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Temperature effect on gel swelling: a fast transient fluorescence study

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Abstract

Fast transient fluorescence (FTRF) technique was employed for studying the swelling of disk shaped poly(methyl methacrylate) (PMMA) gels which were prepared by free-radical copolymerization of methyl (methacrylate) (MMA) and ethylene glycol dimethacrylate at 80°C. The FTRF technique, which measures lifetimes, is more powerful in gel swelling experiments than the steady-state fluorescence technique where fluorescence intensity is measured. Swelling experiments were performed by using pyrene (Py) doped PMMA gels in chloroform at various temperatures. Decay curves of Py were used to monitor during in situ swelling experiments. Double exponential fits were performed to measure the long (τ_2) and short (τ_1) components of Py lifetimes which belong to the Py molecules inside and outside the PMMA gels. It was observed that τ_2 values inside the gel decrease as swelling proceeds; however, τ_1 lifetimes outside the gel stay constant during slow release. An equation is derived for low-quenching efficiencies to interpret the behavior of Py lifetimes inside the gel during swelling. The Li–Tanaka equation was used to determine the cooperative, D_c diffusion coefficients at various temperatures. It was observed that the D_c value increases as the temperature is increased. The activation energy ΔE was measured for the gel swelling process, and found to be 22 kcal mol^{-1}.

Keywords: Poly(methyl methacrylate) gels; Fast transient fluorescence; Gel swelling

1. Introduction

Gels are known to exist generally in two forms, swollen or shrunken. Volume phase transitions occur between these forms either continuously or with sudden jumps between them [1,2]. The equilibrium swelling of gels in solvent has been extensively studied [3–5]. The swelling kinetics of physical and chemical gels are very important in many technological applications, especially in pharmaceutical industries in designing slow-release devices for oral drugs. In the agricultural industry, for producing storable foods, and in medical applications, in developing artificial organs, the knowledge of the volume transitions of gels is quite important.

The total free energy of a chemical gel consists of bulk and shear energies [6–10]. 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 a given temperature. On the other hand, the shear energy that keeps the gel in shape can be characterized by the shear modulus G. Here, the shear energy minimizes the nonisotropic deformations in the gel. The theory of the kinetics of swelling for a spherical chemical gel was first developed by Tanaka and Filmore [11] where the assumption is made that the shear modulus G is negligible compared to the osmotic bulk modulus. Later, Peters and Candau [12] derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming a nonnegligible shear modulus and Li and Tanaka [6] 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.

Fluorescence methods have been employed to study gelation and the kinetics of swelling of chemical and physical gels [13–23]. Measuring the Stokes shift of a polarity sensitive fluorescence species, the gelation during epoxy curing was monitored as a function of cure time [13]. Time-resolved and steady-state fluorescence techniques were employed to study isotactic polystyrene in its gel state [14] where excimer spectra were used to monitor the existence of two different conformations in the gel state of polystyrene. The pyrene (Py) derivative was used as a fluorescence molecule to monitor the polymerization, aging and drying of aluminosilicate gels [15]. In situ observations of the sol–gel phase transition in free-radical crosslinking copolymerization (FCC), using the steady-state fluorescence (SSF) technique was reported by us [16–19].

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The same technique was also performed for studying the swelling and drying kinetics in disk-shaped gels [20,21]. Recently, fast transient fluorescence (FTRF) technique was used for monitoring the swelling of poly(methyl methacrylate) (PMMA) gels [22].

The aim of this work is to study gel swelling at the molecular level, where excited Py molecules are quenched by the penetrant solvent molecules in the range of a few angstroms. The penetration of the solvent molecules into a disk-shaped gel formed by FCC of methyl (methacrylate) (MMA) and ethylene glycol dimethacrylate (EGDM) was studied using FTRF technique which measures lifetimes. Fluorescence decay profiles of Py were measured when the gel was illuminated directly by the exciting light and the decay profiles were fitted to the double exponential laws to obtain long and short lifetimes of Py. The strobe master system (SMS) was used for lifetime measurements of Py inside and outside the gel. Lifetime measurements with SMS take a much shorter time than with the single photon counting system and Phase instruments. This advantage of SMS allows one to make at least hundreds of measurements during the swelling process of the gels. This is the reason why we named this technique as fast transient fluorescence (FTRF), which provides many advantages compared to other lifetime measuring techniques. Measuring lifetimes directly provides swelling parameters which can also be obtained using the SSF technique in which many corrections have to be done to clarify the art effects. It was observed that as the gel swells, the lifetimes of Py inside the gel decrease, which can be modeled using the low-quenching Stern–Volmer equation. However, the lifetimes of Py outside the gel stayed constant during slow release. Cooperative, D_c diffusion coefficients were determined at various temperatures by employing the Li–Tanaka and Stern–Volmer equations, and found to have increased from 0.8 to 20×10^{-4} cm^2 s^{-1} by increasing the temperature from 25 to 50°C. The Arrhenius relation between D_c and the temperature T produced the swelling activation energy ΔE as 22 kcal mol^{-1}.

2. Kinetics of swelling

Li and Tanaka showed that the kinetics of swelling of a polymer network or gel obey the following relation [6]:

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

where $W(t_s)$ and W_∞ are the solvent uptake at swelling time t_s and at infinite equilibrium, respectively. Here B_n represents a constant related to the ratio of the shear modulus G and the longitudinal osmotic modulus M, which is defined by the combination of shear and osmotic bulk modulii as $M = 4/3G + K$ [9,10]. τ_n is the swelling rate constant. In the limit of a large t_s or if the first term τ_c is much larger than the rest of τ_n, all the high-order terms ($n \geq 2$) in Eq. (1) can be neglected, then Eq. (1) becomes

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

Here B_1 is given by the following relation [6]:

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

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 represent 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

The radical copolymerization of MMA and EGDM was performed in bulk at 80°C in the presence of 2,2′-azobisisobutyrronitrile (AIBN) as an initiator. Py was added as a fluorescence probe during the gelation process. AIBN (0.26 wt%) was dissolved in MMA and this stock solution was divided and transferred into round glass tubes of 9.5 mm internal diameter. All the samples were deoxygenated by bubbling nitrogen for 10 min and then radical copolymerization of MMA and EGDM was performed. Here, the Py concentration was taken as 4×10^{-4} M. 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. Chloroform (Merck) was distilled twice over sodium and used for the swelling processes.

Fluorescence decay experiments were performed using Photon Technology International (PTI) SMS. In the strobe or pulse sampling technique [23,24], 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 off the PMT and measuring the emission intensity over a 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

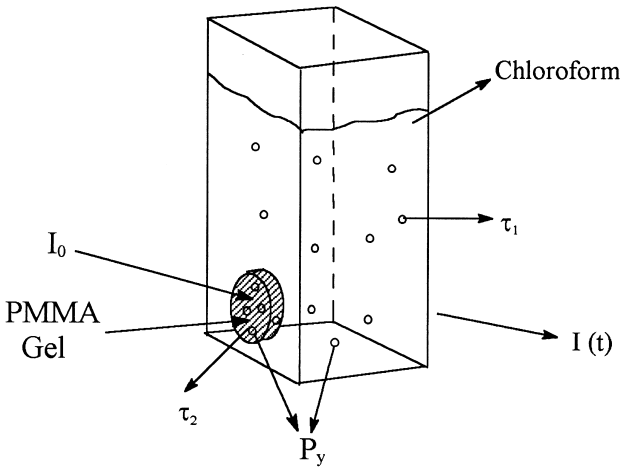

Fig. 1. Fluorescence cell in PTI SMS for monitoring of gel swelling. I_0 and $I(t)$ are the excitation and the emission intensities at 345 and 395 nm, respectively. τ_2 and τ_1 are the lifetimes of Py when it was inside and outside the gel sample, respectively.

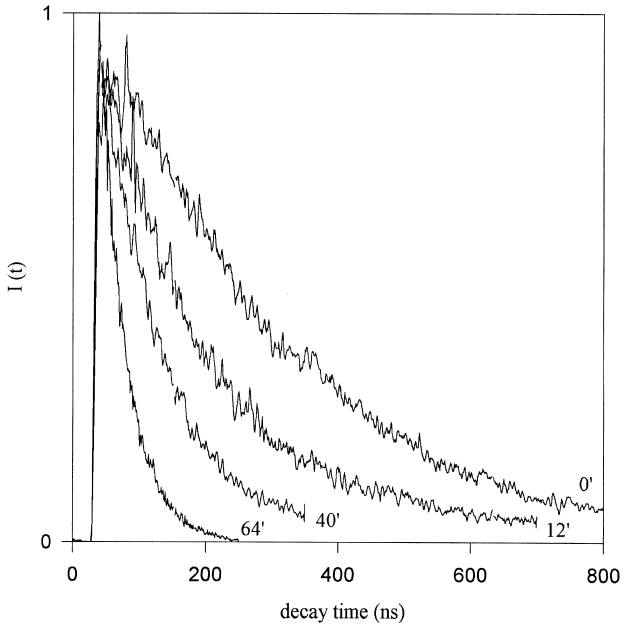

Fig. 2. Fluorescence decay profiles $I(t)$ of Py at various swelling steps for a gel swelled at 50°C. The number on each decay curve presents the swelling time in minutes.

dependent, the strobe instrument is much faster than SPC, and even faster than the phase 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 the swelling of the PMMA gel which takes around several hours.

In situ swelling experiments were carried out in the SMS of PTI, employing a pulsed lamp source (0.5 atm of N_2). Pys were excited at 345 nm and fluorescence decay curves were obtained at 390 nm during in situ swelling experiments which were performed at temperatures of 25, 30, 35, 40, 45 and 50°C. At each temperature, the disk-shaped gel sample was placed in a $1 \times 1\ cm^2$ quartz cell, where it was attached to one side of the cell by pressing a disk with thick steel wire. The quartz cell was filled with chloroform and placed in the SMS where fluorescence decay measurements were performed at 90° angle as shown in Fig. 1. In the swelling experiments, six identical disk-shaped gels were used which were dried and cut from a cylindrical gel obtained from FCC. The fluorescence decay data were collected over three decades of decay and fitted by nonlinear least squares using the 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.

4. Results and discussion

Decay curves of Py obtained from SMS in various swelling times t_s for the gel swelled at 50°C are presented in Fig. 2. In order to probe the swelling process during solvent uptake, the fluorescence decay curves were measured and fitted to the sum of the two exponentials:

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

where τ_1 and τ_2 are the long and short components of Py lifetimes, respectively, and A_1 and A_2 the corresponding amplitudes of the decay curve. In other words, τ_2 and τ_1 are the lifetimes of Py when the Pys are inside and outside the gel sample, respectively. As seen in Fig. 2, when the swelling time t_s increases the excited Pys decay faster and faster, which indicates that as the solvent uptake is increased the quenching of excited Pys by chloroform increases. In Fig. 3(a), (b), (c) and (d), τ_1 and τ_2 values are plotted versus t_s for the gels swelled at 35, 40, 45 and 50°C, respectively, where it is seen that the τ_1 values do not change much but the τ_2 values decrease as t_s increases. Here, the role of the solvent is to add the quasi-continuum of states needed to satisfy the 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. [25] studied the influence of solvent viscosity on the fluorescence characteristics of Py solutions in various solvents and observed that the rate of monomer internal quenching is affected by the solvent quality.

In order to quantify the swelling data, the area under the second part of the fluorescence decay curve is calculated using Eq. (6) according to the following relation:

$$\langle I \rangle = \int_{t_1}^{t_2} I\, dt = \tau_2 A_2, \tag{7}$$

where the integral is taken from the peak (t_1) to the end point (t_2) of the decay curve. The $\langle I \rangle$ values are calculated for the

gels swelled at various temperatures and it is observed that these values decrease as the swelling time t_s increases. This indicates that the quenching rate of Py molecules increases as the chloroform molecules penetrate into the gel. Here at the beginning, before solvent penetration starts, Py intensity is called $\langle I_0 \rangle$. After solvent penetration is started, some excited Py molecules are quenched and the intensity decreases to $\langle I \rangle$ at time t_s where the amount of solvent uptake is W. At the equilibrium state of swelling, Py intensity decreases to $\langle I_\infty \rangle$, where solvent uptake by the swollen gel is W_∞. The relation between the solvent uptake W and the Py intensity $\langle I \rangle$ during the swelling process is then given by the following relation:

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

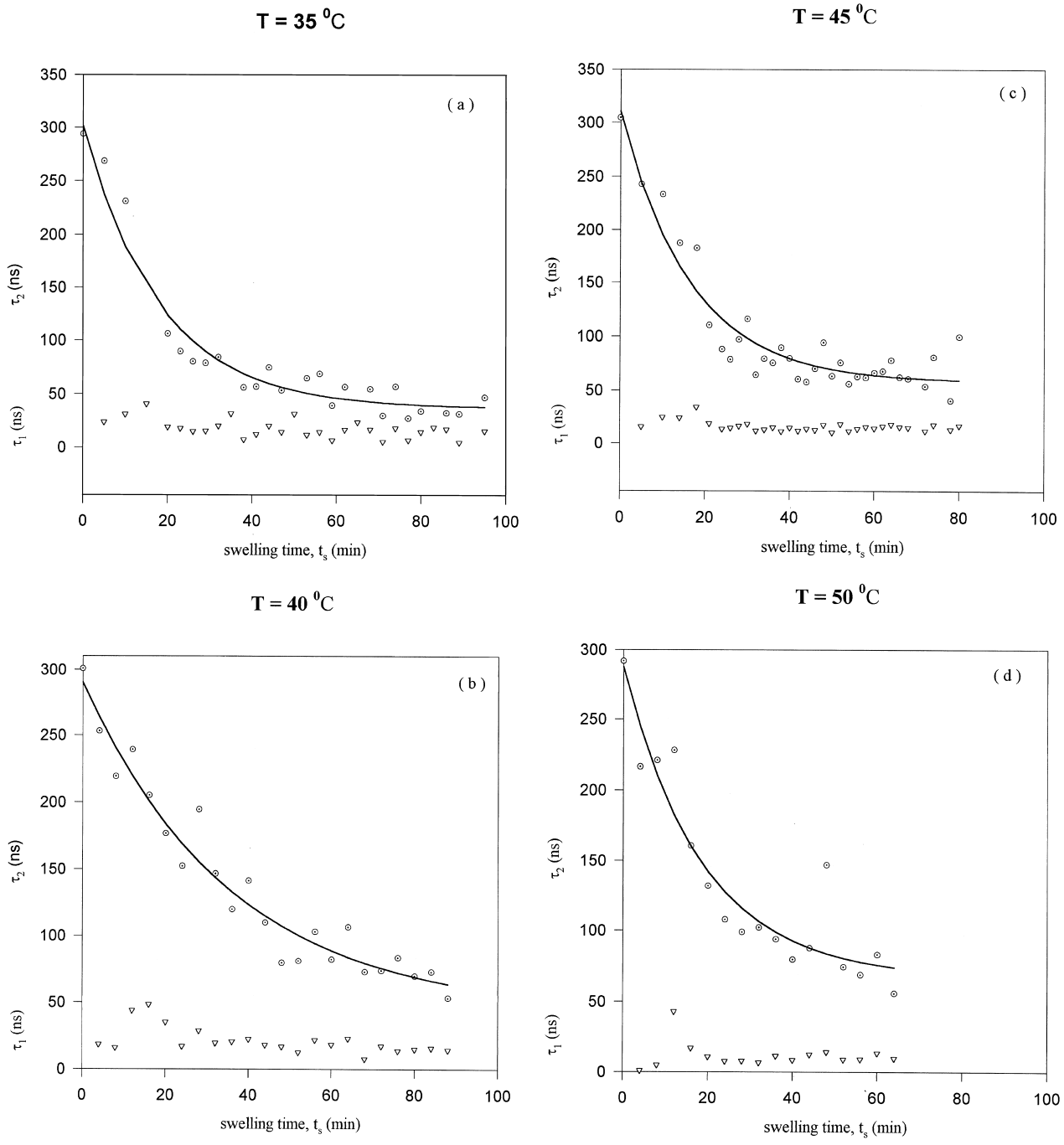

Fig. 3. The plot of the measured τ_2 and τ_1 values versus swelling time t_s for the gels swelled at: (a) 35; (b) 40; (c) 45; and (d) 50°C. τ_1 and τ_2 values were obtained by fitting the $I(t)$ data to Eq. (6) at each temperature.

Since $I > I_\infty$, 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 the oxygen uptake by PMMA spheres [26,27]. Combining Eq. (9) with Eq. (2) and assuming that the number of unquenched Py molecules is proportional to $\langle I \rangle$, the following relation can be obtained:

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

$\langle I \rangle$ data are fitted to Eq. (10) for the gels swelled at 35, 40, 45 and 50°C in Fig. 4 where quite linear relations are obtained. Linear regression of the curves in Fig. 4 provides

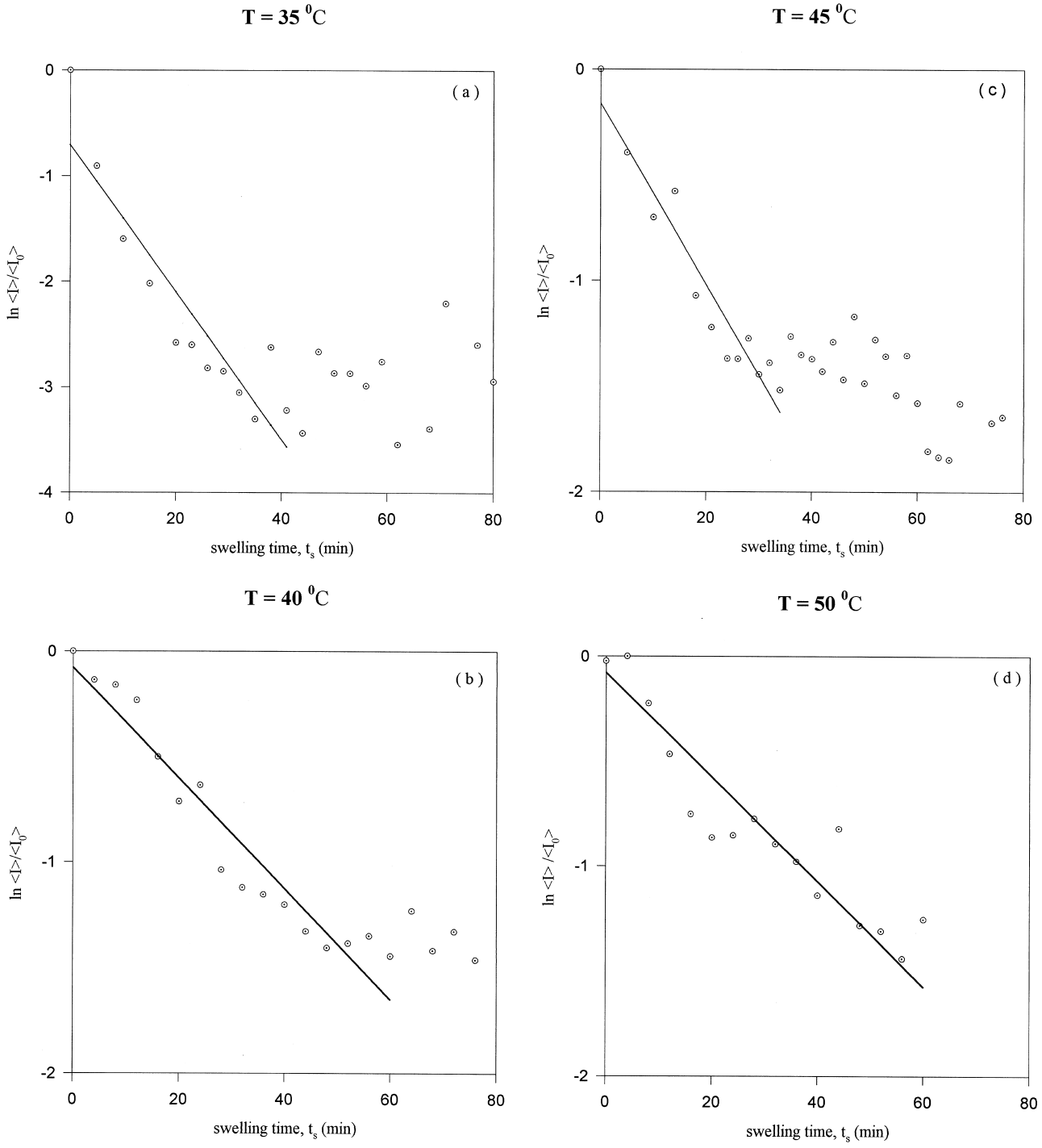

Fig. 4. Fit of the $\langle I \rangle$ data to Eq. (10) for the gel samples swelled at: (a) 35; (b) 40; (c) 45; and (d) 50°C. The slope of the curves produced the τ_c values.

Table 1

Temperature (°C)	B_1	α_1	D_c (cm^2s^{-1}) τ_2
25	0.37	2.3	0.8×10^{-5}
30	0.91	1.1	3.5×10^{-5}
35	0.5	2.3	3.63×10^{-5}
40	0.926	1.0	11.2×10^{-5}
45	0.8	1.55	9.13×10^{-5}
50	0.925	1.0	20.6×10^{-5}

us with the B_1 values from Eq. (10). Taking into account the dependence of B_1 to R, we obtain the R values, and from the α_1–R dependence the α_1 values were produced [6].

In order to quantify the results in Fig. 3(a)–(d) where exponential decrease in τ_2 is observed as the swelling time t_s is increased, the Stern–Volmer type of quenching mechanism may be proposed for the fluorescence decay of Py in the gel sample. According to the Stern–Volmer law, τ_2 lifetimes can be written as [25]:

$$\tau_2^{-1} = \tau_{02}^{-1} + \kappa[W], \tag{11}$$

where τ_{02} is the lifetime of Py in the dry gel in which no quenching has taken place, κ the quenching rate constant and $[W]$ the solvent concentration in the gel after solvent uptake has started. For low-quenching efficiency, where $\tau_{02}\kappa[W] < 1$, Eq. (11) becomes

$$\tau_2 \approx \tau_{02}(1 - \tau_{02}\kappa[W]). \tag{12}$$

Integrating Eq. (12) over the differential volume dv of the gel from its initial (a_0) to final (a_∞) thicknesses, and substituting Eq. (2), the following useful relation is obtained:

$$\frac{\tau_2}{\tau_{02}} = 1 - C + CB_1\, e^{-(t_s/\tau_c)}. \tag{13}$$

Here, $C = \tau_{02}\kappa W_\infty/v$, where v is the swollen volume of the gel. Eq. (13) can be fitted to the normalized lifetimes of Py in Fig. 3 (the solid line) and τ_c values were obtained for the gel samples swelled at 35, 40, 45 and 50°C. Using the known α_1 values from the previous calculations, D_c values were obtained from Eq. (5) are listed in Table 1. Here $\tau_{02} =$ 300 ns was used for the normalization. Similar analyses were made for the gel samples swelled at 25 and 30°C and D_c values were obtained, and are listed in Table 1. Here, it has to be noted that B_1 and α_1 values from the $\langle I\rangle$ data are used to calculate D_c values in the lifetime data. The observed D_c values are consistent with our previous observations of PMMA gel swelled in chloroform [28].

In this work, it is believed that the lifetime data are found to be more reliable than the intensity ($\langle I\rangle$) data; as a result, the D_c values obtained from τ_2 versus t_s plots are trusted more. As seen in Table 1, the D_c values increase as the temperature is increased, which indicates that the D_c–T relation may obey the following Arrhenius relation:

$$D_c = D_{c0}\exp(-\Delta E/kT), \tag{14}$$

where ΔE is the activation energy for swelling, k the Boltzmann's constant and D_{c0} the cooperative diffusion coefficient at $T = \infty$. The logarithmic form of the D_c data is plotted versus T^{-1} in Fig. 5 where the slope of the linear relation produces the activation energy ΔE for the swelling gel as 22 kcal mol^{-1}.

In summary, this paper presents the FTRF technique to be used to measure cooperative diffusion coefficients during the swelling of a polymeric gel at various temperatures. Here, one can argue that measuring lifetimes by using FTRF in swelling gel provides data which can be used with no correction. However, the data obtained by using the steady-state fluorescence method need quite an amount of correction in intensity due to certain art effects [29]. In this work, τ_2 data were used to obtained D_c values which provide us with the swelling activation energy. Here, it is believed that $\Delta E = 22$ kcal mol^{-1} is the total energy (bulk and shear energies) of the gel needed for swelling.

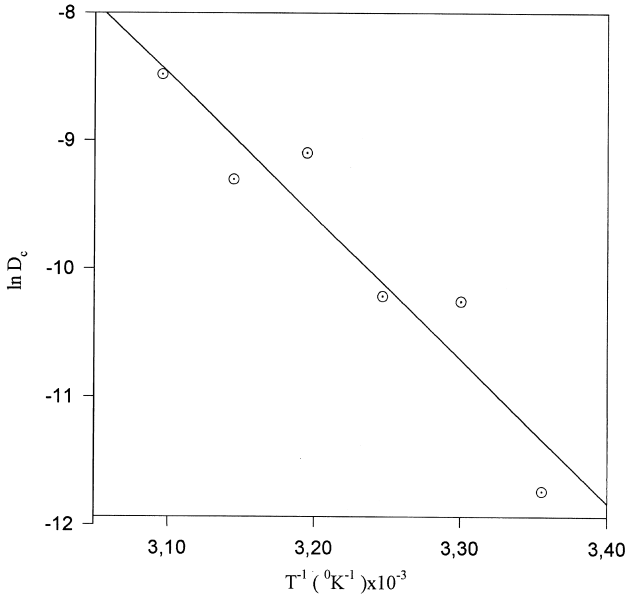

Fig. 5. Plot of D_c values versus temperature T according to Eq. (14). The slope of the linear relation produces the activation energy ΔE for swelling of the gel.

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