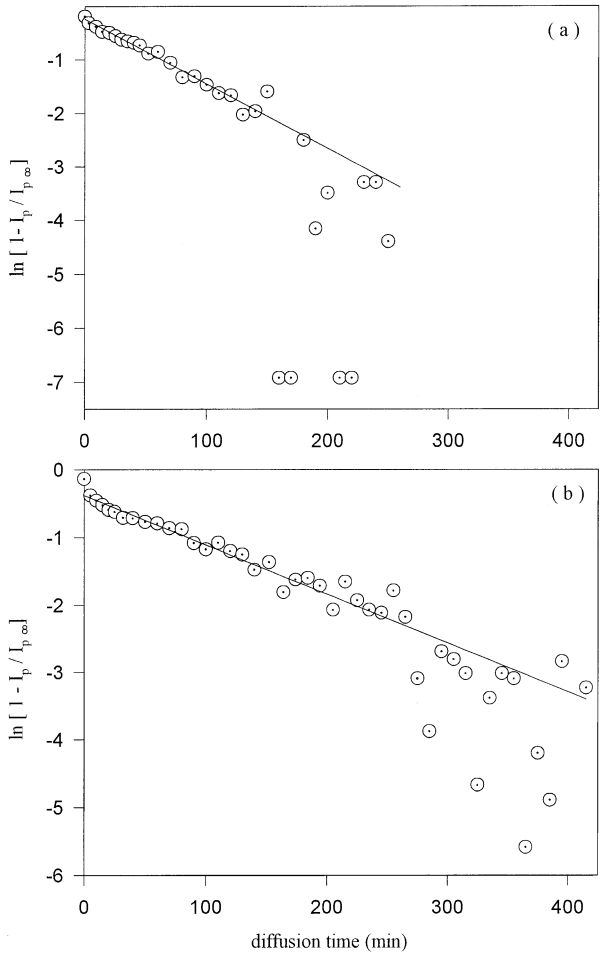


Figure 7. Linear regressions of the data presented in Figure 6a,b. B_1 and τ_c values were obtained from the intersections and slope of the plots.

values in Figure 8b supports the above findings, namely diffusion of high molecular weight Py-PSt chains into PSt gel is much slower than diffusion of low molecular weight chains. Mobility of Py-PSt chains in loose gels is also much higher than in dense gels. Here, one would like to see the relation between D_c and M_n. The log D_c−log M_n plot in Figure 9 shows a good linear relation. The slope of the linear relation in Figure 9 produces −0.99 ± 0.05 and −0.91 ± 0.06 for densely and loosely formed gels, respectively, which can be offer us the following relationship between D_c and M_n values:

$$D_c \approx M_n^{-1} \tag{8}$$

To interpret the relation in eq 8, the molecular weights, M_c, between cross-links of the PSt gels were determined by using Flory−Rehner equation.[24] M_c = 17 000 and 12 500 g mol^{-1} were calculated for the loose (0.5% EGDM) and dense (1.0% EGDM) gels, respectively. Since the molecular weights of the Py-PSt chains are much lower than the M_c values for both gels, then one may conclude that the reptation motion should be ruled out for the diffusion model. In other words, Py-PSt chains diffuse into the PSt gels similar to small molecules obeying Fickian diffusion and eq 8. In fact it has been well established that the diffusion coefficients of dispersed dyes in cellulose acetate decrease with increase in molecular weights.[52] Besides that molar masses of Py-PSt chains are much lower than the entanglement molecular weight of PSt, which also predict that Py-PSt chains obey Fickian diffusion and diffuse in the PSt gel like a small molecule.

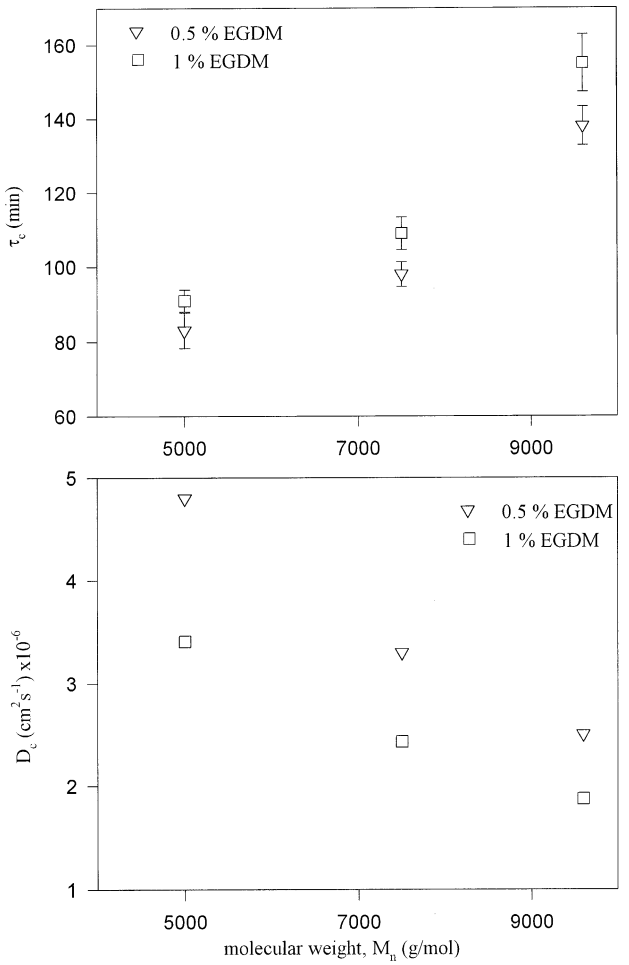


Figure 8. Plots of (a) τ_c and (b) D_c values versus molecular weight, M_n, for the gel samples listed in Table 1.

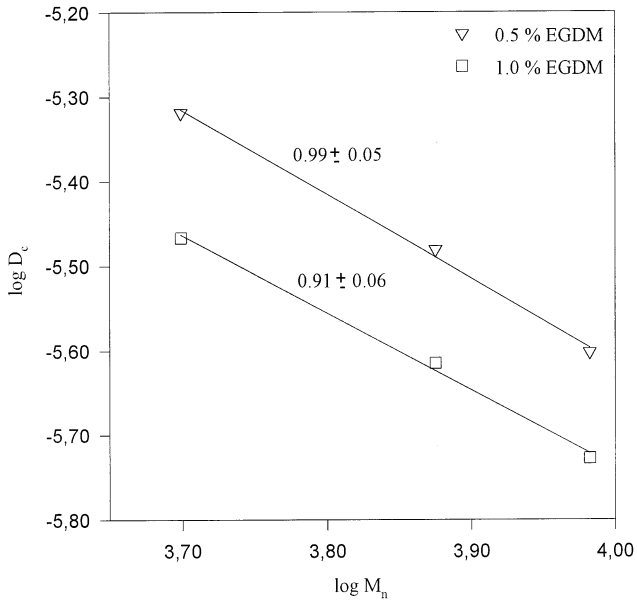


Figure 9. log−log plot of D_c versus M_n. The slope of the linear relation produces the values of −0.99 and −0.91 for the gel samples containing 0.5 and 1.0% EGDM contents, respectively.

On the other hand, toluene-guided Py diffusion into the PSt gel made with 1.5% EGDM has produced larger D_c values (0.63×10^{-5} cm^2 s^{-1})[53] than that were observed in this work. The comparison of these values can predict that polymer chain diffusion is much slower than the small molecule diffusion into the similar gel−solvent systems.

In summary, this work presents the molecular weight dependence of polymer penetration into the polymeric gels immersed in a good solvent. It is observed that higher molecular weight chains diffuse into the polymer network much slower than the low molecular weight chains. On the other hand, low molecular weight polymer chains diffuse much quicker than high molecular weight polymer chains in the polymer network during their diffusion. Here it is believed that direct fluorescence technique can be used for real-time monitoring of the diffusion processes. In this technique in-situ fluorescence experiments are easy to perform and provide us quite sensitive results to investigate diffusion of polymer chains during gel swelling in homopolymer solution. Here it has to be also noted that preparation of pyrene end-capped polystyrene via ATRP using PMBP as the initiator and CuBr/2,2′-bipyridine as the catalyst was reported first time. The produced polymer chains have narrow molecular weight distribution as a result of ATRP, which was desired for studying the diffusion mechanism in a polymeric gel. It was also shown by ^{1}H NMR and GPC that one pyrene group is attached to a single PSt chain which allowed us to monitor individual chain diffusion in the gel system.

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