Modeling of Swelling by Fluorescence Technique in Poly(methyl methacrylate) Gels

Ö. PEKCAN, Y. YILMAZ

Istanbul Technical University, Department of Physics, 80626 Maslak, İstanbul Turkey

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ABSTRACT: A novel technique based on *in-situ* steady-state fluorescence (SSF) measurements is introduced for studying swelling processes in gels formed by free radical cross-linking copolymerization (FCC) of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) in toluene. Gels were prepared at 75°C for various toluene contents with pyrene (Py) as a fluorescence probe. After drying these gels, swelling and desorption experiments were performed in toluene at 50°C by real-time monitoring of Py fluorescence intensity. A correction method was developed to obtain pure swelling curves, by using desorption curves of Py molecules. Li–Tanaka equation was employed to produce swelling parameters. Cooperative diffusion coefficients (D_c) were measured and found to be around 10^{-6} cm^2/s for gels swollen in toluene. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1777–1784, 1997

Key words: fluorescence; swelling; gel; desorption; cooperative diffusion

INTRODUCTION

The swelling process of chemically cross-linked gels can be understood by considering the osmotic pressure versus the restraining force.[1–5] 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 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,[6] where the assumption is made that the shear modulus G is negligible compared to the osmotic bulk modulus. Later, Peters and Candau[7] has derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming non-negligible shear modulus. Recently, Li and Tanaka[1] 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 among which are neutron scattering,[8] quasielastic light-scattering,[7] macroscopic experiments[2] 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,[10] where peak ratios in emission spectra were monitored during these processes. The volume phase transition of poly(acrylamide) gels were monitored by fluorescence anisotropy and lifetime measurements of dansyl groups.[11] Recently, we reported *in situ* observations of the sol-

Correspondence to: O. Pekcan

gel phase transition in free-radical crosslinking copolymerization, using the steady-state fluorescence (SSF) technique.[12,13]

In this work, swelling parameters of gels formed by free radical crosslinking copolymerization (FCC) of methyl methacrylate (MMA), and ethylene glycol dimethacrylate are reported. Pyrene (P_y) was used as a fluorescence probe to monitor swelling and desorption processes in real time during *in situ* fluorescence experiments. Desorption curves are subtracted from the swelling curves to obtain pure swelling behavior of these gels.

KINETICS OF SWELLING

Li and Tanaka showed that the kinetics of swelling and shrinking of a polymer network or gel obey the following relation:[1]

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

where $W(t)$ and W_∞ are the swelling or solvent uptake at time t and at infinite equilibrium, respectively. Here B_n represents a constant related to the ratio of shear modulus G and longitudinal osmatic modulus; M which is defined by the combination of shear and osmotic bulk moduli as[4,5] $M = \frac{4}{3}G + K$. τ_n is the swelling rate constant. In the limit of large t or if τ_1 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

$$\frac{W(t)}{W_\infty} = 1 - B_1 e^{t/\tau_1} \qquad (2)$$

Here B_1 is given by the following relation:[1]

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

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

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

In eq. (2), τ_1 is related to the collective cooperative diffusion coefficient D_c of a gel disk at the surface and given by the relation[2]

$$\tau_1 = \frac{3a^2}{D_c \alpha_1^2} \qquad (5)$$

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

EXPERIMENTS

The radical copolymerization of MMA and EGDM was performed in toluene solution at 75°C in the presence of 2,2′-azobisisobutyronitrile (AIBN) as an initiator. P_y 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 15 mm internal diameter. Six different samples were prepared using this stock solution with various toluene contents for solution polymerization. Details of the samples are listed in Table I. All samples were deoxygenated by bubbling nitrogen for 10 minutes, and then radical

Table I Swelling Parameters of Disk Shaped Gels[a]

Gels	1	2	3	4	5	6
Toluene vol %	0.10	0.13	0.15	0.20	0.23	0.30
τ_1 (s)	3062	3631	1538	1545	1021	962
B_1	0.87	0.86	0.59	0.67	0.74	0.78
α_1	1.33	1.40	2.16	2.0	1.77	1.64
$D_c \times 10^{-6}$ (cm^2/s)	8.62	10.32	6.67	6.34	12.37	16.08
a (cm)	0.12	0.15	0.12	0.11	0.11	0.11

[a] τ_1 and B_1 values were obtained from eq. (8) by linear regression of the swelling data in Figure 8.

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 $4 \times 10^{-4} M$.

EGDM has been commonly used as crosslinker in the synthesis of polymeric networks.[14] 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 (Merck), was distilled twice over sodium.

SSF measurements were carried out using a Perkin Elmer Model LS-50 spectrofluorimeter equipped with temperature controller. All measurements were made at the 90°C position, and slit widths were kept at 2.5 mm. *In situ* swelling and desorption experiments were both performed in a 1 × 1 cm quartz cell at 50°C. Gel samples were attached at one side of a quartz cell filled with toluene. This cell was placed in the spectrofluorimeter, and fluorescence emission was monitored at a 90°C angle so that, during the swelling experiment, only the gel was illuminated by the excitation light. During desorption experiments, gel samples were shifted slightly to upward position so that only the cell with toluene was illuminated by the excitation light. Here, the fluorescence emission from P_y molecules was monitored, which are desorbed from the swelling gels. Figure 1(a) and (b) present the fluorescence cell and the gel positions in swelling and desorption experiments, respectively. In both experiments, disk shaped gels were used, which were dried and cut from the cylindrical gels obtained from FCC.

During the swelling and desorption experiments, the cell was illuminated with 345 nm excitation light, and P_y intensity was monitored at 375 nm using the time drive mode of the spectrofluorimeter. In the swelling experiment, no shift was observed in the wavelength of maximum intensity of P_y. Gel samples, are kept their transparencies during these experiments. Typical fluorescence spectra of a gel before and after swelling are shown in Figure 2.

In swelling experiments, continuous volume transitions are expected, which should result in a continuous decrease in P_y during swelling. Here one may expect that as solvent uptake (W) increases, desorption of P_y molecules from the swollen gel increases; as a result, P_y intensity from the gel decreases. On the other hand, during desorption experiments, one may expect an increase in P_y intensity, due to increasing amount of P_y molecules that are released into toluene in the cell.

RESULTS AND DISCUSSIONS

P_y intensities, I_p, versus swelling time are plotted in Figure 3 for the gels prepared by toluene poly-

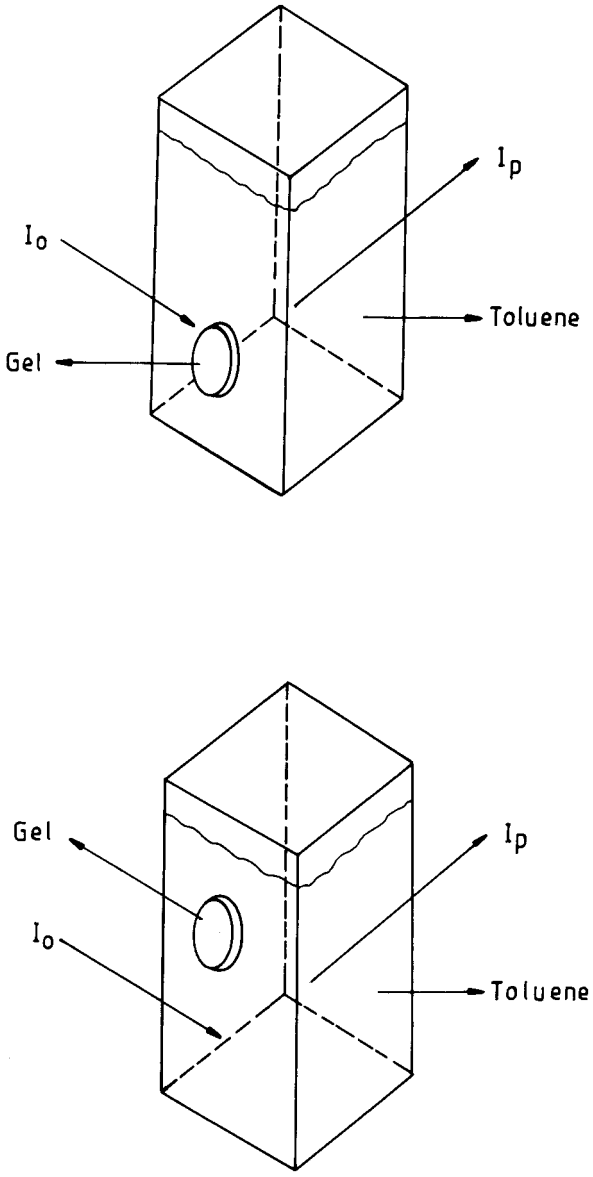

Figure 1 Fluorescence cell in LS-50 Perkin Elmer pectrofluorimeter. Monitoring of (a) gel swelling, and (b) slow release process. I_o and I_p are the excitation and emission intensities at 345 and 375 nm, respectively.

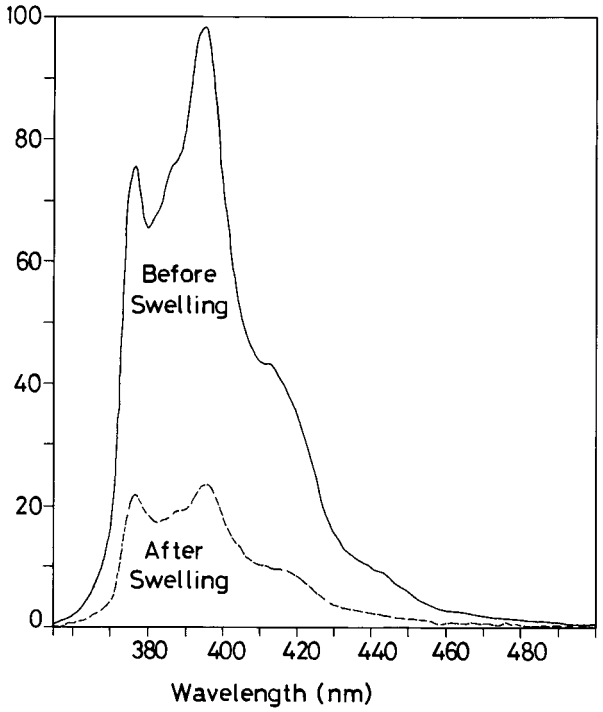

Figure 2 Emission spectra of pyrene (P_y) taken before and after the swelling process is completed. P_y is excited at 345 nm.

merization. The numbers in Figure 3 correspond to gel samples listed in Table I. It is interesting to note that solvent uptake is much faster in loosely formed gels (5 and 6) than densely formed gel (1).

The swelling curves in Figure 3 were obtained during *in situ* fluorescence experiments described in Figure 1(a), where at the beginning, all P_y molecules are in the gel and I_{os} are obtained. After solvent penetration starts, some P_y molecules are washed out from the swollen part of the gel into the cell; as a result, P_y intensity I_s from glassy gel decreases as the swelling time increase. At the equilibrium state of swelling, P_y intensity from glassy gel reaches to $I_{\infty s}$ value, where the solvent uptake by swollen gel is W_∞. The representation of these swelling stages is shown in Figure 4, where the intensity from the desorbed P_y molecules are presented by I_d. The relation between solvent uptake W and fluorescence intensity I_s from the glass part of gel is given by the following relation:

$$\frac{W}{W_\infty} = \frac{I_{os} - I_s}{I_{os} - I_{\infty s}} \qquad (6)$$

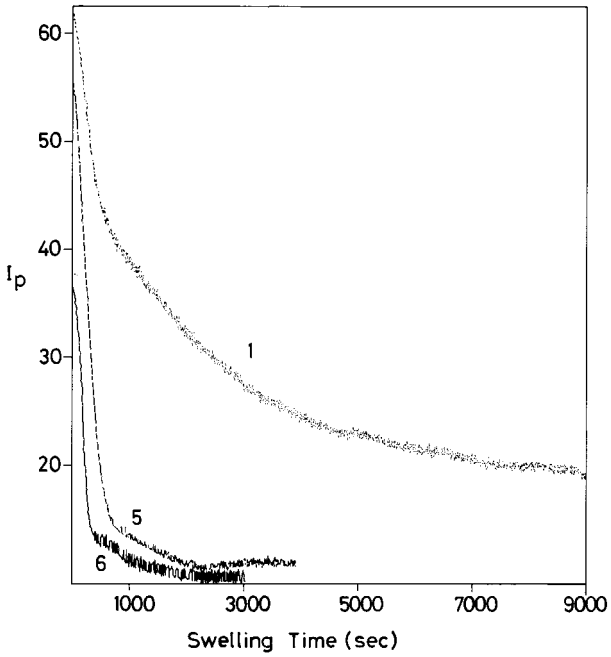

Figure 3 Total pyrene intensity I_p versus slow release time for the gel samples listed in Table I. The gel in the cell was illuminated at 345 nm during swelling measurements. Data for the plot were obtained using the time drive mode of the spectrofluorimeter.

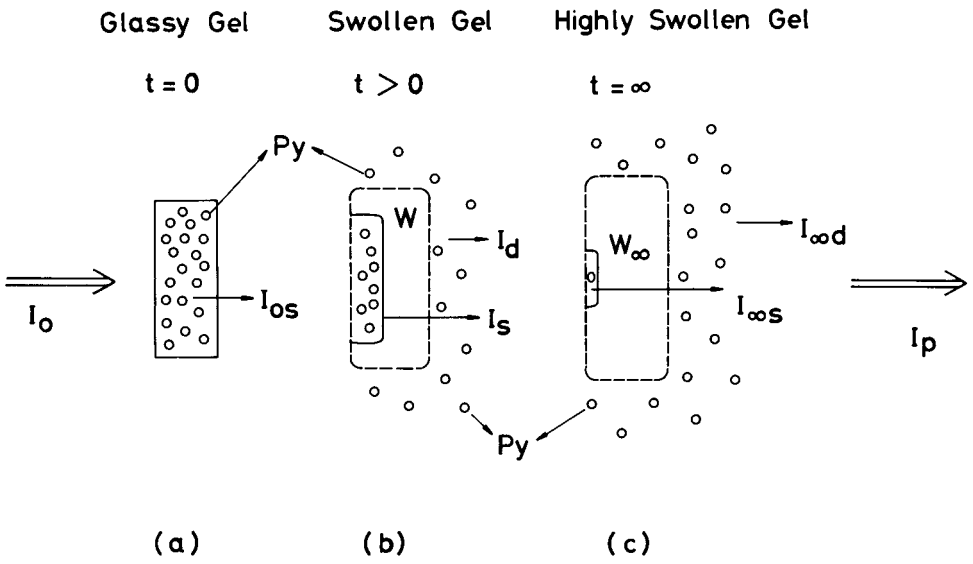

Figure 4 Representation of the swelling processes in the gel during solvent uptake. Fluorescence intensities from P_y molecules are also presented. (a) Gel before swelling, where I_{os} is the fluorescence intensity from glassy gel at $t = 0$. (b) Swollen gel, where I_s and I_d present the fluorescence intensities from glassy gel and desorbed P_y molecules at $t > 0$, and W is the solvent uptake. (c) Highly swollen gel, where $I_{\infty s}$ and $I_{\infty d}$ are the fluorescence intensities at $t = \infty$, and W_∞ is the solvent uptake at $t = \infty$.

Since $I_{os} \gg I_{\infty s}$, eq. (6) becomes

$$\frac{W}{W_\infty} = 1 - \frac{I_s}{I_{os}} \tag{7}$$

This relation predicts that as W increases, I_s decreases and is quite similar to the equation, used to monitor oxygen uptake by poly(methyl methacrylate) and poly vinyl acetate spheres.[15,16] Here, it is assumed that P_y molecules are completely washed out from the swollen part of the gel. Combining eq. (7) with eq. (2), the following useful relation can be obtained:

$$\ln(I_s/I_{os}) = \ln B_1 - t/\tau_1 \tag{8}$$

If one thinks that the fluorescence intensity curves in Figure 3 are originated only from the gels, then eq. (8) has to be obeyed by the data. The digitized form of the data in Figure 3 are plotted in Figure 5 using eq. (8), where we fail to observe the linear relation in the swelling curves, which is not surprising because, during the swelling experiments, desorbing P_y molecules also contribute to the florescence intensity, which prevents us to observe pure swelling curves, as shown in Figure 4. In fact, the data in Figure 3 present the total P_y intensity, I_p curves, during *in situ* swelling experiments, which are presented by the following relations at times:

$$\begin{aligned} t = 0, &\quad I_{op} = I_{os} + I_{od} \\ t > 0, &\quad I_p = I_s + I_d \\ t > \infty, &\quad I_{op} = I_{\infty s} + I_{\infty d} \end{aligned} \tag{9}$$

where I_d is the P_y intensity from the desorbing P_y molecules, as shown in Figure 4. Plots of I_d versus desorbing time for three different gels are shown in Figure 6, which are obtained from the experiments performed according to Figure 1(b). In Figure 6, I_d increases as the desorbing time increases for all the gel samples. Here, numbers represent the gels given in Table I and Figure 3. Since I_d is directly proportional to the number of P_y molecules in toluene, the behavior of the intensity curves in Figure 6 suggests that P_y molecules are desorbed much faster from loosely formed gels (5 and 6) than from densely formed gel (1).

In order to produce the pure swelling intensity (I_s) curves, data in Figure 3 are subtracted from the data in Figure 6 according to eq. (9) and plotted in Figure 7. In order to see the correctness of the pure swelling curves, data in Figure 7 are

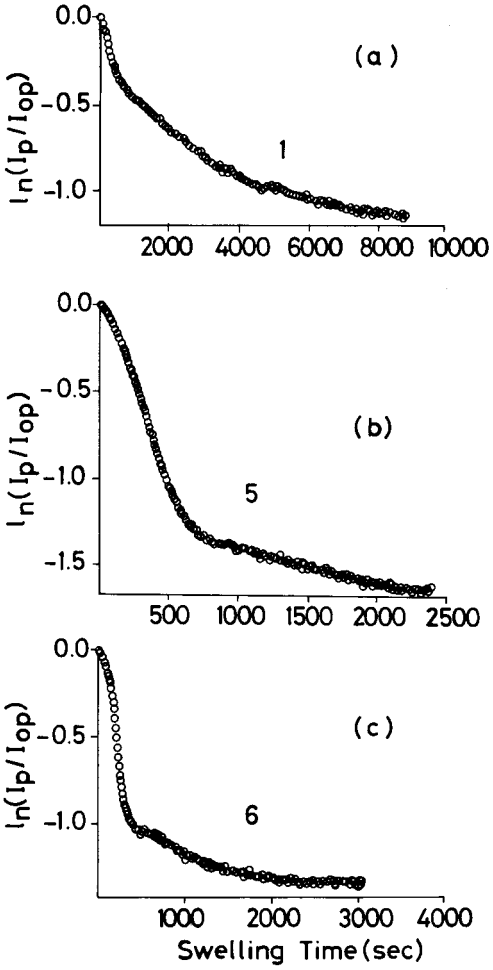

Figure 5 Logarithmic plot of digitized data in Figure 3 (a)–(c) present the data for the gel samples marked with 1, 5, and 6 in Figure 3 and Table I.

digitized according to eq. (8) and plotted in Figure 8, where nice linear relations are obtained except at very short and long time regions. Long time deviations are explained by the saturation of solvent uptake. Short time deviations may correspond to fast relaxation processes in the gel at the early swelling stage. Linear regression of curves in Figure 8 at an intermediate time region provides us with B_1 and τ_1 values from eq. (8). Fits are shown in Figure 9. Taking into account the dependence of B_1 on R, one obtains R values, and from $\alpha_1 - R$ dependence α values were produced.[1] Then, using eq. (5), cooperative diffusion coefficients D_c were determined for these disc shaped gels. Experimentally obtained parameters τ_1 and B_1, together with α_1 and D_c values, are summarized in Table I, where a values are also presented

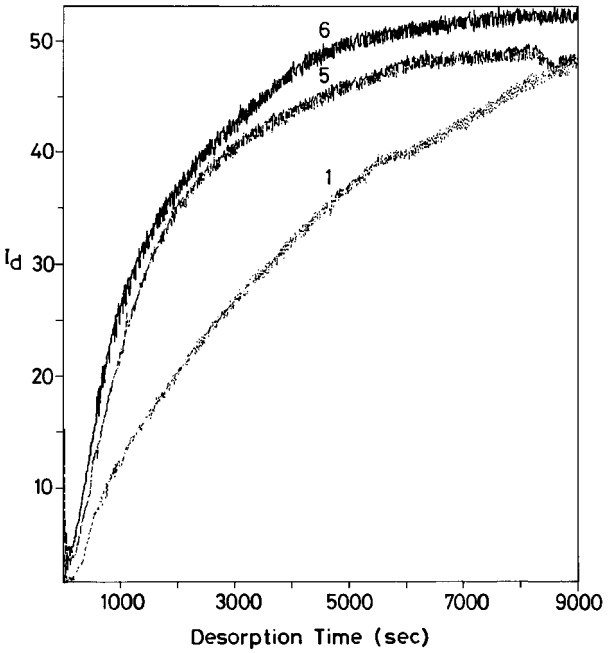

Figure 6 P_y intensity I_d from desorbing P_y molecules versus desorbing time for the gel samples listed in Table I. The cell was illuminated at 345 nm during desorption measurements. Data were obtained using time drive mode of the spectrofluorimeter.

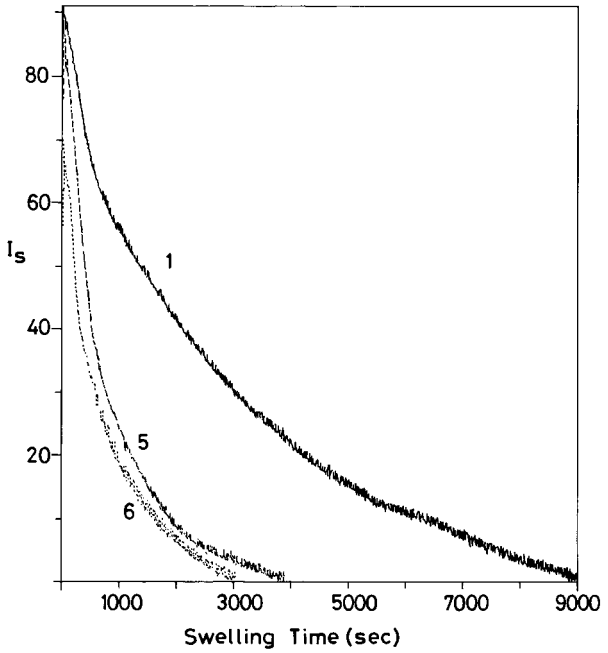

Figure 7 P_y intensity I_s from the glassy part of the gel, which is obtained by subtracting the data in Figure 3 from the data in Figure 6.

for each gel. Here, one should have noticed that measured D_c values present larger numbers for loosely formed gels than for densely formed gels. As expected, τ_1 values in Table I, however, show reverse dependence on D_c values; i.e., loosely formed gels have smaller τ_1 values than densely formed gels. This result can be understood by realizing the fact that loosely formed gel have more vacant spaces, which can take more solvent easily and need less time to reach a fully swollen state.

CONCLUSION

In this short article, preliminary results of the fluorescence technique for real-time monitoring of swelling processes in gels are presented. It is shown that, in this technique, *in-situ* fluorescence experiments are easy to perform and provide us quite sensitive results to measure the swelling parameters of gels. Here, one has to be careful to monitor swelling curves, which are highly screened by curves of P_y molecules desorbing from the swelling gels.

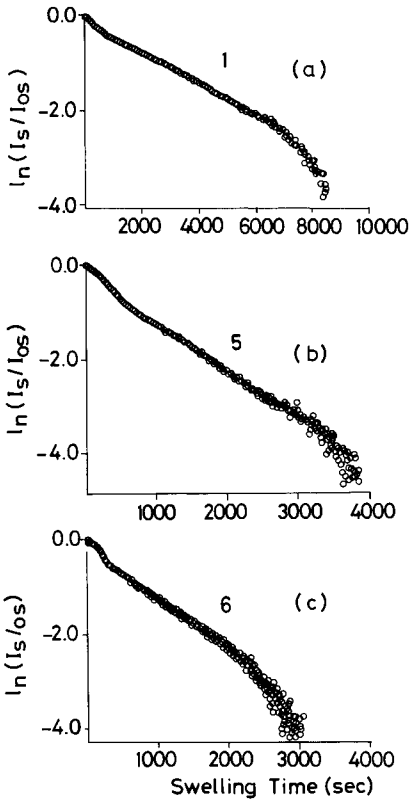

Figure 8 Logarithmic plot of the digitized data of Figure 7, which obey eq. (8). Data for the gel samples marked with 1, 5, and 6 in Figure 7 and Table I are presented in (a), (b), and (c).

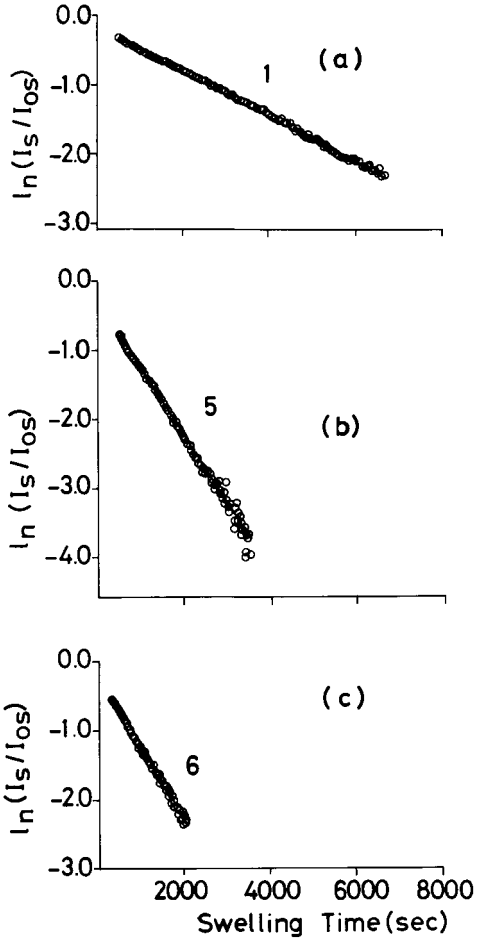

Figure 9 Lineer regressions of the data presented in Figure 8 at the intermediate time regions. B_1 and τ_1 values were obtained from the intersections and the slopes of the plots in (a), (b), and (c) for the gels marked with 1, 5, and 6 in Figure 8.

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