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B. Yönel[a]; M. Erdoğan[a]; Ö. Pekcan[a]
[a] Department of Physics, Istanbul Technical University, Maslak, Turkey

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Fast Transient Fluorescence (FTRF) Technique for Swelling of Gels in Solvent Mixtures

B. Yönel, M. Erdoğan, and Ö. Pekcan*

Department of Physics, Istanbul Technical University,
Maslak, Istanbul, Turkey

ABSTRACT

Strobe Master System (SMS), is introduced for studying THE swelling of disc shaped gels in chloroform–heptane mixtures. 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 existence of P were measured using (SMS) during *in situ* swelling processes. Various percents of chloroform in chloroform–heptane mixtures were used as a swelling agent. For the duration, τ_2 of P in the gel were found to be decreased as swelling proceeded. Li–Tanaka's equation was employed to determine the time constants, τ_c and cooperative diffusion coefficients, D_c which were found to be decreased and increased respectively by increasing the chloroform content in the solvent mixtures.

INTRODUCTION

Fluorescence dyes can be used to study local environments, basically with two types of experiments. When the dye is simply added to the system as a small molecule, the dye is referred to as a probe which is available commercially. Consequently, such experiments are easy to carry out, but are often difficult to interpret because one has to know where the

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*Correspondence: Ö. Pekcan, Department of Physics, Istanbul Technical University, Maslak, Istanbul, 80626, Turkey; E-mail: pekcan@itu.edu.tr.

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dye is located in the system. If one can prepare an experiment which allows the dye to be attached covalently to a specific component of a system such as a polymer chain segment, the dyes are referred to as labels. The question can be raised whether the presence of the dye disturbs the system or disturbs its own local environments in the system. Disturbances are most common where high dye concentration leads to aggregation, and in crystalline systems where the order in the system can be affected by the dye. Disturbances are much less likely when the fluorescent dye is incorporated into an amorphous fluid or glassy phase.

Volume phase transitions in gels may occur from dry to swollen states either continuously, or by sudden jumps from one state to the other.[1,2] The equilibrium swelling of gels in solvent has been studied extensively.[3–5] The swelling process of chemically cross-linked gels can be understood by considering the osmotic pressure vs. the restraining elastic force.[6–8] 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 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. The shear energy minimizes the nonisotropic deformations in the gel. The theory of swelling kinetics for a spherical chemical gel was first developed by Tanaka and Filmore,[9] where the assumption is made that the shear modulus G is negligible compared to the osmatic bulk modulus. Peters and Candau[10] derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming non-negligible 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. 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,[11] quasielastic light-scattering[10] macroscopic experiments[7] and *in situ* interferometric[12] measurements. Time resolved and steady-state fluorescence techniques were employed to study isotactic polystyrene in its gel state[13] where excimer spectra were used to monitor the behavior of two different corformations in the gel state of polystyrene. A pyrene derivative was used as a fluorescence molecule for monitoring the polymerization, aging and drying of aluminosilicate gels.[14] These results were interpreted in terms of chemical changes occurring during the sol–gel transition and the interactions between the chromophores and the sol–gel matrix.

In situ observations of the sol–gel transition in free-radical crosslinking copolymerization, using the steady-state fluorescence technique, were reported.[15,16] The same technique was also applied for studying swelling and drying kinetics in disc shaped gels.[17,18] Recently, fast transient fluorescence technique (FTRF) was used to monitor the swelling of poly(methyl methacrylate) (PMMA) gels.[19,20]

In this work, swelling of gels formed by free radical copolymerization (FCC) of methyl-methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) was studied in chloroform–heptane mixtures using the FTRF technique. Lifetimes of pyrene (P) which is embedded in the gel were followed during the *in situ* swelling processes. A Strobe Master System (SMS) was used for duration measurements of P in the gel. Duration measurements with SMS takes a much shorter time than is required in single photon counting systems and phase instruments. This advantage of SMS allows one to make hundreds of measurements during the swelling process of gels. For this reason, we named this technique Fast Transient Fluorescence (FTRF), which gives us many advantages compared to other existing measuring techniques. It is observed that as the gel swells the existence of P in the gel decreases which can be modeled by the using low quenching Stern–Volmer equation. Cooperative diffusion coefficients, D_c were determined in respect to the chloroform content in the chloroform–heptane mixtures by employing the Li–Tanaka equation.

KINETICS OF SWELLING

It has been suggested[6] 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_∞ are the swelling or solvent uptake at time t and infinite equilibrium, respectively. W(t) can also be considered as volume difference of the gel at the times 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 independent of time t. Here B_n is given by following relationship[6]:

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

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 modulus, K, $M = K + 4G/3$, and α_n are the roots of the Bessel function 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 of the zeroth and first order.

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 relationship[7]

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

Here, the diffusion coefficient D_c is given by $D_c = M/f = (K + 4G/3)/f$, f is the friction coefficient describing the viscous interaction between the polymer and the solvent, and *a* represent half of the disc thickness in the final infinite equilibrium which can experimentally be 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 final stage of the swelling. If $n > 1$, α_n increases and τ_n decreases very rapidly [see Eq. (4)]. Therefore, the kinetics of swelling in the limit of large t, or if τ_1 is much larger than the rest of τ_n, all higher order terms ($n \geq 2$) in Eq. (1) can be neglected, and the swelling and shrinking can be represented by first order kinetics.[6] In this case, Eq. (1) simplifies to:

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

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

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 proves the mentioned the first order kinetics. The higher order terms ($n \geq 2$) can be considered as fast decaying perturbation to the first order kinetics of swelling in the limit of large t.

EXPERIMENTAL

EGDM has been commonly used as a crosslinker in the synthesis of polymeric networks. 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 swelling agent chloroform (Merck), was distilled twice over sodium.

The radical copolymerization of MMA and EGDM was performed at 65°C in the presence of 2,2′-azobisisobutyronitrile (AIBN) (0.26 wt%) as an initiator. P was added as a fluorescence probe during the gelation process. The sample was deoxygenated by bubbling nitrogen through the solution for 10 min, then the radical copolymerization of MMA and EGDM was performed at 65 ± 2°C. The EGDM content was kept at 0.035 vol%, and the P concentration was taken as 4×10^{-4} M. After completed gelation, the cylindrical gel sample was dried under vacuum and cut into the disc shaped gels for the swelling experiments.

Fluorescence decay experiments were performed using a Photon Technology International (PTI) Strobe Master System (SMS). In the strobe, or pulse sampling technique[21,22] the sample is energized by a pulsed light source. The name arises from the Photo Multiplier Tube (PMT) that is gated or *strobed* by a voltage pulse that is synchronized with the pulsed light source. The intensity of the fluorescence emission is measured in a very narrow time window on each pulse and saved in a computer. The time window is moved to a larger time after each pulse. The strobe has the effect of turning of the PMT and measuring the emission intensity over a very short time window. When the data have been sampled over an appropriate range of time, a decay curve of fluorescence intensity as a function of time can be established.

The *in situ* swelling experiment was carried out in the SMS of PTI, by 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 395 nm during the *in situ* swelling experiment which was performed at room temperature. A disc shaped gel sample was placed in

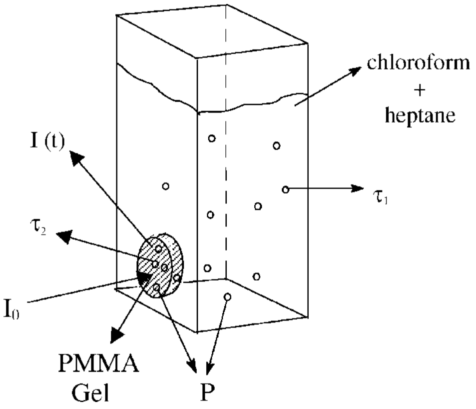

Figure 1. Cartoon representation of the gel position in the fluorescence cell. I_0 and I are the incident and fluorescence light beams respectively. Small dots present the Pyrene molecules. τ_2 and τ_1 are the pyrene lifetimes inside and outside the gel.

a 1 cm × 1 cm quartz cell filled with chloroform–heptane mixtures for swelling process. The position of the disc shaped gel and the incident and fluorescence light beams are shown in Fig. 1 for illustration. The fluorescence decay data were collected over three decades in time and fitted by nonlinear least squares of exponential functions using a deconvolution

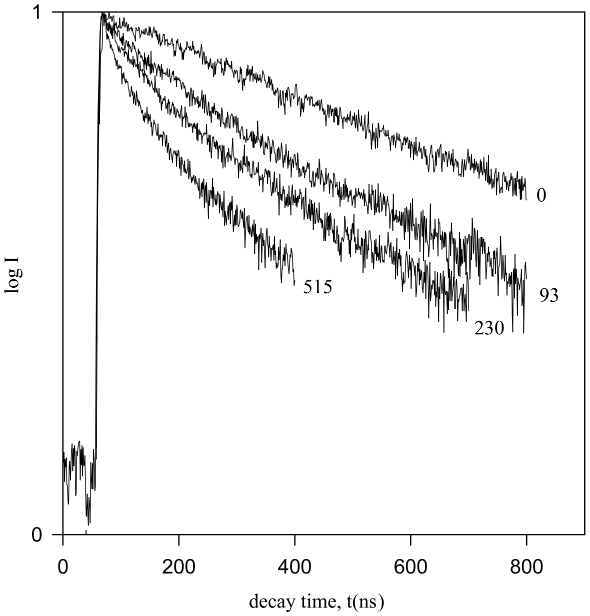

Figure 2. Fluorescence profiles at various swelling steps. The number on each curve present the swelling time in minutes.

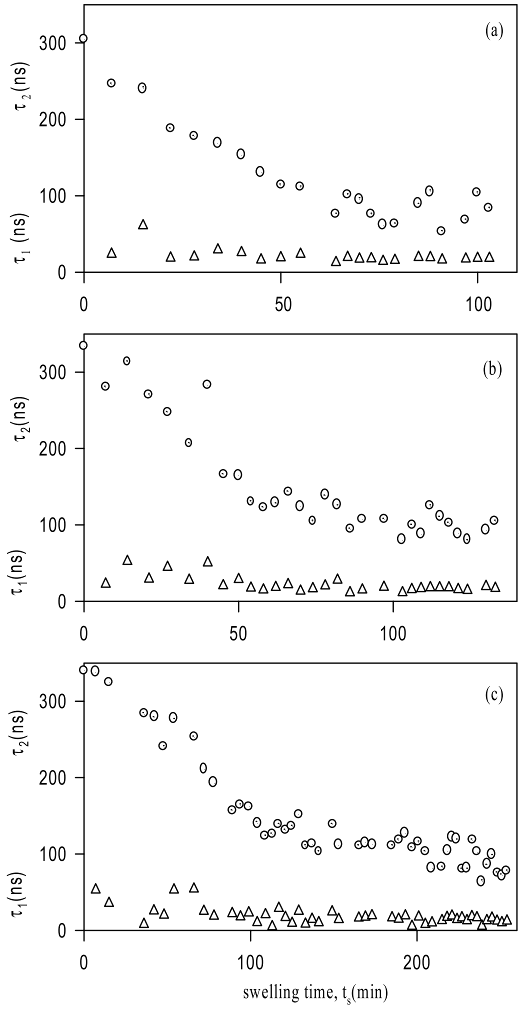

Figure 3. The plot of the measured τ_1 and τ_2 values versus swelling time, t_s for a—100, b—90, c—80% of chloroform contents.

method with a dry gel as a scatterer standard. The quality of the data fit to the model is checked by χ^2 ($\chi^2 \leq 1.10$), the distribution of the weighted residuals and the autocorrelation of the residuals.

RESULTS AND DISCUSSIONS

Figure 2 presents the fluorescence decay profiles at various swelling stages (0, 93, 230 and 515 min). As the swelling time, t_s is increased, the excited pyrenes decay faster and

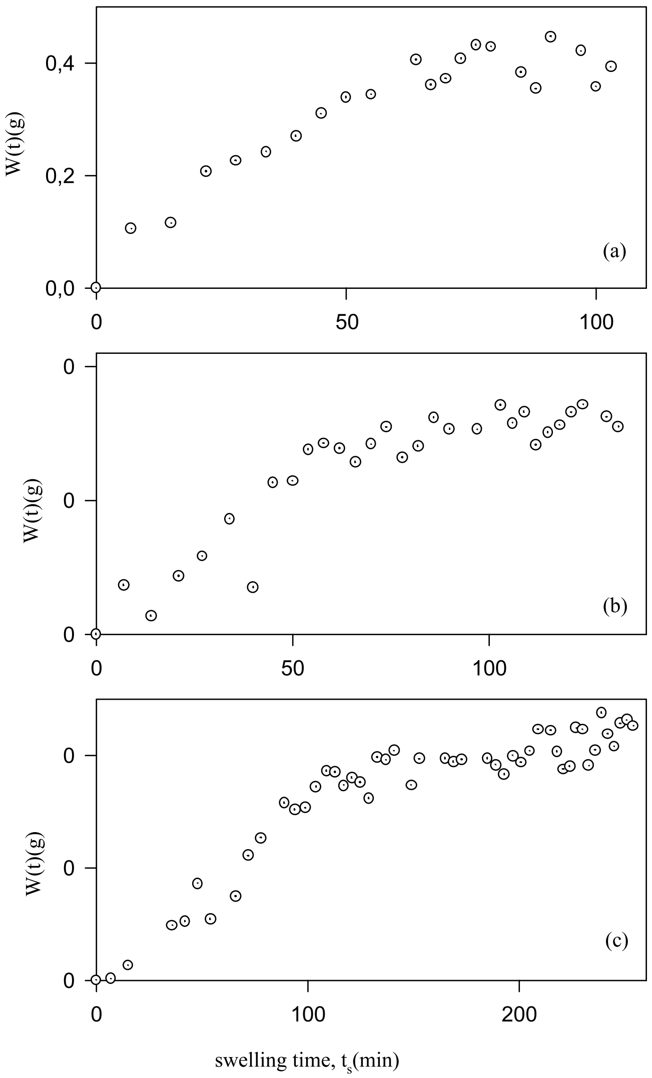

Figure 4. Plot of the solvent uptake, W vs. swelling time, t_s for a—100, b—90, c—80% of chloroform contents.

faster. It indicates that as the solvent uptake is increased, the quenching of excited pyrenes also increase. In order to probe the swelling process during solvent uptake, the fluorescence decay curves were measured and fitted to the sum of two exponentials:

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

where τ_1 and τ_2 are the pyrene lifetimes outside and inside of the gel. A_1 and A_2 are the corresponding amplitudes of the decay curves. Here, the role of the solvent in quenching is to add the quasi-continuum of states needed to satisfy energy resonance

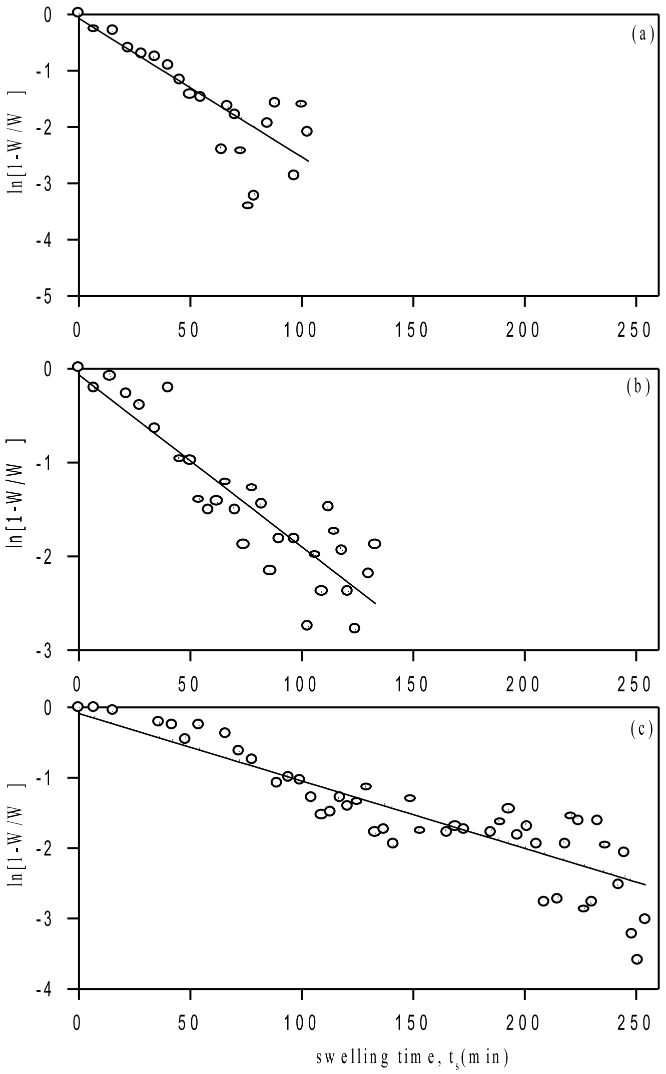

Figure 5. Fit of the data in Fig. 4 to Eq. (12). The slope of the curve produced τ_c values which are listed in Table 1.

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.* studied the influence of solvent viscosity on the fluorescence characteristics of pyrene solutions in various solvents and observed that the monomer internal quenching rate is affected by the solvent quality.[23]

The measured τ_1 and τ_2 values for the gel samples swollen in various chloroform–heptane mixtures are plotted versus swelling time, t_s in Fig. 3. The τ_1 values did not change much, but the τ_2 values decreased as t_s is increased. The decrease in τ_2 arises from solvent

Table 1.

% Chloroform	Δm (g)	a_∞ (cm)	τ_c (s)	B_1	α_1	D_c ($\times 10^{-5}$ cm^2 s^{-1})
100	0,40	0.29	2460	0.94	0.87	3.38
95	0,36	0.28	5040	0.97	0.64	2.95
90	0,16	0.27	3276	0.94	0.87	2.20
85	0,14	0.31	4200	0.93	0.95	1.96
80	0,21	0.3	6240	0.91	1	1.08
70	0,16	0.34	8640	0.93	0.95	1.14
60	0,17	0.31	9120	0.85	1.27	0.49
40	0,13	0.29	12000	0.89	1.15	0.39
20	0,02	0.23	23370	0.9	1.14	0.12

Experimentally measured; maximum solvent uptake, Δm; final disc thickness, a_∞; time constant, τ_c and cooperative diffusion coefficient, D_c.

quenching while the gel swells. As the chloroform content is increased in solvent mixture, τ_2 decrease increasingly faster, i.e., in Fig. 3a, τ_2 decreases much more rapidly than in Fig. 3b,c. The effect of solvent quality 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 in the gel sample during the swelling process.[24] The following relationship for the existence in the gel was satisfied.

$$\tau_2^{-1} = \tau_{20}^{-1} + k_q[W] \tag{8}$$

where τ_{20} is the duration of P in dry gel in which no quenching has taken place, k_q is the quenching rate constant and [W], the solvent concentration in the gel for a certain solvent uptake. For low quenching efficiency, i.e., $\tau_{20}k_q[W] < 1$, Eq. (8) becomes

$$\tau_2 \approx \tau_{20}(1 - \tau_{20}k_q[W]) \tag{9}$$

The solvent uptake, W is obtained from volume integration:

$$W = \int_{a_0}^{a_\infty} [W] d\nu \tag{10}$$

Where $d\nu$ 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:

$$W = \left(1 - \frac{\tau_2}{\tau_{20}}\right)\frac{\nu}{k_q\tau_{20}} \tag{11}$$

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 gels swollen in 100, 90 and 80% chloroform contents are shown in Fig. 4a–c, respectively. These are typical solvent uptake curves following the Li–Tanaka Equation [Eq. (5)].

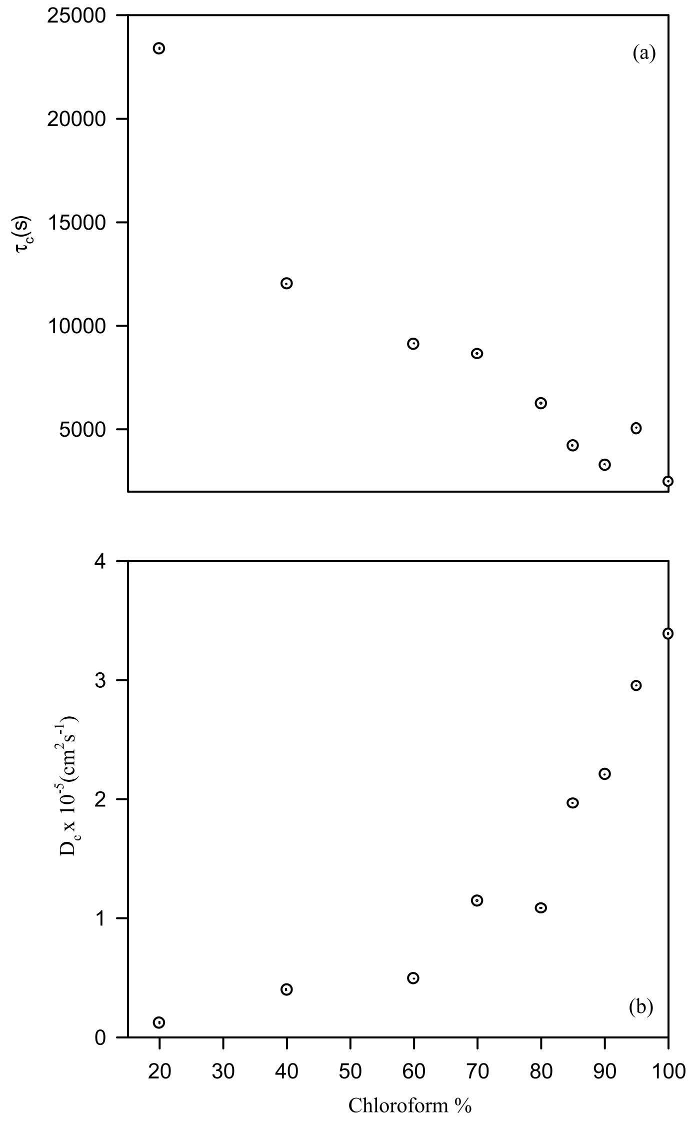

Figure 6. The plot of a—τ_c and b—D_c values versus chloroform %.

The logarithmic data in Fig. 4 were fitted to the corresponding relationship of Eq. (5):

$$\ln\left(1-\frac{W}{W_\infty}\right)=\ln B_1-\frac{t_s}{\tau_c} \tag{12}$$

The fits are presented in Fig. 5, from which B_1 and τ_c values were obtained. These are listed in Table 1. The plot of τ_c vs. the chloroform percentage is shown in Fig. 6a. As

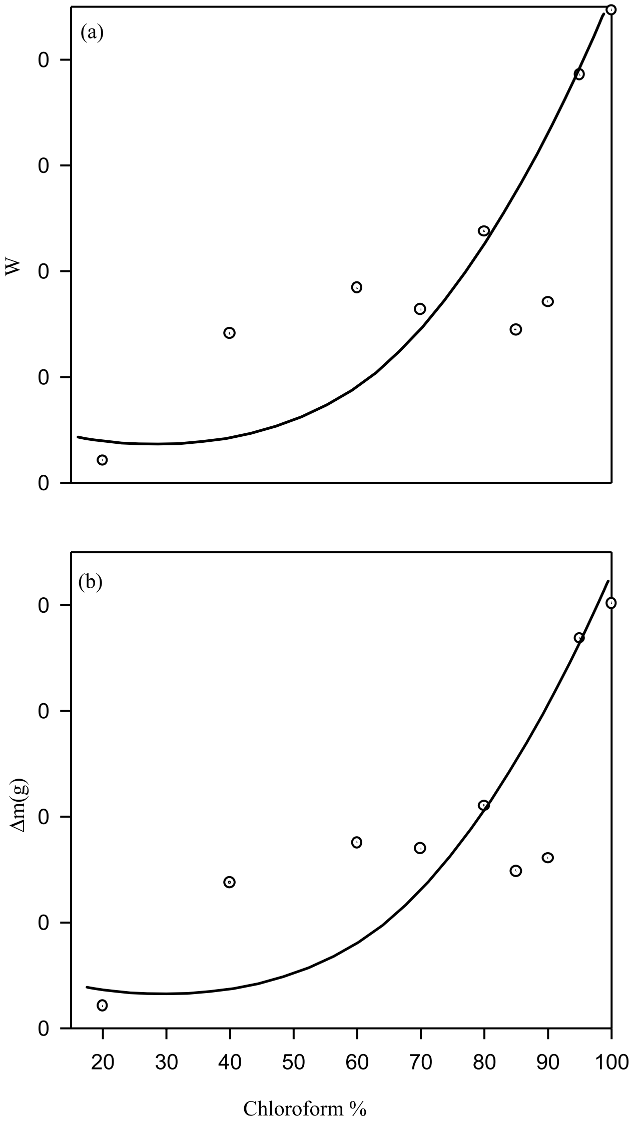

Figure 7. The plot of maximum solvent uptakes measured a—from existing measurements, b—from weighing measurements using micro-balance.

expected, the penetration of solvent molecules slows down as the heptane content is increased. A decrease in the solvent quality prevents the gel from swelling. Knowing B_1, one can obtain α_1 and from Eq. (4), D_c. These data are ploted in Fig. 6b vs. chloroform content. The behavior of D_c in Fig. 6b is evidence for gel segments which move faster in a thermodynamically high quality solvent, i.e., in chloroform containing solvents, gel segments diffuse considerably faster.

W_∞ values could be obtained from the equilibrium regions in Fig. 4 and are plotted in Fig. 7a. Figure 7b presents the observed Δm values which were obtained by subtracting the final weight of the gel from its initial weight. In fact, the Δm and W_∞ values are the parameters similar to each other but measured by different techniques. As shown in Figs. 7a,b they behave quite similarly with regard of the chloroform content. Comparing Fig. 6b with Fig. 7, it is seen that in poor solvent quality (high heptane content) the gel does not swell much. The segments move rather slowly compared to those in gels swollen in the good solvent quality (high chloroform content).

CONCLUSION

We showed that the FTRF technique can be used to measure cooperative diffusion coefficients, D_c, of the segment as a function of solvent quality during swelling a polymeric gel. One may speculate that measuring duration by FTRF in swelling gels may provide data which could be used for determining the rate of solvent penetration. In this paper, we introduced the FTRF method to study gel swelling in solvents of various quality. Solvents of poor solution quality penetrates the gel much more slowly than a solvent of good solution quality. Gels swell much faster and to a larger extent in high quality solvent than in bad quality solvents.

REFERENCES

1. Dusek, K.; Peterson, D. Transition in swollen polymer networks induced by intramolecular condensation. J. Polym. Sci. **1968**, *A2*, 1209.
2. Tanaka, T.; Fillmore, D.; Sun, S.T.; Nishio, I.; Swislow, G.; Shah, A. Phase transitions in ionic gels. Phys. Rev. Lett. **1980**, *45*, 1636.
3. Tobolsky, A.V.; Goobel, J.C. The equation of state for rubber elasticity. The effect of swelling on the front factor. Macromolecules **1970**, *3*, 556.
4. Schild, A.G. Poly(N-isopropylacrylamide) experiment, theory and application. Prog. Polym. Sci. **1992**, *17*, 163.
5. Amiya, T.; Tanaka, T. Phase transition in crosslinked gels of natural polymers. Macromolecules **1987**, *20*, 1162.
6. Li, Y.; Tanaka, T.J. Kinetics of swelling and shrinking of gels. Chem. Phys. **1990**, *92*, 1365.
7. Zrinyi, M.; Rosta, J.; Horkay, F. Studies on the swelling and shrinking kinetics of chemically crosslinked disc-shaped poly(vinyl acetate) gels. Macromolecules **1993**, *26*, 3097.
8. Candau, S.; Bastide, J.; Delsanti, M. Structural elastic and dynamic properties of swollen polymer network. Adv. Polym. Sci. **1982**, *44*, 27.
9. Tanaka, T.; Filmore, D. Kinetics of swelling of gels. J. Chem. Phys. **1979**, *20*, 1214.
10. Peters, A.; Candau, S.J. Kinetics of swelling of spherical and cylindrical gels. Macromolecules **1988**, *21*, 2278.

11. Bastide, J.; Duoplessix, R.; Picot, C.; Candau, S. Small angle neutron scattering and light spectroscopy investigation of polystyrene gels under osmotic deswelling. Macromolecules **1984**, *17*, 83.
12. Wu, C.; Yan, C.Y. Studies on the swelling and drying kinetics of thin gelatin gel films in situ interferometry. Macromolecules **1994**, *27*, 4516.
13. Wandelt, B.; Birch, D.J.S.; Imhof, R.E.; Holmes, A.S.; Pethnick, R.A. Photophysical studies of isotactic polystyrene in its gel state. Macromolecules **1991**, *24*, 5141.
14. Panxviel, J.C.; Dunn, B.; Zink, J.J. Fluorescence study of alumino silicate sols and gels doped with hydroxy trisulfonated pyrene. J. Phys. Chem. **1989**, *93*, 2134.
15. Pekcan, Ö.; Yilmaz, Y.; Okay, O. In situ fluorescence experiments to test reliability of random bond and site bond percolation models during sol-gel transition in free-radical crosslinking copolymerization. Polymer **1996**, *37*, 2049.
16. Pekcan, Ö.; Yilmaz, Y.; Okay, O. Determination of reaction activation energy durin gelation in free-radical crosslinking copolymerization using steady-state fluorescence method. J. Appl. Polym. Sci. **1996**, *61*, 2279.
17. Pekcan, Ö.; Yilmaz, Y. Fluorescence methos to study gelation swelling and drying processes in gels formed by solution free-radical crosslinking copolymerization. Prog. Colloid Polym. Sci. **1996**, *102*, 89.
18. Pekcan, Ö.; Yilmaz, Y. In-situ fluorescence experiments to study swelling and slow release kinetics of disc-shaped poly(methyl methacrylate) gels made at various crosslinker density. Polymer **1998**, *39*, 5351.
19. Pekcan, Ö.; Kaya, D.; Erdoğan, M. Fast transient fluorescence technique for monitoring swelling of poly(methyl methacrylate) gels. Polymer **2000**, *41*, 4915.
20. Erdoğan, M.; Pekcan, Ö. Temperature effects on gel swelling; a fast transient fluorescence study. Polymer **2001**, *42*, 4973.
21. Lakowicz, J.R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983.
22. Ware, W.R.; James, D.R.; Siemiarczuk, A. Stroboskopic optical boxcar technique for the determination of fluorescence lifetimes. Rev. Sci. Instrum. **1992**, *63*, 1710.
23. Birks, J.B.; Lumb, M.D.; Mumra, J.H. Exoimer fluorescence (V), influence of the solvent viscosity and temperature. Proc. R. Soc. A **1964**, *280*, 289.
24. Birks, J.B. *Photophysics of Aromatic Molecules*; John Wiley-Interscience: London, 1970; 90.

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