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Polymer 41 (2000) 4915–4921

polymer

Fast transient fluorescence technique for monitoring swelling of poly(methyl methacrylate) gels

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Received 24 August 1998; received in revised form 6 February 1999; accepted 29 September 1999

Abstract

A fast transient fluorescence technique (FTRF) which uses the Strobe Master System (SMS), is introduced for studying swelling of a cylindrical poly(methyl methacrylate) (PMMA) gel. PMMA gel was prepared by free radical copolymerization of methyl (methacrylate) (MMA) and ethylene glycol dimethacrylate (EGDM). Pyrene (P_y) was introduced as a fluorescence probe during polymerization and lifetimes of P_y were measured during in situ swelling process. Chloroform was used as a swelling agent. An equation is derived for low quenching efficiencies to interpret the behavior of mean lifetimes $\langle\tau\rangle$ during swelling. It was observed that $\langle\tau\rangle$ values decreased as swelling proceeded. The Li–Tanaka equation was used to determine the cooperative, D_c and mutual D_m diffusion coefficients, which were found to be around 10^{-5} and 10^{-7} cm^2 ns^{-1}, respectively.

Keywords: Poly(methyl metacrylate) gels; Fast transient fluorescence technique; Swelling

1. Introduction

For about the last two decades, the transient fluorescence (TRF) technique for measuring fluorescence decay has been routinely applied to study many polymeric systems [1–5]. TRF spectroscopy with a non-radiative direct energy transfer (DET) and quenching has been used to characterize internal morphologies of composite materials [6,7]. It has been reported that the local, fractal like structures of interpenetrating network morphology in blend-like particles can be studied by TRF spectroscopy. Film formation from donor and acceptor labeled latex particles has been studied using DET in conjunction with TRF technique [8–10]. A single photon counting method in conjunction with DET was used to study the diffusion of small dye molecules within the interphase domain of dye labeled poly(methyl methacrylate) (PMMA) particles sterically stabilized by polyisobutylene, where mean lifetimes of fluorescing donor molecules were measured to monitor diffusion [11,12]. The Fickian model for diffusion was employed to determine diffusion coefficients.

Volume phase transitions in gels may occur from dry to swollen states either continuously, or by sudden jumps between them [13,14]. The equilibrium swelling of gels in solvent has been extensively studied [15–17]. The swelling process of chemically cross-linked gels can be understood by considering the competition between the osmotic pressure and the restraining force [18–22]. 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 a polymer at a given temperature. On the other hand, the shear energy that keeps the gel in shape can be characterized by shear modulus G. Here, shear energy minimizes the nonisotropic deformations in the gel. The theory of kinetics of swelling for a spherical chemical gel was first developed by Tanaka and Filmore [23], where the assumption is made that the shear modulus G is negligible compared to the osmotic bulk modulus. Latter, Peters and Candau [24] have derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming non-negligible shear modulus. Recently, Li and Tanaka [18] have developed a model where the shear modulus plays an important role that 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.

Several experimental techniques have been employed to study the kinetics of swelling, shrinking and drying of chemical and physical gels, e.g. neutron scattering [25],

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0032-3861/00/$ - see front matter
PII: S0032-3861(99)00721-1

quasielastic light-scattering [24], macroscopic experiments [26] and in situ interferometric measurements. Using the fluorescence technique, a pyrene derivative was employed as a fluorescence probe to monitor the polymerization, aging and drying of aluminosilicate gels [27], where peak ratios in emission spectra were monitored during these processes. The volume phase transitions of poly(acrylamide) gels were monitored by fluorescence anisotropy and lifetime measurements of dansly groups [28]. We have reported in situ observations of the sol–gel phase transition in free-radical crosslinking copolymerization (FCC), using the in situ steady-state fluorescence (SSF) technique [29,30]. Recently, SSF measurements on swelling of gels formed by FCC of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) have been reported, where pyrene (P_y) was used as a fluorescence probe to monitor swelling, desorption and drying processes in real time during in situ fluorescence experiments [31–33].

In this work, swelling of a gel formed by FCC of MMA and EGDM was studied using FTRF technique. Lifetimes of P_y embedded in the gel were monitored during in situ swelling processes. The Strobe Master system (SMS) was used for lifetime measurements of P_y in the gel. Lifetime measurements with SMS take much less time than with single photon counting systems and phase instruments. This advantage of SMS allows one to make at least hundreds of measurements during the swelling process of gels. That is the reason we named this technique as Fast Transient Fluorescence (FTRF), which gives us many advantages compared to other lifetime measuring techniques. It is observed that, as the gel swells, the lifetime of P_y decreases, which can be modeled using the low quenching Stern–Volmer equation. Cooperative, D_c and mutual D_m diffusion coefficients were determined by employing Li–Tanaka equation and found to be around 10^{-5} and 10^{-7} $cm^2\,s^{-1}$, respectively.

2. Kinetics of swelling

Li and Tanaka [18] showed that the kinetics of swelling and shrinking of a polymer network or gel obey the following relation:

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

where $W(t_s)$ and W_∞ are the solvent uptake at the swelling time, t_s and at infinite equilibrium, respectively. Here B_n represents a constant related to the ratio of shear modulus G and longitudinal osmotic modulus, M is defined by the combination of shear and osmotic bulk modulus as [4,5] $M = 4/3G + K$ and τ_n is the swelling rate constant. In the limit of large t_s, or if the first term τ_c is much larger than the rest of τ_n, all high-order terms ($n \geq 2$) in Eq. (1) can be neglected, then Eq. (1) becomes

$$\frac{W(t)}{W_\infty} = 1 - B_1 \, e^{-t_s/\tau_c} \tag{2}$$

Here B_1 is given by the following relation [18]:

$$B_1 = \frac{2(3-4R)}{\alpha_1^2 - (4R-1)(3-4R)} \tag{3}$$

where $R = G/M$ and α_1 is given as a function of R, i.e.

$$R = \frac{1}{4}\left[1 + \frac{\alpha_1 J_0(\alpha_1)}{J_1(\alpha_1)}\right] \tag{4}$$

where J_0 and J_1 present Bessel functions. In Eq. (2), τ_c is related to the collective cooperative diffusion coefficient D_c of a gel disk at the surface and given by the relation [19]

$$\tau_c = \frac{3a^2}{D_c \alpha_1^2} \tag{5}$$

Here, a represents half of the disk thickness in the final infinite equilibrium state, which can be experimentally determined.

3. Experiments

EGDM has been commonly used as a crosslinker in the synthesis of polymeric networks. Here, for our use, the monomers MMA (Merck) and EGDM (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 polymerization solvent toluene and swelling agent chloroform (Merck), was distilled twice over sodium.

The radical copolymerization of MMA and EGDM was performed in toluene solution at 75°C in the presence of 2,2′-azobisisobutyronitrile (AIBN) (0.26 wt%) as an initiator. P_y was added as a fluorescence probe during the gelation process. The sample was deoxygenated by bubbling nitrogen for 10 min, and then radical copolymerization of MMA and EGDM was performed at 75 ± 2°C. Here, EGDM content was kept as 0.01 vol.%, and P_y concentration was taken as 4×10^{-4} M. After gelation was completed, the gel sample was dried under vacuum for the swelling experiment.

Fluorescence decay experiments were performed using the Photon Technology International (PTI) Strobe Master System (SMS). In the strobe, or pulse sampling technique [34,35], the sample is excited with a pulsed light source. The name comes about because 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 emission is measured in a very narrow time window on each pulse and saved in a computer. The time window is moved after each pulse. The strobe has the effect of turning on the PMT and measuring the emission intensity over a

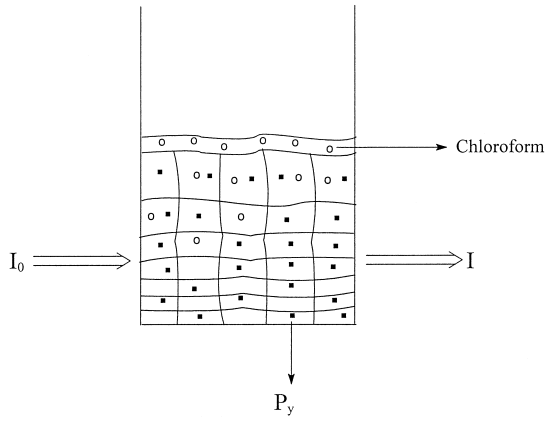

Fig. 1. Cartoon representation of the gel during swelling.

very short 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.

Since the strobe technique is intensity-dependent, the strobe instrument is much faster than SPC and even faster than a phase measuring instrument. The strobe instrument is much simpler to use than SPC and the data is easier to interpret than the phase system. Because of these advantages SMS is used to monitor swelling of PMMA gels over a period of several hours.

An in situ swelling experiment was carried out in the SMS of PTI, employing a pulsed lamp source (0.5 atm of N_2). Pyrenes in the gel sample were excited at 345 nm and fluorescence decay curves were obtained at 390 nm during in situ swelling experiments which were performed at room temperature. A cylindrical gel sample was placed in a round quartz cell and chloroform was added on top of the gel during swelling process. The thin level of chloroform above the gel was kept constant during swelling. The position of the gel, the level of chloroform and the incident light beam for inducing fluorescence are shown in Fig. 1. The fluorescence decay data were collected over 3 decades of time and fitted by nonlinear least squares using a deconvolution method, with a dry gel as a scatterer standard. The uniqueness of the fit of the data to the model is determined by χ^2 ($\chi^2 \leq 1.10$), the distribution of the weighted residuals and the autocorrelation of the residuals.

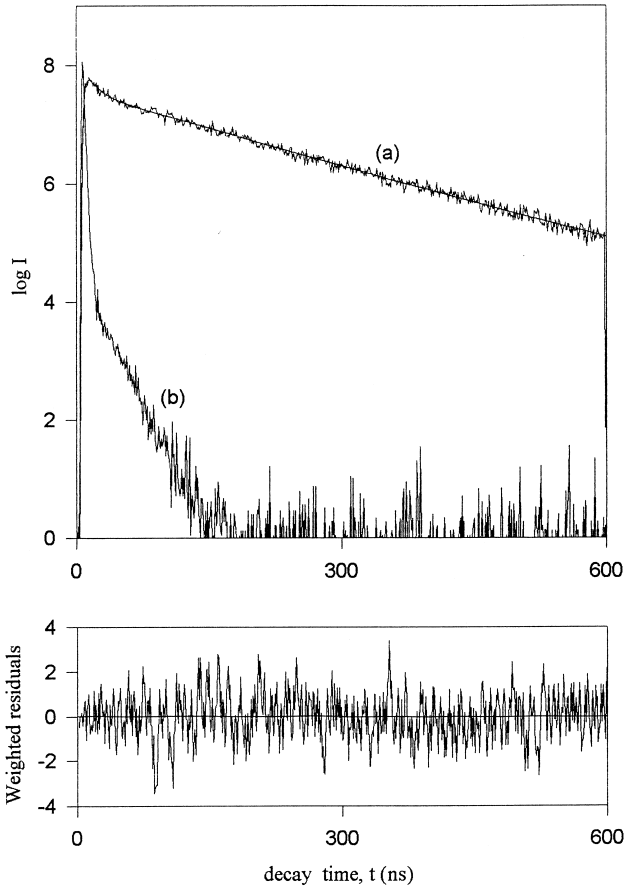

Fig. 2. Fluorescence decay curve (a) of pyrene in PMMA gel. The incident light pulse (b) is also shown.

4. Results and discussions

A typical decay curve of P_y, obtained from SMS is shown in Fig. 2. In order to probe the swelling process during solvent uptake, the fluorescence decay curves were measured and were fitted to the sum of two exponentials

$$I(t) = A_1 \, e^{-t/\tau_1} + A_2 \, e^{-t/\tau_2} \quad (6)$$

where τ_1 and τ_2 are the long and short components of pyrene lifetimes and A_1 and A_2 are the corresponding amplitudes of the decay curves. Fig. 3 presents the fluorescence decay profiles at various swelling steps (0, 300, 450 and 600 min). It can be seen that as the swelling time t_s, is increased, excited pyrenes decay faster and faster which indicates that as solvent uptake is increased quenching of excited pyrenes increase. Here the role of the solvent is to add the quasi-continuum of states needed to satisfy energy resonance conditions, i.e. the solvent acts as an energy sink for rapid vibrational relaxation which occurs after the rate limiting transition from the initial state. Birks et al. [36] 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. We have reported the viscosity effect on low frequency intermolecular vibrational energies of excited naphthalene in swollen PMMA latex particles [37].

The measured A_1, A_2 and τ_1, τ_2 values for the gel sample are plotted versus swelling time t_s in Fig. 4a and b, respectively. It can be seen that A_1, A_2 and τ_1 values do not change much; however, τ_2 values decrease as solvent uptake is increased. In order to quantify the above observation, the area under the fluorescence decay curve is calculated using Eq. (6) according to the following

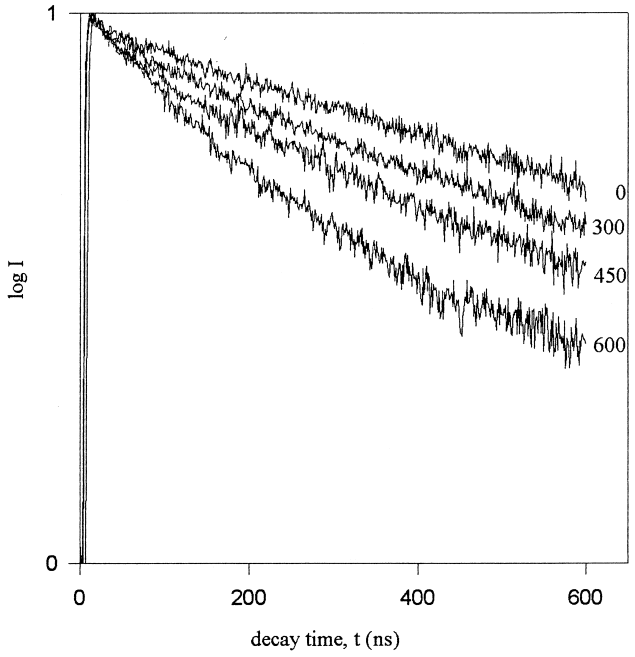

Fig. 3. Fluorescence profiles at various swelling steps. The number on each curve present the swelling time in minutes.

relation:

$$\langle I\rangle = \int_{t_1}^{t_2} I\,\mathrm{d}t = \tau_1 A_1 + \tau_2 A_2 \tag{7}$$

where the integral is taken from the peak (t_1) to the end point (t_2) of the decay curve. The calculated $\langle I\rangle$ values are plotted logarithmically versus swelling time t_s in Fig. 5. It can be seen that $\langle I\rangle$ values decreased as the swelling time t_s increased. This indicates that quenching rate of P_y molecules increased as chloroform molecules penetrate into the gel. Here at the beginning, before solvent penetration starts, the P_y intensity is called $\langle I_0\rangle$. After solvent penetration starts, some excited P_y molecules are quenched and intensity decreases to $\langle I\rangle$ at time t_s where amount of solvent uptake is W. At the equilibrium state of swelling, the P_y intensity decreased to $\langle I_\infty\rangle$, where the solvent uptake by swollen gel is W_∞. The relation between solvent uptake W and P_y intensities $\langle I\rangle$ from the gel during the swelling process is given by the following relation:

$$\frac{W}{W_\infty} = \frac{\langle I_0\rangle - \langle I\rangle}{\langle I_\infty\rangle - \langle I_\infty\rangle} \tag{8}$$

since $I_0 \gg I_\infty$, Eq. (8) becomes

$$\frac{W}{W_\infty} = 1 - \frac{\langle I\rangle}{\langle I_0\rangle} \tag{9}$$

This relation predicts that as W increases, $\langle I\rangle$ decreases and is quite similar to the equation used to monitor oxygen uptake by PMMA spheres [38,39]. Combining Eq. (9) with Eq. (2) and assuming that the number of quenched P_y molecules are proportional to $\langle I\rangle$, the following relation

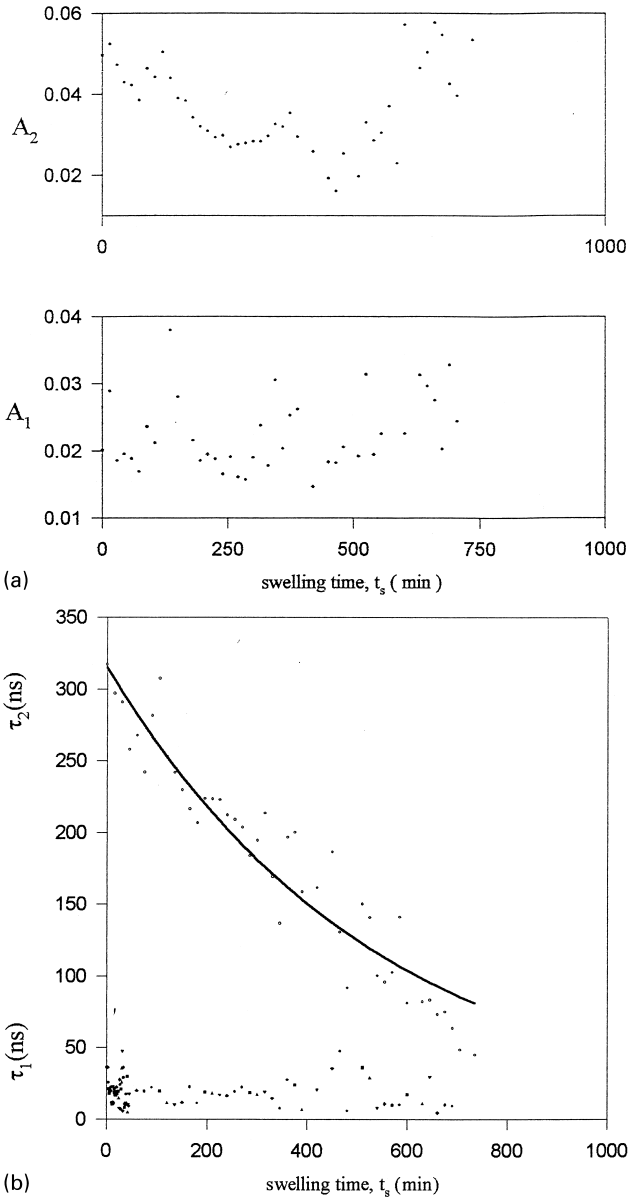

Fig. 4. The plot of the measured (a) A_1 and A_2, (b) τ_1 and τ_2 values versus swelling time, t_s. A_1, A_2, τ_1 and τ_2 values were obtained by fitting the data in Fig. 3 to Eq. (6).

can be obtained:

$$\ln\left[\frac{\langle I\rangle}{\langle I_0\rangle}\right] = \ln B_1 - \frac{t_s}{\tau_c} \tag{10}$$

The data are plotted in Fig. 6 according to Eq. (10) where a quite linear relation is obtained. Linear regression of curves in Fig. 6 provide us with B_1 and τ_c values from Eq. (10). Taking into account the dependence of B_1 and R, one obtains R values, and from α_1–R dependence α values were produced [18]. Then, using Eq. (5), cooperative diffusion coefficient D_c was determined for the gel sample.

The area, I under the fluorescence decay curves is also directly measured from the proper software of PTI. The normalized I values are plotted in Fig. 7. Now Eq. (10)

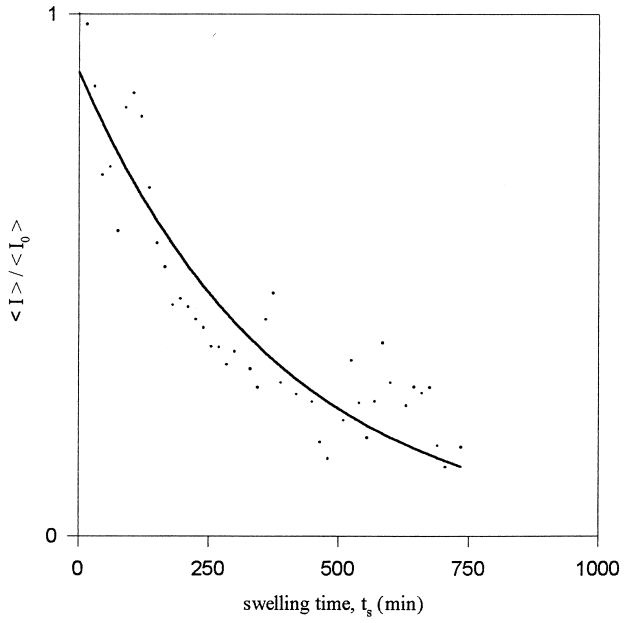

Fig. 5. Plot of the normalized $\langle I \rangle$ values calculated according to Eq. (7), versus swelling time, t_s.

can be written as follows:

$$\ln\left(\frac{I}{I_0}\right) = \ln B_1 - \frac{t_s}{\tau_c} \tag{11}$$

The data are fitted to Eq. (11) in Fig. 8 to produce new B_1 and τ_c values. Using Eq. (5) and the same procedure as was used above, a new D_c value is obtained. The D_c and τ_c values obtained from two different recipes are listed in Table 1.

Mean lifetimes of P_y can be calculated from the following

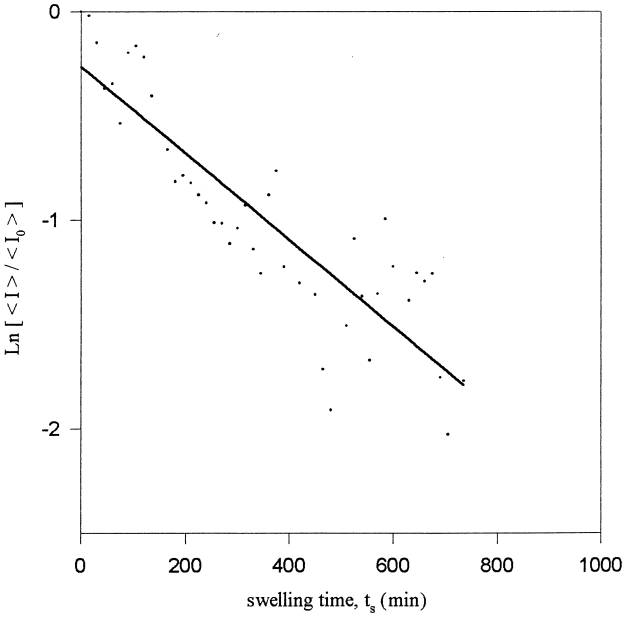

Fig. 6. Fit of the data in Fig. 5 to Eq. (10). The slope of the curve produced τ_c value, which is listed in Table 1.

Table 1

	I/I_0	$\langle I \rangle / \langle I_0 \rangle$	$\langle \tau \rangle / \tau$
% toluene	0.225	0.225	0.225
a_0 (cm)	0.35	0.35	0.35
a_∞ (cm)	0.5	0.5	0.5
W_∞ (g)	0.6708	0.6708	0.6708
B_1	0.95	0.77	0.95
			0.77
τ_1 (min)	526	476	553
R	0.71	0.43	0.71
			0.43
α	0.8	1.5	0.8
			1.5
D_c ($cm^2\ s^{-1}$)	3.5×10^{-5}	1.0×10^{-5}	3.5×10^{-5}
			1.0×10^{-5}
κ ($M^{-1}\ s^{-1}$)	–	–	5.5×10^{5}
			1.2×10^{5}

relation:

$$\langle \tau \rangle = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \tag{12}$$

Using the τ_i and A_i values, $\langle \tau \rangle$ values were obtained from Eq. (12) and are plotted in Fig. 9, where exponential decrease in $\langle \tau \rangle$ is observed as the swelling time t_s is increased. In order to quantify the above results, the Stern–Volmer type quenching mechanism may be proposed for the fluorescence decay of P_y in the gel sample during swelling process [40], where the following law for lifetime is satisfied:

$$\tau^{-1} = \tau_0^{-1} + \kappa[W] \tag{13}$$

where τ_0 is the lifetime of P_y in dry gel in which no quenching has taken place; κ is the quenching rate constant; and $[W]$ is the solvent concentration in the gel after solvent uptake has started. For low quenching efficiency, where $\tau_0\kappa[W] \ll 1$, Eq. (13) becomes

$$\tau \approx \tau_0(1 - \tau_0\kappa[W]) \tag{14}$$

The mean lifetime of P_y can be obtained approximately using the volume integration as follows:

$$\langle \tau \rangle = \frac{\int_{a_0}^{a_\infty} \tau\, d\upsilon}{\int_{a_0}^{a_\infty} d\upsilon} \tag{15}$$

where $d\upsilon$ is the differential volume in the gel. The integration is taken from initial a_0 to final a_∞ thickness of the gel. Performing the integration and inserting Eq. (2) in Eq. (15) the following relation is obtained:

$$\frac{\langle \tau \rangle}{\tau_0} = 1 - C + CB_1\, e^{-t_s/\tau_c} \tag{16}$$

where $C = \tau_0\kappa W_\infty/\upsilon$. Here υ is the swollen volume of the gel and the solvent uptake is calculated over differential

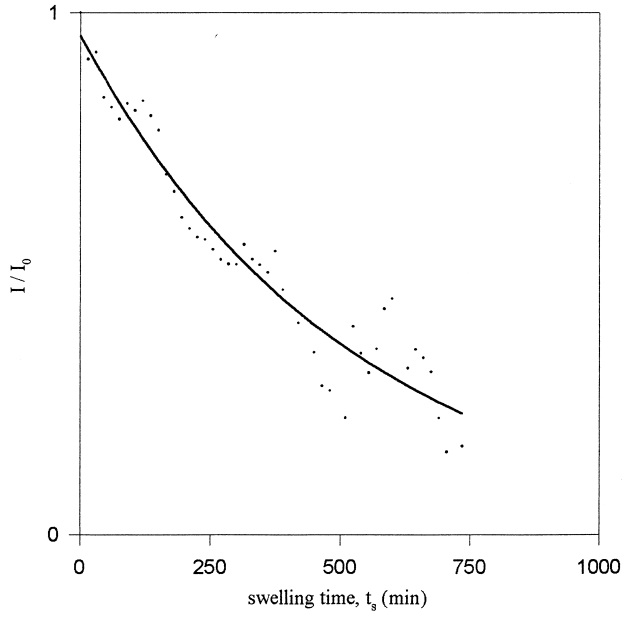

Fig. 7. Plot of the normalized intensity, I versus swelling time, t_s. I values are obtained directly from the area under the curves in Fig. 3.

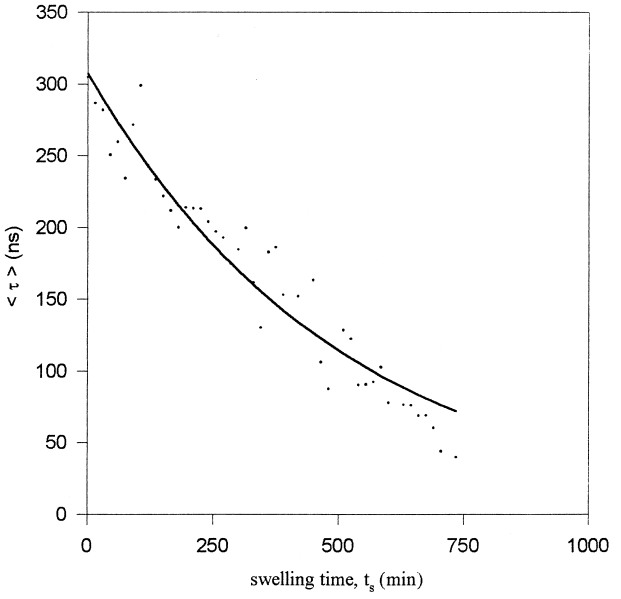

Fig. 9. The plot of the measured mean lifetimes, $\langle\tau\rangle$ versus swelling time, t_s. $\langle\tau\rangle$ values were calculated by using Eq. (12). The fit of the data to Eq. (16) is also presented.

volume as

$$W = \int_{a_0}^{a_\infty} [W]\, \mathrm{d}\upsilon \tag{17}$$

Eq. (16) can be fitted to the normalized mean lifetime of P_y in Fig. 9. τ_c is measured from the slope of the curve in Fig. 9. Using known B_1 values from the previous calculations, the D_c and κ values are obtained and listed in Table 1. Here $\tau_0 = 304$ ns was used for calculating the quenching rate constant κ. In Table 1, the measured τ_c values differ from each other depending on the method used. Comparing Figs. 6, 8 and 9, the best fit to data is observed in Fig. 9; as a result, $\tau_c = 553$ min is found to be more reliable than the others. D_c values are also different, depending on the method of measurement. Here it has to be noticed that B_1 values from the first two methods are used to calculate D_c value in the first method. The observed D_c values are consistent with out previous observations of PMMA gel swelled in chloroform [33].

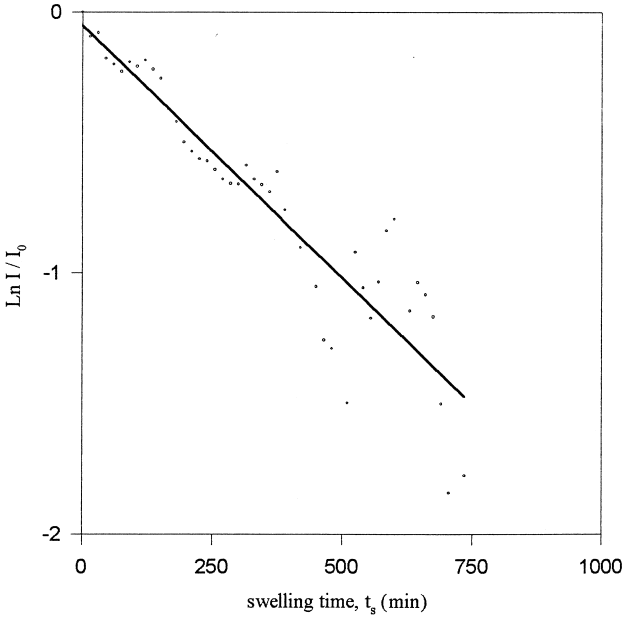

Fig. 8. Fit of the data in Fig. 7 to Eq. (11). The slope of the curve produced τ_c value, which is listed in Table 1.

The quenching rate constant κ was found to be 5.5×10^5 or 1.2×10^5 M^{-1} s^{-1}, depending on the method of producing B_1; κ is given by the following relation [41]:

$$\kappa = \frac{4\pi N_A D_m R_p}{1000} \tag{18}$$

where $D_m = D_p + D_{ch}$ is the sum of the mutual diffusion coefficients of chromophore (P_y) and quencher (chloroform), respectively, $R = R_p + R_{ch}$ is the sum of their interaction radii, N_A is the Avogadro number and p is a factor describing the reaction probability per collision. Here D_p and D_{ch} are the mutual diffusion coefficients and R_p and R_{ch} are the radii of P_y and chloroform molecules, respectively. The sum of the mutual diffusion coefficient was calculated from Eq. (18) by using the average κ value and found to be $D_m = 5.7 \times 10^{-7}$ cm^2 s^{-1}, where R is taken as 7.8 Å (i.e. $R_p = 3.98$ Å and $R_{ch} \neq 3.88$ Å) and p is assumed to be unity. The observed mutual diffusion coefficient, D_m is typical for a small molecule diffusing in a swollen rubbery environment [1,42] and is much smaller than the cooperative diffusion coefficient, D_c. This result is expected, because an element of swollen network moves much faster, due to the restraining forces, than the P_y and chloroform molecules in the swollen, viscous environment.

In summary, in this paper we have shown that the FTRF technique can be used to measure cooperative and mutual diffusion coefficients during swelling of a polymeric gel. Here one can argue that measuring lifetimes by using FTRF in a swelling gel provides data that can be used with no correction. However, data obtained by using steady state fluorescence method need a significant amount of correction in intensity due to certain art effects [31,32]. In conclusion, we introduced a novel FTRF method to study gel swelling which produces more reliable results than other techniques. The FTRF method can also be used to study gelation and polymerization processes, because fluorescence lifetimes are very sensitive to environment and SMS is fast enough to monitor gelation and polymerization processes which take hours.

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