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ORIGINAL PAPER

Effect of LCST on the swelling of PAAm-NIPA copolymers: a fluorescence study

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Abstract Temperature sensitive copolymers were prepared by free radical crosslinking copolymerization in aqueous solution with different molar percentage of *N*-isopropylacrylamide (NIPA) and acrylamide (AAm) monomers. *N,N′*-methylenebis (acrylamide) (BIS) and ammonium persulfate (APS) were used as a crosslinker and an initiator, respectively. The steady-state fluorescence (SSF) technique was used to determine the low critical phase transition temperature (LCST) for PAAm-NIPA copolymers. Swelling experiments were performed in water at various temperatures by real time monitoring of pyranine (*Py*) fluorescence intensity, *I* which decreased as swelling proceeded. The Stern–Volmer equation is modified for low quenching efficiencies to interpret the behavior of pyranine intensity during the swelling of PAAm-NIPA copolymers. The Li–Tanaka equation was used to determine the swelling time constants, τ_1 and the cooperative diffusion coefficients, D_0 from fluorescence intensity, weight and volume variations of the copolymers at various temperatures. It was observed that τ_1 first increased up to LCST, and then decreased; naturally D_0 decreased up to LCST and then increased upon increasing temperature. It was understood that (LCST) increases as PAAm contents increase in the PAAm-NIPA copolymers.

Keywords Swelling · Fluorescence · NIPA · Polyacrylamide · Copolymer · LCST

Abbreviations

Py	Pyranine
NIPA	*N*-isopropylacrylamide

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AAm	Acrylamide
APS	Ammonium persulfate
LCST	Low critical phase transition temperature
DSC	Differential scanning calorimetry
SEM	Scanning electron microscopy
TEMED	Tetramethylethylenediamine
D_0	Cooperative diffusion coefficients
τ_1	Swelling time constants

Introduction

Hydrogel is a hydrophilic three-dimensional network polymer, so it cannot dissolve when it hold a large amount of water and biochemical fluid [1]. As an example, polyacrylamide (PAAm) hydrogels are mainly obtained by free radical crosslinking copolymerization (FCC) of AAm in the presence of *N*,*N*′-methylene bis (acrylamide) (BIS) as the crosslinker. Since the monomers are solid at the polymerization temperature, the reactions are necessarily carried out in an aqueous solution of the monomers. On the other hand, poly (*N*-isopropylacrylamide) (NIPA) hydrogel is a typical temperature sensitive gel exhibiting volume phase transition in an aqueous solution [2–5]. The incorporation of hydrophobic comonomers leads to a low LCST and hydrophilic comonomers to a high LCST. Effect of comonomers hydrophilicity and ionization on the LCST of *N*-isopropylacrylamide copolymers was performed by differential scanning calorimetry (DSC). It was concluded that the changes in LCST caused by the incorporation of comonomers were due to changed in overall hydrophilicity of the polymer and were not due to a direct influence of comonomers hydrophilicity or charge on the structuring of water around hydrophobic groups, respectively [6]. Thermal properties of copolymers containing *N*-isopropylacrylamide were investigated by DSC and swelling measurements. The roles of water molecules and ionic groups in the network were discussed in relation to the volume phase transition [7, 8]. Synthesis and properties of poly (*N*-isopropylacrylamide) and poly (*N*-isopropylacrylamide-*co*-acrylamide) copolymers were prepared by radiation polymerization. It was investigated that lower critical solution temperature (LCST) of the hydrogels was changed by pH, ionic strength, and hydrophilic monomer (acrylamide) [9]. Swelling behavior of polyacrylamide-NIPA copolymers was discussed on the basis of the incorporated structure of guest particles (the spheres of NIPA gel with submicrometer diameter, which were synthesized by an emulsion-polymerized reaction in water) depending on the concentration of guest particles, acetone concentration, and temperature [10]. Synthesis, swelling, and interaction with ionic surfactants of thermosensitive poly (*N*-isopropylacrylamide-*co*-acrylamide) copolymers were modeled by Fickian mechanism [5] and the effect of the crosslinking degree on the morphology of poly(NIPA-*co*-AAc) copolymers were performed by scanning electron microscopy(SEM) [11].

The swelling kinetics of gels developed by Tanaka and Fillmore [12] and obtained from the kinetics of swelling agrees in terms of experimental accuracy with previous

experiments by Peters and Candau [13]. The steady-state fluorescence technique was employed to study the swelling of polyacrylamide gels at various temperatures [14] and with various crosslinker contents [15]. The results presented in this reference show that the fluorescence method can be used to measure the swelling time constants and the cooperative diffusion coefficients at a molecular level during swelling of polyacrylamide gel in water [14]. The Li-Tanaka model was used to measure these parameters. It was observed that the time constant decreased and the diffusion coefficient increased as the swelling temperature was increased and crosslinker content was increased, respectively. The Photon transmission technique was used to study the volume phase transition of polyacrylamide [16]. It was presented that polyacrylamide gels prepared with various *N*,*N*′-methylene bis (acrylamide) (BIS) concentrations in pure water were completely dried and then swollen in water [17]. The transmitted light intensity, I_{tr} from the gel increased in the initial stages when PAAm gels were immersed in water and then decreased exponentially as the swelling time increased. The decrease in I_{tr} was modeled using the Li–Tanaka equation [18], and it was attributed to the lattice heterogeneities which might originate between "frozen blob clusters" and holes in the swelling gel [19]. On the other hand, the phase behavior of poly (*N*-isopropylacrylamide) has been extensively studied as a representative gel exhibiting nearly critical phase transition [20, 21]. The effect of preparation temperature on phase transitions of *N*-isopropylacrylamide gel was studied by Pekcan and Kara [22], showed that when the temperature was increased above the set temperature during the phase transition process, and NIPA gel remembered its own heterogeneities which were gained during the gel formation process. Phase transitions of NIPA gels were prepared with various crosslinker contents [23], and the spinodal phase transition of NIPA gels was obtained by a suitable technique which could be used to study the heterogeneous gel systems.

This article examines the effect of temperature on the swelling process of PAAm-NIPA copolymers by using the steady-state fluorescence technique. The Stern–Volmer equation combined with Li–Tanaka equation was used to explain the behavior of the swelling of PAAm-NIPA copolymers at different temperatures. The swelling time constants, τ_1, and the cooperative diffusion coefficients, D_0, were determined for the swelling of PAAm-NIPA copolymers prepared at various acrylamide and NIPA contents. Supporting gravimetrical and volumetrical swelling experiments were also supported the results of the fluorescence measurements of PAAm-NIPA copolymers. It was observed that τ_1 first increased up to LCST, and then decreased; naturally D_0 decreased up to LCST and then increased by increasing temperature. We predicted that as PAAm increases in the PAAm-NIPA copolymers, the LCST increases.

Theory

Stern–Volmer model

The Stern–Volmer type of quenching mechanism can be proposed for the fluorescence intensity in the sample under consideration. According to the Stern–Volmer law, fluorescence intensity can be written as [24],

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \tag{1}$$

Here, k_q is the quenching rate constant, τ_0 is the lifetime of the fluorescence probe with no quenching has taken place, and $[Q]$ is the quencher content and I_0 is the fluorescence intensity for the zero quencher content. This is referred to as the Stern–Volmer equation.

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

$$I \approx I_0 \left(1 - \tau_0 k_q [Q]\right) \tag{2}$$

If one integrates Eq. 2 over the differential volume (dv) of the sample from the initial a_0 to final a_∞ thickness, then reorganization of the relation produces the following useful equation.

$$W = \int_{a_0}^{a_\infty} [W] \mathrm{d}\upsilon \tag{3}$$

In our case, the amount of water diffusion, W is calculated over the differential volume by replacing Q with W as

$$W = \left(1 - \frac{I}{I_0}\right) \frac{\upsilon}{k_q \tau_0} \tag{4}$$

Here it is assumed that water molecules are the only quencher for the excited pyranine molecules in our system. Where υ is the volume at the equilibrium swelling state, which can be measured experimentally, k_q was obtained from separate measurements by using Eq. 1 where the infinity equilibrium value of water diffusion, W, was used for each sample. Since τ_0 (5 ns) is already known for pyranine molecules, then the measured values of I, W, and V at the equilibrium swelling condition can be used to calculate k_q for each swelling experiment separately.

Li–Tanaka model

Volume phase transitions in gels may occur from dry to swollen states either continuously, or by sudden jumps between them. In a dried state, a gel is a solid material which swells until it reaches the swelling equilibrium when a solvent is added. The solvent molecules are kept in the three dimensional mesh and the combination of the mesh and solvent molecules creates a "world" having characteristic properties which can be either isolated from isochore or linked to isobar. The volume phase transition was experimentally discovered for a partially ionized acrylamide gel in a mixture of acetone and water by Tanaka [25]. The theory of the kinetics of the swelling of a crosslinked polymeric network has been derived by Tanaka and Fillmore [12]. Li and Tanaka [26] proposed a two process mechanism based on the assumption that gel swelling and shrinking are not a pure diffusion process. The shear modulus plays an important role: it keeps the system in

shape due to coupling of any change in different directions. As a result of this, the geometry of the gel plays an important role [27].

The kinetics of the swelling of a gel is comprehensively described by the behavior of the displacement vector as a function of space and time. The equation of motion has been suggested the following relation [26]

$$\frac{\partial \vec{u}}{\partial t} = D_0 \vec{\nabla}^2 \vec{u} \tag{5}$$

where $\vec{u}$ is the displacement vector measured from the final equilibrium location after the gel is fully swollen ($\vec{u} = 0$ at $t = \infty$). $D_0 = (K + 4\mu/3)/f$ is the cooperative diffusion coefficient. Here t denotes the time and K is the bulk modulus. The high value of the friction coefficient, f between the network and solvent overdamps the motion of the network, resulting in a diffusion-like relaxation.

Swelling experiments of disk-shaped gels have shown that the relative changes of diameter and thickness are the same, indicating that the gel swelling processes are not pure diffusion processes. This feature was due to the shear modulus of the network keeping the system in shape by minimizing the non-isotropic deformation. Since, during a shear relaxation process, there is no relative motion and hence no friction between gel network and solvent, the system can instantly adjust its shape to minimize the total shear energy. For a disk-shaped gel, any change in diameter is coupled to 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 diffusion. The shear energy, on the other hand, can be minimized instantly by readjusting the shape of the gel [26]. As long as the shear modulus μ is not zero, the change of the total shear energy in response to any small change in shape that maintains constant volume element within the gel should be zero,

$$\delta F_{\mathrm{sh}} = 0 \tag{6}$$

Each small diffusion process determined by Eq. 5 must couple to a small shear process given by Eq. 6 producing the following relation for a disk-shaped gel

$$\frac{u_r(r,t)}{r} = \frac{u_z(a,t)}{a} \tag{7}$$

where r is the radius and a is the half thickness of the gel. Equation 7 indicates that the relative change in shape of the gel is isotropic, i.e., the swelling rates of a disc in the axial (z) and radial (r) directions are the same.

Simultaneous solution of Eqs. 5 and 6 produces the following equations for the swelling of a disk gel in axial and radial directions [26].

$$u_z(z,t) = u_z(z,\infty) \sum_n B_n \mathrm{e}^{-t/\tau_n} \tag{8a}$$

$$u_r(r,t) = u_r(r,\infty) \frac{z}{a} \sum_n B_n \mathrm{e}^{-t/\tau_n} \tag{8b}$$

where the axial and radial displacements are expressed as a series of components, each of them decaying exponentially with a time constant, τ_n. The first terms of the

expressions are dominant at large t that is at the last stage of swelling. Eq. 8 can also be written in terms of water uptakes W and W_f at time t and equilibrium, respectively, as follows:

$$1 - \frac{W}{W_f} = \sum_{n=1}^{\infty} B_n \exp(-t/\tau_n) \tag{9}$$

In the limit of large, t or if τ_1 is much larger than the rest of τ_n, all higher terms ($n \geq 2$) in Eq. 9 can be omitted and the swelling kinetics is given by the following relation

$$\frac{W}{W_f} = 1 - B_1 \exp(-t/\tau_1) \tag{10}$$

where B_1 is given by the following relation:

$$B_1 = \frac{2(3 - 4R)}{\alpha_1^2 - (4R - 1)(3 - 4R)} \tag{11}$$

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

$$R = \frac{1}{4}\left[1 + \frac{\alpha_1 J_0(\alpha_1)}{J_1(\alpha_1)}\right] \tag{12}$$

where J_0 and J_1 represent Bessel functions. It should be noted from Eq. 9 that $\sum B_n = 1$; therefore B_1 should be less than 1. B_1 is related to the ratio, R [26], of the shear modulus, μ and longitudinal osmotic modulus, $M = (K + 4\mu/3)$. Once the value of B_I is obtained, one can determine the value of $R = \mu/M$. Here we have to note that Eq. 10 can also be obtained by using theoretical results; in the case of $R \to 3/4$ ($\mu/K \to \infty$), the swelling time constant $\tau_1 \approx (3/4 - R)^{-1}$goes to infinity and all B_n go to zero except B_1, which goes to unity. τ_1 is related to the cooperative diffusion coefficient, D_0 at the surface of a gel disk by

$$D_0 = \frac{3a_f^2}{\tau_I \alpha_1^2} \tag{13}$$

where α_1 is a function of R only [26], and a_f stands for the half thickness of the gel in the final equilibrium state. Hence, D_0 can be calculated.

Experimental

Materials

Copolymer was prepared with various molar percentages of PAAm and NIPA in distilled water at room temperature by keeping 2 M. 0.01 g of BIS (*N,N′*-methylenebisacrylamide, Merck), 0.008 g of APS (ammonium persulfate, Merck), and 2 μL of TEMED (tetramethylethylenediamine, Merck) were dissolved in 5 mL distilled water (pH 6.5). Pyranine (*Py*) concentration was kept constant at

4×10^{-4} M for all experiments. The solution was stirred (200 rpm) for 15 min to achieve a homogenous solution. All samples were deoxygenated by bubbling nitrogen for 10 min just before the polymerization process [28]. The swelling experiments of disk-shaped PAAm-NIPA copolymers prepared with various molar percentages of (100 PAAm %, 90 PAAm % + 10 NIPA %, 75 PAAm % + 25 NIPA %, 50 PAAm % + 50 NIPA %, 25 PAAm% + 75 NIPA %, 10 PAAm % + 90 NIPA %, 100 NIPA %) were performed in water at temperatures of 20, 30, 40, 50, and 60 °C.

Fluorescence measurements

After drying these copolymers, swelling experiments of disk-shaped PAAm-NIPA copolymers were performed at various temperatures in the water. The fluorescence intensity measurements were carried out using a Model LS-50 spectrometer from Perkin-Elmer, equipped with a temperature controller. All measurements were made at 90° position and spectral bandwidths were kept at 5 nm. Disk-shaped copolymers were placed on the wall of a 1 cm path length, square quartz cell filled with water for the swelling experiments. We used *Py* in the PAAm-NIPA copolymers as a fluorescence probe. The *Py* is a derivative of pyrene including three SO_3^- groups which can form bonds with positive charges on the copolymers. The *Py* can be attached to the gel by Coulombic attractions [29].

The copolymers were excited at 340 nm during in situ experiments and emission intensities of the pyranine were monitored at 427 nm as a function of swelling time. As the water diffusion was increased, the fluorescence intensity, I_{em} decreased and the scattered light intensity, I_{sc} increased due to the increase in turbidity of the swelling gel. The position of the PAAm-NIPA copolymer which was behind the hole in the cell and fixed by stainless steel wire and the incoming light beam for the fluorescence measurements are shown in Fig. 1 during the swelling of the copolymer in distilled water. One side of the quartz cell was covered by black cardboard with a circular hole which was used to define the incoming light beam and limit its size to the initial dimensions of the gel disc. At the same time, the gravimetric measurements were performed by measuring weight. The distance and thickness of the PAAm-NIPA copolymer were also measured to calculate the volume of the PAAm-NIPA copolymer from the formula for a cylinder's volume.

Results and discussion

Figure 2 presents the fluorescence spectra of pyranine from PAAm-NIPA copolymers in 0 and 60 min during the swelling process of 10% NIPA content in pure water at 50 °C where it is seen that as the water uptake is increased, the fluorescence intensity, I_{em} decreased and the scattered light intensity, I_{sc} increased. In order to elaborate the above findings, first of all we have to be mentioned that two different phenomena causes the decrease in the fluorescence emission intensity, I_{em}; first one is the quenching of excited pyranines and the other one is the scattering of light

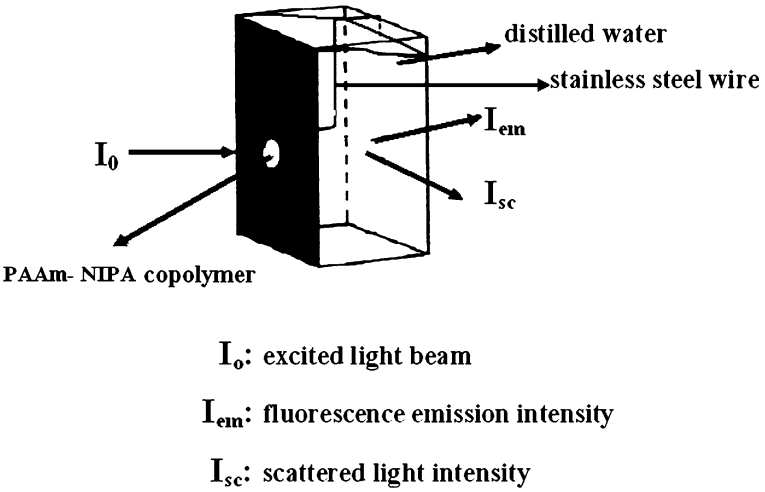

Fig. 1 The position of PAAm-NIPA copolymer in the fluorescence cell during swelling in water. I_0 is excitation, I_{sc} is scattered, and I_{em} is emission maximum light intensities at 340 and 427 nm, respectively. The PAAm-NIPA copolymer is behind the *circular hole* in the *black cardboard* and fixed by stainless steel wire in the cell

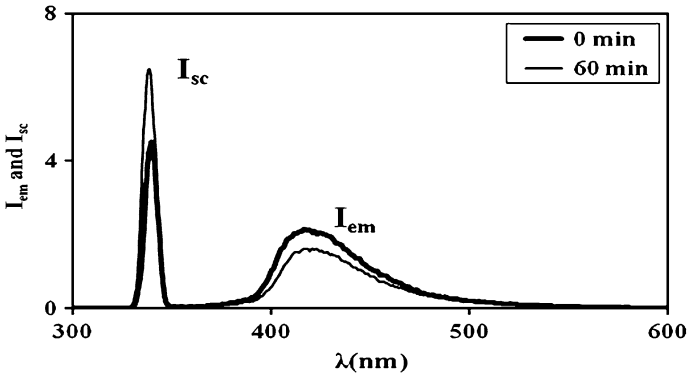

Fig. 2 Fluorescence spectra of pyranine from the copolymer during swelling in water at 50 °C for 10% NIPA content gel sample. Each *curve* indicates the swelling times in different minutes

from the gel due to turbidity. As far as the turbidity is concern, it has been known that the swelling and elastic properties of acrylamide gels are strongly influenced by large scale heterogeneities in the network structure [30, 31]. In the swollen state these imperfections manifest themselves in a non uniformity of polymer concentration. These large-scale concentration heterogeneities do not appear in the dry state but only in the gel at the swollen, equilibrium state [32]. Light scattering experiments by Bastide et al. [33] seem to confirm this picture. A gel can be described as a random distribution of crosslinks on a lattice formed by the interchain contact points. When two junctions are located on neighboring lattice sites, a

"frozen blob" is formed in that region [32]. In the swollen state of a gel, these crosslinks cannot move apart from each other, since they are chemically connected by a chain segment which is in an optimal excluded volume conformation. Frozen blobs are often connected and form clusters of first topological neighbors. As a result the random cross-linking of chains can be described as a site percolation on a blob lattice. When the gel is in a good solvent it swells and frozen blob clusters expand less than the interstitial medium. Here the swelling of gel leads to an excess scattering of light which comes from the contrast between frozen blob clusters and holes created by the dilution. During the dilution process in gel swelling, the partial separation of frozen blob clusters leads to a strong increase of the scattering intensity, I_{sc} or decrease in the transmitted light intensity, I_{tr}.

In situ photon transmission technique for study the aging of acrylamide gels due to multiple swelling was reported from our laboratory, where it was observed that the transmitted light intensity, I_{tr}, decreases continuously when PAAm gel swells. The same technique was employed to study swelling of PAAm gels with various crosslinker concentrations, where decrease in I_{tr} was explained using the frozen blob model [17].

As far as the correction of fluorescence emission is concern, totally empirical formula was introduced [14, 15] to produce the meaningful results for the fluorescence quenching mechanisms. Here the main idea is to eliminate the structural fluctuation due to the frozen blobs and holes during swelling by using I_{sc}, i.e., one has to produce the corrected fluorescence intensity, I by dividing emission intensity, I_{em} to scattering intensity, I_{sc} to exclude the effect of turbidity of the gel on the fluorescence emission intensity and elaborate the Stern–Volmer model by using solely fluorescence intensity, I.

Figure 3 shows the variations of the corrected pyranine intensities, I ($=I_{em}/I_{sc}$) of PAAm-NIPA copolymers versus swelling time during swelling process for 90% NIPA content copolymers for 30 and 50 °C. As the swelling time, t, increased, quenching of excited pyranines increased due to water uptake. It should also be noted that quenching became more efficient at higher NIPA contents. In order to quantify these results, a collision type of quenching mechanism may be proposed for the fluorescence intensity, I, in the gel sample during the swelling process by using Eq. 2. W can be calculated by using Eq. 4 and the measured I values at each step of the swelling [24]. Here, it is assumed that the k_q values do not vary during the swelling processes, i.e., the quenching process solely originates from the water molecules. Plots of water uptake, W, versus swelling time are presented in Fig. 4a. The logarithmic form of the data in Fig. 4a was fitted to the following relation produced from Eq. 10

$$\ln\left(1-\frac{W}{W_f}\right)=\ln B_1-\frac{t}{\tau_1} \tag{14}$$

Here, τ_1 is the swelling time constant, measured by the fluorescence technique and B_1 is related to the ratio of the shear modulus, μ and longitudinal osmotic modulus, M by Eq. 11. Using Eq. 14 linear regression of the curves in Fig. 4a

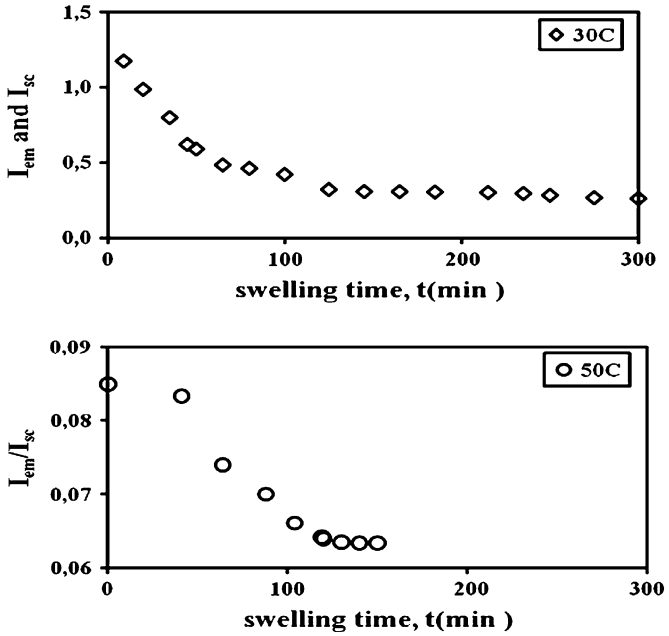

Fig. 3 Corrected fluorescence intensities of pyranine, I (= I_{em}/I_{sc}) versus swelling time, t during the swelling process at **a** 30, and **b** 50 °C for 90% NIPA content copolymers, respectively

provided us with B_1 and τ_{1I} values. Taking into account the dependence of B_1 on R, one obtains R values and from the α_1-R dependence α_I value was based on the method described by Li and Tanaka [26]. Then, using Eq. 13, cooperative diffusion coefficients D_0 were determined for these disk-shaped copolymers and found to be around 10^{-9} m^2/s. Experimentally obtained τ_{1I} and D_{0I} values are summarized in Table 1. It should be noticed that D_{0I} values decreased until LCST, and then increased above LCST by increasing temperature as shown in Fig. 5a. Figure 6 presents the variation of LCST versus NIPA content where it is seen that LCST temperature approaches to its original value (∼30 °C) as the NIPA content is increased. The curve in Fig. 6 was produced using Table 1 and/or Fig. 5 where LCST corresponds to the temperature at which D_{0I} is the minimum for each NIPA content gel sample.

The plots of the water uptake, W, versus swelling time measured gravimetrically for two of the PAAm-NIPA copolymers swollen in water are shown in Fig. 4b. These are typical solvent uptake curves, obeying the Li–Tanaka equation, Eq. 10. The logarithmic forms of the data in Fig. 4b were fitted by using Eq. 14, from which B_1 and the gravimetric time constant, τ_{1w} were determined. Then, using Eq. 13, the gravimetric cooperative diffusion coefficient D_{0w}, was determined and is listed in Table 1 with the τ_{1w} values. A similar behavior in D_{0w} as for D_{0I} was observed, i.e., the LCST increased by increasing acrylamide content in the copolymers as shown in Fig. 6.

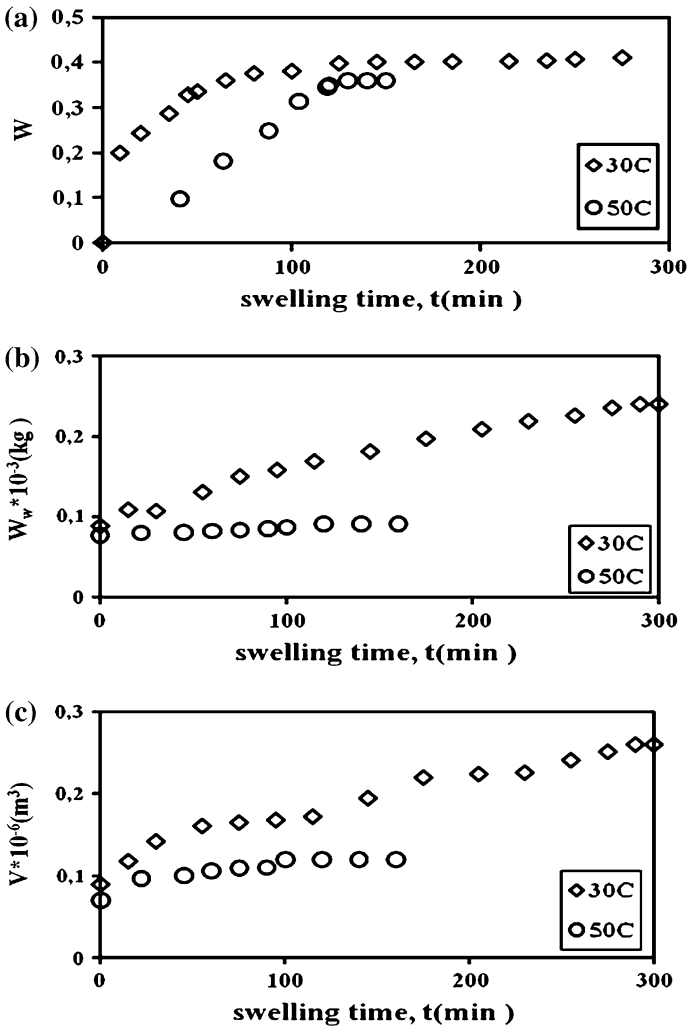

Fig. 4 **a** The plots of fluorescence data by using Eq. 4, versus swelling time, *t*, for PAAm-NIPA copolymers swollen in water measured by fluorescence technique, **b** the plots of the water uptake, *W*, variation versus swelling time, *t*, for PAAm-NIPA copolymers swollen in water measured by gravimetrically technique, and **c** The plots of the volume, *V*, variation versus swelling time, *t*, for PAAm-NIPA copolymers swollen in water measured by volumetric technique at 30, and 50 °C for 90% NIPA content copolymers, respectively

The volume, *v*, variations of the PAAm-NIPA copolymers during the swelling process were also measured. The plots of the volume, *v*, versus swelling time for PAAm-NIPA copolymers swollen in water are presented in Fig. 4c, which are again typical solvent uptake curves, obeying the Li–Tanaka equation, Eq. 10. The logarithmic forms of the data in Fig. 4c were fitted by using Eq. 14 from which B_1 and volumetric time constants, τ_{1v} were determined. Here it is assumed that the relation between *W* and *v* was linear, then using Eq. 13 the volumetric cooperative

Table 1 Experimentally measured parameters of PAAm-NIPA copolymers for various temperature and with various molar percentages of NIPA content during swelling process

Molar % NIPA	T (°C)	τ_{1I} (min)	$D_{0_I} \times 10^{-9}$ (m^2/s)	τ_{1w} (min)	$D_{0w} \times 10^{-9}$ (m^2/s)	τ_{1v} (min)	$D_{0v} \times 10^{-9}$ (m^2/s)
0	20	88.00	1.48	217.77	0.25	250.00	0.21
	30	85.00	0.95	250.00	0.47	232.55	0.28
	40	48.50	4.00	73.00	0.50	189.00	0.35
	50	37.70	7.10	58.00	0.60	70.00	0.50
	60	25.00	7.30	47.00	1.20	47.00	0.85
10	20	76.92	1.45	223.90	1.51	200.00	2.31
	30	90.00	1.00	232.55	1.42	212.76	1.95
	40	153.84	0.92	256.41	0.82	243.90	1.33
	50	200.00	0.52	263.15	0.54	250.00	0.67
	60	171.42	0.67	235.84	0.55	232.55	0.83
25	20	117.64	1.38	250	0.93	222.22	1.92
	30	125.00	0.91	263.15	0.80	232.55	1.62
	40	166.66	0.83	270.27	0.65	250.00	0.62
	50	256.41	0.58	277.77	0.47	277.77	0.38
	60	250.00	0.65	263.90	0.52	259.06	0.53
50	20	181.81	0.74	270.27	0.91	243.90	1.89
	30	250.00	0.65	285.71	0.74	250.00	1.51
	40	270.27	0.49	289.01	0.58	263.15	0.59
	50	294.11	0.46	294.11	0.45	307.69	0.44
	60	270.27	0.60	263.15	0.48	285.71	0.48
75	20	250.00	0.58	285.71	0.73	285.71	1.51
	30	270.27	0.45	294.11	0.65	294.11	0.92
	40	294.11	0.35	322.58	0.32	322.58	0.37
	50	289.01	0.42	307.69	0.44	312.50	0.41
	60	277.77	0.40	294.11	0.46	294.11	0.47
90	20	270.27	0.42	303.00	0.63	312.50	0.54
	30	370.37	0.25	333.33	0.25	333.33	0.25
	40	285.71	0.32	322.58	0.46	322.58	0.33
	50	294.11	0.37	312.50	0.48	312.50	0.40
	60	285.71	0.38	307.69	0.50	307.69	0.46
100	20	Opaque	Opaque	307.69	0.60	318.00	0.52
	30			338.98	0.21	338.98	0.08
	40			333.33	0.35	333.33	0.25
	50			325.73	0.37	325.73	0.37
	60			325.73	0.45	325.73	0.45

τ_{II} The Li–Tanaka time constant of fluorescence measurement, τ_{Iw} The Li–Tanaka time constant of gravimetric measurement, τ_{Iv} The Li–Tanaka time constant of volumetric measurement, D_{0I} fluorescence cooperative diffusion coefficient, D_{0w} gravimetric cooperative diffusion coefficient, D_{0v} volumetric cooperative diffusion coefficient

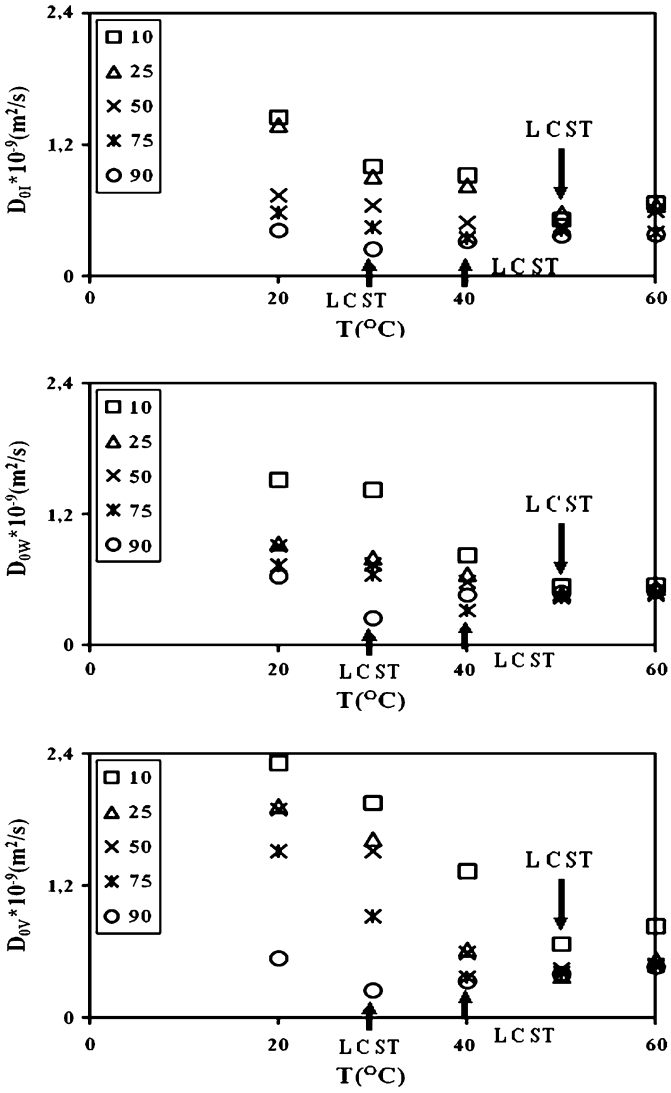

Fig. 5 The behavior of D_0 against temperature. The junction of *broken lines* presents the LCST from each samples **a** fluorescence, **b** gravimetrically, and **c** volumetric techniques for different NIPA contents, respectively

diffusion coefficients, D_{0v} were produced and are listed in Table 1 with the τ_{1v} values. Figure 5b, c presents the behaviors of D_0 values against temperature, measured by gravimetrical and volumetric techniques, respectively. Here the observed LCST is plotted in Fig. 6 against NIPA content; where similar argument can be made for fluorescence measurement.

The swelling time constants, τ_1 with respect to temperature measured by fluorescence, gravimetric and volumetric techniques are all presented similar

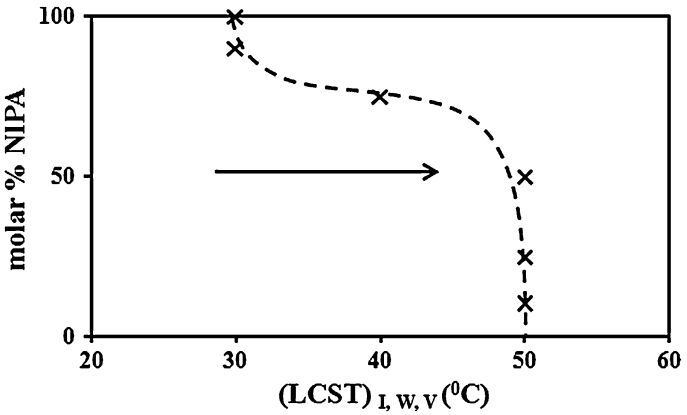

Fig. 6 Plot of NIPA content versus LCST. It is seen that as NIPA content is increased LCST approaches to original value (∼30 °C) for fluorescence, gravimetrically, and volumetric techniques, respectively

behaviors, i.e., gel swells faster above and below LCST during water uptake process. In other words, the largest Li–Tanaka time constant has been observed at LCST for each NIPA contents as shown in Table 1.

On the other hand, as seen in Fig. 5, cooperative diffusion coefficients are decreased up to LCST, and then increased above LCST for a given NIPA content gel. This is because the incorporation of hydrophobic comonomers leads to lower LCST, however, hydrophilic comonomers present higher LCST. It has been found that copolymerizing NIPA (NIPA exhibits it's LCST in water at 31 °C) with acrylamide (hydrophilic) leads to a higher LCST and a lower endothermic heat of phase separation. This part can be explained by knowing that the crosslinked gel poly (*N*-isopropylacrylamide) (NIPA) has been shown to exhibit discontinuous volume transitions in water in response to an increase in temperature [34]. Here, one can argue that PAAm-NIPA copolymers collapse at LCST of NIPA by presenting lowest D_0 values, i.e., slow diffusion and segmental motion, at where gel swell slowly. Increasing NIPA content in copolymer decreases LCST to its original value (∼30 °C).

Conclusion

The results in this study have shown that the fluorescence method can be used to monitor swelling kinetics of PAAm-NIPA copolymers in water for various temperatures. This technique was employed to measure the swelling time constants, τ_1, and the cooperative diffusion coefficients, D_0 for copolymers prepared with various percentages of PAAm and NIPA contents. The Li–Tanaka model was applied to measure these parameters and results were interpreted in terms of the swelling time constants, τ_1 and the cooperative diffusion coefficient, D_0 as the NIPA content increased. It is observed that the decrease in LCST is due to the increase in NIPA content in the PAAm-NIPA copolymers. LCST approaches its original value

($\sim$30 °C) at highest NIPA content where D_0 value found to be its minimum. It has to be noted that τ_1 values measured by using fluorescence technique are smaller than the values measured by volumetric and gravimetric techniques, which may predict the observation of different mechanisms of the swelling gel. It is obvious that the fluorescence technique measures the behavior of the microstructure of the gel, i.e., since pyranine molecules are bounded to the polymer chains, segmental motion of the gel network can be monitored by using fluorescence technique which detects the swelling of the gel at a molecular level. However, volumetric and gravimetric measurements provide us with the information of the macroscopic (i.e., bulk) behavior of the gel. According to the above presented argument, one may suggest that chain segments move much faster presenting short response time (τ_1) than the bulk polymeric material itself during the swelling process.

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