Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 45 (2004) 2551–2558

polymer

www.elsevier.com/locate/polymer

Fast transient fluorescence method for measuring swelling and drying activation energies of a polystyrene gel

M. Erdoğan[a], Ö. Pekcan[b,*]

[a]*Department of Physics, Balikesir University, Soma Cd. 10100 Balikesir, Turkey*
[b]*Department of Physics, Faculty of Science and Letters, Istanbul Technical University, Maslak, Istanbul 80626, Turkey*

Received 22 September 2003; received in revised form 29 January 2004; accepted 4 February 2004

Abstract

The time-resolved, fast transient fluorescence (TRF) technique which uses a strobe master system (SMS), was employed for studying swelling and drying of disc-shaped polystyrene gels. Disc-shaped gels were prepared by free-radical crosslinking copolymerization of styrene and ethylene glycol dimethacrylate. Pyrene was introduced as a fluorescence probe during polymerization and lifetimes, τ of pyrene were measured during in situ swelling and drying processes. Chloroform was used as an organic vapor agent to induce gel swelling at various temperatures. It was observed that τ values decreased as swelling is proceeded. Li–Tanaka equation was used to determine the swelling time constant, τ_c and cooperative diffusion coefficients, D_c for the swelling processes. It is observed that lifetimes, τ of pyrene increased during drying process and an empirical equation was introduced to determine the desorption coefficient, D for drying at various temperatures. The activation energies, ΔE were measured for the swelling and drying processes and found to be 80.0 and 33.5 kJ mol^{-1}, respectively.

Keywords: Polystyrene; Diffusion; Activation energy

---

1. Introduction

The swelling and drying kinetics of physical and chemical gels are very important in many technological applications: in the pharmaceutical industry in designing slow-release devices for oral drugs; understanding the mechanism of swelling and drying kinetics is highly desirable in the use of cosmetics ingredients; in the agricultural industry for producing storable foods; and in medical applications in developing artificial organs. The degree of swelling of chemically crosslinked polymer is determined by several factors, such as polymer–solvent interaction, crosslinking density, conditions during network formation etc. The final degree of swelling can also be affected by existing physical crosslinks, and is controlled by temperature, solvents nature and composition.

Two network phases of different degree of swelling can exist and the transition from one state of network to the other is called volume phase transition [1]. The continuous swelling is directly related to visco elastic properties of a gel. The gel elasticity and the friction between the network and solvent play an important role on the kinetics of the gel swelling [2,3]. It has been known that the relaxation time of swelling is proportional to the square of a linear size of the gel [1] which has been confirmed experimentally [3]. One of the most important features of the gel swelling process is that it is isotropic, i.e. when the radius increases 10%, the axial length increases 10% in long cylindrical gel. The elastic and swelling properties of permanent networks can be understood by considering two opposing effects, the osmotic pressure and restraining force. 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 non-isotropic deformation. The characteristic coefficient of these forces is the shear modulus, G, which can be most directly evaluated by stress–strain measurements [4,5]. 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

---

* Corresponding author. Tel.: +90-212-285-3213; fax: +90-212-285-6366.

E-mail address: pekcan@itu.edu.tr (O. Pekcan).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.02.026

different direction. This model predicts that the geometry of the gel is an important factor, and swelling is not a pure diffusion process. Nuclear magnetic resonance stray field imaging technique was used to study swelling and vapor diffusion in xanthan powder. Three region model, where diffusion obeys Fick's law was suggested as an analytical model to fit the experimental results [7]. The equilibrium swelling of polystyrene networks by linear polystyrene was investigated by the ion beam technique of helium-3 nuclear reaction analysis [8]. These data analyzed in the framework of the Flory–Rehner theory. Recently, solvent uptake and swelling of ultrathin polyacrylamide films was studied in the presence of saturated vapor of water at room temperature using gravimetric and X-ray reflectivity methods [9]. It was observed that solvent uptake faster process compared to swelling which is governed by the Fickian dynamics of the diffusion of water molecules into the free volume of the polymer structure.

Fluorescence methods, such as steady state spectroscopy, fluorescence anisotropy and transient fluorescence (TRF) measurements have shown to be quite effective in the investigation for the microscopic environment around a chromophore. The first fluorescence study on polymer gel was carried out by Horie et al. to investigate the hydrophobicity and dynamic characteristics of crosslinked polystyrene with dansyl probe [10]. The volume phase transition of acrylamide gel induced by the change in solvent composition and/or pH was investigated using fluorescence depolarization technique. The microscopic structure of dansyl-labelled dimethylacrylamide-methacrylic acid copolymer gel was investigated to understand the nature of the multiple phase by using fluorescence spectroscopy, where multiple phase behavior were characterized by distinct degrees of swelling [11]. On the other hand, the TRF technique for measuring fluorescence decay has been routinely applied to study many polymeric systems. TRF spectroscopy with a non-radiative direct energy transfer (DET) and quenching has been used to characterize internal morphologies of composite materials. It has been reported that the local, fractal like structures of interpenetrating network morphology in blend-like particles can be studied by TRF spectroscopy [12]. Steady state and TRF techniques were applied to drying process of selected silane gels in oxygen free atmosphere. A kinetic model of drying was suggested and drying rate constants were determined [13]. Recently, fast transient fluorescence (FTRF) technique was used in our laboratory to study polymer dissolution [14], gel swelling [15] and drying [16] and gelation [17] processes. We have also reported temperature effect on gel swelling for the poly(methyl methacrylate) (PMMA) gels [18] in chloroform. In these studies, Strobe Master System (SMS) was used and a model was employed for low quenching efficiencies to measure lifetimes of pyrene (P) which was used as a fluorescence probe.

In this work, organic vapor induced swelling and their air drying of disc-shaped gels formed by free-radical cross-linking copolymerization (FCC) of styrene (S) and ethylene glycol dimethacrylate (EGDM) was studied using FTRF technique. Lifetimes of P embedded in the polystyrene (PS) gel were monitored during in situ swelling and drying processes. The SMS was used for lifetime measurements of P in the gel. Lifetimes can be measured with SMS technique at least hundreds times during the swelling and drying process of gels. That is the reason, we named this technique as FTRF, which gives us many advantages compare to other lifetime measuring techniques. It is observed that, as gel swells and dries, the lifetime of P decreases and then increases, respectively. These behaviors can be modeled using the low quenching Stern–Volmer equation. In this work vapor induced swelling of the PS gel was treated using Li–Tanaka model, which has been commonly applied for solvent–gel systems. Cooperative, D_c diffusion coefficients were determined by employing Li–Tanaka model. Drying of PS gels were quantified by employing moving boundary model from which desorption coefficients, D were determined.

2. Kinetics of swelling

It has been suggested [6] that the kinetics of swelling 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

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

Eq. (5) allows us to determine the parameters B_1 and τ_c. 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.

3. Experiments

EGDM has been commonly used as crosslinker in the synthesis of polymeric networks. Here, for our use, the monomer S (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 initiator 2,2′-azobisisobutyrronitrile (AIBN, Merk) was recrystallized twice from methanol.

The free-radical crosslinking copolymerization of S with EGDM was performed at 70 °C in the presence of 2,2′-azobisisobutyrronitrile (AIBN) (0.26 wt%) as an initiator. P was added as a fluorescence probe during the gelation process. Samples were deoxygenated by bubbling nitrogen for 10 min, and then radical copolymerization of S with EGDM was performed at 70 ± 2 °C. Here, EGDM content was kept as 0.015 vol%, and P concentration was taken as 4×10^{-4} M. After gelations are completed, the PS gel samples were dried under vacuum for the swelling experiment. Gel swelling experiments were performed at various temperatures. After the swelling processes were accomplished all gel samples were dried in air to investigate the drying mechanism at various temperatures.

Fluorescence decay experiments were performed using the Photon Technology International (PTI) SMS. In the strobe, or pulse sampling technique [19,20], the sample is excited with a pulsed light source. The name comes about because the Photo Multiplier Tube (PMT) is gated or strobed by a voltage pulse that is synchronized with the pulsed light source. The intensity of fluorescence emission is measured in a very narrow time window on each pulse and saved in a computer. The time window is moved after each pulse. The strobe has the effect of turning on the PMT and measuring the emission intensity over a very short time window. When the data has been sampled over the appropriate range of time, a decay curve of fluorescence intensity versus time can be constructed.

Since the strobe technique is intensity dependent, the strobe instrument is much faster than single photon counting (SPC) and even faster than a phase measuring instrument. The strobe instrument is much simpler to use than SPC and the data is easier to interpret than the phase system. Because of these advantages SMS is used to monitor swelling and drying of PS gels over a period of several hours.

In situ swelling and drying experiments under chloroform vapor and air were carried out, respectively, in the SMS of PTI, employing a pulsed lamp source (0.5 atm of N_2). Pyrenes in the PS gels were excited at 345 nm and fluorescence decay curves were collected at 395 nm during in situ swelling and drying experiments, which were performed at various temperatures. No shift was observed at the 395 nm during both swelling and drying processes. A disc-shaped gel samples were placed in the wall of 1×1 quartz cell with chloroform at the bottom for the swelling experiments. Vapor–gel system was deoxygenated by bubbling nitrogen for 10 min at room temperature to avoid oxygen quenching processes. Then the cell was sealed against oxygen penetration during swelling experiments. The position of the gel, the level of chloroform and the incident light beam for the fluorescence measurements are shown in Fig. 1(a) during swelling. In Fig. 1(b) the position of the cell during drying in air is presented. The fluorescence decay data were collected over three decades of time and fitted by 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 $\chi^2(\chi^2 \leq 1.10)$, the distribution of the weighted residuals and the autocorrelation of the residuals.

4. Results and discussions

4.1. Swelling

In order to probe vapor induced swelling and air drying processes, the fluorescence decay curves were measured and fitted to the mono exponential functions

$$I(t) = A \exp(-t/\tau) \tag{6}$$

where τ and A are the pyrene lifetime and the corresponding amplitude of the decay curves. Fig. 2(a) and (b) present the fluorescence decay profiles for various swelling (0, 30, 65 and 125 min) and drying (40, 132, 297 and 564 min) steps,

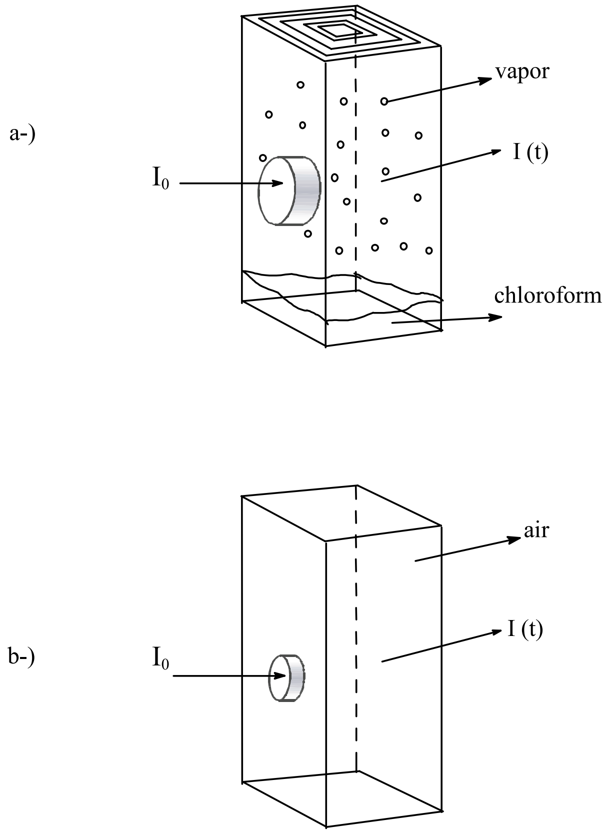

Fig. 1. The position of PS gel in the fluorescence cell (a) during swelling under chloroform vapor and (b) during drying in air. I_0 is the excitation and $I(t)$ is the emission intensities at 345 and 395 nm, respectively.

respectively. It can be seen that as the swelling time t_s, is increased, excited pyrenes decay faster and faster which indicates that as chloroform vapor uptake is increased quenching of excited pyrenes increases. On the other hand, it can be seen that as the drying time t_d, is increased excited pyrenes decay slower by indicating that chloroform vapor evaporates.

The normalized τ values for the gels swelling at 25, 35 and 45 °C, are plotted versus swelling time t_s, in Fig. 3(a). It can be seen that in all samples τ values decrease as vapor uptake is increased. The increase in temperature causes faster decrease in τ values. In order to quantify these results the collisional type of quenching mechanism may be proposed for the fluorescence decay of P in the gel sample during swelling process, where the following relations are given [21],

$$P + h\nu \rightarrow P^*$$

excitation of ground state pyrene, P to excited state of pyrene, P^*

$$P^* + Q \rightleftharpoons (P^*Q) \rightarrow P + Q$$

collisional quenching of P^* to P by Q

$$P^* \rightarrow P + h\nu$$

the decay of P^*, here Q presents the quencher (chloroform) molecules. The quenching rate constant, k_q for these processes are given by Smoluchowski equation as [22]

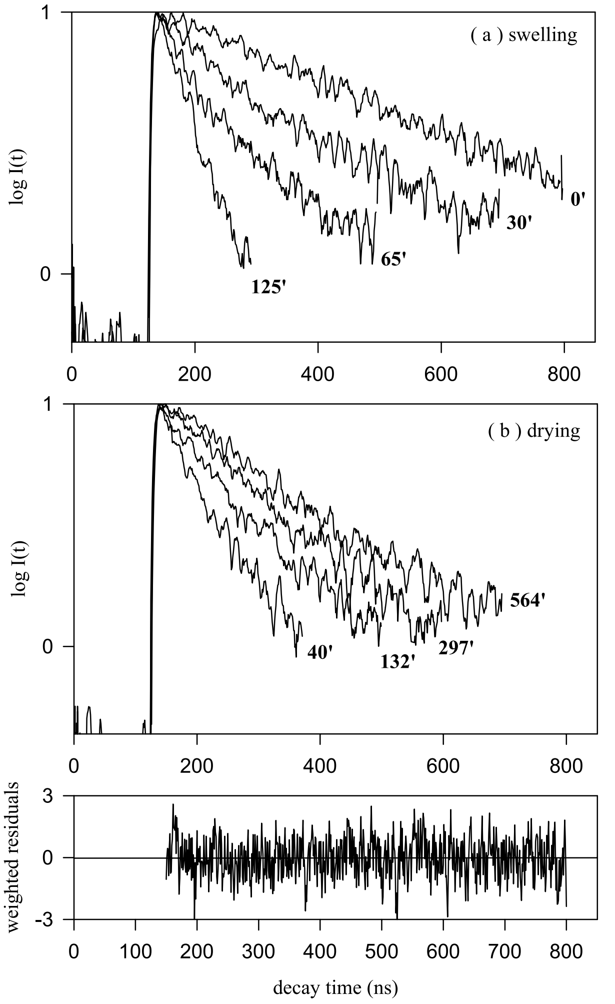

Fig. 2. Fluorescence decay profiles of pyrene in PS gel during (a) swelling and (b) drying. Numbers on each decay curve present the swelling, t_s and drying, t_d times, in minute. The box below the decay curves show the typical weighted residuals for a single experiment.

$$k_q = \frac{4\pi N_A D_M R}{1000} \tag{7}$$

where $D_m = D_p + D_s$ is the sum of the mutual diffusion coefficients of P and solvent molecules, $R = R_p + R_s$ is the sum of their interaction radii, N_A is the Avagadro's number.

The rate equation for P^* with delta function excitation can be written as

$$\frac{[P^*]}{dt} = -(\tau_0^{-1} + k_q[Q]) + \delta(t - t_0)[P] \tag{8}$$

Here [ ] represent the concentration of P^* and Q molecules, τ_0 is the lifetime of P in dry gel in which no quenching has taken place and $\delta(t - t_0)$ is the light pulse of SMS. Solution of Eq. (8) produce Eq. (6), where

$$\tau^{-1} = \tau_0^{-1} + k_q[Q] \tag{9}$$

For low quenching efficiency, $(\tau_0 k_q[Q] \ll 1)$, Eq. (9)

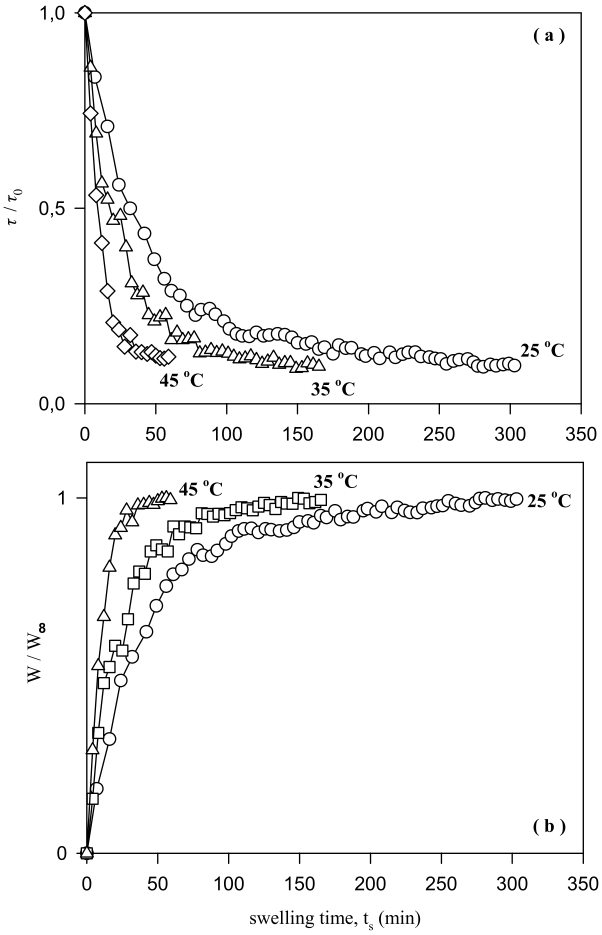

Fig. 3. (a) The plots of normalized pyrene lifetimes, τ versus swelling time, t_s for the gel swollen at 25, 35 and 45 °C. τ values were obtained by fitting the $I(t)$ data to Eq. (6). (b) The plots of normalized vapor uptake, W versus swelling time, t_s for the gel swollen at 25, 35 and 45 °C.

becomes

$$\tau \approx \tau_0(1 - \tau_0 k_q[\mathrm{Q}]) \qquad (10)$$

If one integrates Eq. (10) over the differential volume (dv) of the gel from the initial, a_0 to final a_∞ thickness and then, reorganization of the relation produces the following useful equation.

$$W = \left(1 - \frac{\tau}{\tau_0}\right)\frac{v}{k_q \tau_0} \qquad (11)$$

Here vapor uptake, W is calculated over differential volume by replacing Q with W as

$$W = \int_{a_0}^{a_\infty} [W]\mathrm{d}v \qquad (12)$$

where v is the swollen volume of the gel at the equilibrium swelling, which can be measured experimentally. k_q was obtained from separate measurements by using Eq. (11) where the infinity equilibrium value of vapor uptake, W_∞ was used at each temperature. Since τ_0 ($\approx$300 ns) is already known from the dry gel, and measured values of v and τ at equilibrium swelling condition can be used to calculate k_q at each temperature separately (see Table 1). The average value of k_q is found to be around $0.9 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Once k_q values are measured, the vapor uptakes, W can be calculated from the measured τ values at each swelling step. Here, it is assumed that k_q values do not vary during swelling processes, i.e. the quenching process solely originates from the chloroform molecules.

The plots of the vapor uptake, W for the gels swollen at 25, 35 and 45 °C in chloroform vapor are shown in Fig. 3(b), which are typical vapor uptake curves, obey Li–Tanaka equation (Eq. (5)). Logarithmic form of the data in Fig. 3(b) are fitted to the following relation, produced from Eq. (5).

$$\ln\left[1 - \frac{W}{W_\infty}\right] = \ln B_1 - \frac{t_s}{\tau_c} \qquad (13)$$

The fits are presented in Fig. 4, from where B_1 and τ_c values are determined and are listed in Table 1, where it is seen that as the temperature is increased penetration of vapor molecules into the gel increase, as expected. By knowing B_1 values one can obtain α_1 values and then from Eq. (4) D_c values are produced and listed in Table 1. The behavior of D_c versus temperature predicts that gel segments move much faster at high temperature during the vapor penetration. As seen in Table 1, the D_c values increase as the temperature is increased, which predicts that the $D_c - T$ relation may obey the following Arrhenius law:

$$D_c = D_{co}\exp(-\Delta E_s/kT) \qquad (14)$$

where the ΔE_s is the activation energy for swelling, k the Boltzmann's constant and D_{co} the cooperative diffusion coefficient at $T = \infty$. The logarithmic form of the D_c data are plotted versus T^{-1} in Fig. 5 where the slope of the linear relation produces the activation energy ΔE_s for the swelling gel as 80.0 kJ mol^{-1}.

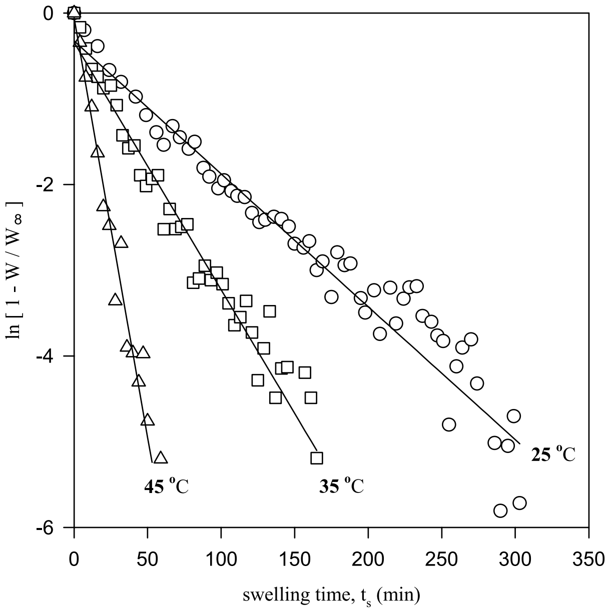

Fig. 4. Linear regression of the data in Fig. 3(b) according to Eq. (13) for the gels swollen at 25, 35 and 45 °C.

Table 1
Swelling parameters

Temperature (°C)	m_i (g)	m_f (g)	d_i (cm)	d_f (cm)	B_1	k_q ($M^{-1}s^{-1}$) × 10^5	τ_c (min)	D_c ($cm^2\ s^{-1}$) × 10^{-5}	D_m ($cm^2\ s^{-1}$) × 10^{-7}
50	0.062	0.168	0.20	0.26	0.86	1.0	8.9	5.08	1.75
45	0.067	0.166	0.21	0.26	0.85	1.0	10.5	4.24	1.72
40	0.065	0.167	0.20	0.26	0.80	1.1	17.6	1.85	7.85
35	0.067	0.211	0.21	0.28	0.71	0.9	34.7	0.78	1.45
30	0.066	0.178	0.21	0.27	0.60	0.9	47.1	1.15	1.50
25	0.064	0.247	0.20	0.27	0.72	0.7	64.5	0.40	1.24

m_i, d_i, initial weight and thickness of the PS gels; m_f, d_f, final weight and thickness of the PS gels; τ_c, swelling time constant; D_c, collective diffusion coefficient. D_m, mutual diffusion coefficient.

The sum of the mutual diffusion coefficients were calculated form Eq. (7) by using the k_q values and found to be around $D_m \cong 10^{-7}$ cm^2 s^{-1}, where R is taken as 8 Å. The observed mutual diffusion coefficients, D_m are listed in Table 1 that are typical for a small molecule diffusing in a swollen rubbery environment [23]. It is interesting to note that D_m values are much smaller than the cooperative diffusion coefficient, D_c. This result is expected, because an element of swollen network moves much faster, due to the restraining forces, than the P and chloroform molecules in the swollen, viscous environment.

4.2. Drying

Drying processes were monitored from the fluorescence decay curves of P in the PS gels. Mono exponential decays were fitted to Eq. (6) and τ values were produced. Fig. 6(a) shows a typical τ values versus drying time t_d data for the gel dried at 40 °C in air. It is seen in Fig. 6(a) that τ values increase as chloroform vapor evaporates from the gel sample (by indicating decrease in quenching of P during drying). According to Eq. (10) as the quencher, ($Q \approx W$) concentration decreases, τ values increase. In order to quantify this behavior, Eq. (11) can be employed to calculate the amount of vapor release, W' from the PS gels. Here it has to be noted that drying phenomena in gels has not yet been completely modeled. Because drying process is not as simple as swelling, at least in solvent. In this work, however, by using vapor, drying process is tried

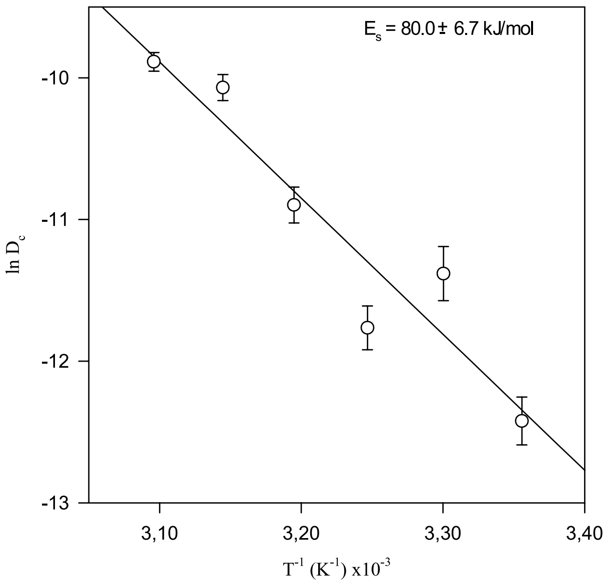

Fig. 5. The logarithmic plot of D_c values versus temperature T^{-1} according to Eq. (14). The slope of the linear relation produces the activation energy as $\Delta E_s = 80.0$ kJ mol^{-1} for swelling of the gel.

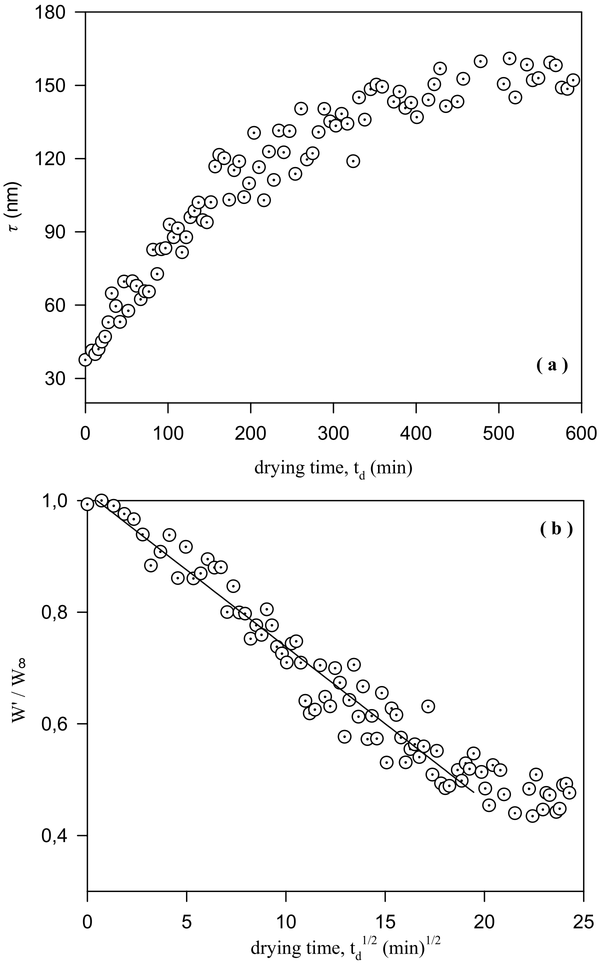

Fig. 6. (a) The plots of pyrene lifetimes, τ during drying versus drying time, t_d for the gel dried at 40 °C in air. τ values were obtained by fitting the $I(t)$ data to Eq. (6). (b) The plots of vapor release, W' from the gel dried at 40 °C in air versus square root of drying time, t_d. The slope of the linear relation in Eq. (16) produces desorption coefficient, D.

to be simplified, but still it is not modeled by considering elastic forces of the gel. During drying, it is assumed that there are two regions exist in the gel, i.e. less concentrated region near the surface separates itself from the high concentrated region by a boundary which moves during drying towards the center of the gel and as the boundary moves, vapor molecules evaporates from the surface of the gel into air. Then, the behavior of W' against t_d can be explained by considering a model in which diffusion occurs in two regions separated by moving interface [24]. The moving interface can be marked by a discontinuous change in concentration as in the absorption by a liquid of a single component from a mixture of gases or by a discontinuity in the gradient of concentration as in the progressive freezing of a liquid. Discontinuities have been observed in several practical systems, for instance when two metals interdifuse [24]. The sharp advancing boundary is well known in many polymer–solvent systems [25], which is considered as a discontinuity for some purposes. When the diffusion coefficient is discontinuous at a concentration c, i.e. the diffusion coefficient is zero below c and constant and finite above c, then the total amount, M_t of diffusing substance desorbed from unit area of a plane sheet of thickness d at time t, is given by the following relation

$$\frac{M_t}{M_\infty} = 2\left[\frac{D}{\pi d^2}\right]^{1/2} t^{1/2} \tag{15}$$

where D is constant diffusion coefficient at concentration c_1. Here $M_\infty = dc_1$ is the equilibrium value of M_t. If one assumes that the diffusion coefficient of polymer segments in the gel is negligible with compared to the desorption coefficient, D of vapor into air, then Eq. (15) can be written to employ our data in Fig. 6(a) as follows

$$\frac{W'}{W_\infty} = 2\left[\frac{D}{\pi d^2}\right]^{1/2} t_d^{1/2} \tag{16}$$

here it is assumed that M_t is proportional to the amount of vapor released at time, t_d.

The plot of normalized W' versus $t_d^{1/2}$ is presented in Fig. 6(b) for the gel dried at 40 °C. The desorption coefficient, D are obtained from the slope of linear relation in Fig. 6(b) using Eq. (16). Similarly treatments are performed for the other gel samples and measured D values are listed in Table 2, where it is observed that desorption coefficient increase as the temperature is increased. This result is expected since gel segments move much faster at high temperature, which cause faster evaporation of chloroform vapor from the gel. The drying activation energy, ΔE_d can be evaluated by using the following Arrhenius relation.

$$D = D_0 \exp(-\Delta E_d/kT) \tag{17}$$

where k the Boltzmann's constant and D_0 the cooperative diffusion coefficient at $T = \infty$. The logarithmic form of Eq. (17) is presented in Fig. 7 from where ΔE_d is found to be as 33.5 kJ mol^{-1}. From here, one can immediately conclude that the drying activation energy, ΔE_d is found to be smaller than the swelling activation energy, ΔE_s, i.e. gels under consideration need more energy to swell than to dry. Most probably during swelling elastic forces oppose vapor penetration, as a result diffusing molecule need more energy to overcome the elastic forces. However, during drying elastic forces are in favor of vapor evaporation, then gel spend less energy to be accomplishing drying process.

Several studies related to diffusion of aqueous and non-aqueous agents into polymeric networks have been reported in literature where corresponding activation energies are presented. Water sorption of networks based on 2-hydroxyethyl methacrylate-triethylenglycol dimethacrylate copolymers was investigated [26] gravimetrically and the apparent activation energy was found to be independent of composition of the networks, given a value of 15.5 kJ mol^{-1}. Solvent transport aromatic hydrocarbons through both crosslinked and uncrosslinked poly(ethylene-co-vinyl acetate) membranes has been investigated by using gravimetric technique [27]. The activation energies for the process of diffusion, sorption and permeation have been

Table 2
Drying parameters

Temperature (°C)	m_i (g)	m_f (g)	d_i (cm)	d_f (cm)	D (cm^2 s^{-1}) × 10^{-5}
50	0.168	0.078	0.26	0.205	7.00
45	0.166	0.085	0.26	0.215	6.36
40	0.167	0.083	0.26	0.205	4.97
35	0.211	0.089	0.28	0.210	3.37
30	0.178	0.089	0.27	0.215	3.08
25	0.247	0.083	0.27	0.205	2.70

m_i, d_i, initial weight and thickness of the PS gels; m_f, d_f, final weight and thickness of the PS gels; D, desorption coefficients.

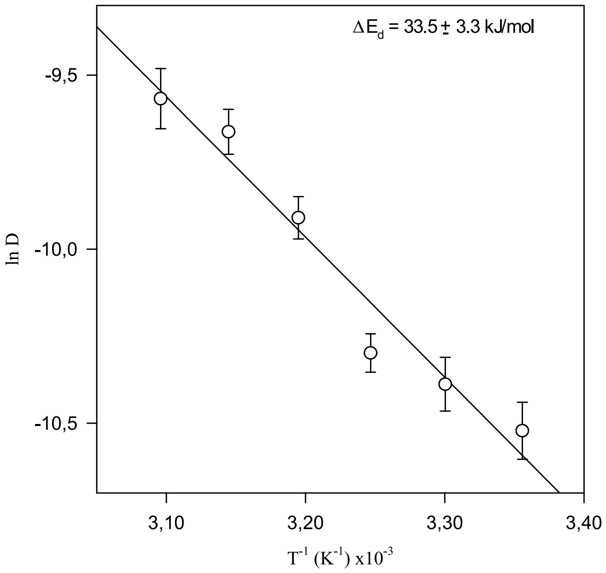

Fig. 7. Plot of the logarithmic form of Eq. (17) for the data in Table 2. Drying activation energy, $\Delta E_d = 33.5$ kJ mol^{-1} is obtained from the slope of the straight line.

measured and found to be in between 3 and 20 kJ mol^{-1} depending on the penetrant size. An investigation of sorption kinetics and diffusion of chloroalkanes into tetrafluoro ethylene/propylene copolymer membranes was reported [28], where activation energy of diffusion for chloroform was found to be around 15 kJ mol^{-1}. Diffusion and permeation properties of substituted benzenes through variety of membranes formed from blends of nitrile rubber and natural rubber have been studied in the temperature interval of 28–70 °C and the values of activation energies were measured to be around 10 kJ mol^{-1} [29]. These activation energies all correspond to typical diffusion processes and much lower than our finding (80.0 kJ mol^{-1}). The difference between literature values and our finding most probably originates from the difference between solvent and vapor penetration processes. From here one may conclude that high concentration gradient during solvent penetration lowers the value of the activation energy, however, system needs more energy during vapor sorption due to low concentration gradient. Resent work [30] oxygen diffusion in copolymers of ethylene and norbornene support these findings where the diffusion activation energy was found to be around 35–40 kJ mol^{-1} over the range of 5–35 °C temperature.

References

[1] Dusek K. Adv Polym Sci 1993;I:109.
[2] Peters A, Candau SJ. Macromolecules 1988;21:2278.
[3] Chiarelli P, De Possi D. Prog Colloid Polym Sci 1988;78:4.
[4] Dusek K, Prins W. Adv Polym Sci 1969;6:1.
[5] Candau S, Bastide J, Delsanti M. Adv Polym Sci 1982;7:44.
[6] Li Y, Tanaka T. J Chem Phys 1990;92(2):1365.
[7] Goerke U, Chamberlain AHL, Crilly EA, McDonald PJ. Phys Rew E 2000;62(4):5353.
[8] Russ T, Brenn R, Geoghegan M. Macromolecules 2003;36:127.
[9] Singh A, Mukherjee M. Macromolecules 2003;36:8728.
[10] Horie K, Mita I, Kawabata J, Nakahama S, Hirao A, Yamazaki N. Polym J 1980;12:319.
[11] Annaka M, Noda H, Motokawa R, Nakahira T. Polymer 2001;42:9887.
[12] Pekcan Ö. Chem Phys 1993;177:619.
[13] Miller E. J Photochem Photobiol, A 2002;152:249.
[14] Uğur Ş, Pekcan Ö. Polymer 2000;41:1571.
[15] Erdoğan M, Pekcan Ö. Polymer 2003;44:2129.
[16] Erdoğan M, Pekcan Ö. Compos Interface 2003;10(6):547.
[17] Kaya D, Pekcan Ö, Yilmaz Y. Phase Transit 2003;76(6):543.
[18] Erdoğan M, Pekcan Ö. Polymer 2001;42:4973.
[19] Lakowicz JR. Principles of fluorescence spectroscopy. New York: Plenum Press; 1983.
[20] Ware WR, James DR, Siemiarczuk S. Rev Sci Instrum 1992;63:1710.
[21] Birks JB. Photophysics of aromatic molecules. New York: Wiley/Interscience; 1971.
[22] Birks JB, Lumb MD, Munro IH. Proc R Soc A 1964;277:289.
[23] Pekcan Ö, Winnik MA, Egan LS, Croucher MD. Macromolecules 1983;16:669.
[24] Cranck J. Mathematics of diffusion. Oxford: Clarendon Press; 1975.
[25] Hartley GS. Trans Faraday Soc 1946;42:136.
[26] Peniche C, Cohen ME, Vazquer B, Roman JS. Polymer 1997;38(24):5977.
[27] Kumar SA, Tomas S, Kumaran MG. Polymer 1997;38(18):4629.
[28] Aminabhari TM, Harlapur SF, Balundgi RH, Ortega JD. Polymer 1998;39(5):1067.
[29] Mathai AE, Singh RP, Thomas SJ. Membr Sci 2002;202:35.
[30] Poulsen L, Zebger I, Klinger M, Larsen PS, Ogilby RP. Macromolecules 2003;36:7189.