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Slow Release of Trapped Homopolymers from a Swelling Polymeric Gel: A Fluorescence Study

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In-situ steady-state fluorescence experiments were performed for studying slow release of pyrene-labeled polystyrene chains from polystyrene gels formed by free-radical crosslinking copolymerization. Atom transfer radical polymerization was used to produce the pyrene end-capped polystyrene chains. In order to load the pyrene end-capped polystyrene chains into the gel, disc-shaped gels were left in toluene solutions of pyrene end-capped polystyrene chains of various molecular weights. These swollen gels were redried in air and then immersed in pure toluene solution for monitoring slow release from the gel. These reswelling experiments were performed at room temperature in real time by monitoring the pyrene emission intensity using steady-state fluorescence measurements. Slow-release diffusion coefficients were measured and found to decrease as the crosslink density of the gels increased. It was observed that higher molecular weight pyrene end-capped polystyrene chains released much faster than low molecular ones during the slow-release process.

Keywords slow release, diffusion, fluorescence, gels swelling

Introduction

Modern advances in diffusion of molecules through polymeric materials are not limited to gases and other small molecules. A major current field involves controlled slow release for drug delivery. The slow-release kinetics of physical and chemical gels are very important in many technological applications, especially in pharmaceutical and agricultural industries. When a crosslinked polymer is placed in contact with a compatible solvent, the solvent penetrates into the polymer and forms a swollen phase. The slow-release process of chemically crosslinked gels can be understood by considering the osmotic pressure vs. the restraining force.[1–5] The total free energy of a chemical gel consists of bulk and shear energies. In fact, in a swollen gel, the 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 given temperature. On the other hand, the shear energy, which keeps the gel in shape, can be characterized by the shear modulus G. Here, shear energy minimizes the nonisotropic deformations in gel. The theory of kinetics of swelling for a spherical chemical gel was first developed by Tanaka and Filmore[6] who assumed that the shear modulus, G, is negligible

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compared to the osmotic bulk modulus. Later, Peters and Candau[7] derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming nonnegligible shear modulus. Recently, Li and Tanaka[1] developed a model where the shear modulus plays the important role of keeping the gel in shape due to coupling of any change in different directions. This model predicts that the geometry of the gel is an important factor, and swelling is not a pure diffusion process.

Fluorescence techniques, such as steady-state spectroscopy, fluorescence anisotropy, and fluorescence decay measurements are powerful tools for studies of molecular diffusion or molecular interaction. Due to high sensitivity, versatility of information, and commercially available instrumentation, fluorescence techniques have been extensively applied in many areas such as biomedicine, biology, science of materials, etc.[8] Fluorescence dyes have been used in two basic types of experiments. When the dye is simply added to the system as a small molecule, the dye is referred to as a probe; these are available commercially. As a consequence, such experiments are easy to carry out, but often difficult to interpret, because one has to know where the dye is located in the system. If one can prepare an experiment that allows the dye to be attached covalently to a specific component of a system, such as a polymer chain segment, such dyes are referred to as labels. The question is whether or not the presence of the dye perturbs the system or perturbs its own local environments within the system. Perturbation is most common where high dye concentration leads to aggregation, and in crystalline systems where the order in the system can be affected by the dye. Perturbations are much less likely when the fluorescent dye is incorporated into an amorphous fluid or glassy phase.

Fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and nonradiative processes.[9] If the possibility of perturbation due to oxygen is excluded, the radiative probabilities are found to be relatively independent of environment and even of the kind of molecules. Environmental effects on nonradiative transitions, which are primarily intramolecular in nature, are believed to arise from the breakdown of the Born-Oppenheimer approximation.[10] The role of the solvent in such a situation is to add the quasi-continuum of states needed to satisfy energy resonance conditions. The solvent acts as an energy sink for rapid vibrational relaxation, which occurs after the rate limiting transition from the initial state. Years ago, Birks et al. studied the influence of solvent viscosity on the fluorescence characteristics of pyrene solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality.[11] As the temperature of liquid solution is varied, the environment about the molecule changes, and much of the change in absorption spectra and fluorescence yields in solution can be related to the changes in solvent viscosity. A matrix that changes little with temperature will enable one to study molecular properties themselves without changing the environmental influence.

Among the various techniques to polymerize vinyl monomers, ranging from ionic to group transfer, the most convenient remains free-radical polymerization since it is easy to perform. Its mild reaction conditions and applicability to the wide range of polymerizable monomers make it suitable for both industry and research laboratories. However, the main disadvantage of classical free-radical polymerization is that it does not allow structure and molecular weight control. The produced polymers are generally polydisperse, and the molecular weights are difficult to control. These features are indeed accessible through living anionic or cationic processes, but these techniques require rigorous conditions and delicate procedures. One of the most widely studied controlled radical polymerization techniques is Atom Transfer Radical Polymerization (ATRP).[12–14] The ATRP process

uses an alkyl halide as initiator, and a metal in its lower oxidation state with complexing ligands. The process involves the successive transfer of the halide from the dormant polymer chain to the ligated metal complex, thus establishing a dynamic equilibrium between active and dormant species. The ATRP technique has proven to be a powerful tool in the synthesis of polymers with narrow polydispersities and controlled molecular weight.

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,[15] quasielastic light-scattering,[15] macroscopic experiments,[2] and in situ interferometric[16] measurements. Recently, an in situ steady-state fluorescence method has been used to study sol-gel phase transitions in a free-radical crosslinking copolymerization process[17–19] and swelling and drying processes in various gel systems.[20,21] The same technique was also applied for studying release of camptothecin from agar hydrogel.[22,23]

Experimental

The slow-release process of Pyrene end-capped Polystyrene (Py-PSt) homopolymers trapped in Polystyrene (PSt) gels was studied in pure toluene solution. The PSt gels with various crosslinker content were prepared by Free-radical Crosslinking Copolymerization (FCC) of styrene and Ethylene Glycol Dimethacrylate (EGDM). Polymer solutions were prepared by dissolving Py-PSt chains having various molecular weights in toluene. The PSt gels, swollen in this solution, were left in air to dry. Dried polystyrene gels containing the Py-PSt chains were then immersed in pure toluene solution and allowed to reswell. In-situ Steady-State Fluorescence (SSF) experiments were performed by monitoring the Pyrene (Py) fluorescence emission spectra outside of the gel during slow release. Slow-release diffusion coefficients (D) were measured and found to decrease as the crosslinker density of the gels was increased. However, the D values increased as the molecular weight, M_n of the Py-PSt chains was increased.

The 1-Pyrene aldehyde, $NaBH_4$, 2-bromopropanoyl bromide (Aldrich), pyridine (py) (Lab-scan), CuBr (Aldrich), 2,2′-bipyridine (Bpy) (Aldrich) and EGDM (Merck) were used as received. Styrene was purified by the usual methods and distilled in vacuo over CaH_2. The 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Dichloromethane (CH_2Cl_2) (Lab-scan) was distilled over CaH_2 prior to use. The 1-Pyrenylmethyl-2-Bromopropanoate (PMBP) was prepared as described previously.[24]

Synthesis of Pyrene–End-Capped Polystyrene[24]

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. The CuBr (0.0285 g, 0.2 mmol), Bpy (0.0927g, 0.6 mmol), and initiator PMBP (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 was filtered off and dried in vacuo. Reaction conditions and the results are given in Table 1.

Analysis of the Polymers

The ^{1}H-NMR spectra were recorded on a Bruker 250-MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Gel Permeation Chromatography

Table 1
Reaction conditions and molecular weights of end-capped polystyrene prepared by the atom transfer radical polymerization of polystyrene[a]

Polymer	Reactant ratio[b]	Conversion (%)	$M_{n,th}$	$M_{n,GPC}$ (PDI)[c]	$M^{d}_{n,NMR}$
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 4h; 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 anthracene group is incorporated into each polymer chain.

(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, 2, and 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 Styrene (St) and EGDM was performed in the presence of AIBN (0.26-wt%) as an initiator. Samples were deoxygenated by bubbling nitrogen for 10min, 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 disc-shaped gels for the swelling experiments to load Py-PSt chains. Here, two different gels with the two different EGDM contents (0.5- and 1.0-vol.%) were used for the slow-release experiments.

Results and Discussion

Steady-state fluorescence (SSF) measurements were carried out using a Perkin Elmer Model LS-50 Spectroflurimeter. All measurements were made at 90° position, and slit widths for excitation and emission were both kept at 10 nm. In situ slow-release experiments were performed in a 1×1 cm quartz cell at room temperature. Gel sample were attached to one side of the quartz cell by pressing the disc with thin steel wire. The quartz cell was filled with pure toluene solution for the slow-release experiments. This cell was placed in the spectrofluorimeter, and fluorescence emission was monitored at a 90° angle. Figure 1 shows the position of the gel samples during the slow-release process. During the fluorescence measurements, the wavelength of the excitation light was kept at 345 nm, and pyrene emission intensities at wavelength of 395nm were monitored for each slow-release step. The Py spectra from Py-PSt1, Py-PSt2, and Py-PSt3 in 0.5% EGDM content gels are shown in Fig. 2-a, Fig. 2-b, and Fig. 2-c at various slow-release times, respectively. One may expect that, as solvent uptake increases, slow release of Py-PSt molecules from the swollen gel increases; as a result, Py intensity in the surrounding solution increases due to increasing amount of Py molecules in the solvent in the cell. In order to quantify the fluorescence data, the maximum Py intensity, I_p at 395nm was used during the slow-release experiments. No shift was observed in the wavelength of the maximum intensity, I_p of Py, as shown in Fig. 2.

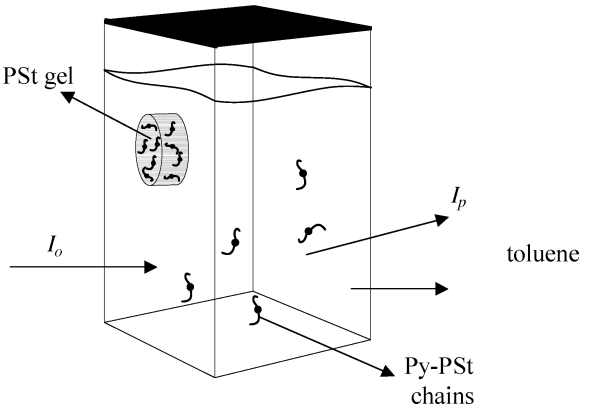

Figure 1. Fluorescence quartz cell in LS-50 Perkin Elmer spectrofluorimeter for monitoring of slow-release processes. I_0 and I_p are the excitation and emission intensities at 345 nm and 395 nm, respectively.

The pyrene emission intensities I_p (at 395nm) from the Py-PSt1, Py-PSt2, and Py-PSt3 in pure toluene solution for the 0.5% EGDM content gel against slow-release time, t_s, are plotted in Figs. 3-a, 3-b, and 3-c, respectively. Since pyrene intensity, I_p, is proportional to the amount of the fluorescing Py-PSt chains in the toluene solution, the behavior of intensity curves in Fig. 3 may suggest that the longer the release time,

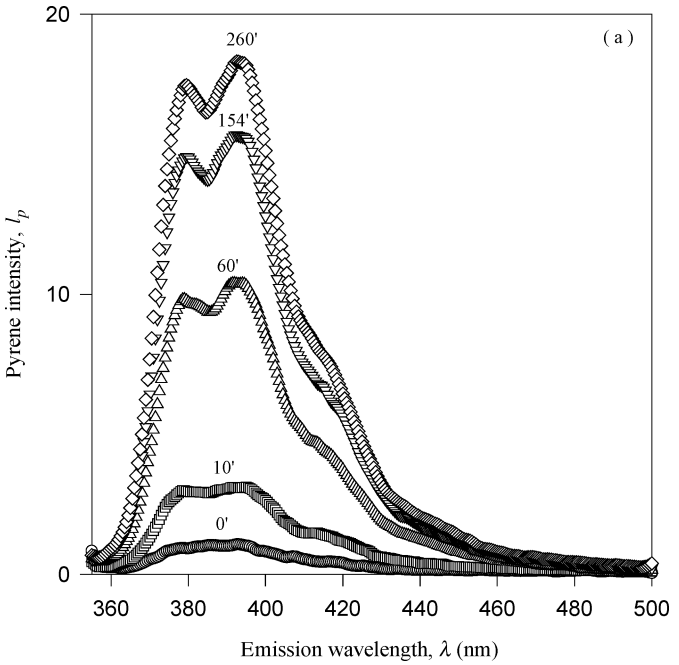

Figure 2. Pyrene emission spectra, produced for a: Py-PSt1; b: Py-PSt2; and c: Py-PSt3, in pure toluene solution from 0.5% EGDM content gel at various slow-release times. Numbers on each curve indicate time of slow release in minutes. *(Continued)*

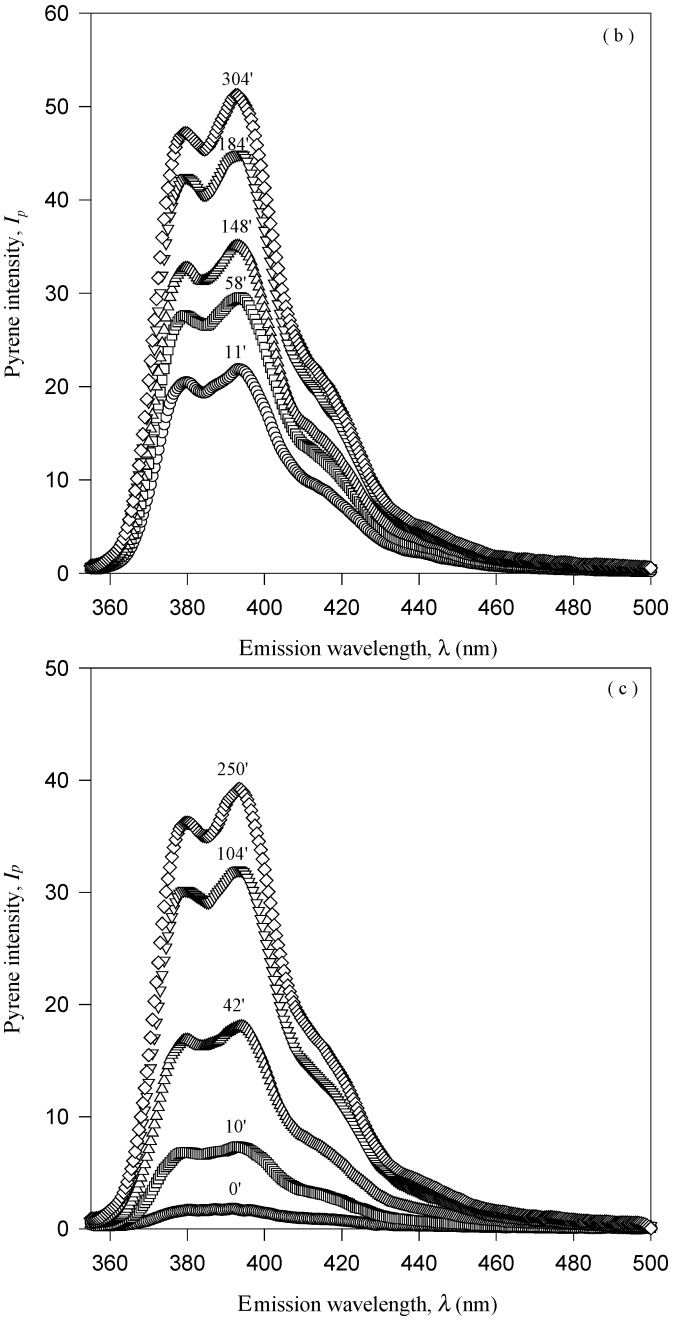

Figure 2. (Continued)

the more the Py-PSt molecules have been released to surrounding solution from PSt gel.

The fraction, $\frac{M_t}{M_\infty}$, of the amount of Py-PSt chains released at time, t, can be employed to quantify the slow-release data for PSt gels. Here, M_t and M_∞ are the amount of flourescing chains released at time t, and at thermodynamic equilibrium or at infinitely long time. In the

present work, the emission intensities, I_p and , I_∞, from the surrounding solution at time t, and at time infinity (i.e., when the intensity aproached a constant value), were obtained by using fluorescence measurements. The relation between the fraction, $\frac{M_t}{M_\infty}$, of the released Py-PSt chains from gel and emission intensity from surrounding solution can be simply

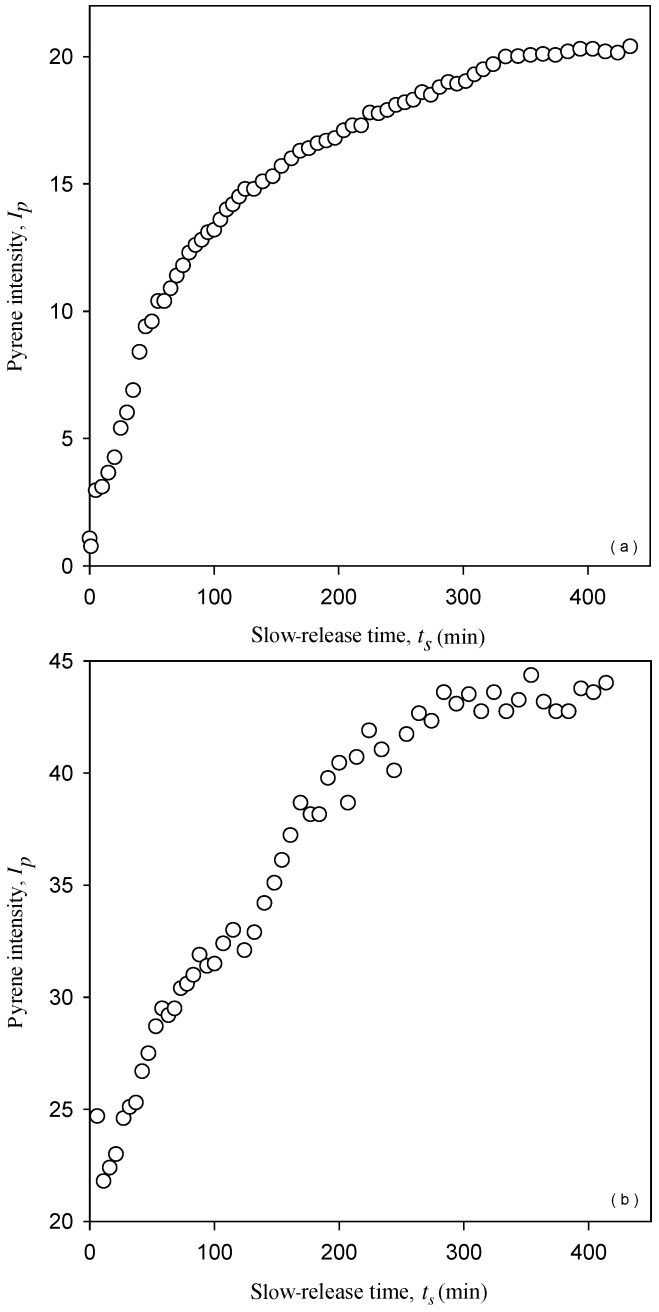

Figure 3. Plots of the pyrene emission intensities, for a: Py-PSt1; b: Py-PSt2; and c: Py-PSt3, in pure toluene solution from 0.5% EGDM content against the slow release time. *(Continued)*

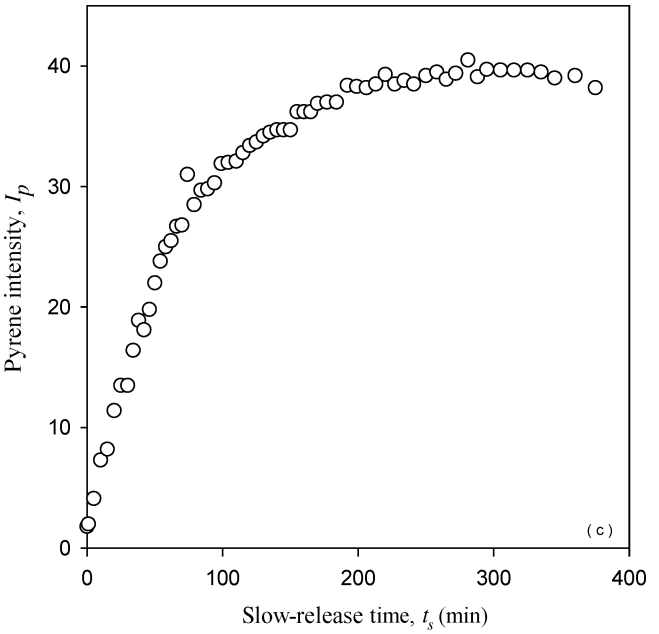

Figure 3. (Continued)

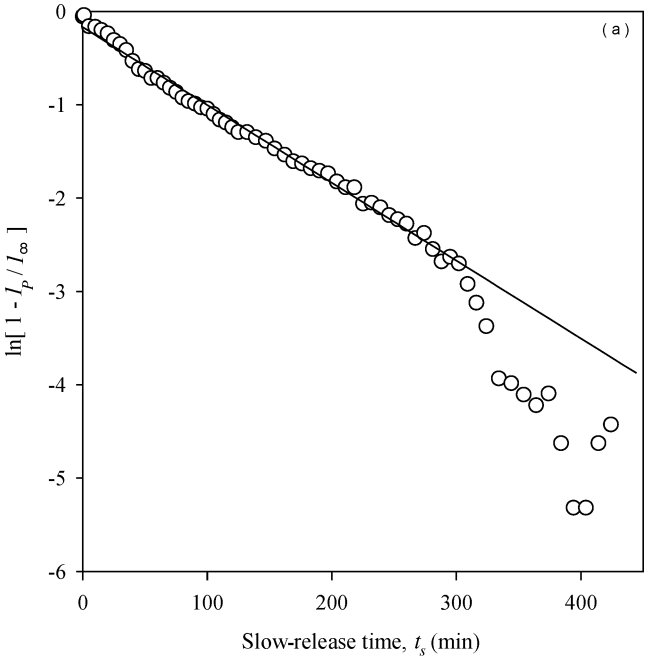

Figure 4. Linear regressions of the data presented in Figs. 2-a, 2-b, and 2-c. Slow-release diffusion coefficients (D) were obtained from slope of the plots. *(Continued)*

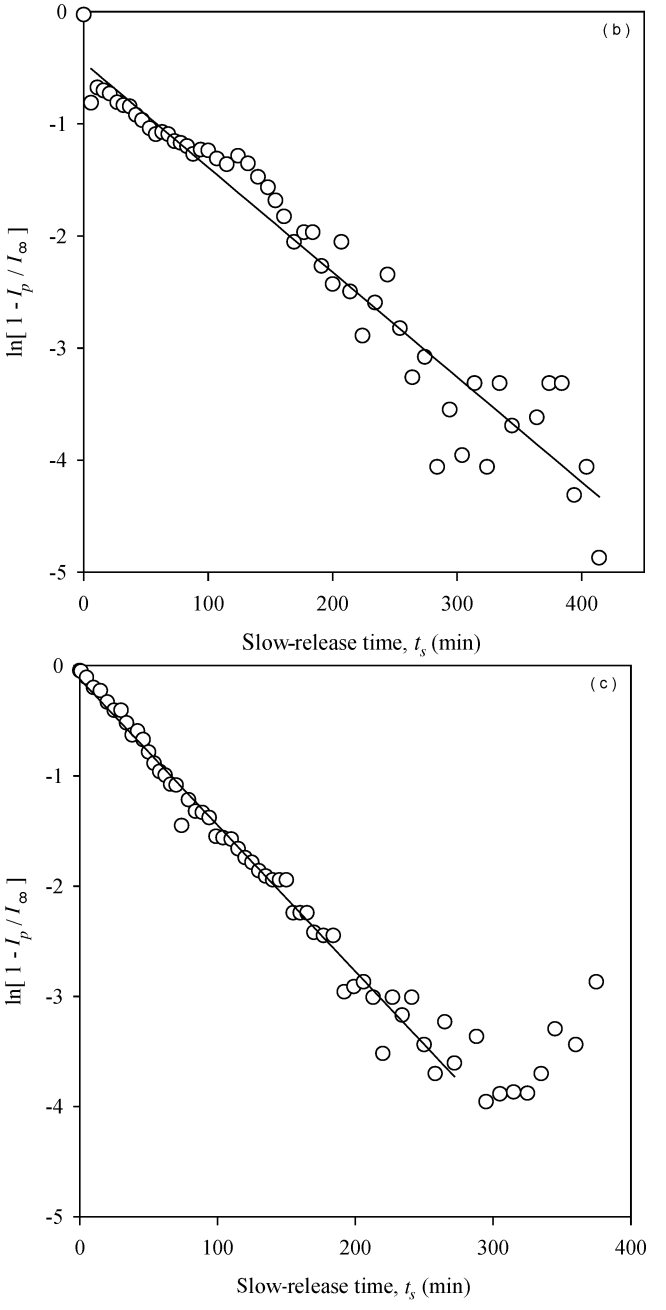

Figure 4. (Continued)

expressed as follows[25,26]:

$$\frac{M_t}{M_\infty} \approx \frac{I_p}{I_\infty}. \tag{1}$$

The release of a substance from polymeric gels can be classically assumed to take place by diffusion.[27] The diffusion coefficient thus appears as a key parameter if a device

Table 2
Release of Py-PSt chains from PSt gels; slow-release diffusion coefficients and initial values of gels thicknesses and weights

M_w	m_i (g)	a_0 (cm)	D ($cm^2\ s^{-1}$) $\times\ 10^{-5}$
	EGDM (vol. %) 0.5		
5000 (Py-PS1)	0,07	0,21	3,90
7500 (Py-PS2)	0,07	0,21	4,40
9600 (Py-PS3)	0,07	0,21	5,90
	EGDM (vol. %) 1.0		
5000 (Py-PS1)	0,07	0,21	3,40
7500 (Py-PS2)	0,07	0,21	3,60
9600 (Py-PS3)	0,07	0,21	4,70

is designed to release a solute at a predetermined rate. Here, the slow-release process can be treated using the Fickian diffusion model.[28] The behavior of slow-release curves (I_p) in Fig. 3 support this suggestion. The solution to the Fick's second law in the form of a trigonometric series for a thin slab is given by the following relation[28]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2 D\pi^2}{a_0^2}t\right), \tag{2}$$

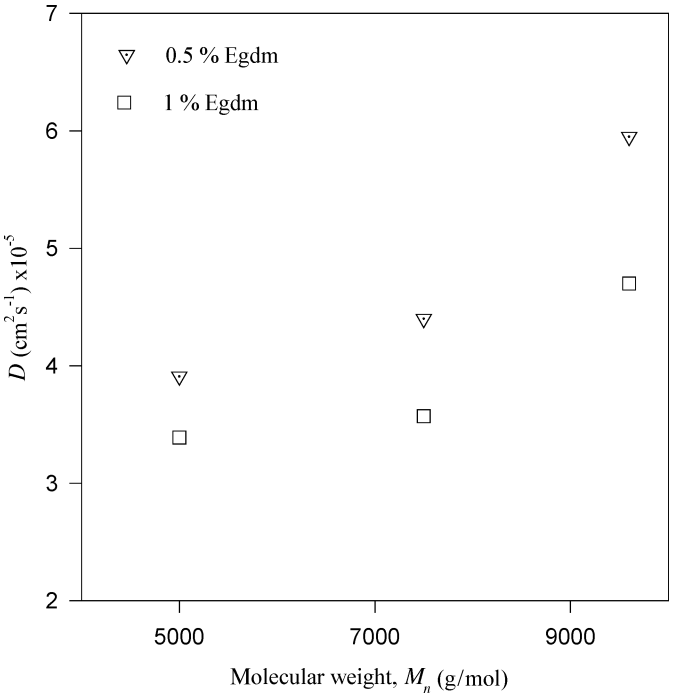

Figure 5. Plot of slow-release diffusion coefficients, D, vs. molecular weight, M_n, for the gel samples containing 0.5 and 1.0% EGDM contents, respectively.

where D can be called the slow-release diffusion coefficient, and a_0 is taken as the initial thickness of the swollen gel. Here, for our use, the thin discs used are assumed to be thin slabs. By taking only the first term ($n = 0$) in the summation series and using Equation (1), Equation (2) can be simplified to Equation (3):

$$\ln\left[1 - \frac{I_p}{I_\infty}\right] = \ln\left[\frac{8}{\pi^2}\right] - \frac{D\pi^2}{a_0^2}t \tag{3}$$

The slow-release diffusion coefficients, D for Py-PSt molecules, can be obtained using Equation (3). The I_p/I_∞ data in Fig. 3 are fitted to Equation (3) in Figs. 4-a, 4-b, and 4-c for Py-PSt1, Py-PSt2, and Py-PSt3 in the 0.5% EGDM content gel. The slope of the linear curves produce the D values, which are listed in Table 2. As seen in Fig. 4, linear fits are quite successful, which indicates that the slow-release model employed is reliable for the present gel systems. The D values for the 1.0% EGDM content gel samples are also provided in Table 2. Figure 5 presents the plot of slow-release diffusion coefficients, D vs. molecular weight, M_n, of the Py-PSt molecules for the 0.5 and 1.0% EGDM content gel samples. The release time of low-molecular-weight Py-PSt chains into the surrounding

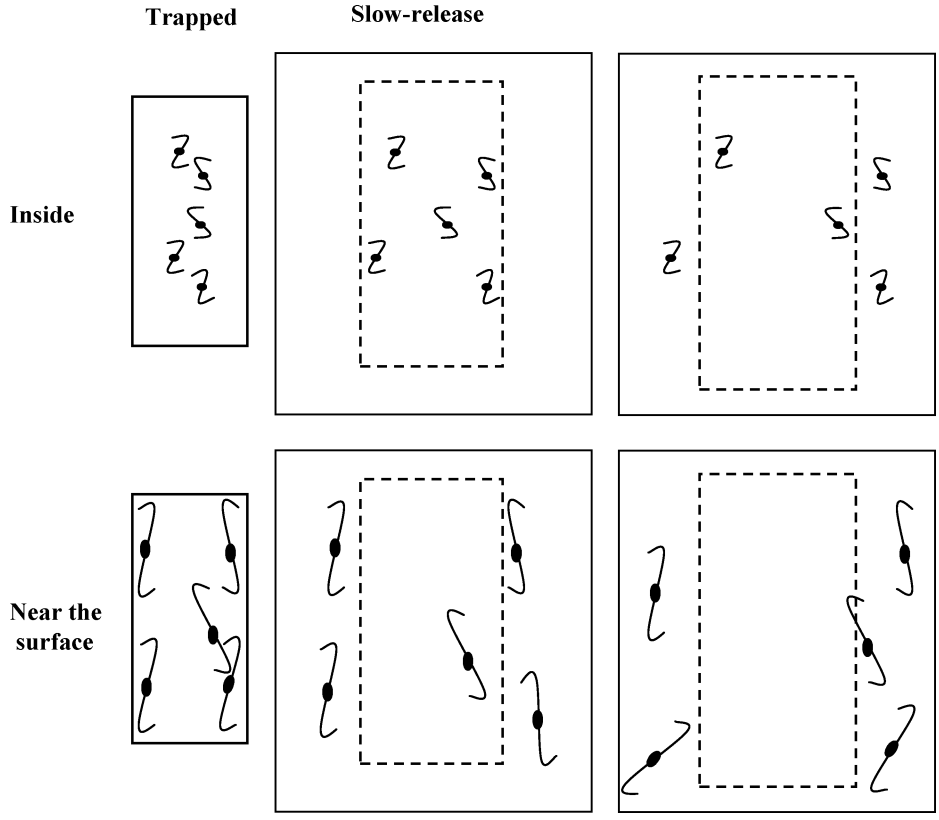

Figure 6. Cartoon representation of Py-PSt chains after loading into PSt gel. In the first column, low molecular weight Py-PSt chains locate much deeper in the gel than high molecular weight chains, which locate near the surface of the gel. Second and third columns represent release of Py-PSt chains into surrounding solution during slow release processes.

solution from the gels is much slower than that of the high-molecular-weight chains. In other words, high-molecular-weight Py-PSt chains diffuse into surrounding solvent much faster than low-molecular-weight chains. This behavior of slow-release diffusion coefficients, D, can be explained as follows: during the process of trapping of Py-PSt chains into the gel, high-molecular-weight Py-PSt chains are not able to penetrate deeply into the gel sample, as depicted in Fig. 6, while low-molecular-weight Py-PSt chains are able to penetrate more deeply into the gel sample. As a result, high-molecular-weight Py-PSt chains can only locate near the gel surface, whereas low-molecular-weight Py-PSt chains can locate more deeply inside the gel during loading of Py-PSt chains into gel samples. During the slow-release process, high-molecular-weight Py-PSt chains trapped near the gel surface can then be released much faster than low-molecular-weight Py-PSt chains located inside the gel. On the other hand, slow-release coefficients (D) for the high crosslinker gel samples are found to be smaller than those of low crosslinker samples, as expected. Because highly crosslinked gel swells much more slowly than low crosslinked gel, therefore slow release from high crosslinked gel has to be slower than low crosslinked gel.

Conclusion

In summary, this work presents the molecular weight dependence of slow-release coefficients (D) of polymer chains released from gel into solvent. It is observed that diffusion of high molecular weight chains from gel into solvent is much faster than low molecular weight chains during the slow-release process. These results also showed that the fluorescence method can be used for real time monitoring of the slow-release processes.

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