Fast Transient Fluorescence (FTRF) Technique to Study Swelling of Densely and Loosely Formed Gels

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ABSTRACT: A Strobe Master System (SMS) is introduced for studying the swelling of cylindrical densely (DG) and loosely (LG) formed gels. Gels were prepared by free radical copolymerization of methyl (methacrylate) (MMA) and ethylene glycol dimethacrylate (EGDM). Pyrene (P) was introduced as a fluorescence probe during polymerization, and the lifetimes of P were measured using (SMS) during *in situ* swelling processes. Chloroform was used as a swelling agent. A model is derived for low quenching efficiencies to measure mean lifetimes $\langle\tau\rangle$ of P, and it was observed that $\langle\tau\rangle$ values decreased as the swelling proceeded. The Li-Tanaka equation was employed to determined the time constants, τ_c, and cooperative diffusion coefficients, D_c, which were found to be around 400 min and 10^{-5} cm^2s^{-1}, respectively. No differences were detected in τ_c and D_c values of DG and LG gels. Quenching rate constants, κ, and the mutual diffusion coefficient, D_m, were measured and found to be around 10^5 $M^{-1}s^{-1}$ and 10^{-10} cm^2s^{-1} for DG and LG gel samples. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1494–1502, 2000

Key words: fast transient fluorescence (FTRF); swelling; densely and loosely formed gels

INTRODUCTION

Fluorescent dyes can be used to study local environments, basically with two types of experiments. When the dye was simply added to the system as a small molecule, the dye was referred to as a probe, which is 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 can be raised is: does the presence of the dye perturb the system or perturb its own local environments in the system. Perturbation is most common where high dye concentration leads to aggregation, and the 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.

For about 2 decades the transient fluorescence (TRF) technique for measuring fluorescence decay has been routinely applied to study many polymeric systems using dyes both as a probe and/or as labels.[1–7] TRF spectroscopy, with direct energy transfer (DET), and the quenching method, has been used to characterize internal morphologies of composite polymeric materials.[6,7] Film formation from donor- and acceptor-labeled latex particles was studied using DET in conjunction with TRF.[8–10] A single-photon counting (SPC) technique that produces decay curves and measures lifetimes in conjunction with DET was used to

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study the diffusion of small dye molecules within the interphase domain of anthracene- and/or phenantrene-labeled poly(methyl methacrylate) (PMMA) particles.[11,12] Mean lifetimes of fluorescing donor dye molecules were measured during diffusion. A Fickian model for diffusion was employed to produce diffusion coefficients, at room and above glass transition temperatures.

Polymer networks or gels are known to generally exist in two forms—swollen and shrunken. Volume transitions occur between these forms either continuously or with sudden jumps between them.[13,14] The equilibrium swelling and shrinking of gels in solvents have been extensively studied.[15,17] The swelling, shrinking, and drying 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 use of cosmetic ingredients, understanding the kinetics is highly desirable. In agricultural industry for producing storable foods and in medical applications in developing artificial organs, the knowledge of the gel kinetics is an important requirement for the scientist in the field.

The swelling properties of chemically crosslinked gels can be understood by considering the osmotic pressure vs. 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 osmoticbulk modulus κ, which is defined in terms of the swelling pressure and the volume fraction of the 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, 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 et al.,[23] where the assumption is made that the shear modulus, G, is negligible compared to the osmotic bulk modulus. Later, Peters et al.[24] derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming a nonnegligible shear modulus. Recently, Li and Tanaka[6] 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.

Many different experimental techniques have been used to study the kinetics of swelling and shrinking of chemical and physical gels, among which are neutron scattering,[25] quasielastic light scattering,[24] macroscopic experiments,[19] and *in situ* interferometric[26] measurements. Time-resolved and steady-state fluorescence techniques were employed to study isotactic polystyrene in its gel state[27] where excimer spectra was used to monitor the existence of two different conformations in the gel state of the polystyrene. Pyrene derivate was used as a fluorescence molecule to monitor the polymerization, aging, and drying of aluminosilicate gels.[28] These results were interpreted in terms of the chemical changes occurring during the sol-gel process, and the interactions between the chromophores and the sol-gel matrix. Recently, we reported *in situ* observations of the sol-gel phase transition in free radical crosslinking copolymerization using the fluorescence technique.[29–31] The same technique was also performed for studying swelling and drying kinetics in disc-shaped gels.[32,33]

In this work, swelling of densely (DG) and loosely (LG) formed gels by FCC of MMA and EGDM was studied using the Fast Transient Fluorescence (FTRF) technique. Lifetimes of P, which is embedded in the cylindrical PMMA gels, were monitored during the *in situ* swelling processes. A Strope Master system (SMS) of Photon Technology International (PTI) was used for lifetime measurements of P in gels. Lifetime measurement with SMS takes a much shorter time than single-photon counting and phase instruments. This advantage of SMS allows one to make hundreds of measurements during the swelling process of gels. That is the reason we named this technique Fast transient Fluorescence (FTRF), which gives us many advantages compare to other lifetime-measuring techniques. It is observed that as gels swell, the lifetime of P decreases, which can be a model according to the Li-Tanaka equation using a low quenching approximation.

THEORETICAL CONSIDERATIONS

It has been suggested[18] that the kinetics of swelling and shrinking of a polymer network or gel should obey the following relation,

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

where $W(t)$ and $W(\infty)$ are the swelling or solvent uptake at time t and at infinite equilibrium, respectively. $W(t)$ can also be considered as a volume difference of the gel between time t 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 indepent of time t. Here, B_n is given by the following relation.[6]

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

Here, 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

$$R = \frac{1}{4}\left[1 + \frac{\alpha_n J_0(\alpha_n)}{J_1(\alpha_n)}\right] \tag{3}$$

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 disk at the surface, and given by the relation[7]

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

Here the diffusion coefficient D_c is given by $D_c = M/f = (K + 4G/3)/f$, where f is the friction coefficient describing the viscous interaction between the polymer and the solvent, and a representation of half of the disc thickness in the final infinite equilibrium that 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 correspond to the last stage of the swelling. As it is seen from eq. (4), τ_n is inversely proportional to the squared of α_n, where α_ns are the roots of the Bessel functionals. If $n > 1$, α_n increases and τ_n decreases very rapidly. Therefore, the kinetics of swelling in the limit of a large t, or if τ_1 is much larger than the rest of τ_n,[6] 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.[14] In this case, eq. (1) can be written as

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

Equation 5 allows us to determine the parameters B_1 and τ_c.

Here, it is important to note that eq. (5) satisfies the following equation

$$\frac{dW(t)}{dt} = \frac{1}{\tau_c}(W_\infty - W) \tag{6}$$

which suggests that the process of swelling should obey the first-order kinetics. The higher order terms ($n \geq 2$) can be considered as fast decaying perturbative additions to the first-order kinetics of the swelling in the limit of large t.

EXPERIMENTS

EGDM has been commonly used as crosslinker in the synthesis of polymeric networks.[33] Here, for our use, the monomers MMA (Merck) and EGDM (Merck) were free 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. Then radical copolymerization of MMA and EGDM was performed in toluene at 80°C in the presence of 2,2′-azobisisobutyronitrile (AIBN) as an initiator. 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 samples were deoxygenated by bubbling nitrogen for 10 min, and then radical copolymerization of MMA and EGDM was performed. P was added as a fluorescence probe before the gelation process during sample preparation. Here, P concentration was taken as $4 \times 10^{-4}M$. Four different samples were prepared using this stock solution with four different toluene contents. These gels are named as G1, G2, G3, and G4, depending on the toluene content. Here, G1 and G2 samples are called as densely (DG) formed gels that contain higher amount of MMA. G3 and G4 gels are loosely (LG) formed gels, containing fewer amounts of MMA compared to DG gels. These gels are all in cylindrical shape. Details of the samples are listed in Table I.

Fluorescent decay experiments were performed using the Photon Technology International (PTI) Strobe Master System (SMS) presented in Figure 1. In the strope, or pulse-sam-

Table I Experimentally Obtained Swelling Parameters of DG and LG Gels

Gel	G1	G2	G3	G4
Toluene content (%)	0.1	0.125	0.225	0.250
MMA content (%)	0.9	0.875	0.775	0.75
W_∞ (gr)	1.15	0.58	0.67	0.83
a_0 (cm)	0.3	0.26	0.35	0.35
a_∞ (cm)	0.59	0.55	0.5	0.55
τ_c (min) $\langle I\rangle/\langle I_0\rangle$	446	280	476	447
β_1	0.80	0.79	0.76	0.89
τ_c (min) $\langle \tau\rangle/\langle \tau_0\rangle$	961	425	507	380
D_c (cm^2s^{-1}) $\langle I\rangle/\langle I_0\rangle$	2×10^{-5}	2×10^{-5}	0.9×10^{-5}	2.3×10^{-5}
D_c (cm^2s^{-1}) $\langle \tau\rangle/\langle \tau_0\rangle$	0.9×10^{-5}	1.31×10^{-5}	8.05×10^{-6}	2.7×10^{-6}
κ ($M^{-1}s^{-1}$)	4.7×10^5	10.7×10^5	6.65×10^5	3.2×10^5
D_m (cm^2s^{-1})	7.97×10^{-10}	18×10^{-10}	11.3×10^{-10}	5.4×10^{-10}

$\langle I\rangle/\langle I_0\rangle$ and $\langle \tau\rangle/\langle \tau_0\rangle$ values indicate the equation that used to measure the corresponding parameters.

pling 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 fluorescent emission is measured in a very narrow time window on each pulse, and saved in a computer. The window is moved after each pulse. The strobe has the effect of turning the PMT and measuring the emission intensity over a very short time window. When the data have been sampled over the appropriate range of time, a decay curve of fluorescent intensity vs. time can be constructed. Because the strope technique is intensity dependent, the strobe instrument is much faster than the SPC, and even faster than the phase instrument. The strobe instrument is much simpler to use than the SPC, and the data is easier to interpret than the phase system. Because of these advantages, SMS is used to monitor the swelling of PMMA, gels which takes several hours.

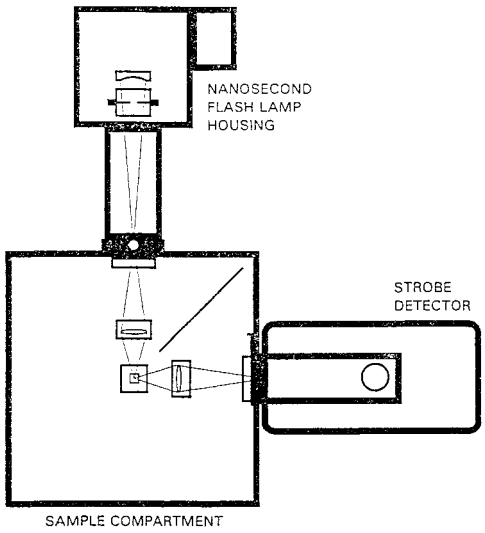

Figure 1 Strobe Master Fluorescence Lifetime Spectrometer of Photon Technology International (PTI).

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 the *in situ* swelling experiment, which was performed at room temperature. Gel samples were placed in a round quartz cell, and chloroform was added on top of the gel during the swelling process. Here, the level of chloroform is kept constant during swelling. The fluorescence decay data were collected over 3 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.

RESULT AND DISCUSSIONS

Typical decay curves of P at various swelling steps obtained from SMS are shown in Figure 2(a) and (b) for G1 and G3 gels, respectively. The fluorescent decay curves were fitted to the sum of two exponentials:

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (7)$$

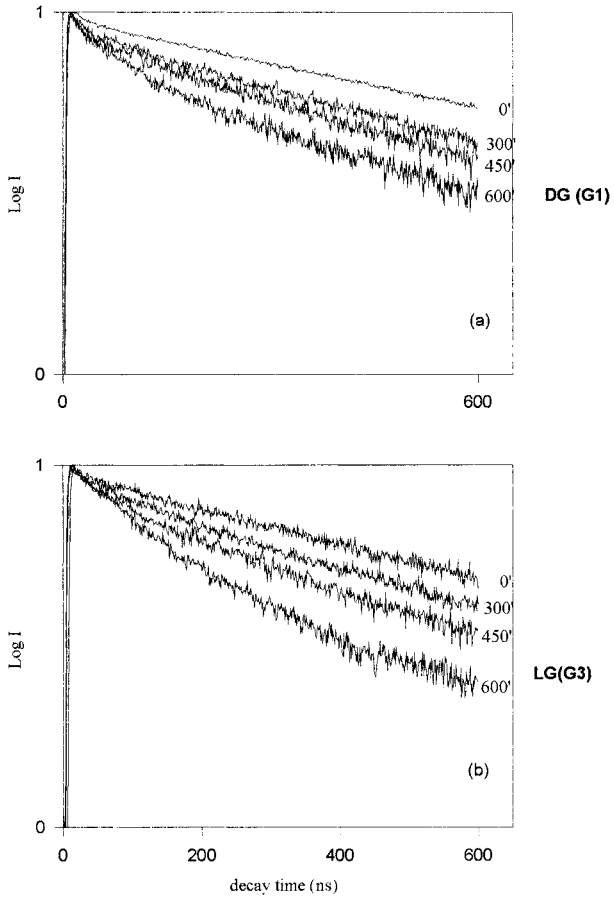

Figure 2 Decay curves of Pyrene in (a) G1, (b) G3 gels during swelling process. Numbers on each decay curve present the swelling time, t_s, in minute.

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. In Figure 2(a) and (b) it is observed that as the swelling time, t_s, is increased, excited pyrenes decay faster and faster by indicating 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 the rapid vibrational relaxation that 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 the monomer internal quenching is affected by the solvent quality. We have reported the viscosity effect on low-frequency intermolecular vibrational energies of excited naphthalene in swollen PMMA latex particles.[37]

To quantify the above observation, the area under the fluorescent decay curves are calculated using eq. (7) according to the following integration

$$\langle I \rangle = \int_{t_1}^{t_2} I dt = \tau_1 A_1 + \tau_2 A_2 \tag{8}$$

where the integral is taking from the peak (t_1) to the end point (t_2) of the decay curve. Normalized $\langle I \rangle$ values are plotted in Figure 3(a) and (b) for G1 and G3 gels, respectively, where it is seen that $\langle I \rangle$ values decrease as the swelling time, t_s, is increased, which indicates that quenching of P molecules increases as chloroform penetration is increased. At the beginning, before solvent penetration starts, P intensity is called $\langle I_0 \rangle$. After solvent penetration starts, some excited P molecules are quenched and intensity decreased to $\langle I \rangle$ at time t_s where solvent uptake is W. At the equilibrium state of swelling P, intensity decreased to $\langle I_\infty \rangle$, where solvent uptake by swollen gel is W_∞. The relation between solvent uptake W and P intensities during the swelling process is given by following relation

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

Because $\langle I_0 \rangle \gg \langle I_\infty \rangle$, eq. (9) becomes

$$\frac{W}{W_\infty} = 1 - \frac{\langle I \rangle}{\langle I_0 \rangle} \tag{10}$$

Combining eq. (10) with eq. (5), and assuming that number of quenched P molecules are proportional to $\langle I \rangle$, the following relation is obtained

$$\ln\left[\frac{\langle I \rangle}{\langle I_0 \rangle}\right] = \ln B_1 - \frac{t_s}{\tau_c} \tag{11}$$

Data in Figure 3(a) and (b) are plotted in Figure 4(a) and (b) according to eq. (11). Linear regression of curves in Figure 4(a) and (b) produce B_1 and τ_c values from eq. (11). Taking into account the dependence of B_1 and R, one obtains R values, and from $\alpha_1 - R$ dependence α-values were obtained.[38] Then, using eq. (5), the cooperative diffusion coefficient D_c was determined for the G1 and G3 gel samples. The same procedure is applied for the other gel samples (G2 and G4),

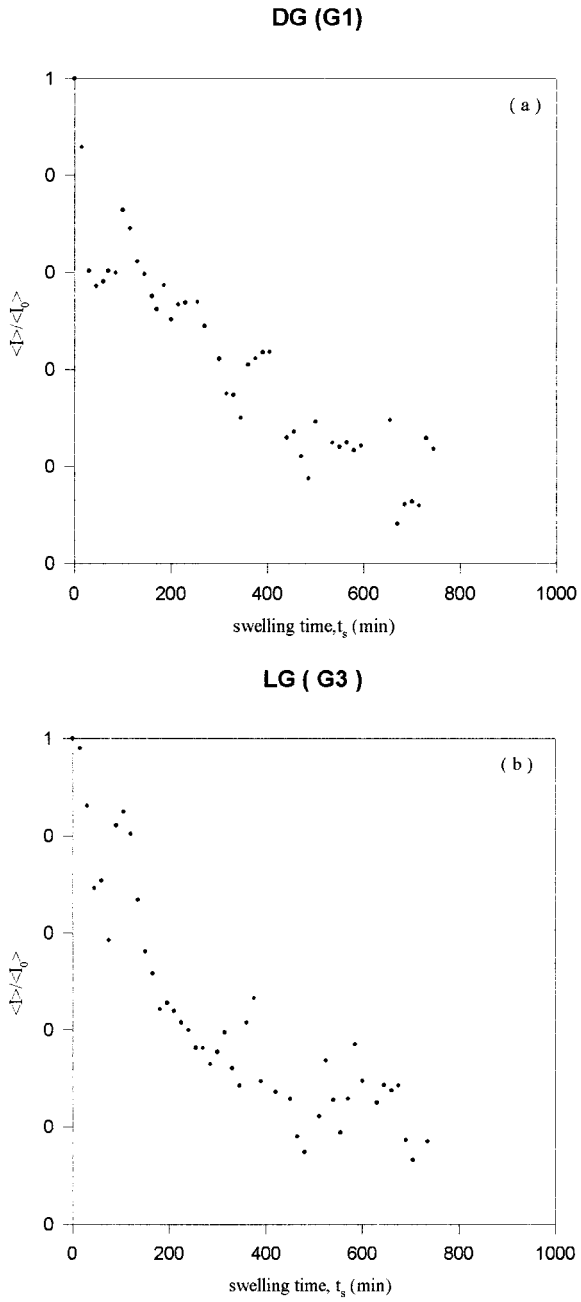

Figure 3 The normalized area under the fluorescence decay curves $\langle I \rangle$ are plotted vs. swelling time t_s for (a) G1 and (b) G3 samples, respectively.

and the measured τ_c, B_1, and D_c values are listed in Table I. It is seen that these values do not change much for the DG and LG gels.

Mean lifetimes of P were calculated from the relation

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

Using the τ_i and A_i values $\langle \tau \rangle$ values are obtained from eq. (12), and are plotted in Figure 5(a) and (b) for G1 and G3 gels where the exponential decrease of $\langle \tau \rangle$ is observed as the swelling time, t_s is increased. To quantify the above results, a Stern-Volmer type of quenching mechanism[39] may be proposed for the fluorescent decay of P in DG and LG gel samples during the swelling pro-

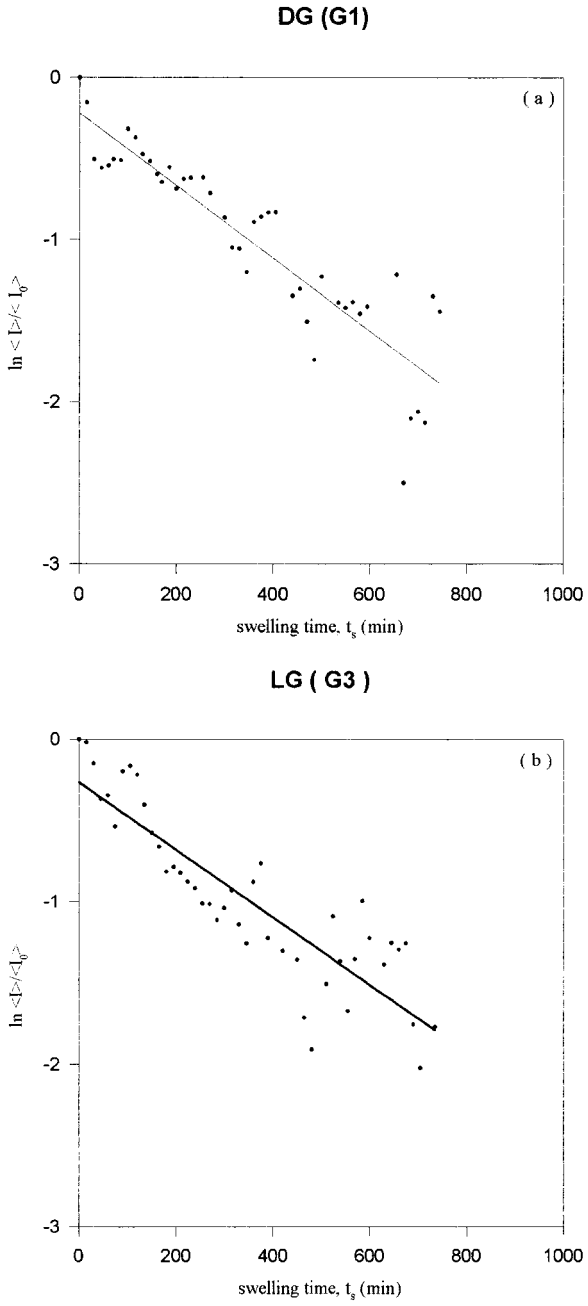

Figure 4 Linear regression of the data in Figure 3(a) according to eq. (11) for the (a) G1 and (b) G3 samples, respectively.

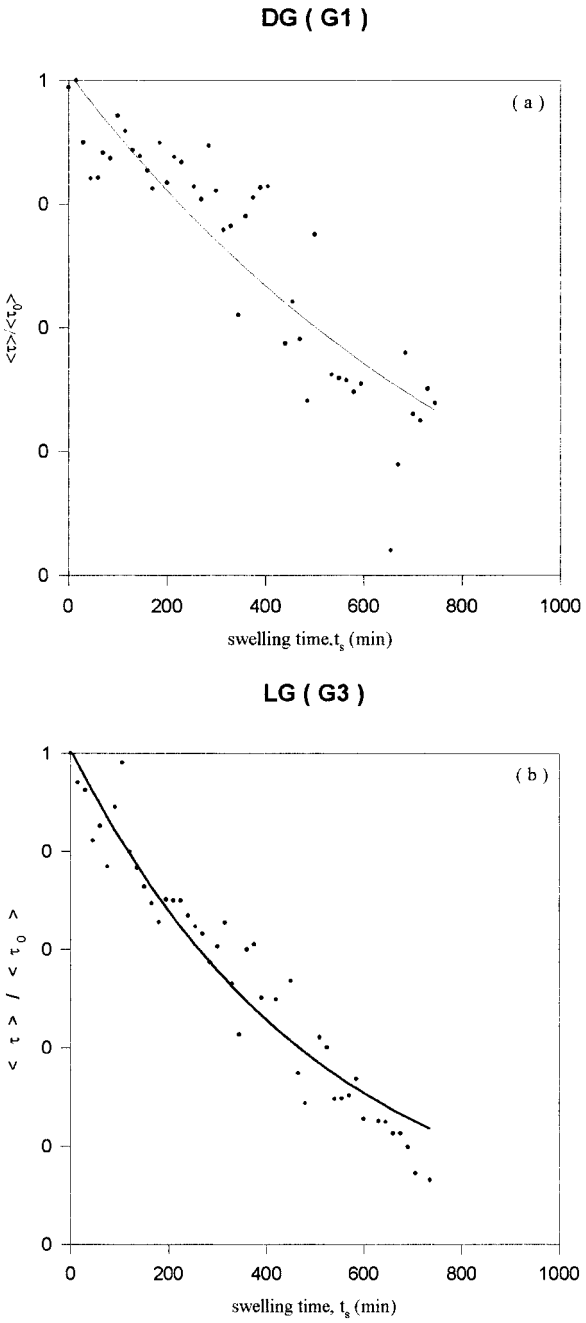

Figure 5 Normalized mean lifetimes $\langle\tau\rangle$ of P are which obtained from eq. (12) and are plotted vs. swelling time, t_s, for (a) G1 and (b) G3 samples, respectively.

cess, where the following law for the lifetime is satisfied.

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

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

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

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

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

where d 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, the following relation is obtained.

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

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

$$W = \int_{a_0}^{a} [W] dv \tag{17}$$

Equation (16) can be fitted to the normalized mean lifetimes of P in Figure 5(a) and (b) for G1 and G3 gel samples. Using known B_1 values τ_c, D_c, and κ parameters are obtained, and are listed in Table I for all DG and LG samples. Here, one should have noticed that measured D_c, τ_c, and κ values are found to be similar for all gel samples.

The quenching rate constant, κ, which is found to be as $10^5 M^{-1}\text{s}^{-1}$, is given by the following relation[39]

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

where $D_m = D_p + D_{ch}$ is the sum of the mutual diffusion coefficients of chromophore (P) and quencher (chloroform), respectively, $R = R_p + R_{ch}$ is the sum of their interaction radii, N_A is the Avagadro's number, and p is a factor describ-

ing 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 and chloroform molecules, respectively. The sum of the mutual diffusion coefficient was calculated form eq. (18) by using the average κ value, and was found to be around $D_m = 10^{-10}$ cm^{2}s^{-1}, where R is taken as 7.8 Å (i.e., $R_p = 3.98$ Å and $R_{ch} = 3.88$ 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] and is much smaller than the cooperative diffusion coefficient, D_c. This result is expected, because the element of swollen network moves much faster—due to the restraining forces—than the P and chloroform molecules in the swollen, viscous environment.

As the network is swollen by absorption of solvent, the chains between the network junction are required to assume elongated configurations, and a force akin to the swelling process. As the swelling proceeds, this force increases and the dilution force decreases. The force of retraction in a stretched network structure also depends on the degree of crosslinking.[40] In this work, because the crosslinker density was kept constant for all gels, no structural differences are expected. The fact that DG and LG gels show similar τ_c, D_c, and D_m values can be understood by realizing the fact that both gels have a similar degree of crosslinking. The only differences in DG and LG gels are the vacancies in the structure that were formed during the solution polymerization by varying the toluene content. During swelling, these vacancies are filled up by chloroform. Penetration of chloroform into the network in DG and LG gels in time should be similar, due to the same degree of crosslinking; as a result, all gels present similar τ_c, D_c, and D_m values. The cartoon representation of the swelling of DG and LG gels is presented in Figure 6, where the DG gel presents fewer vacancies than the LG gel; however, the network structure of both gels are similar. After swelling [see Fig. 6(b)], it is seen that network structures do not change in either gel.

In conclusion this work presents a novel technique (FTRF) for studying gel swelling using fluorescent probes. In this technique, two advantages have to be mentioned compare to the other techniques. In Fast transient fluorescence, which uses SMS, lifetime measurement takes much shorter time than single-photon counting and phase instrument techniques. This advantage allows one to measure hundreds of lifetimes during the gel swelling process. The second and the most important advantage of the FTRF technique is that one does not need to make any turbidity corrections, which are very critical in using the steady-state fluorescence (SSF) technique,[32,33] because in SSF, intensity measurements are made; however, in FTRF, lifetimes are measured.

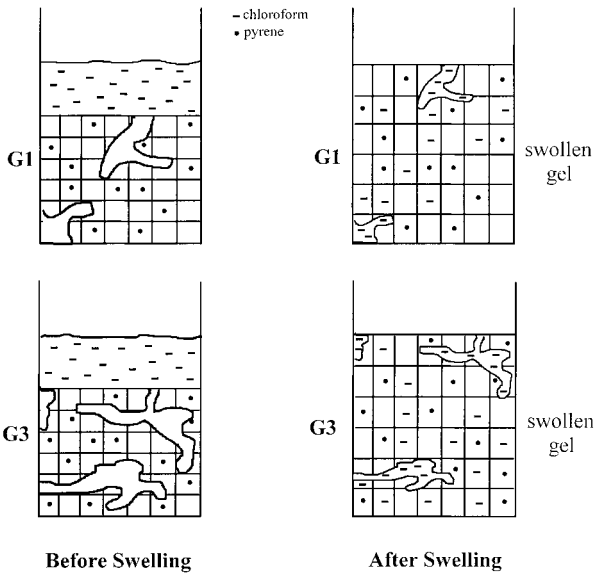

Figure 6 The cartoon representation of swelling of DG and LG gels are presented for G1 and G3 samples, respectively.

Here, one can predict that the FTRF technique can be used to monitor sol-gel phase transition in real time, which take minutes, during which at least 10 to 20 lifetime measurements can be carried out. If one can perform DET measurements at the percolation threshold[29,30] during sol-gel transition, one may succeed in determining the fractal dimension of a percolation cluster. This kind of study may help one to compare gelation models, which have been quite a debate in the last few decade.

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