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Molecular weight effect on swelling of polymer gels in homopolymer solutions: a fluorescence study

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Abstract

A novel technique based on in situ steady state fluorescence measurements is introduced for studying swelling processes of gels formed by free radical crosslinking copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) in homopolymer solutions. Gels were prepared at 55 ± 2 °C for various EGDM contents. After drying these gels, swelling experiments were performed in chloroform solution of anthracene labeled poly(methyl methacrylate) (An-PMMA) in various molecular weights at room temperature by real time monitoring of anthracene fluorescence intensity. Anthracene labeled PMMA chains having various molecular weights were prepared by atom transfer radical polymerization at 90 °C. During the swelling experiments, it was observed that anthracene emission intensities increased due to trapping of An-PMMA chains into the gel as the swelling time is increased. The trapping of An-PMMA chains in swollen gel, increase by obeying parabolic law in time. Penetration time constant, τ of PMMA chains were measured and found to be increased as the crosslinker density of gel is increased. It is observed that τ values are much higher for high molecular weight An-PMMA chains than low molecular weight chains in all gel samples.

Keywords: Polymer gels; Steady state fluorescence; Methyl methacrylate

1. Introduction

Investigation of phase equilibrium in ternary systems involving crosslinked gel, a linear polymer and a solvent has been of interests for many years. In general swelling of crosslinked polymer network by mobile polymer chains in solvent can be interpreted by Flory–Rehner theory [1]. It has been found that the Flory–Huggins interaction parameter for the pure swollen network is usually much larger than in the corresponding uncrosslinked 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 [2]. Bastide et al. studied the volume change of polystyrene gel in toluene solution of mobile polystyrene at high and low concentrations and interpreted the shrinking behavior of the gels on the basis of scaling concepts [3]. An equation of state for ternary systems was derived [4] 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 [5]. Concentration dependent collapse of single chains in the semi-dilute solution of incompatible polymer was studied theoretically [6] and experimentally [7]. For a long time, common belief has been that the mobile chains do not penetrate into gel, even if they are compatible with the crosslinked 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 based on the extended Flory model and the scaling theory where three different regimes were distinguished [8].

The equilibrium swelling of gels in pure solvents have been extensively studied [9–11]. The swelling kinetics of chemically crosslinked gels can be understood by considering the osmotic pressure versus the restraining force [12–16]. 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

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Table 1
An-PMMA1 (m_i and m_f: initial and final weights of a gel, d_i and d_f: initial and final thicknesses of a gel, τ: time constant)

Vol% EGDM	m_i (g)	m_f (g)	d_i (cm)	d_f (cm)	τ (min)
2.5	0.12	0.42	0.23	0.37	183
5	0.11	0.24	0.21	0.28	175
7.5	0.12	0.22	0.24	0.30	102
10	0.11	0.18	0.21	0.26	313
12.5	0.12	0.20	0.22	0.25	301
15	0.11	0.16	0.22	0.25	400
20	0.10	0.16	0.20	0.22	227

Table 2
An-PMMA2 (m_i and m_f: initial and final weights of a gel, d_i and d_f: initial and final thicknesses of a gel, τ: time constant)

Vol% EGDM	m_i (g)	m_f (g)	d_i (cm)	d_f (cm)	τ (min)
2.5	0.12	0.37	0.24	0.37	108
5	0.12	0.28	0.24	0.33	144
7.5	0.12	0.20	0.24	0.30	163
10	0.12	0.17	0.24	0.27	449
12.5	0.13	0.23	0.23	0.26	384
15	0.12	0.16	0.24	0.26	636
20	0.10	0.15	0.20	0.24	393

minimizes the non-isotropic deformations in gel. The theory of kinetics of swelling for a spherical chemical gel was first developed by Tanaka et al. [17] where the assumption is made that the shear modulus, G is negligible compared to the osmotic bulk modulus. Later, Peters et al. [18] derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming non-negligible shear modulus. Li and Tanaka [12] 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 [19], quasi-elastic light-scattering [18] and in situ interferometric [20] measurements. The steady state fluorescence (SSF) technique was recently applied for studying swelling and drying kinetics in disc shape gels [21–23]. Fast transient fluorescence [24,25] and optical transmission [26] techniques were also used in our laboratory to study swelling kinetics in pure solutions.

In all these experiments fluorescence probes were used which are introduced into the gels. In this work, our aim is to study swelling of gels in polymer solutions where polymer chains are labeled with fluorescence dyes. There have been several methods for introducing the fluorescence labels to the polymers, in which functionalization is achieved at different stages of the particular polymerization involved i.e. initiation, propagation or termination [27–30]. Recently, the controlled/living radical polymerization, such as copper catalyst mediated atom transfer radical polymerization (ATRP), has been utilized for the synthesis of well-defined narrow polydispersity polymers [31–33]. A living polymerization initiated with a label-containing species should give rise to the polymer with a chromophore at the end of each chain. In this work swelling processes of gels in various crosslinker content formed by free radical crosslinking copolymerization (FCC) of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) were studied in polymer solutions. Polymer solution was prepared using anthracene (An) labeled poly(methyl methacrylate) (PMMA) chains in various molecular weights in chloroform. PMMA samples bearing anthryl label at chain ends were prepared in three different molecular weights using 9-anthryl methyl-2-bromo-2-methyl propanoate as an initiator in ATRP. In situ SSF experiments were performed by monitoring of An fluorescence intensity, I_f during swelling processes. I_f intensities were measured from the An labeled polymers trapped into the swollen gel. Increase in I_f were monitored with respect to elapsed time during penetration of An labeled PMMA chain into the gels made at various EGDM contents. It was observed that high molecular An labeled PMMA chains penetrate much slower than low molecular weight chains into these gels. Our goal in the present work is to study the swelling process in polymeric solution to determine the molecular weight effect on polymer penetration into the gels.

2. Experiments

2.1. Gelation

EGDM has been commonly used as crosslinker in the synthesis of polymeric networks. Here, for our use, the monomers MMA (Merck) were freed from the inhibitor by shaking with a 10% aqueous KOH solution, washing with water and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride.

The radical copolymerization of MMA and EGDM was performed at 55 ± 2 °C in the presence of 2,2′-azobisisobutyrronitrile (AIBN) (0.26 wt%) as an initiator. Samples were deoxygenated by bubbling nitrogen for 10 min and then radical copolymerization of MMA and EGDM was performed at 55 ± 2 °C. Here various amounts of EGDM were used to prepare seven different gels. After gelations are completed, the gel samples were dried under vacuum and cut into disc shape gels for the swelling experiments. EGDM contents are given in Tables 1–3.

2.2. Synthesis of 9-anthrylmethyl 2-bromo-2-methyl propanoate

To a round bottom flask were added 9-anthracene methanol (1 g, 4.8 mmol), triethylamine (0.98 ml, 7 mmol), and 20 ml of dry THF. To the reaction mixture, stirred at 0 °C under nitrogen was added drop-wise 2-bromo isobutyryl bromide (0.87 ml, 7 mmol) in 10 ml of dry THF over a

Table 3
An-PMMA3 (m_i and m_f: initial and final weights of a gel, d_i and d_f: initial and final thicknesses of a gel, τ: time constant)

Vol% EGDM	m_i (g)	m_f (g)	d_i (cm)	d_f (cm)	τ (min)
2.5	0.12	0.36	0.24	0.33	155
5	0.13	0.30	0.24	0.32	195
7.5	0.12	0.23	0.23	0.28	144
10	0.12	0.21	0.23	0.27	269
12.5	0.12	0.25	0.22	0.27	357
15	0.10	0.19	0.21	0.24	289
20	0.10	0.17	0.20	0.23	389

period of 45 min. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after THF evaporation, crude product was dissolved in dichloromethane and washed successfully with dilute Na_2CO_3 (sodium carbonate) aqueous solution for three times and dried over anhydrous sodium sulfate (Na_2CO_3). CH_2Cl_2 was removed and the yellow oil was crystallized from hexane two times. Light yellow crystals were obtained with 60% of yield. ^{1}H NMR ($CDCl_3$): δ 7.43–8.52 ppm (m, 9 ArH of anthracene) 6.21 ppm (s, 2H, CH_2–O), 1.87 ppm (s, $(CH_3)_2$–C–Br).

2.3. Synthesis of poly(methyl methacrylate)

The general procedure for ATRP was as follows: to a Schlenk tube equipped with magnetic stirring bar, ligand, catalyst, degassed monomer, solvent and initiator were added in the order mentioned. Tube was degassed by freeze–pump–thaw cycles, left under vacuum and placed in thermostated oil bath at a given temperature, 90 °C. After polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer was evaporated under reduced pressure. Poly(methyl methacrylate), PMMA samples were dissolved in THF and precipitated in methanol, filtered and dried in vacuum oven at 50 °C for overnight. This procedure was repeated at least twice for each sample in order to remove unbounded initiator species if there are. The conversions were determined gravimetrically. PMMA was prepared in 50 vol% diphenylether (DPE) solution at 90 °C using CuCl/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst and 9-anthryl methyl 2-bromo-2methyl propanoate, as the initiator.

2.4. Characterization of polymers

Size exclusion analyses (g.p.c.) were performed with an Agilent Model 1100 instrument consisting of pump and RI detector and three Waters styragel columns (HR 4, HR 3, HR 2). THF was eluent at a flow rate of 0.3 ml min^{-1} at 30 °C. The molecular weight of polymers was calculated with the aid of polystyrene standards. ^{1}H NMR spectrum was recorded on a Bruker spectrometer (250 MHz for proton). UV–Vis spectra were recorded on a Perkin–Elmer Lambda 2 spectrometer in CH_2Cl_2 solutions.

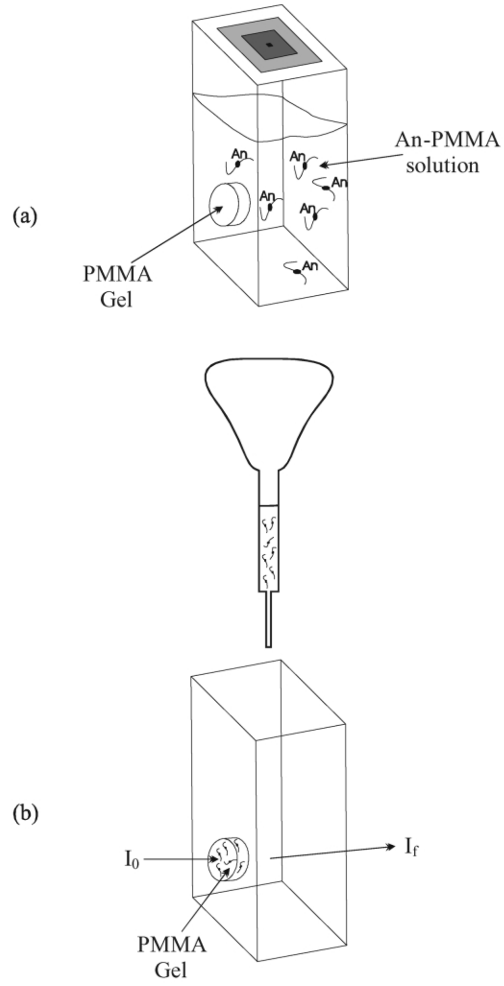


Fig. 1. Fluorescence cell in spectroflurimeter for monitoring of gel swelling. (a) Gel was allowed to swell. (b) Solution was taken out by pipette for fluorescence measurements.

2.5. Fluorescence and swelling measurements

SSF measurements were carried out using Perkin–Elmer Model LS-50 Spectroflurimeter. All measurements were made at 90° position and band-pass was set to 10 nm. In situ swelling experiments were performed in a 1 × 1 cm^2 quartz cell at room temperature. Gel sample were attached to one side of the quartz cell by pressing the disc with thin steel wire. Initially the quartz cell was filled with chloroform solution of An labeled PMMA (An-PMMA). This cell was placed in the spectrofluorimeter. Gels were allowed to swell in 10 min time interval and then solution was removed by a pipette for fluorescence measurements. Fluorescence spectra from An was measured after each 10 min swelling time intervals. These snap shot swelling experiments were repeated during the penetration of An-PMMA into the swollen gels. Fig. 1a and b shows the swelling process

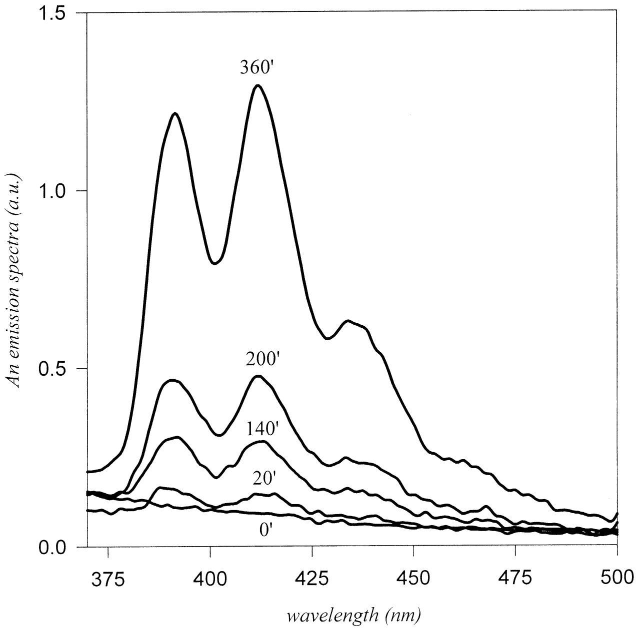
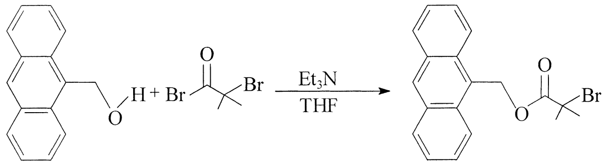


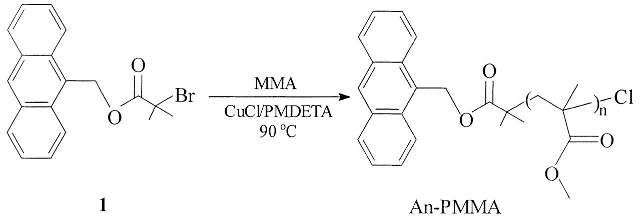
Fig. 2. Anthracene emission spectra produced from An-PMMA2 chains in 12.5% EGDM content gel at various swelling steps. Number on each curve presents time of swelling in minutes.

and fluorescence measurements, respectively. Increase in An spectral intensity was monitored against these sequential 10 min time intervals in which penetration of An labeled PMMA chains into the gel was detected. These experiments were repeated for the gels prepared with various EGDM contents. Swelling experiments were performed for each gel in chloroform solution of An-PMMA polymer chains with three different molecular weights. The initial thickness d_i of the disc shaped gels were around 0.20–0.25 cm. Variation in disc thicknesses were also monitored together with the variation in the weight of the gels during the swelling experiments. The initial and final values of the gel thicknesses, d_i and d_f and weights, m_i and m_f are given against EGDM contents in Tables 1–3 for three different molecular weights of An-PMMA polymers.

During the fluorescence measurements the wavelength of the excitation light was kept at 348 nm and Anthracene spectra were monitored at each swelling step. The An spectra from An-PMMA2 in 12.5% EGDM content gel are shown in Fig. 2 at various times of swelling steps. In order to quantify the fluorescence data the maximum intensity, I_f at 414 nm was used during swelling experiments. No shift was observed in the wavelength of maximum intensity I_f of An and gel samples were kept with their transparencies during the swelling experiments.



Scheme 1.



Scheme 2.

3. Results and discussions

The synthetic approach for the preparation of the functional initiator, 9-anthryl methyl-2-bromo-2-methyl propanoate (**1**) is depicted in Scheme 1. ^{1}H NMR spectrum confirmed the structure of (**1**). See Section 2.

Anthracene labeled initiator (**1**) was used to perform the

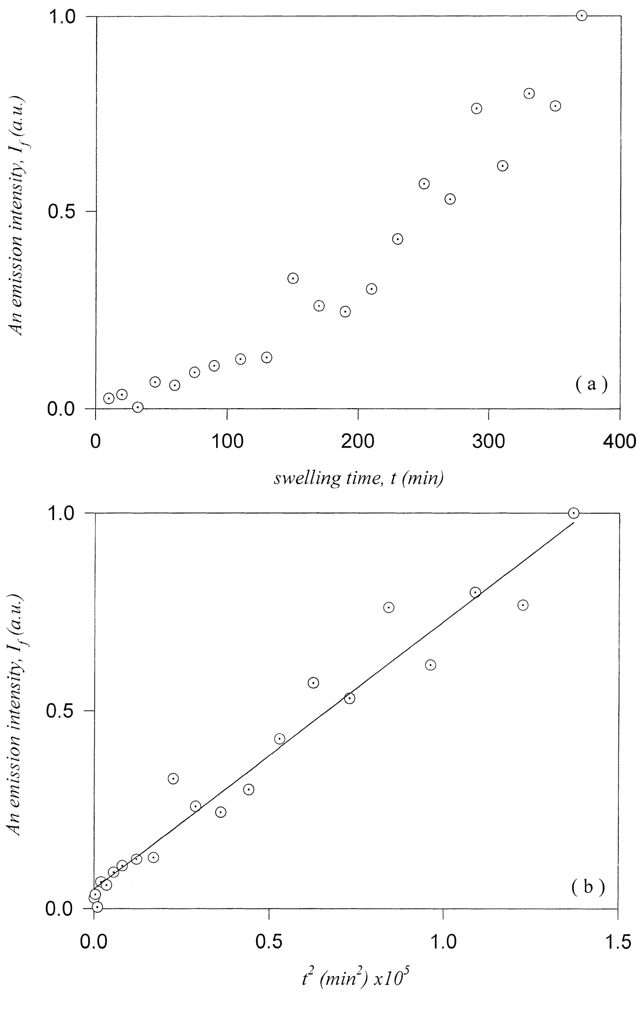


Fig. 3. Plots of the normalized anthracene emission intensities, I_f against (a) swelling time, t and (b) t^2. The slope of the linear relation in (b) produces the inverse square of time constant, τ.

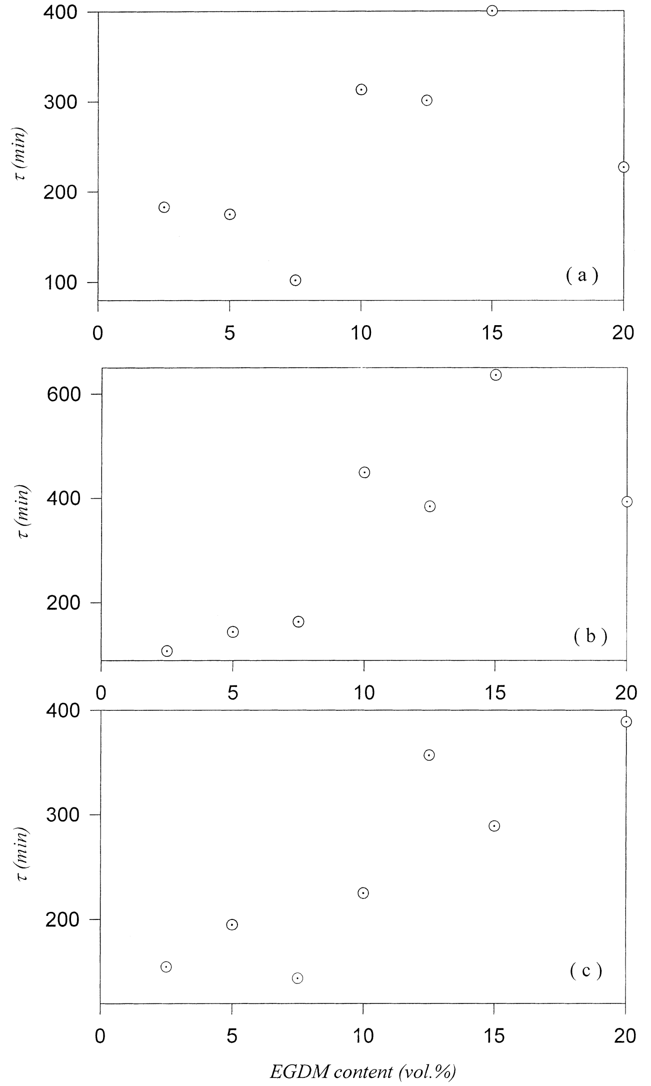


Fig. 4. Plots of the time constant, τ versus EGDM content for (a) An-PMMA1, (b) An-PMMA2 and (c) An-PMMA3 chains.

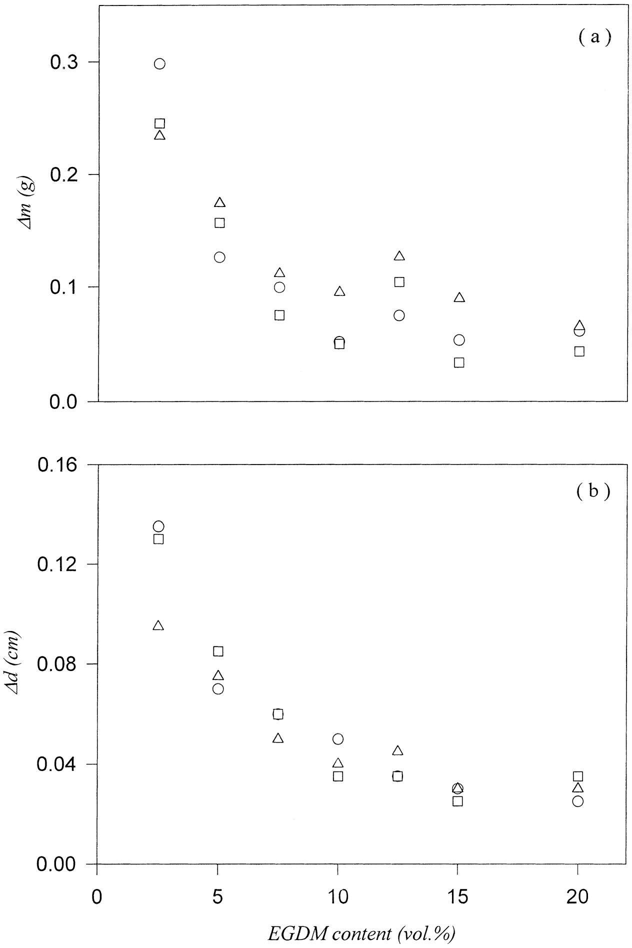


Fig. 5. Plots of the variation of (a) weights, Δm and (b) thicknesses, Δd of the gels prepared with various EGDM content. Symbols ○, □ and △ stand for An-PMMA1, An-PMMA2 and An-PMMA3 chains, respectively.

controlled polymerization of MMA in conjuction with CuCl complexed by PMDETA as catalyst at 90 °C in 50 vol% diphenyl ether. This led to the formation of anthracene labeled PMMAs (An-PMMA)s. Syntheses of PMMA was carried out as shown in Scheme 2.

As shown in Table 4, the molecular weight of resulting PMMA chains determined by g.p.c is in reasonable agreement with those obtained from theoretical and UV calculations. The molecular weights of anthracene labeled PMMA were calculated from their UV absorption spectra by using Beer's Law ($\varepsilon_{366\ \mathrm{nm}} = 7257\ \mathrm{l\ mol^{-1}\ cm^{-1}}$).

The normalized anthracene emission intensities, I_f from the An-PMMA2 in 12.5% EGDM content gel versus swelling time are plotted in Fig. 3a. The points in Fig. 3a were obtained during in situ fluorescence experiments described in Fig. 1b, where An-PMMA2 chains were trapped in the swollen gel. As seen in Fig. 3a that trapping of An-PMMA2 chains in the swollen gel increase by obeying parabolic law, as the swelling time is increased. Here the law of penetration of polymer chains follows different behavior than the

Table 4
Synthesis of poly(methyl methacrylate) at 90 °C ($[M_0] = 4.67$ M, $[M_0]/[I_0] = 200$, $[I_0]$: [Cu(I)] : [Ligand] = 1 : 1 : 1, Initiator = (**1**), Cu(I) = CuCl, Ligand = PMDETA)

Polymer	Time (min)	Conversion (%)	Mn_{theo}[a]	$Mn_{\mathrm{g.p.c}}$	Mn_{uv}	MWD
An-PMMA1	30	40	8000	12 800	10 300	1.05
An-PMMA2	120	70	14 000	21 700	18 000	1.11
An-PMMA3	150	80	16 000	28 900	21 000	1.08

[a] Molecular weight was calculated on the basis of the polystyrene (PS) standards.

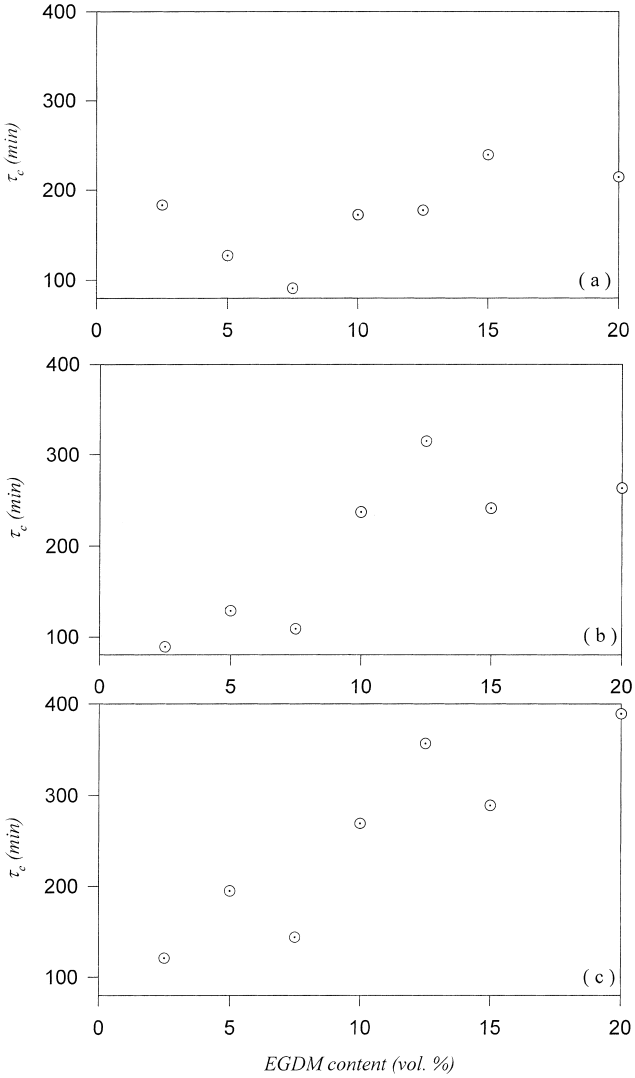


Fig. 6. Plots of the corrected time constants, τ_c versus EGDM content for (a) An-PMMA1, (b) An-PMMA2 and (c) An-PMMA3 chains.

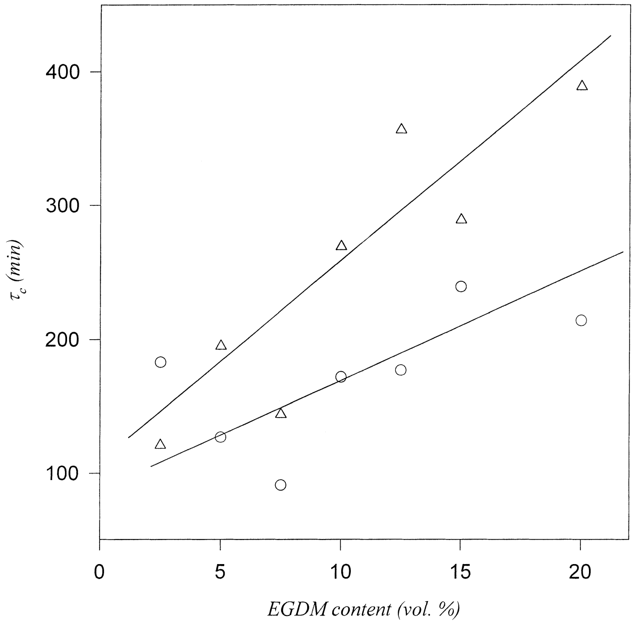


Fig. 7. Plots of the corrected time constants, τ_c versus EGDM contents for An-PMMA1 and An-PMMA3 chains. Symbols ○ and △ stand for An-PMMA1 and An-PMMA3 chains, respectively.

Li–Tanaka equation which is obeyed by swelling of gel in small molecular solvents. The data in Fig. 3a are plotted in Fig. 3b according to the following equation

$$I_f = a + bt^2 \tag{1}$$

where a and b are constants related to the penetration behavior of An-PMMA chains. The slopes of the linear relations in Fig. 3b produce the b values which are interpreted as inverse square of time constant, τ as follows:

$$b = \tau^{-2} \tag{2}$$

Here, τ is the measure of penetration time of An-PMMA chains into swollen gel. The produced τ values are given in Tables 1–3 for An-PMMA1, An-PMMA2 and An-PMMA3 chains, respectively. Fig. 4a–c shows the τ values versus EGDM content for the above An-PMMA chains. In all cases τ values increase as the EGDM content is increased. In order to reach more precise τ values some corrections are needed, because some gels swell more than others, even if they have same amount of EGDM content. Fig. 5a and b shows $\Delta m = (m_f - m_i)$ and $\Delta d = (d_f - d_i)$ values versus EGDM content, respectively, where it is seen that swelling varies at each EGDM value depending on the molecular weight of the penetrant An-PMMA chains. The following formula was used to produce the corrected time constants τ_c:

$$\tau_c = \tau \frac{\Delta m}{\Delta m_0} \tag{3}$$

where Δm is the amount of swelling of a gel and Δm_0 is the maximum amount of swelling of a gel for each EGDM content. Fig. 6a–c shows the corrected τ_c values according to Eq. (3) for various molecular weights of An-PMMA chains. In order to see the molecular weight effect on polymer penetration corrected time constants, τ_c versus EGDM content An-PMMA1 and An-PMMA3 are compared in Fig. 7. It is seen that higher molecular weight An-PMMA chains penetrate much slower than low molecular weight An-PMMA chains into the gel. In the mean time, it is observed that it takes longer to penetrate into the densely formed gels than loosely formed gels in all cases.

In summary, this work presents molecular weight effect on polymer penetration into the polymeric gels immersed in good solvent. It is observed that higher molecular weight chains penetrate into the gel much slower than the low molecular weight chains. Here it is believed that fluorescence technique is quite powerful to study gel swelling in homopolymer solution.

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