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Swelling of heterogels in good solvents; a fast transient fluorescence study

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Abstract

The swelling of disc-shaped heterogels were studied using Fast Transient Fluorescence Technique (FTRF). Disc-shaped heterogels were prepared by combination of methyl-methacrylate (MMA) and styrene (S) with ethylene glycol dimethacrylate (EGDM) as a crosslinker agent in the presence of 2,2′-azobisisobutyronitrile (AIBN). Pyrene (P_y) was introduced as an extrinsic floroprobe during polymerisation. Lifetimes of P_y were measured during in situ swelling processes of heterogels in good solvents to determine the relation between the diffusion and solvent quality. An equation is derived for low-quenching efficiencies to interpret the behavior of lifetime of P_y during swelling. Li–Tanaka equation was employed to determine the cooperative diffusion coefficients, D_c in heterogels, which were found to be strongly correlated with the chosen solvent and the polymeric material in the heterogel system.

Keywords: Swelling; Fast transient fluorescence technique; Solvent quality

1. Introduction

The equilibrium swelling of gels in solvents have been extensively studied [1–3]. The swelling kinetics of chemically cross-linked gels can be understood by considering the osmotic pressure versus the restraining force [4–8]. 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 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 non-isotropic deformations in gel. The theory of kinetics of swelling for a spherical chemical gel was first developed by Tanaka et al. [9] where the assumption is made that the shear modulus, G is negligible compared to the osmotic bulk modulus. Later, Peters et al. [10] derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming non-negligible shear modulus. Recently, Li and Tanaka [4] 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 directions. This model predicts that the geometry of the gel is an important factor, and swelling is not a pure diffusion process.

In material science, it has been a well known practice to improve the properties of one material by mixing it with another material. For example the mechanical properties of metal alloys are much superior to those of pure metals. In polymer science this is rather more difficult to do as few polymers can be mixed or blended satisfactorily. Usually the properties of the blends are more inferior compared to the pure polymers. One approach is to synthesize chains, which have more than one type of monomer unit. Copolymers, which are made by this method, can have in higher qualities, which may be much better than those of the parent homopolymers. The qualities of the copolymer can be improved by the various arrangements of the monomer units on the polymer chain i.e. there are several ways in which the monomers can be arranged in the polymer chain. Most common types of copolymers are random, alternating, block and graft copolymers. Different monomer units similar to copolymer can also construct gels. In chemical gelation, the molecules crosslink into larger clusters by forming covalent bonds in various ways. Free-radical crosslinking copolymerization (FCC) has been widely used to synthesize polymer gels.

Several experimental techniques have been employed to

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study the kinetics of swelling, shrinking and drying of chemical and physical gels among which are neutron scattering [11], quasielastic light-scattering [10], macroscopic experiments and in situ interferometric [12] measurements. In situ observations of sol–gel phase transition in free-radical crosslinking copolymerization, were reported by using the steady state and fast transient fluorescence (SSF and FTRF) techniques [13–15]. The same techniques were also applied for studying swelling and drying kinetics in disc shape gels [16–18].

In this work swelling processes of gels formed by free radical crosslinking copolymerization (FCC) from the mixture of methyl methcrylate (MMA) and styrene (S) with ethylene glycol dimethacrylate were studied. Pyrene (P_y) was used as a fluorescence probe to monitor swelling processes during in situ FTRF experiments in chloroform and toluene which are known to be good solvent for poly(methyl-methacrylate) and polystyrene, respectively. The purpose of the present work is to study the swelling processes of heterogels in good solvents to determine the relation between the gel mobility and solvent quality. In order to do that gel parameters such as time constant, τ_1 and collective diffusion coefficient, D_c were measured and used to understand gel swelling mechanism and gel mobility, respectively. Both τ_1 and D_c values were found to be strongly correlated with the chosen solvent and polymeric material in the heterogel system.

2. Theoretical considerations

It is known that the kinetics of swelling of a polymer network or gel should obey the following relation [4],

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

where $W(t_s)$ and W_∞ are the swelling or solvent uptake at time t_s and at equilibrium, respectively. $W(t_s)$ can also be considered as a volume differences of the gel between the time t_s 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_s. Here B_n is given by the following relation [4].

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

where 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 cooperative diffusion coefficient D_c of a gel disc at the surface and is given by the relation [5]

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

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 a represents half of the disc 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_ns 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_1 is much larger than the rest of τ_n^4 all high-order terms ($n \geq 2$) in Eq. (1) can be dropped so that the swelling and shrinking can be represented by the first order kinetics [12]. In this case Eq. (1) can be written as

$$\frac{W(t_s)}{W_\infty} = 1 - B_1 \, e^{-t_s/\tau_1} \tag{5}$$

Eq. (5) allows us to determine the parameters B_1 and τ_1.

3. Fast transient fluorescence technique

When an organic dye absorbs light, it becomes electronically excited, then fluorescence occurs from the lowest excited singlet state and decays over a time scale typically of nanoseconds [19,20]. In addition, unimolecular decay pathways for deexcitation of excited state, there are a variety of bimolecular interactions, which can lead to deactivation. These are referred to collectively as quenching processes, which enhance the rate of decay of an excited state intensity. For dilute solutions of dye molecules in isotropic media, exponential decays are common. Because of these features, fluorescence dyes can be used to study local environments. For about two decades the transient fluorescence (TRF) technique for measuring fluorescence decay has been routinely applied to study many polymeric systems using organic dyes [21–25]. FTRF technique, which is based on the strobe, or pulse sampling technique [26] was recently used to study gelation of styrene (S) [27] and methyl-methacrylate (MMA) [28] in free radical crosslinking copolymerisation (FCC). In this technique, the photo multiplier tube (PMT) is gated or strobed by a voltage pulse that is synchronized with the pulsed light source. The intensity of fluorescence

Table 1
Swelling parameters of heterogels swollen in chloroform

Styrene con. (vol.%)		m_i (g)	m_f (g)	τ_1 (min)	B_1	$D_c \times 10^{-5}$ (cm^2 s^{-1})
100	PS	0.083	0.366	34.9	0.62	0.79
70	PSM7	0.083	0.359	27.4	0.85	2.28
50	PSM5	0.082	0.463	30.8	0.85	2.06
40	PSM4	0.088	0.397	27.6	0.71	1.27
30	PSM3	0.113	0.499	23.1	0.94	7.05
20	PSM2	0.089	0.407	27.8	0.90	3.49
10	PSM1	0.126	0.496	15.9	0.93	9.19

m_i—initial weight; m_f—final weight; τ_1—time constant; B_1—pre exponential factor; D_c—collective diffusion coefficient.

Table 2
Swelling parameters of heterogels swollen in toluene

Styrene con. (vol.%)		m_i (g)	m_f (g)	τ_1 (min)	B_1	$D_c \times 10^{-5}$ (cm^2 s^{-1})
100	PS	0.064	0.221	89.2	0.83	0.63
80	PSM8	0.065	0.208	110.8	0.88	0.58
70	PSM7	0.070	0.213	149.4	0.88	0.50
50	PSM5	0.067	0.190	175.6	0.89	0.44
45	PSM4.5	0.071	0.175	218.2	0.91	0.37
40	PSM4	0.071	0.193	310.1	0.94	0.41
30	PSM2	0.072	0.134	287.5	0.88	0.21

m_i—initial weight; m_f—final weight; τ_1—time constant; B_1—pre exponential factor; D_c—collective diffusion coefficient.

emission of an organic dye is measured in a very narrow time window. When the data has been sampled over the appropriate range of time, a decay curve of fluorescence intensity versus time can be constructed. Because the strobe technique is intensity-dependent, the strobe instrument is much faster than single photon counting (SPC) [21–25] and even faster than a phase instrument techniques. The strobe instrument is much simpler to use than SPC and data is easier to interpret than with a phase systems. Because of these advantages, strobe instrument is used to monitor gelation processes, which take less than an hour.

The rate equation for an excited organic dye with pulse excitation can be written as

$$\frac{d[F^*]}{dt} = -\tau^{-1}[F^*] + L(t - t')[F] \quad (6)$$

where $[F^*]$ and $[F]$ represents the concentration of excited and ground state dye molecules and $L(t - t')$ is the light pulse of the strobe instrument. The lifetime τ of fluorescence molecule is given by the following relation, which is called Stern–Volmer equation [19,20]

$$\tau^{-1} = \tau_0^{-1} + k_q[Q]. \quad (7)$$

where k_q is the quenching rate constant and [Q] is the

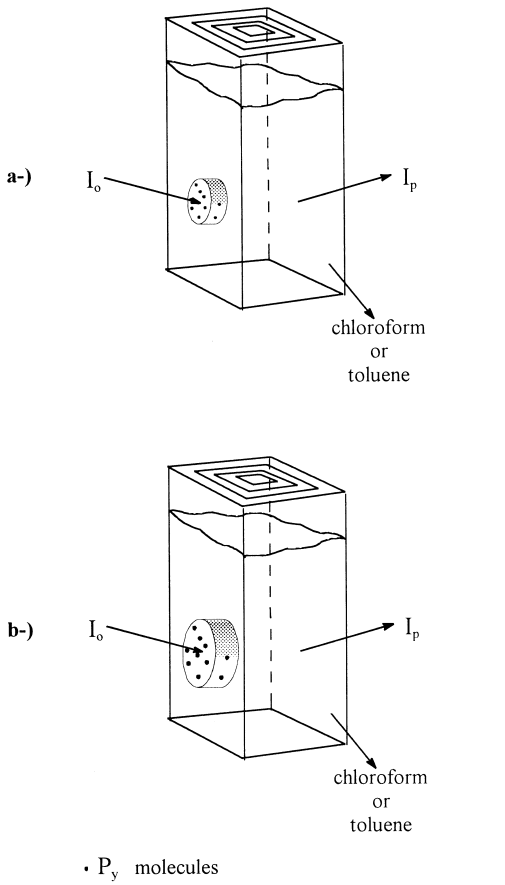

Fig. 1. The position of heterogel in the fluorescence cell (a) before, (b) after swelling. I_0 is the excitation and I_p is the emission intensities of pyrene at 345 and 395 nm, respectively.

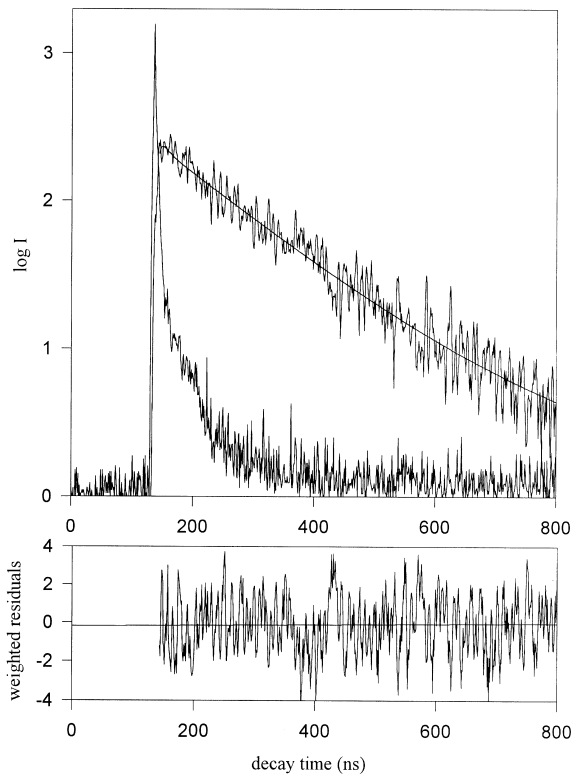

Fig. 2. Flourescence decay curve of pyrene in dry PSM1 heterogel. The sharp peak is the incident light pulse.

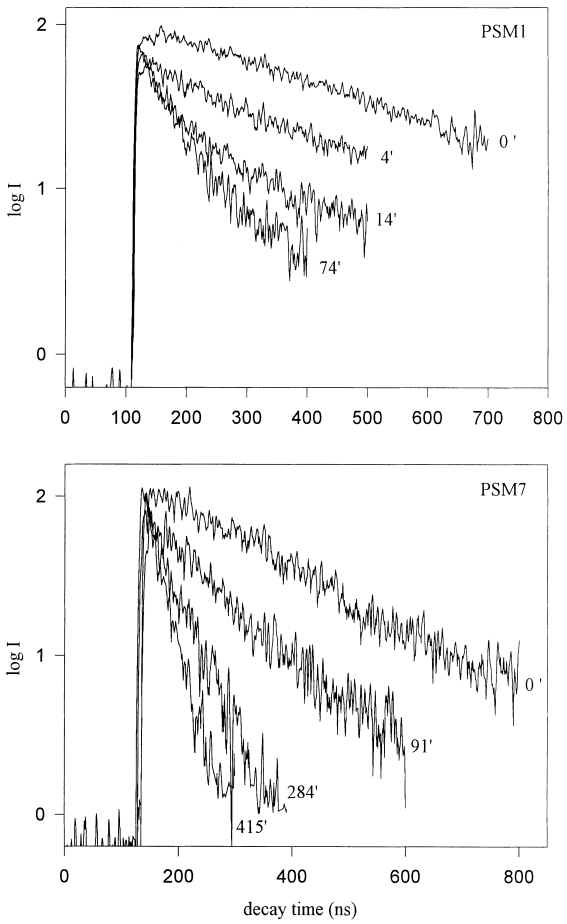

Fig. 3. Fluorescence decay profiles of pyrene in swollen heterogels (a) PSM1 in chloroform and (b) PSM7 in toluene. Numbers on each decay curve present the swelling time, t_s in minute.

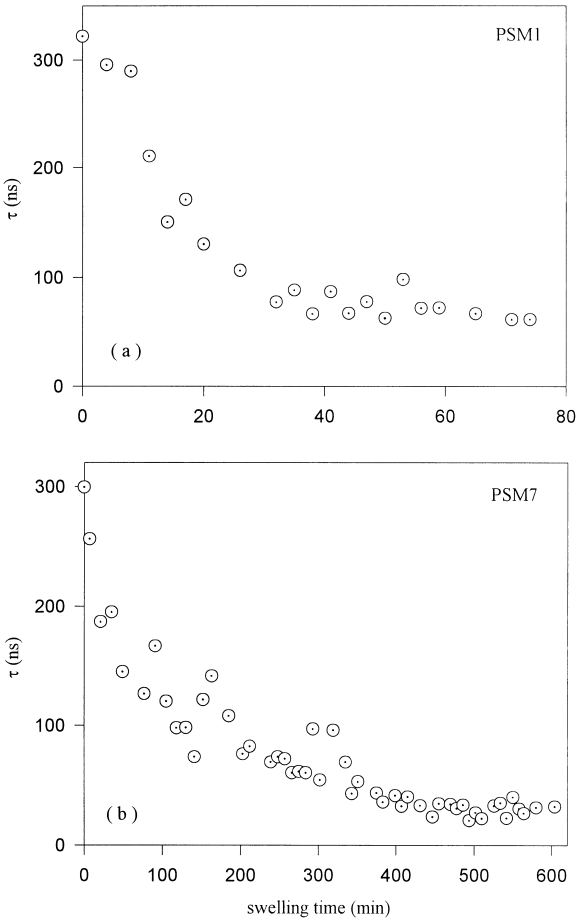

Fig. 4. The plots of the measured τ values versus swelling time, t_s for the swollen heterogel (a) PSM1 in chloroform and (b) PSM7 in toluene.

quencher concentration. Solution of Eq. (6) produces the decaying fluorescence intensity as [19,20]

$$I(t) = C \exp\left(-\frac{t}{\tau}\right) \tag{8}$$

where C is the preexponential factor. The observed fluorescence decay of a sample, $\phi(t)$ is related to the actual fluorescence decay, $I(t)$ given in Eq. (8) and the light pulse $L(t)$ by the convolution integral [21,22]

$$\phi(t) = \int_0^t L(t - t')I(t')\mathrm{d}t' \tag{9}$$

4. Experimental

Heterogels were prepared in FCC of MMA and S mixtures with ethylene glycol dimethacrylate (EGDM). EGDM has been commonly used as crosslinker in the synthesis of polymeric networks. Here, for our use, the monomers MMA (Merck), S (Merck) and EGDM (Merck) were freed from the inhibitor by shaking with a 5% aqueous NaOH solution, washing with water and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride. The initiator, 2,2′-azobisisobutyronitrile (AIBN, Merck), was recrystallized twice from methanol. The free radical copolymerization of MMA and S with EGDM were performed in bulk in the presence of AIBN as an initiator. Seven different heterogels were prepared at 70 °C temperature in constant (1.5% v/v) EGDM content with various combinations of MMA and S. MMA and S contents for mixtures and their symbols are presented in Tables 1 and 2 for the gels swollen in chloroform and toluene, respectively. In all these gels the initiator concentration was held constant at 0.26 wt%, the P_y concentration was taken as 4×10^{-4} M and the samples were deoxygenated by bubbling nitrogen for 10 min before FCC.

The steady state fluorescence (SSF) and FTRF techniques were used to characterize these heterogels [29]. The increase in P_y intensity (in SSF measurements) and P_y lifetimes (in FTRF measurements) as a function of gelation time were monitored during free radical crosslinking copolymerization. Because of the incompatible nature of S monomers with MMA, the system becomes heterogeneous upon the increase in S content. The results were interpreted on the basis of the percolation theory. The critical exponents γ and β for the weight average degree of polymerization and gel fraction at the sol–gel transition were observed up to a

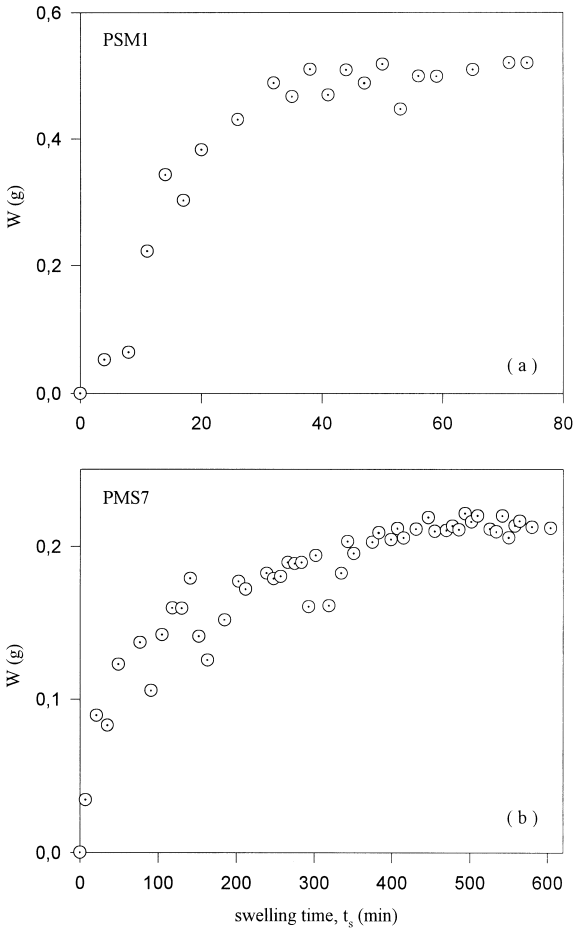

Fig. 5. The plots of the solvent uptake, W versus swelling time, t_s for (a) PSM1 in chloroform, (b) PSM7 in toluene.

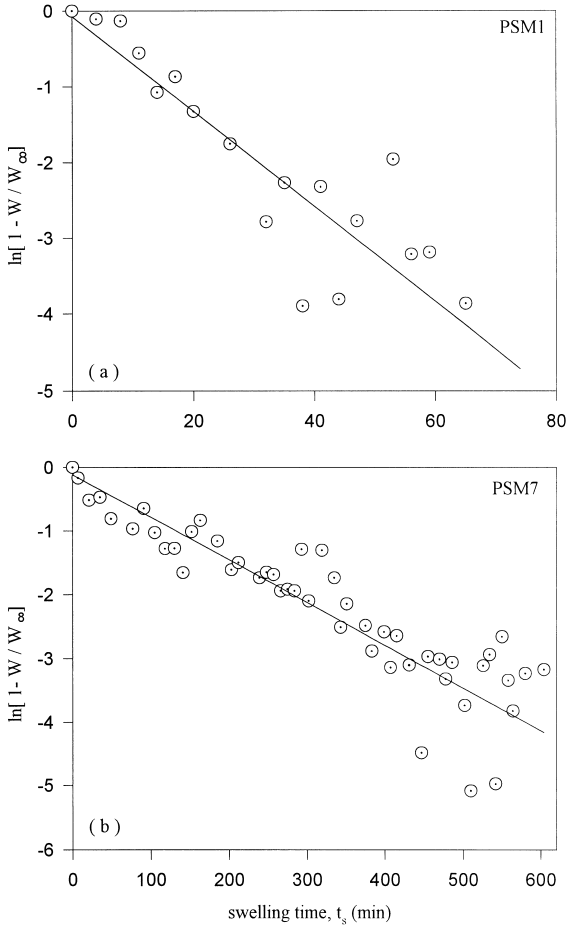

Fig. 6. Linear regression of the data in Fig. 5 according to Eq. (13) for (a) PSM1 in chloroform and (b) PSM7 in toluene.

45% (v/v) of S content above which the exponents are deviated from their expected values. The fact that the exponents deviate from the percolation values above 45% (v/v) of S is due to heterogeneity. Since the S rich parts quench the P_y intensity and the lifetime of P_y, then the whole part of the interconnected network cannot be monitored. The P_y intensity can only monitor the MMA rich part of the system. The hetero-structure of the MMA-S system has been found to be a fractal with the dimension of 2.5 above 45% (v/v) S content. Fractal dimension measurement also supports that MMA–S mixture goes to a disordered phase as the S content is increased above the 45% v/v of S.

Chloroform and toluene were chosen as swelling agent, which have the solubility parameter, δ of 19 and 18.2 $MPa^{1/2}$, respectively. These values of δ for the solvents are able to make the chloroform and toluene good solvent for PMMA ($\delta_p = 19\ MPa^{1/2}$) and PS ($\delta_p = 18.5\ MPa^{1/2}$), respectively.

In situ fluorescence decay experiments from which P_y lifetimes were determined were performed using Photon Technology International's (PTI) Strobe Master System (SMS). All lifetime measurements were made at 90° to the incident beam and the slit widths were kept at 10 nm. The swelling experiments were performed in a fluorescence cell filled chloroform and/or toluene, which was placed in the SMS, and fluorescence decays were collected over three decades of decay time. The sample was illuminated with 345 nm excitation light and pyrene fluorescence emission was detected at 395 nm. The position of the heterogel during swelling is shown in Fig. 1. Deconvolution of $I(t)$ from Eq. (9) is performed using iterative linear-least-squared fitting technique. The uniqueness of the fit of the data to the model is determined by χ^2 ($\chi^2 < 1.20$), the distribution of weighted residuals, and the autocorrelation of the residuals.

5. Results and discussion

In order to monitor the swelling processes fluorescence decay curves are measured and fitted to Eq. (8) by employing in Eq. (9). A typical decay curve and its fit are shown in Fig. 2 for the PSM1 sample before swelling. Fig. 3a and b shows the fluorescence decay profiles of P_y of PSM1 and PSM7 at various swelling steps in chloroform and toluene, respectively.

It is observed that as the swelling time increases, excited pyrenes decay faster and faster by indicating that quenching

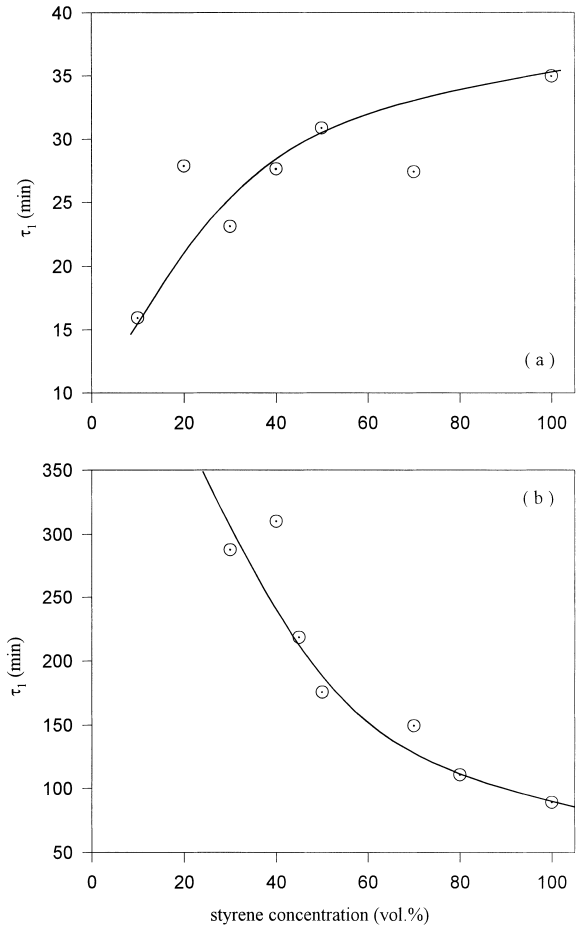

Fig. 7. The plots of the τ_1 values versus styrene concentration for the heterogels swollen in (a) chloroform and (b) toluene.

of excited pyrenes increase in the swelling gel. τ values were produced at each swelling steps using least square analysis. The measured τ values during swelling are plotted versus swelling time, t_s in Fig. 4a and b for the PSM1 and PSM7 samples in chloroform and toluene, respectively.

The effect of solvent penetration can be interpreted by applying quenching mechanisms to the produced data where the Stern–Volmer type of quenching mechanism may be assumed for the fluorescence decay of P_y in the gel sample during the swelling process. For low quenching efficiency, i.e. $\tau_0 k_q[W] < 1$, Eq. (7) becomes

$$\tau \approx \tau_0(1 - \tau_0 k_q[W]) \tag{10}$$

where [W] is the solvent concentration in the gel. The solvent uptake, W is obtained from volume integration

$$W = \int_{a_0}^{a_\infty} [W]\mathrm{d}\nu \tag{11}$$

where $\mathrm{d}\nu$ is the differential volume in the gel. The integration is taken from initial, a_0 to final a_∞ thickness of the disc shaped gel. Performing the integration, the following relation is obtained.

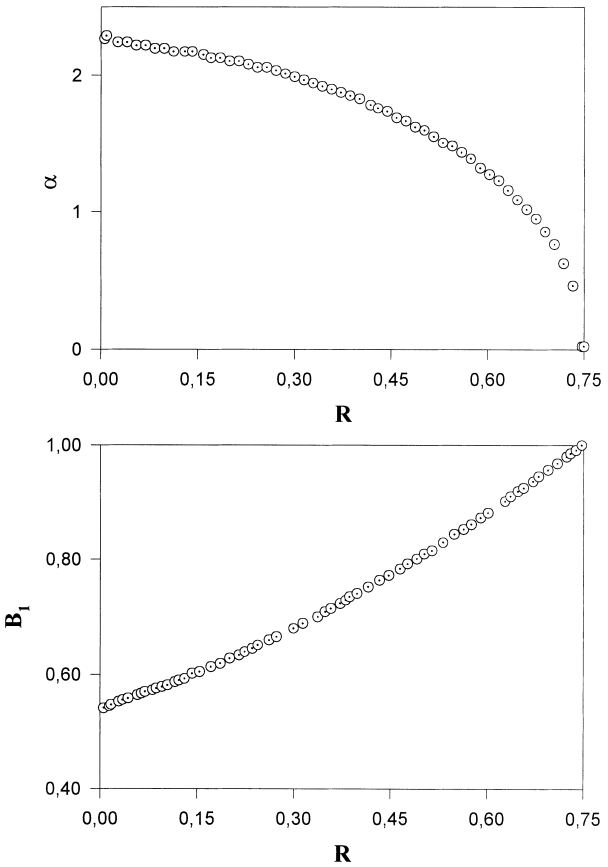

Fig. 8. Determination of α_1 can be done by using these theoretical results by knowing B_1.

$$W = \left(1 - \frac{\tau}{\tau_0}\right)\frac{\nu}{k_q \tau_0} \tag{12}$$

Here ν is the swollen volume of the gel, which can be measured experimentally. k_q was obtained from separate measurements.

The plots of solvent uptake, W, for the PSM1 and PSM7 gels swollen in chloroform and toluene are shown in Fig. 5a and b, respectively. These are typical solvent uptake curves which obeyed Li–Tanaka equation (Eq. (5)). The logarithmic data in Fig. 5 were fitted to the corresponding relationship of Eq. (5)

$$\ln\left(1 - \frac{W}{W_\infty}\right) = \ln B_1 - \frac{t_s}{\tau_1} \tag{13}$$

The fits are shown in Fig. 6, from which B_1 and τ_1 values were obtained. These are listed in Tables 1 and 2 for the gels swollen in chloroform and toluene, respectively.

The plots of τ_1 versus styrene content (vol.%) are shown in Fig. 7a and b for the gel samples swollen in chloroform and toluene, respectively. The immediate conclusion from Fig. 7 can be reached that penetration of chloroform into the heterogels are at least an order of magnitude faster than penetration of toluene into the

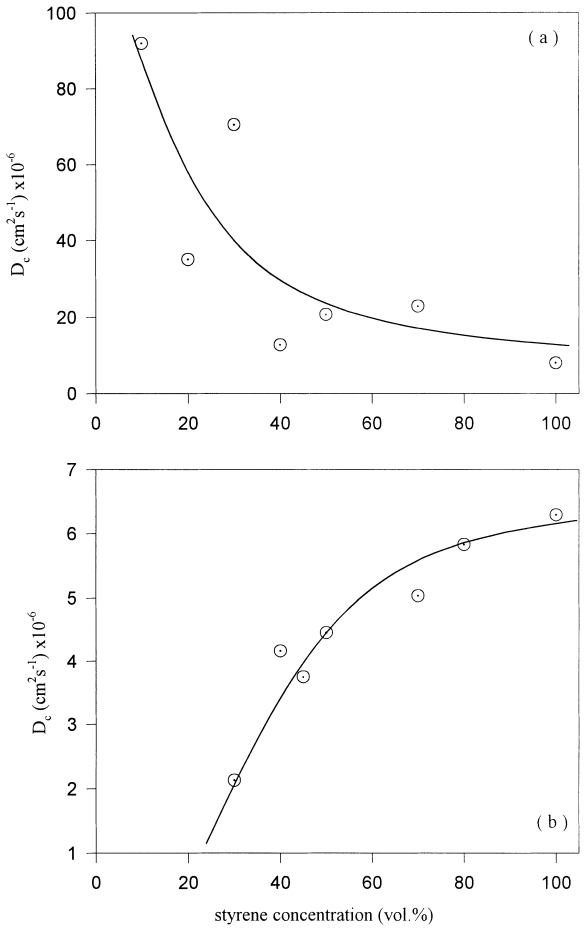

Fig. 9. The plot of the collective cooperative diffusion coefficient, D_c versus styrene concentration for the heterogels swollen in (a) chloroform and (b) toluene.

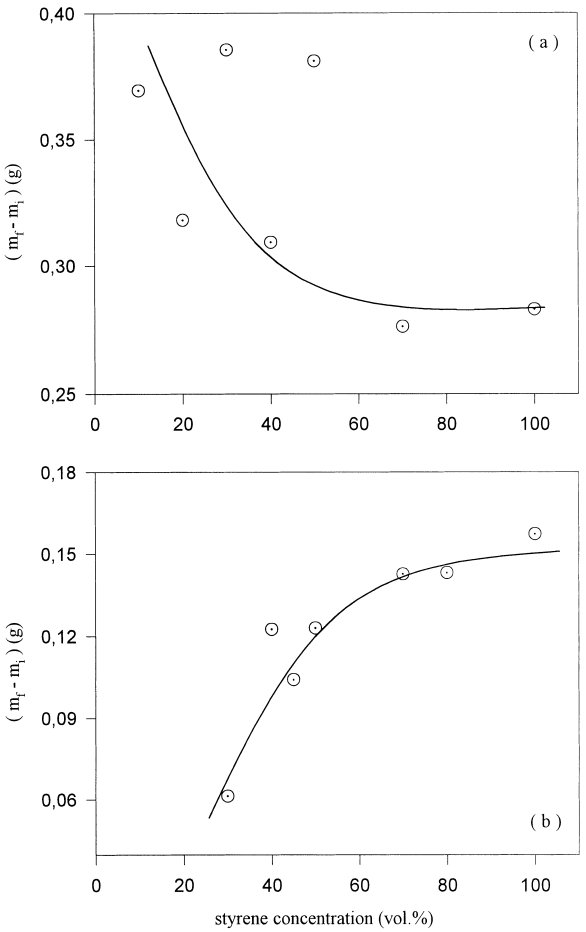

Fig. 10. The variation of final and initial mass differences versus styrene concentration for the heterogels swollen in (a) chloroform and (b) toluene.

similar gels. It is seen in Fig. 7a that as the styrene content is increased penetration of chloroform molecules slows down, which indicate that low solubility of chloroform in styrene rich heterogel prevents penetration of solvent molecules into the network. However, high solubility of toluene in PS compared to PMMA allows toluene molecules to penetrate into the network much faster in PS rich heterogels than PMMA rich heterogels (see Fig. 7b).

Knowing B_1 value, one can obtain α_1. Determination of α_1 values are shown in Fig. 8 which is obtained from Ref. [4]. D_c values were obtained from Eq. (4) and plotted in Fig. 9a and b for the heterogels swollen in chloroform and toluene, respectively. The behavior of D_c in Fig. 9a shows that the gel segments move much faster in PMMA rich network than PS rich network in chloroform. On the other hand, gel segments move much faster when the PS rich network is swollen in toluene as shown in Fig. 9b. The overall behavior of D_c values predict that gel segments move much faster in chloroform swollen network than toluene swollen networks. Fig. 10a and b shows the differences between final and initial weights of the swollen heterogels in chloroform and toluene, respectively. These results indicate that PS rich heterogels absorb less chloroform than the PMMA rich heterogels as shown in Fig. 10a. On the other hand, the behavior of heterogels are opposite in toluene compare to in chloroform i.e. PS rich heterogels absorb more toluene than PMMA rich heterogels (see Fig. 10b). All these swelling properties of heterogels can be explained with the solubility parameters of PS, PMMA, chloroform and toluene. It is obvious that PMMA rich heterogels swell much faster and easier in chloroform than in toluene. Finally, PS rich networks are well behaved in toluene than in chloroform. Here we have to point out that the interconnected network-like structure of these heterogels allowed both chloroform and/or toluene penetrate deep into the gel system. In other words, these gels swell homogeneously by predicting the interconnected network like morphology formed during gel preparation.

In conclusion, this work has shown that the swelling behavior of heterogels are quite sensitive to the solvent quality of the swelling agent. It is also shown that FTRF technique can be easily used to study the swelling behavior of the heterogels prepared with the mixture of MMA and styrene.

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