

Swelling and Drying Kinetics of Polytetrahydrofuran and Polytetrahydrofuran–Poly (methyl methacrylate) Gels: A Photon Transmission Study

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ABSTRACT: A bifunctional polytetrahydrofuran (PTHF) macromonomer was synthesized by termination of the living polymerization of tetrahydrofuran (THF) initiated by triflic anhydride and the subsequent termination by sodium methacrylate. The PTHF macromonomer thus prepared was polymerized and copolymerized with methyl methacrylate (MMA) by free-radical polymerization to yield a network and a segmented network of PTHF, both being homogeneous, respectively. These PTHF and PTHF–PMMA gels were used for swelling experiments in chloroform and chloroform vapor. Drying processes were monitored after removing the gels from the solvent and solvent vapor. Photon transmission from PTHF and PTHF–PMMA gels was monitored during swelling and drying processes using a UV-

visible (UVV) spectrophotometer. Transmitted light intensities, I_{tr} , from these gels increased when they were immersed in chloroform and/or subjected to its vapor. The increase in I_{tr} was attributed to the homogeneous lattice structure of PTHF and PTHF–PMMA gels which appeared during swelling. The increase in I_{tr} was modeled using the Li–Tanaka equation from which time constants, τ_1 , and cooperative diffusion coefficients, D_C , were determined. A decrease in I_{tr} after removing chloroform and/or its vapor from the cell was observed and attributed to the decrease in homogeneity of lattice structures during drying of the corresponding gels. Time constants, τ_2 , for the drying processes were also determined. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 632–640, 2003

INTRODUCTION

One of the most important features of the gel-swelling process is that it is isotropic; for example, in a long cylindrical gel when the radius increases 10%, the axial length increases 10%. In general, the elastic and swelling properties of permanent networks can be understood by considering two opposing effects: the osmotic pressure and the restraining force.^{1–3} Usually, the total free energy of a chemically crosslinked network can be separated into two terms: the bulk and the shear energies. In a swollen network, the characteristic quantity of the bulk free energy is the osmotic bulk modulus, K . The other important energy, the shear energy, keeps the gel in shape by minimizing the nonisotropic deformation. The characteristic coefficient of these forces is the shear modulus, μ , which can be most directly evaluated by stress–strain measurements.^{4,5} Li and Tanaka⁶ 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. The equilibrium swelling and shrinking of gels in solvents have been extensively studied.^{7,8} The swelling, shrinking, and drying kinetics of physical and chemical gels are important in many technological applications. Especially, in pharmaceutical industries, in designing slow-release devices for oral drugs and in using of cosmetic ingredients, understanding the kinetics is highly desirable. In the agricultural industry for producing storable foods and for medical applications for developing artificial organs, knowledge of the gel kinetics is an important requirement for the scientist in the field.

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,⁹ quasi-elastic light-scattering¹⁰ macroscopic experiments¹¹ and *in situ* interferometric¹² 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 existence of two different conformations in the gel state of polystyrene. A pyrene derivative was used as a fluorescence molecule to monitor the polymerization, aging, and drying of aluminosilicate gels.¹⁴ These results were interpreted in

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terms of the chemical changes occurring during the sol-gel process and the interactions between the chromophores and the sol-gel matrix. *In situ* observations of the sol-gel phase transition during free-radical crosslinking copolymerization, using the fluorescence technique were reported.¹⁵⁻¹⁷ The same technique was also performed for studying drying and swelling kinetics in disc-shaped gels.¹⁸⁻²⁰ Modeling of swelling using the fast transient fluorescence (FTRF) technique was recently reported from our laboratory.²⁰⁻²²

Aging of acrylamide (AAm) gels due to multiple swelling was studied using the photon transmission technique, where it was observed that the transmitted light intensity, I_{tr} , decreased continuously as the PAAm gel swelled.²³ The decrease in I_{tr} was attributed to the structural inhomogenities in the PAAm gel. The same technique was employed to study PAAm gel formation in various water²⁴ and crosslinker^{25,26} contents, where it was observed that the I_{tr} intensity decreased during gelation in both cases. The photon transmission technique was recently employed to study the swelling and drying of PAAm gels.^{26,27} It was observed that I_{tr} decreased and then increased during swelling and drying processes, respectively. The behavior of I_{tr} was explained by the lattice heterogenities which create frozen blobs during swelling; however, during drying, frozen blobs disappear and the lattice presents a more homogeneous structure.

In this article, the Li-Tanaka equation was used to interpret the increase in transmitted light intensities, I_{tr} , during the swelling of *polytetrahydrofuran* (PTHF) and PTHF-poly (methyl methacrylate) (PMMA) networks which were prepared by free-radical polymerization and copolymerization with MMA of the PTHF bismacromonomer, respectively, where PTHF-PMMA networks were swollen in chloroform and its vapor more than was the PTHF gel. An increase in I_{tr} during swelling was attributed to the homogenization of the lattice structure of the gel; however, during drying the lattice heterogeneity increased due to coiling up of the network chains. The time constants, τ_1 , and cooperative diffusion coefficients, D_C , were determined for swelling processes using the Li-Tanaka equation. The time constant, τ_2 , for the drying processes were measured by proposing a phenomenological equation for drying.

SWELLING KINETICS

For a disc-shaped gel, any change in diameter is coupled with a change in thickness. The total energy of a gel can be separated into bulk energy and shear energy. The bulk energy is related to the volume change, which is controlled by the diffusion equation.⁶ The shear energy F_{sh} , on the other hand, can be minimized instantly by readjusting the shape of the gel, that is, the change of the shear energy in response to any

small change in shape that maintains a constant volume element within the gel should be zero⁶: $\delta F_{sh} = 0$. Each small diffusion process determined by the diffusion equation must be coupled to a small shear process given that $\delta F_{sh} = 0$.

A simultaneous solution of the diffusion equation and $\delta F_{sh} = 0$ produces the following equation for the swelling of a gel disk⁶:

$$\frac{u(r,t)}{u(r,0)} = \sum_n B_n e^{(-t/\tau_n)} \quad (1)$$

where the displacement vector $u(r,t)$ is expressed as a decomposition into components, each of them decaying exponentially with a time constant, τ_n . The first term of the expression is dominant at a large shear modulus, μ . Equation (1) can also be written in terms of solvent uptakes W and W_∞ at time t and at time infinity, respectively, as follows:

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

where B_1 is given by the following relationship:

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

It should be noted from eq. (1) that $\sum_n B_n = 1$; therefore, B_1 should be less than 1. Here, $R = \mu/M$, where M is the longitudinal osmotic modulus $M = (K + 4\mu/3)$. Once the value B_1 is experimentally obtained, one can determine the value of R , since the dependence of B_1 and R for a disk can be found in the literature.⁶ For example, when $R = 3/4$, B_1 is equal to 1, and if R is smaller than $3/4$, B_1 is always smaller than 1. τ_1 is related to the collective cooperative diffusion coefficient D_C of a gel disk at the surface by

$$D_C = \frac{3a_\infty}{\tau_1 \alpha_1^2} \quad (4)$$

where α_1 is a function of R only and given in the literature⁶ and a_∞ stands for the half-thickness of the gel in the final equilibrium state. If R is known, α_1 can be determined.⁶ Once the quantities τ_1 and B_1 are experimentally obtained, R , α_1 , and D_C can be calculated.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was dried over potassium hydroxide, distilled over sodium wire, and finally distilled over sodium benzophenone ketyl prior to use.

MMA was washed with a 5% aqueous NaOH solution, dried over CaCl_2 , and vacuum-distilled from CaH_2 . Triflic anhydride, benzoyl peroxide (BPO), and ethylene glycol dimethacrylate (EGDM) were used as received. Sodium methacrylate (MANa^+) was obtained by the reaction of sodium hydroxide with an excess of methacrylic acid in an aqueous solution and purified by the reprecipitation from methanol into excess acetone.

Synthesis of PTHF bismacromonomer

The synthesis was carried out under a nitrogen atmosphere. Freshly distilled THF (50 mL) was put into a Schlenk tube heated *in vacuo* with a heat gun and flushed with dry nitrogen. Triflic anhydride (0.62

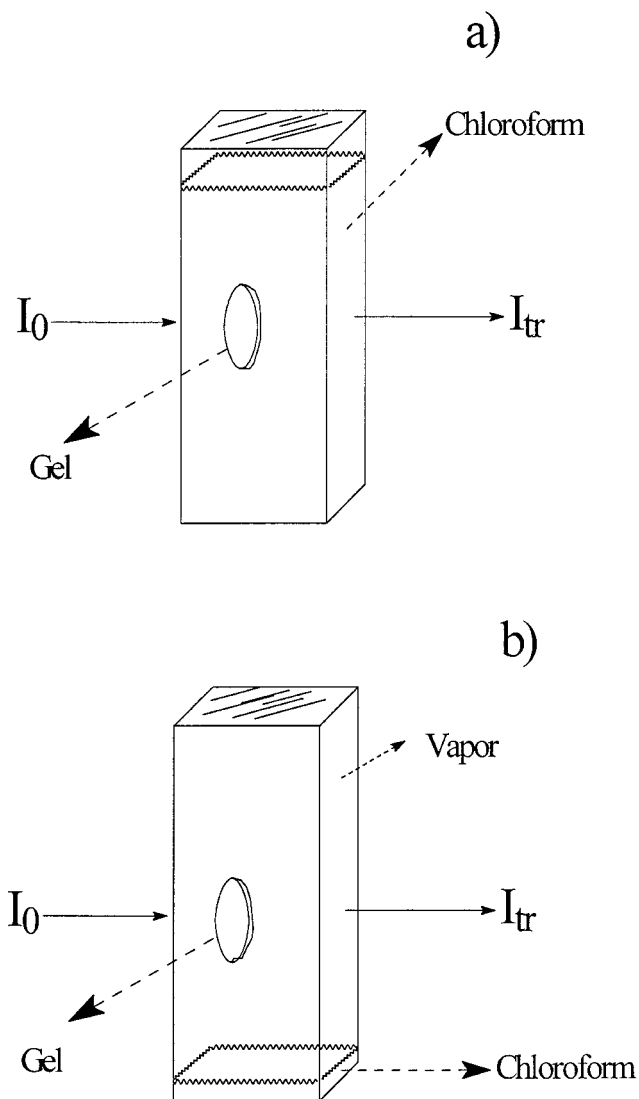


Figure 1 Presentation of the positions of gels in the UV cell when they are subjected to (a) chloroform and (b) chloroform vapor. I_{tr} is the transmitted photon intensity.

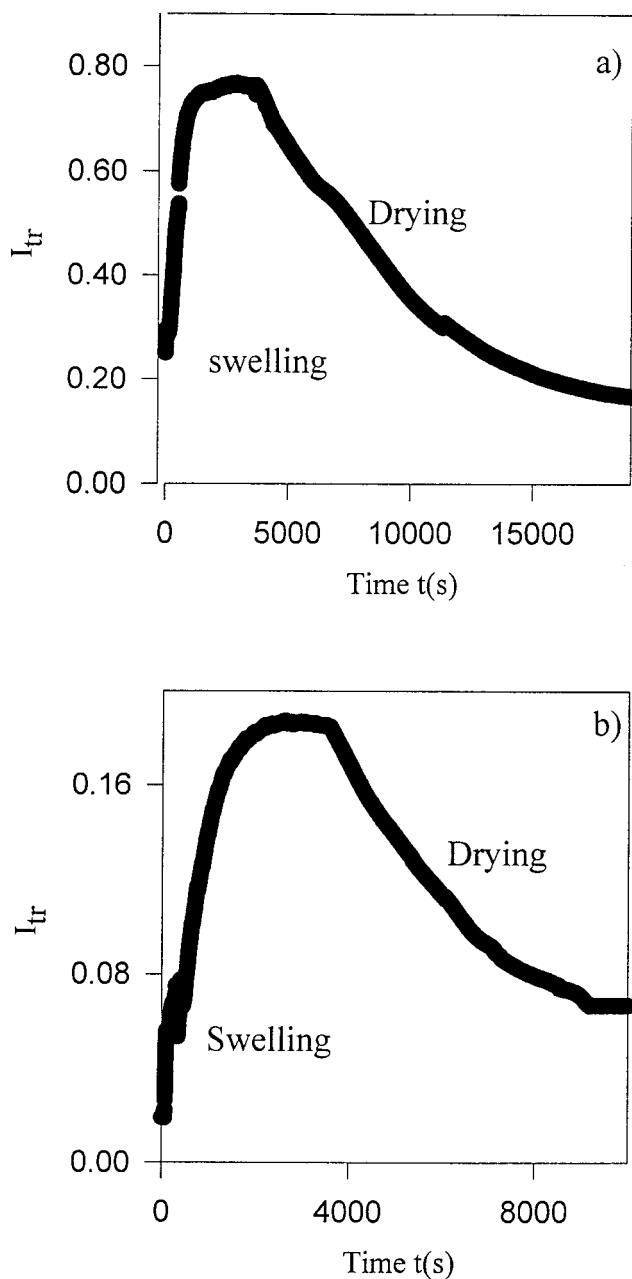


Figure 2 Variation in transmitted photon intensity I_{tr} versus time during swelling and drying of PTHF-PMMA gel (a) in chloroform and (b) in chloroform vapor.

mmol) was added under efficient stirring at 25°C . After 7 min, an aliquot sample was removed with a syringe and poured into methanol for GPC characterization. A suspension of the sodium methacrylate (10 mol equivalent of the initiator concentration) in CaCl_2 was added to the remaining part of the reaction mixture to terminate the polymerization. The reaction mixture was stirred for 2 days and then poured into a methanol/water (1/1) mixture. The precipitated polymer was filtered off and dried *in vacuo*.

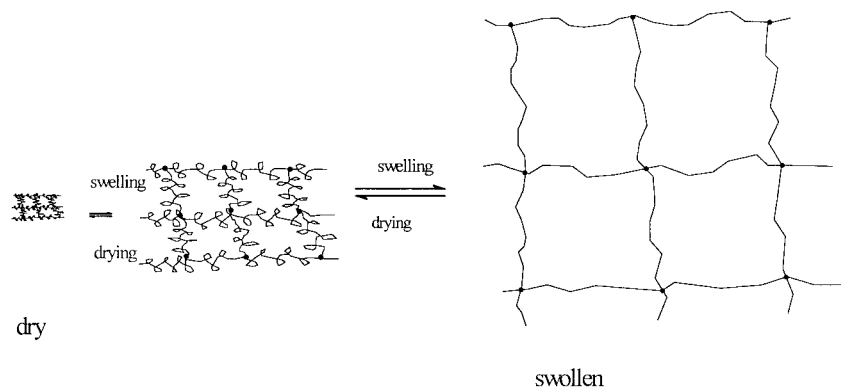


Figure 3. Cartoon representation of swelling and drying processes of gels. Swollen and dried networks present homogeneous (uncoiled) and heterogeneous (coiled) states, respectively.

Synthesis of homogeneous network of PTHF

A solution of 0.7 g of bismethacrylate-terminated PTHF and 10 mg BPO in 1 mL of toluene was prepared. The solution was then poured into a glass mold and held 16 h at 60°C for thermal polymerization. After a given reaction time, a film of the homogeneous network of PTHF was obtained.

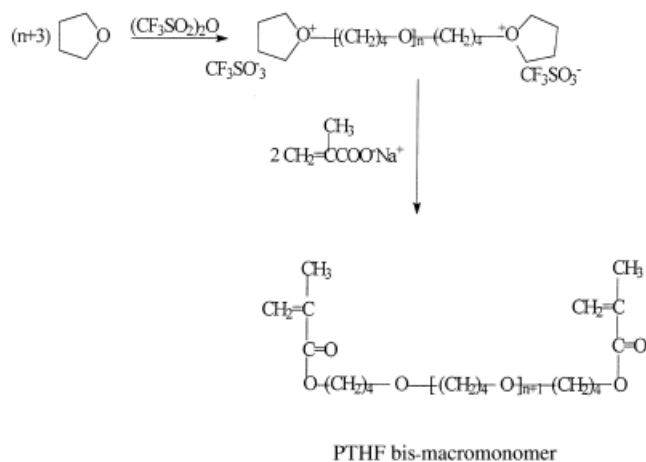
Synthesis of homogeneous segmented networks of PTHF-PMMA

In the case of a segmented network, 2 mmol of MMA and 1.0 wt% BPO were added to bismethacrylate-terminated PTHF. The same procedure was followed for the synthesis of a homonetwork PTHF. After 16 h, a film of net-poly (THF-co-MMA) was obtained.

UV/VIS measurements

Disc-shaped gels prepared by the above procedure were placed into a 1 × 1-cm quartz cell filled with chloroform (CHCl₃) and/or its vapor for *in situ* pho-

ton transmission measurements. Swelling of the gels was monitored in real time using a Perkin-Elmer UV/VIS spectrophotometer. The positions of the gels in UV cells filled with chloroform and its vapor for swelling experiments are presented in Figure 1(a,b), respectively. Drying experiments were performed in air after removing the solvent from the UV cell. Photon transmission intensities, I_{tr} , were measured using the time-drive mode of the spectrophotometer at 350 nm during both swelling and drying of the gels. Typical I_{tr} curves against time, t , are given in Figure 2(a,b) for the PTHF-PMMA gel swollen and dried in chloroform and its vapor, respectively. In Figure 2(a), it is seen that the I_{tr} intensity increased during swelling by reaching the highest transparency, then decreased exponentially during drying. In Figure 2(b), the behavior of swelling and drying repeats itself as in Figure 2(a), except at lower transparencies. An increase in I_{tr} during the swelling process predicts the homogenization of the lattice structure of the PTHF-PMMA gel; however, during drying the gel goes back to its initial more heterogeneous structure. Figure 3 presents the homogeneous (swollen) and heterogeneous (dried) states of the gel due to uncoiling and coiling of the network chains during the swelling and drying processes, respectively.



Scheme 1

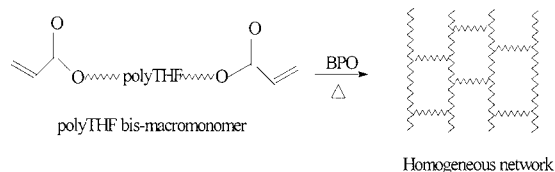
TABLE I
Synthesis of PTHF Bismacromonomer

Code	Reaction time (min)	Conversion (%)	M_n^a	M_n^b	M_w/M_n
PTHF	7	6.6	2960	2970	1.15

[THF] = 12.3 mol L⁻¹; [triflic anhydride] = 0.0124 mol L⁻¹; [MANa⁺] = 0.62 mmol.

^a Determined by GPC based on polystyrene standards and then converted to PTHF data using $M_{PTHF} = 0.592M_{PS}$.

^b Determined by ¹H-NMR.



Scheme 2

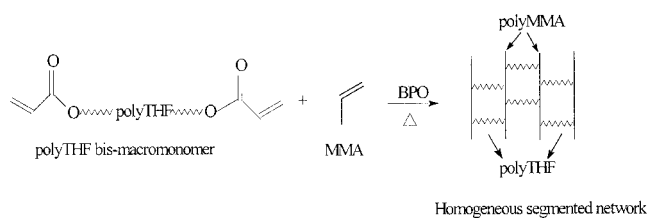
RESULTS AND DISCUSSION

Gelation

The bismacromonomer of PTHF was synthesized by end-capping of the living PTHF chain. For this purpose, polymerization of THF initiated by a bifunctional initiator, triflic anhydride at 25°C, was terminated with the sodium salt of methacrylic acid. The overall reaction is represented in Scheme 1. The results of the synthesis of the bismacromonomer of PTHF is shown in Table I. The bismacromonomer obtained was characterized by GPC measurement and $^1\text{H-NMR}$ analysis. The molecular weight distribution of the obtained polymer by this method was narrow, as expected. The molecular weight, determined by $^1\text{H-NMR}$, was calculated by comparing the integrated areas of the signals corresponding to vinylic protons at 5.9 and 6.6 ppm to the integrated areas of the signals corresponding to the OCH_2 protons of PTHF at 3.4 ppm, assuming two vinyl groups for each polymer chain. The molecular weight, which was determined by $^1\text{H-NMR}$, was in good agreement with that by the GPC method. This result indicated that the macromonomer obtained by this method possesses two vinyl groups per one polymer chain.

A homogeneous PTHF network was prepared by free-radical polymerization of the PTHF bismacromonomer in the presence of BPO as an initiator (Scheme 2). The same procedure for the homogeneous segmented network was followed. By free-radical copolymerization of the PTHF bismacromonomer with MMA, a network with a block copolymer structure was obtained (Scheme 3).

It should be pointed out that the PTHF networks formed from only the bifunctional monomer are highly crosslinked products, whereas the crosslinked density in a segmented network is lower due to the presence of linear PMMA chains in the structure.



Scheme 3

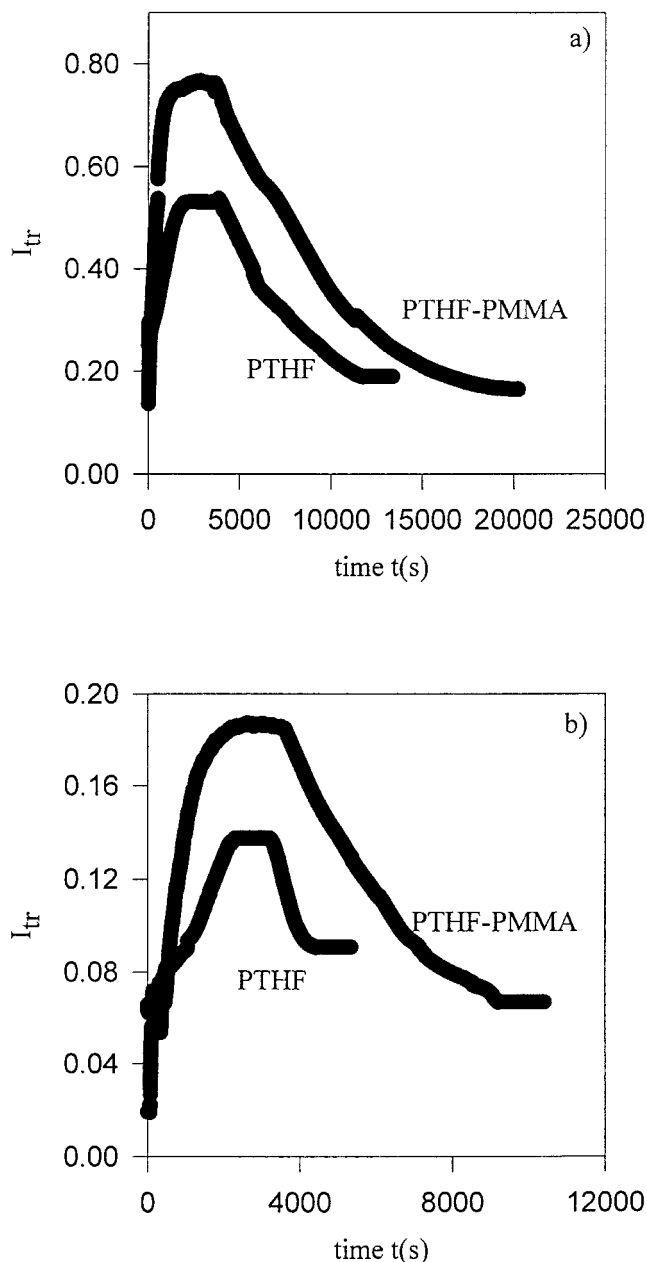


Figure 4 Variation in transmitted photon intensity, I_{tr} , during swelling and drying of PTHF-PMMA and PTHF gels (a) in chloroform and (b) in chloroform vapor.

Swelling

The behavior of I_{tr} from PTHF-PMMA and PTHF gels immersed in chloroform are given in Figure 4(a) during swelling and drying processes. Similar swelling and drying curves of the corresponding gels under chloroform vapor are presented in Figure 4(b). In Figure 4, it is seen that I_{tr} increases as the swelling time t is increased in both PTHF-PMMA and PTHF gels due to increasing homogenization of these gels. The maximum of I_{tr} from the PTHF-PMMA gel was found to be much higher than from the PTHF gel, indicating the relatively loose structure of the former case. In other

words, the PTHF-PMMA gel swells more than does the PTHF gel due to its low crosslinked and loosely formed structure. Cartoon representation of the homogenization of the gel swelling is presented in Figure 3. At the beginning, when the gel is dry, the mean free path of a photon is very short due to the heterogeneities (coiled-up chains) of the lattice. As a result, light is scattered from the gel. However, as the gel swells, the lattice goes to a more homogeneous state (uncoiled chains) and the mean free path of a photon increases. Consequently, nonscattered light travels a long distance in the gel, resulting in an increase in the transmitted light intensity.

The behavior of I_{tr} below the maxima, that is, during swelling, can be quantified by establishing a relation between eq. (2) and I_{tr} . After solvent penetration starts, due to lattice homogenization, transmitted light intensity increases from zero to I_{tr} at time t where the amount of solvent uptake is W . At the equilibrium state of swelling, the transmitted light intensity reaches $I_{tr}(\infty)$, where the solvent uptake by the swollen gel is W_∞ . A similar argument can be made for the vapor uptake. The relation between the solvent uptake W and the transmitted light intensity, I_{tr} , during the swelling of the gel both in the solvent and its vapor can now be given by the following relation:

$$\frac{W}{W_\infty} = \frac{I_{tr}}{I_{tr}(\infty)} \quad (5)$$

This relation simply assumes that homogenization (uncoiling) is proportional to the solvent uptake, W , which predicts that as W increases I_{tr} also increases. By combining eq. (5) with eq. (2) and taking the logarithm of it, the following useful relation can be obtained:

$$\ln\left(1 - \frac{I_{tr}}{I_{tr}(\infty)}\right) = \ln(B_1) - \frac{t}{\tau_1} \quad (6)$$

The swelling portion of the PTHF-PMMA and PTHF data below the maxima, shown in Figure 4(a), are plotted in Figure 5(a,b) according to eq. (6), where quite linear relations are obtained. Linear regression of curves in Figure 5(a,b) provide us with B_1 and τ_1 values. A similar treatment was performed with the swelling portion of the data in Figure 4(b), from which B_1 and τ_1 values were obtained for the PTHF-PMMA and PTHF gels swollen in chloroform vapor. These results are presented in Figure 6(a,b) for the PTHF-PMMA and PTHF gels, respectively. Experimentally obtained B_1 and τ_1 values are listed in Table II for the gels swollen in chloroform and its vapor. Here, one can immediately state that the PTHF-PMMA gel swells much faster than does the PTHF gel both in solvent and in its vapor. The results are quite reson-

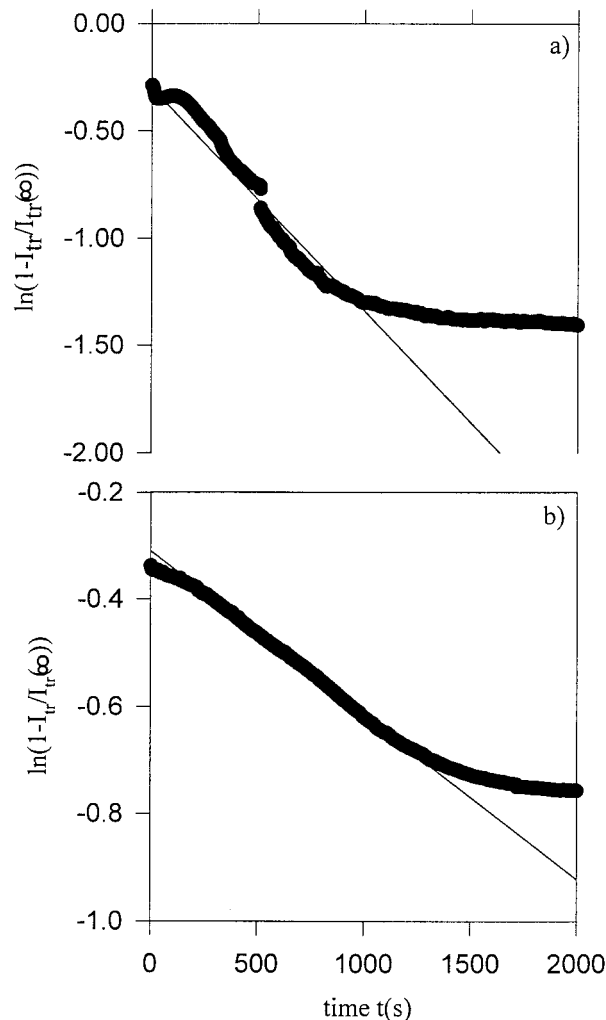


Figure 5 Determination of swelling time constant, τ_1 , from the data in Figure 4(a) using eq. (6) for (a) PTHF-PMMA and (b) PTHF samples. Intercept of straight-line procedure B_1 values.

able, because PTHF-PMMA is loosely formed and expected to swell much faster and more than the densely formed PTHF gel. Taking into account the dependence of B_1 and R , one obtain R values; from $\alpha_1 - R$ dependence, α_1 values were produced.⁶ Then, using eq. (1), cooperative diffusion coefficients D_C were determined for all the gel samples swollen in chloroform and its vapor. The results are listed in Table II together with the τ_1 , a_i , a_∞ and W_∞ values. Here, a_i and a_∞ are the half-thicknesses of the gels before and after swelling. W_∞ is the amount of solvent uptake at the equilibrium of swelling. Here, a_i and a_∞ are measured with callipers and W_∞ values were determined using the digital balance. These behaviors of the gels can be understood by realizing that loosely formed gels are more flexible, because the shear energy is much less in these gels than in densely formed gels. As a result, a loosely formed gel swells much faster and more than does a densely formed gel. The

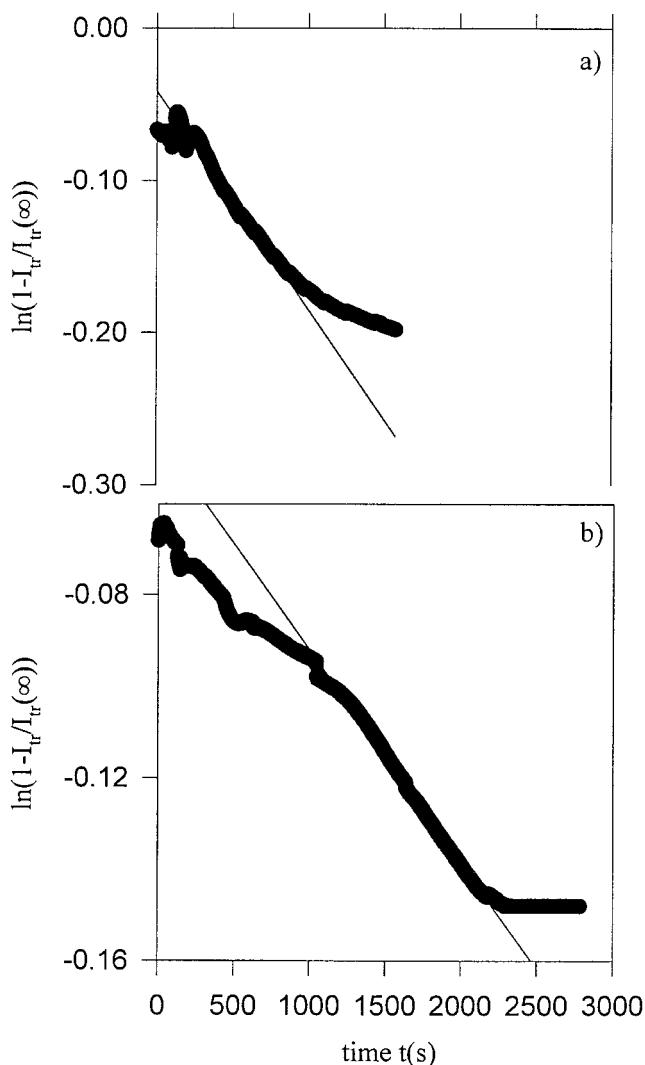


Figure 6 Determination of swelling time constant, τ_1 , from the data in Figure 4(b) using eq. (6) for (a) PTHF-PMMA and (b) PTHF samples. Intercept of straight-line procedure B_1 values.

larger values of D_C for the PTHF-PMMA gels compared to the PTHF gels predict the faster motion of gel segments in the former one. Here, we have to note that gels in a solvent swell much faster than do those in vapor. In the meantime, gel segments move much faster in solvent than in vapor.

Drying

The drying portions of the data in Figure 4 predict that both gels obey the following exponential relation during drying:

$$\frac{I_{tr}}{I_{tr}(\infty)} = e^{-t/\tau_2} \quad (7)$$

where τ_2 is called the drying time constant. Here, it is assumed that the amount of released solvent, W , from the gel is proportional to the transmitted intensity I_{tr} that is, as a solvent evaporates, a gel goes back to its heterogeneous (coiled-up) state; as a result, I_{tr} decreases. The logarithmic form of eq. (7) is used to produce τ_2 values from the drying portions of the data in Figure 4. The results are plotted in Figures 7 and 8 for the PTHF-PMMA and PTHF gels dried from a solvent and its vapor, respectively. Here, we have to note that the time at the maxima of $I_{tr}(\infty)$ is taken as zero, that is, the beginning point of drying. The produced τ_2 values are listed in Table II. It is observed that the loosely formed PTHF-PMMA gel dries much slower than does the densely formed PTHF gel, both from solvent and from its vapor. It should be noted that swelling and drying processes are not symmetrical for the gels swollen in a solvent and its vapor. For example, a gel dries much slower than it swells when it is subjected to a solvent. However, the opposite behavior was observed when a gel was exposed to vapor, that is, it swelled much slower than it dried.

The swelling and drying behavior of these gels, when swollen in a solvent, can be understood by realizing that a gel swells faster due to the existing

TABLE II
Experimentally Obtained Swelling and Drying Parameters (B_1 , τ_1 , D_C and τ_2) of PTHF-PMMA and PTHF Gels

	In solvent		In vapor	
	PTHF-PMMA	PTHF	PTHF-PMMA	PTHF
B_1	0.7394	0.7334	0.9594	0.9554
τ_1 (s)	960	3270	6965	21,520
D_C ($\text{cm}^2\text{s}^{-1} \times 10^{-5}$)	3.2	1.2	1.9	0.8
a_∞ ($\text{cm} \times 10^{-1}$)	1.86	2.11	1.63	1.94
a_i (cm)	0.07	0.10	0.07	0.10
W_∞ (g)	19.55	12.37	14.22	7.05
τ_2 (s)	8410	7460	4950	1875

a_i and a_∞ are initial and final thicknesses, respectively, and W_∞ is the solvent uptake of the gels.

high solvent pressure at the outside of the gel, which causes faster diffusion of the solvent molecules into the network. When the gel is left to dry in air, due to a high solvent uptake, it takes a longer time to release the solvent molecules. In other words, a high concentration gradient can cause a faster solvent uptake. However, the reverse case is not true for the drying process. Most probably, the shear energy plays a more important role than does bulk diffusion during drying. On the other hand, when the gel swells under vapor, due to the low pressure at the outside of the

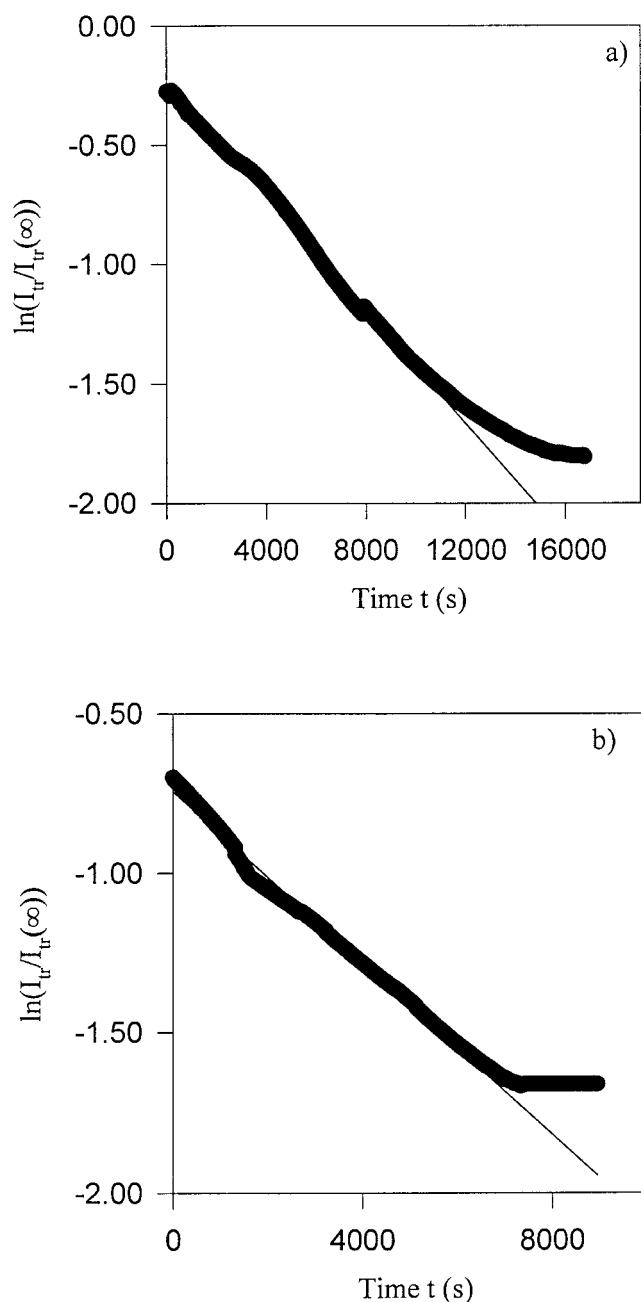


Figure 7 Determination of drying time constant, τ_2 , from the data in Figure 4(a) using eq. (7) for (a) PTHF-PMMA and (b) PTHF samples.

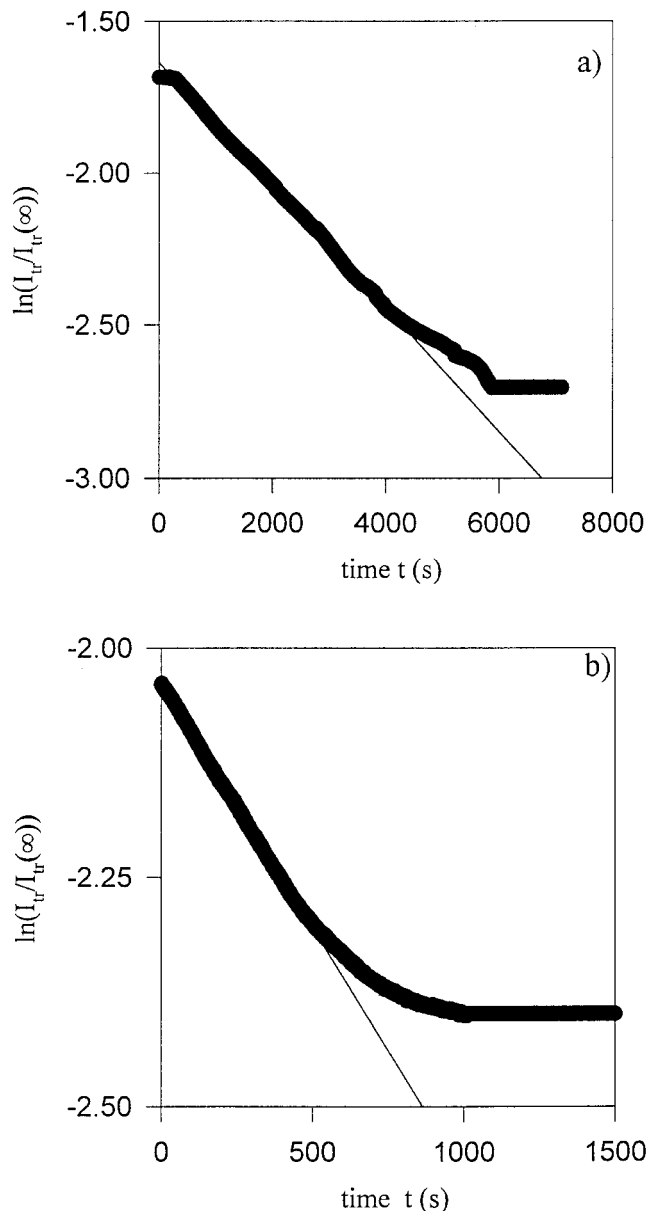


Figure 8 Determination of drying time constant, τ_2 , from the data in Figure 4(b) using eq. (7) for (a) PTHF-PMMA and (b) PTHF samples.

gel, it takes a longer time to swell. However, due to a low uptake of solvent molecules in the gel, it is much easier and faster to release them out of the network during drying.

In conclusion, this work presented a UV/VIS spectrophotometric technique to study the swelling and drying of PTHF-PMMA and PTHF gels when they are exposed to chloroform and its vapor. It is mainly understood that a loosely formed PTHF-PMMA gel swells much faster and more than does a densely formed PTHF gel. It was observed that the transmitted light intensity, I_{tr} , increases as the gels swell. The increase in I_{tr} was attributed to the decrease in the scattered light from the gel due to the lattice homog-

enization (uncoiling chains), which takes place during swelling processes. During drying, I_{tr} decreased exponentially due to the heterogenization (coiling chains) of the network. It was observed that a loosely formed gel dries slower than does a densely formed gel after being swollen in a solvent. It should be emphasized that the swelling kinetics is completely understood by applying the well-established Li–Tanaka model. On the other hand, the drying mechanism still remains to be evaluated and probably needs another model to be developed to explain the drying kinetics more quantitatively. Further studies in this line are in progress.

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