
Investigation of Drying of Poly(*N*-isopropylacrylamide-*co*-acrylamide) by Fluorescence Technique

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ABSTRACT: The steady-state fluorescence technique was performed on drying of various molar percentages of poly(*N*-isopropylacrylamide-*co*-acrylamide) [poly(NIPA-*co*-AAc)] to elucidate the mechanism of temperature-induced phase separation and the effect of monomer content. Poly(NIPA-*co*-AAc) copolymers were prepared by free radical cross-linking copolymerization. The fluorescence intensity, *I*, of pyranine, introduced as a probe, increased as drying time was increased for all samples. The behavior of *I* was modeled by using the Stern–Volmer equation combined with the moving boundary diffusion model. The desorption coefficient, *D*, increased as NIPA content was increased at a given temperature. Gravimetric and volumetric experiments also supported the results of the fluorescence technique. The energy, ΔE , values were measured for the drying processes for each molar percentage of NIPA monomer content by using fluorescence, gravimetric, and volumetric methods, respectively. It is understood that ΔE values decrease by increasing NIPA content, until 50% NIPA, and then increase after 50% NIPA, indicating that the phase separation has occurred at 50% NIPA. © 2012 Wiley Periodicals, Inc.

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Introduction

Special polymers and hydrogels are highly hygroscopic, and the shrinking and/or drying of these materials encompass many fields of technology. The quantity of bound water associated with the polymer varies as per the internal structure of the gel, that is, monomer and cross-linking agent proportions are responsible for both the porous structure and the pore size of the gel. Different models to explain drying mechanisms have been studied by many investigators.^{1,2} Diffusion,³ shear modulus,⁴ and the status of the mechanism and practice of drying mechanisms of gels as stresses and cracking⁵ were investigated.⁶ The drying of polyacrylamide gel and cellulosic paste has been studied by a diffusive drying model.⁷ Water diffusion and drying in polyacrylamide gels were studied using a mathematical model with independent parameters, which analyze the critical physical phenomenon.⁸ The experimental characteristics of a drying curve of plaster slabs were found to depend strongly on the thicknesses of the material.⁹ This study is based on the receding evaporating front model and on the assumption of a parabolic moisture content profile in the diffusion zone of the wet region. Different methods for fitting and smoothing drying curves are compared, which can be used in industrial design.¹⁰ The prediction of the drying kinetics for slab geometry has been proposed by Coumans.¹¹ The structural and thermodynamic properties of hydrophobic material in a spherical cavity were studied by Wallqvist et al.¹²

Several experimental techniques have been employed to study the kinetics of drying of chemical and physical gels, for example, neutron scattering, quasielastic light scattering,¹³ macroscopic experiments,¹⁴ and in situ interferometric measurements.¹⁵ The hydrophobicity and dynamic characteristics of cross-linked polystyrene with a dansyl probe were investigated as the first fluorescence study on polymer gels.¹⁶ Our group reported that the photon transmission technique can be used to study the drying of polyacrylamide (PAAm) gels

with various cross-linker contents¹⁷ and with various water contents.¹⁸ Recently, the steady-state fluorescence technique was employed for studying the drying of polyacrylamide at various temperatures¹⁹ and various cross-linker contents.²⁰

Poly(*N*-isopropylacrylamide), NIPA, is one of the well-known thermal-dependent water-soluble polymers with a lower critical solution temperature (LCST) at 31–35°C, and its network reveals unique thermal volume transitions near LCST.^{21–23} Intermolecular interactions might occur mainly between NIPA molecules and water, when temperature was below the LCST, but when the temperature was above the LCST NIPA molecules may aggregate in water as a result of both the intermolecular interactions within NIPA molecules and the hydrophobic interactions in the system.²⁴ Although the behavior of NIPA gel in aqueous solutions has been extensively investigated,^{21–23} only a few studies have been carried out on its behavior in the solid state. It is of particular interest whether the drying method can alter the physicochemical properties of the dried NIPA gel to influence its thermal-dependent behavior. Drying methods affected the particle sizes, phase transition, deswelling, reswelling processes, and morphology of NIPA microgel beads. Lin et al. investigated that drying methods affected the particle sizes, phase transition, deswelling, reswelling process, and morphology of NIPA microgel beads.²⁴ Deuterium isotope effects on swelling–shrinking states of poly(NIPA-*co*-AAc) copolymers in aqueous solutions were investigated by using fluorescence spectroscopy. These effects in the microenvironment changes of NIPA gel and polyacrylamide gel displayed similar characteristics.²⁵ Lee and Yeh reported the effect of hydrophobic monomer on the swelling behavior and mechanical properties of the copolymeric hydrogels.²⁶ Results showed that the equilibrium swelling ratio and critical gel transition temperature decreased with an increase in the hydrophobic monomer content.

This paper focuses on the drying process of poly(NIPA-*co*-AAc) copolymers to elucidate the mechanism of temperature-induced phase separation and the effect of monomer content during

drying. In the present investigation, we prepared various molar percentages of AAC and NIPA mixtures and employed the steady-state fluorescence technique, during drying at various temperatures. We demonstrated that the drying of poly(NIPA-co-AAc) copolymers was monitored by using the steady-state fluorescence technique and quantified by the moving boundary model combining the Stern–Volmer equation. The effect of monomer content on the mechanism of temperature-induced phase separation was measured. Water desorption coefficients, D , were determined for the drying copolymers prepared with various molar percentages of NIPA content at different temperatures. Drying energies ΔE were measured for each copolymer. It is well understood that phase separation occurred at 50% NIPA.

Theoretical Considerations

STERN–VOLMER KINETICS

Fluorescence or phosphorescence or photochemical reactions with the concentration of a given reagent can be a substrate or a quencher in the Stern–Volmer kinetics, which is broadly applicable to variations of quantum yields of photophysical processes. In the simplest case, a plot of fluorescence intensity versus concentration of quencher [Q] is linear, obeying the following equation²⁷:

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \quad (1)$$

Here, k_q is the quenching rate constant, τ_0 is the lifetime of the fluorescence probe, [Q] is the quencher concentration, and I_0 is the fluorescence intensity for the zero quencher content. This relation is referred to as the Stern–Volmer equation.

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

$$\begin{aligned} \frac{I}{I_0} &= (1 + k_q \tau_0 [Q])^{-1} \\ &= 1 - \tau_0 k_q [Q] + \frac{1}{2} [\tau_0 k_q [Q]]^2 - \dots \end{aligned} \quad (2)$$

Equation (1) becomes

$$I \approx I_0 (1 - \tau_0 k_q [Q]) \quad (3)$$

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

following useful equation:

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

Here, the amount of water desorption, W , is calculated over differential volume by replacing Q with W as

$$W = \int_{a_0}^{a_\infty} [W] d v \quad (5)$$

Here it is assumed that water molecules are the only quencher for the excited pyranine molecules in our system. Where v is the volume at the equilibrium drying state, which can be measured experimentally, k_q is obtained from separate measurements by using Eq. (1), where the infinity equilibrium value of water release, W is used for each sample. The measured values of v and I at equilibrium drying condition are used to calculate k_q for each drying experiments separately.

MOVING BOUNDARY DIFFUSION MODEL

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions. Fick's first and second laws of diffusion were first formulated by Fick, in a direct analogy with the equations of heat conduction.

If the diffusion is one dimensional in the sense that a concentration gradient exists only along the direction of x , C , and $\partial C / \partial x$ are everywhere independent of y and z , that diffusion is governed by the following simple equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (6)$$

where D is the diffusion coefficient measured (m^2/s), C is the concentration of diffusing substance (mol/m^3), and x is the position in the substance (m).

The more general cases in which the diffusion coefficient changes discontinuously from one constant finite value to another at one or more concentrations require a detailed calculation. At the concentration at which a discontinuous change in D occurs, there is also a discontinuity in the concentration gradient and the way in which this move has to be determined. The problem can be stated mathematically as follows:

Suppose that diffusion takes place into a semi-infinite medium and that the surface $x = 0$ is maintained at a constant concentration C_1 . We shall first consider a diffusion coefficient in which a discontinuity occurs at a concentration C_x . For concentrations less than $C_x D = D_2$, and for concentrations greater than $C_x D = D_1$. Suppose that at time t , the discontinuity in the concentration gradient occurring at C_x is at $x = X(t)$; this is a function of t , which has to be determined. At time t , let the concentration in the region $0 < x < X$ be denoted by c_1 and in the region $x > X$ by c_2 . At the discontinuity, the concentrations c_1 and c_2 must be the same and also the mass of diffusing substance must be conserved, so we have

$$c_1 = c_2 = C_x \quad x = X \quad (7)$$

$$D_1 \frac{\partial c_1}{\partial x} = D_2 \frac{\partial c_2}{\partial x} \quad x = X \quad (8)$$

In the region $0 < x < X$,

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} \quad 0 < x < X \quad (9)$$

$$c_1 = C_1 \quad x = 0 \quad (10)$$

and in the region $x > X$,

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2} \quad x > X \quad (11)$$

$$c_2 = C_2 \quad x = \infty \quad (12)$$

These differential equations are solved with Neumann's method at boundary conditions. The solutions satisfy

$$c_1 = C_1 + A \operatorname{erf} \frac{x}{2\sqrt{(D_1 t)}} \quad (13)$$

$$c_2 = C_2 + B \operatorname{erfc} \frac{x}{2\sqrt{(D_2 t)}} \quad (14)$$

where A and B are constants. For all values of t , x must be proportional to $t^{1/2}$

$$x = kt^{1/2} \quad (15)$$

where k is a constant.

After finding constants, the solution of Eq. (8) can be written for non-steady state

$$C = C_1 + \frac{2}{l} \sum_{n=0}^{\infty} e^{-D_1(2n+1)^2\pi^2(t-t_0)/4l^2} \sin \frac{(2n+1)n\pi}{2l} \times \left\{ \frac{2(-1)^{n+1}lC_1}{(2n+1)\pi} + \int_0^l f(x) \sin \frac{(2n+1)n\pi}{2l} dx \right\} s \quad (16)$$

where the surface of the sheet $x = 0$ is maintained at C_1 , the center of the sheet is at $x = l$, and $f(x)$ is the concentration distribution through the sheet at time $t = t_0$.

The total amount M_t , the diffusion substance present in half sheet at time t , is obtained by integrating the right-hand side of Eq. (16) with respect to x between the limits 0 and l and is given by

$$\frac{M_t}{lC_1} = 1 + 2 \sum_{n=0}^{\infty} e^{-D_1(2n+1)^2\pi^2(l-l_0)/4l^2} \times \left\{ \frac{2(-1)^n}{(2n+1)\pi} \int_0^l \frac{1}{lC_1} f(x) \sin \frac{(2n+1)\pi x}{2l} dx - \frac{4}{(2n+1)^2\pi^2} \right\} \quad (17)$$

In the present problem, $f(x)$ is given by Eq. (18) evaluated at time, $t = t_0$, so that

$$f(x) = C_1 \left\{ 1 + \frac{A}{C_1} \operatorname{erf} \frac{x}{2(D_1 t_0)^{1/2}} \right\} \quad (18)$$

where A is a constant. The time t_0 is defined as that at which $x = l$ so that it is related to the solution of Eq. (18) by the expression

$$\left(\frac{D_1 t_0}{l^2} \right)^{1/2} = \frac{D_1^{1/2}}{k} \quad (19)$$

By substituting in Eq. (17) from Eq. (18) and Eq. (19), M_t/lC_1 is expressed as a function of the single variable $D_1 t/l^2$. Equation (8) can be written as

$$\frac{\partial M_t}{\partial t} = - \left(D_1 \frac{\partial c_1}{\partial x} \right)_{x=0} = - \frac{AD_1^{1/2}}{(\pi t)^{1/2}} \quad (20)$$

And hence

$$\frac{M_t}{lC_1} = - \frac{2}{\pi^{1/2}} \frac{A}{C_1} \left(\frac{D_1 t}{l^2} \right)^{1/2} \quad (21)$$

where A is a constant and is negative for sorption.

In this study, drying was modeled by moving boundary diffusion. Diffusion in a system with a moving boundary occurs in two distinct regions separated by a moving interface. The moving interface can be marked by a discontinuous change in the 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 the concentration as in the progressive freezing of a liquid. Furthermore, the movement of the boundary relative to the two regions it separates may be caused by the appearance or disappearance of matter at the boundary in one or both regions, which results in a bodily movement of the matter in one or both regions relative to the boundary. When the diffusion coefficient is discontinuous at a concentration c , that is, the diffusion coefficient is zero below c and constant and finite above c ; then the total amount, M_t , of the diffusing substance desorbed from an unit area of a plane sheet of thickness a at time t is given by the following relation²⁸:

$$\frac{M_t}{M_\infty} = 2 \left[\frac{D}{\pi a^2} \right]^{1/2} t^{1/2} \quad (22)$$

where D is a diffusion coefficient at the concentration c_1 . Here $M_\infty = ac_1$ is the equilibrium value of M_t . If one assumes that the diffusion coefficient of polymer segments in the gel is negligible compared to the desorption coefficient, D , of water vapor into air, then Eq. (22) can be written as

$$\frac{W}{W_\infty} = 2 \left[\frac{D}{\pi a^2} \right]^{1/2} t^{1/2} \quad (23)$$

Here it is assumed that M_t is proportional to the amount of water molecules released, W , at time, t .

Experimental

MATERIALS

Copolymers were prepared with various molar percentages of NIPA and AAc and in distilled water at room temperature by keeping 2 M. 0.01 g of *N, N'*-methylenebisacrylamide (Merck, Turkey), 0.008 g of ammonium persulfate (Merck), and 2 μ L of tetramethylethylenediamine (Merck) were dissolved in 5 mL distilled water (pH 6.5). The pyranine concentration was kept constant at 4×10^{-4} M for all experiments. The solution was stirred (200 rpm) for

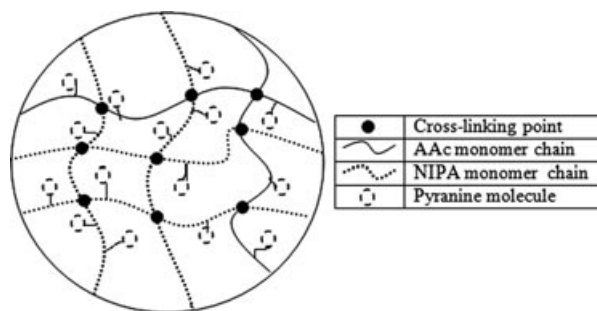


FIGURE 1. A scheme showing the possible bindings of fluorescence probe with the copolymer in two dimensions.

15 min to achieve a homogeneous solution. All samples were deoxygenated by bubbling nitrogen for 10 min just before the polymerization process.²⁹ During the gelation process, pyranine molecules bind to NIPA and AAc chains upon the initiation of the polymerization; thus, the fluorescence spectra of the bonded pyranines shift to the shorter wavelengths.²⁹ A scheme showing the possible bindings of fluorescence probe with copolymer in two dimensions is given in Fig. 1.

In this study, the drying experiments of disc-shaped poly(NIPA-*co*-AAc) copolymers prepared with various molar monomer contents (100% NIPA, 10% AAc + 90% NIPA, 25% AAc + 75% NIPA, 50% AAc + 50% NIPA, 75% AAc + 25% NIPA, 90% AAc + 10% NIPA, 100% AAc) were performed in air at temperatures of 20, 30, 40, 50, and 60°C. As seen from the fluorescence spectra of pyranine, structural changes in the copolymer did not occur during the drying process. On the other hand, only the diameter and thickness of the copolymer gel have been changed.

FLUORESCENCE MEASUREMENTS

The fluorescence intensity measurements were carried out using a model LS-50 spectrometer of Perkin-Elmer (UK), equipped with a temperature controller. All measurements were made at 90° position, and spectral bandwidths were kept at 5 nm. A disc-shaped copolymer was placed on the wall of 1-cm path length square quartz cell for the drying experiments. Pyranines in the poly(NIPA-*co*-AAc) copolymers were excited at 340 nm during in situ experiments, and emission intensities of pyranine were monitored at 427 nm as a function of drying time. The position of the sample for the fluorescence measurements was shown in previous articles.^{19,20} At the same time, a gravimetric

measurement was performed by measuring weight. The diameter and thickness of the poly(NIPA-co-AAc) copolymers were also measured to calculate the volume of the poly(NIPA-co-AAc) copolymers from the formula for a cylinder's volume. The initial thickness is constant for the all samples.

Results and Discussion

Figure 2a shows the typical emission spectra of pyranine from poly(NIPA-co-AAc) copolymers with 10% NIPA monomer content during drying in air at 20°C temperature. It is seen for all experiments that as the drying temperature is increased, the fluorescence intensity, I_{em} , increases relative to the scattered light intensity, I_{sc} . Because the decrease in I_{sc} corresponds to the decrease in turbidity of the drying, the corrected fluorescence intensity, I , was introduced as I_{em}/I_{sc} to eliminate the turbidity effect. As far as the correction of fluorescence emission is concerned, totally empirical formula was introduced to produce the meaningful results for the fluorescence quenching mechanisms.²⁰ Here the main idea is to eliminate

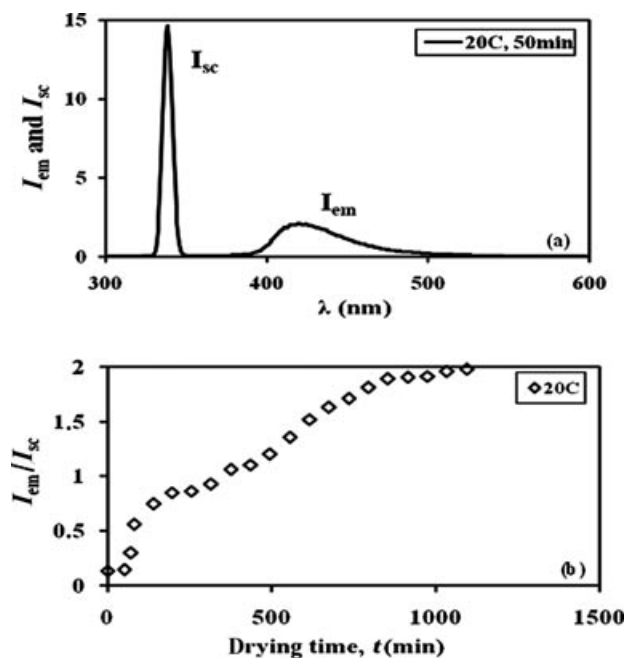


FIGURE 2. (a) Typical emission spectra of pyranine from the copolymer during drying in air at 20°C for 10% NIPA monomer content copolymer at 50 min and (b) corrected fluorescence intensities of pyranine, $I (= I_{em}/I_{sc})$ versus drying time, t , during the drying at 20°C for 90% NIPA monomer content, respectively.

the structural fluctuation due to the frozen blobs and holes¹⁷ during drying by using I_{sc} , that is, 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 copolymers on the fluorescence emission intensity, and elaborate the Stern–Volmer model by using solely fluorescence intensity, I . The variations of I versus drying time, t , during drying of copolymer at 20°C for the 90% NIPA monomer content sample are presented in Fig. 2b. As the drying time, t , is increased, the quenching of excited pyranines decreases due to an increase in the water released from the drying poly (NIPA-co-AAc) copolymers. It is also to be noted that quenching becomes less efficient at higher temperatures. To quantify these results, a collisional type of the quenching mechanism may be proposed for the fluorescence intensity, I , emitted from the copolymer during the drying process by using Eq. (4). For the dry copolymer, W can be calculated from the measured I values in each drying step.²⁷

The plots of W versus t for 10% and 90% NIPA monomer content at 20°C are presented in Fig. 3a, where the fit of the data to Eq. (23) produced the desorption coefficients, D_1 , which are listed in Table I. To examine the effects of copolymers on the

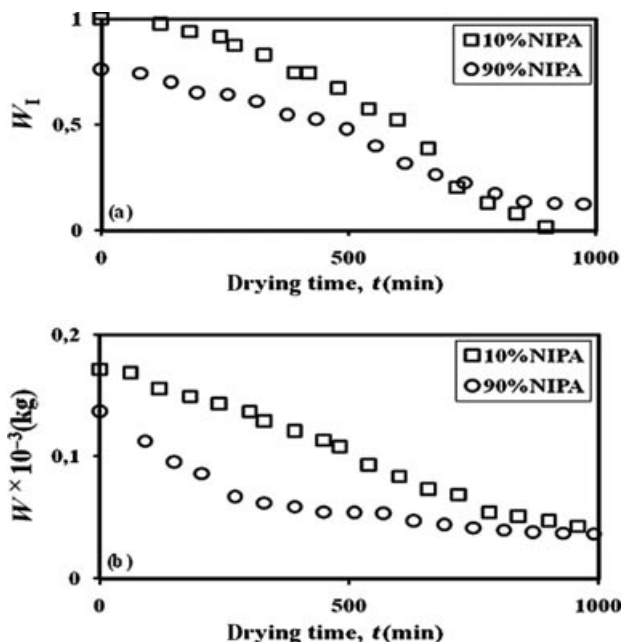


FIGURE 3. Plots of water release versus drying time, t , for poly(NIPA-co-AAc) copolymer dried in air measured by (a) fluorescence and (b) gravimetric technique for 10% and 90% NIPA monomer content copolymers at 20°C, respectively.

TABLE I
Experimentally Measured Parameters of Poly(NIPA-co-AAc) Copolymers for Various Temperatures at Molar Percentage of NIPA Monomer Content during the Drying Process

Molar % NIPA	T (°C)	$D_I \times 10^{-9}$ (m ² /s)	$D_W \times 10^{-9}$ (m ² /s)	$D_V \times 10^{-9}$ (m ² /s)
0	20	12.72	0.38	0.37
	30	14.10	1.29	0.45
	40	15.0	1.40	0.49
	50	26.0	3.40	1.58
	60	48.67	4.40	1.81
10	20	39.45	0.41	0.96
	30	42.22	1.35	1.01
	40	46.81	2.37	1.37
	50	61.23	7.14	3.29
	60	52.30	5.44	2.47
25	20	49.35	0.46	1.12
	30	76.79	2.08	1.35
	40	81.03	2.94	1.53
	50	103.4	8.55	4.81
	60	70.65	7.85	4.41
50	20	63.27	0.58	1.27
	30	84.24	2.56	1.43
	40	104	3.01	1.66
	50	106.65	9.84	6.07
	60	98.48	8.03	5.68
75	20	73.21	0.93	1.55
	30	93.30	3.73	1.89
	40	110.33	11.66	8.40
	50	108.86	10.54	7.96
	60	104.29	9.61	7.01
90	20	85.45	1.01	1.58
	30	140.99	13.26	12.22
	40	125.85	11.91	8.75
	50	114.31	11.30	8.36
	60	110.0	11.24	8.26
100	20	Opaque	1.02	1.61
	30		13.78	13.26
	40		12.34	8.86
	50		12.26	8.65
	60		12.16	8.40

translational motions of water, the desorption coefficient, D , can be used. In drying, desorption is often activated by thermal fields and consequently become a strong function of temperature. On the other hand, LCST behavior is caused by a critical hydrophilic/hydrophobic balance of polymer side groups. In the hydrophilic and hydrophobic regions, the motions of water molecules are highly hindered by the presence of polymer chains. Therefore, the maximum values of the plot of desorption coefficient, D , versus temperature were defined

by the LCST. In Table I, D_I values increased up to LCST and then decreased where LCST is also affected by increasing NIPA monomer contents. On the other hand, D_I values increase by increasing NIPA monomer content at a given temperature.

Water desorption from the drying poly(NIPA-co-AAc) copolymers, prepared at various molar percentages of NIPA monomer contents, was also studied by using the gravimetric methods at different temperatures. The plots of the data are presented in Fig. 3b at 20°C for 10% and 90% NIPA monomer contents. The fits of water release, W , to Eq. (23) for the copolymers dried at 20, 30, 40, 50, and 60°C for various NIPA monomer contents produced the desorption coefficients, D_W , which are listed in Table I. A similar increase and decrease in D_W as that for D_I was observed around LCST.

The measured thickness in Fig. 4a and diameter in Fig. 4b at 20°C for 10% and 90% NIPA monomer contents of the poly(NIPA-co-AAc) copolymers were used to calculate the volume of the poly(NIPA-co-AAc) copolymer from the formula for a cylinder's volume. The initial thickness is constant for the all samples as shown in Fig. 4a. The variations in volume, V , of poly(NIPA-co-AAc) copolymers during the drying process are also calculated. The plots of the volume, V , versus drying time for poly(NIPA-co-AAc) copolymers dried in air are presented in Fig. 4c. The data in Fig. 4(c) are fitted to the following relation produced from Eq. (23):

$$\frac{V}{V_\infty} = 2 \left(\frac{D}{\pi a^2} \right)^{1/2} t_d^{1/2} \quad (24)$$

Here it is assumed that the relation between W and V is linear. Then using Eq. (24), the volumetric desorption coefficients, D_V , were determined and are listed in Table I. Again, the behavior of D_V was found similar to the D_I and D_W behavior against temperature. Here D_W and D_V coefficients are also found to be much larger at high NIPA content copolymers for all temperatures. All these results are summarized in Figs. 5 and 6. In Fig. 5, the largest D values were observed at LCST for all experimental techniques, indicating that collapse of NIPA chains results in faster drying of copolymer due to exclusion of water from the system. On the other hand, Fig. 6 presents the behavior of LCST against NIPA monomer contents, where it is understood that NIPA monomer content is increased as LCST approaches its original value ($\sim 31^\circ\text{C}$), predicting faster drying (high D values) for the copolymer

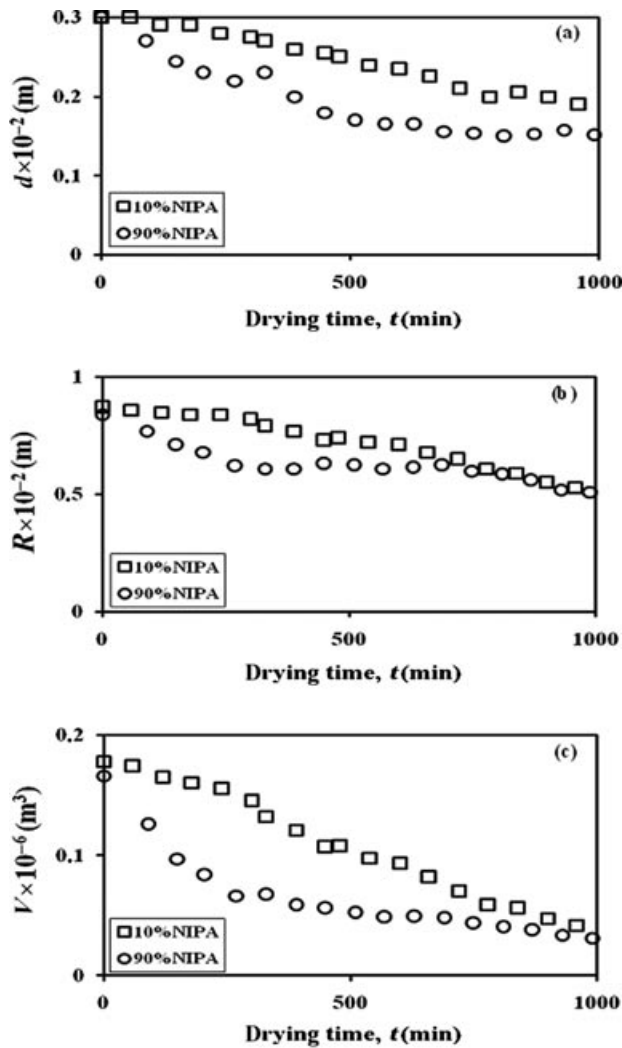


FIGURE 4. Plots of the (a) thickness, (b) diameter, and (c) volume, V , of copolymer versus drying time, t , for poly(NIPA-co-AAc) copolymer dried in air and measured by using the volumetric technique for 10% and 90% NIPA monomer content copolymers at 20°C, respectively.

system. It is obvious that as NIPA monomer content is decreased LCST increased, indicating slower drying from the poly(NIPA-co-AAc) copolymers. In Fig. 6, arrows indicate the critical NIPA concentration for the LCST value passing from low to high NIPA monomer content in the copolymer system.

As seen in Table I, D values measured by using the fluorescence technique are larger than the values measured by volumetric and gravimetric techniques, which may predict the observation of different mechanisms of the drying copolymer. It is obvious that the fluorescence technique measures the behavior of the microstructure of the copolymer; that

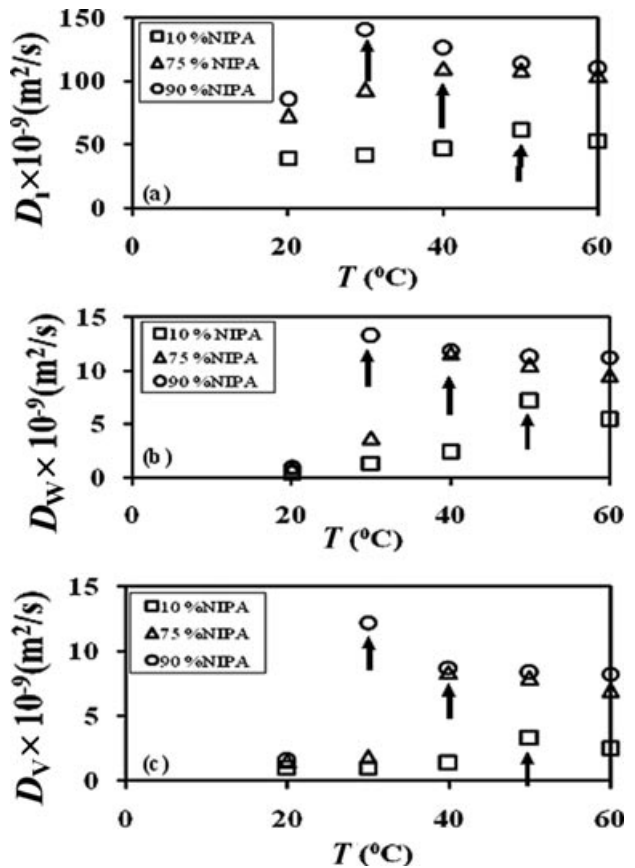


FIGURE 5. Plot of desorption coefficients, D , versus temperature measured by (a) fluorescence, (b) gravimetric and (c) volumetric techniques for 10%, 75%, and 90% NIPA monomer content copolymers, respectively.

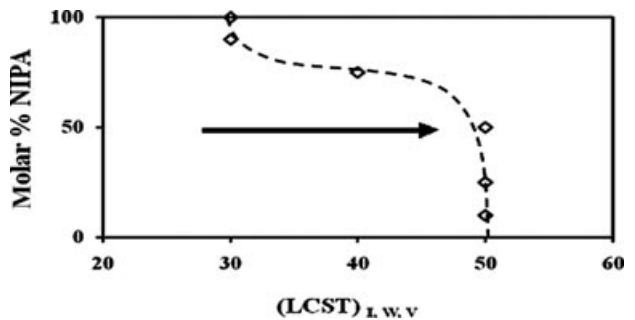


FIGURE 6. Plot of molar percentage of NIPA monomer content versus LCST measured by fluorescence (I), gravimetric (W), and volumetric (V) techniques, respectively.

is, because pyranine molecules are bounded to the polymer chains, segmental motion of the network can be monitored by using the fluorescence technique, which then monitors the drying network of

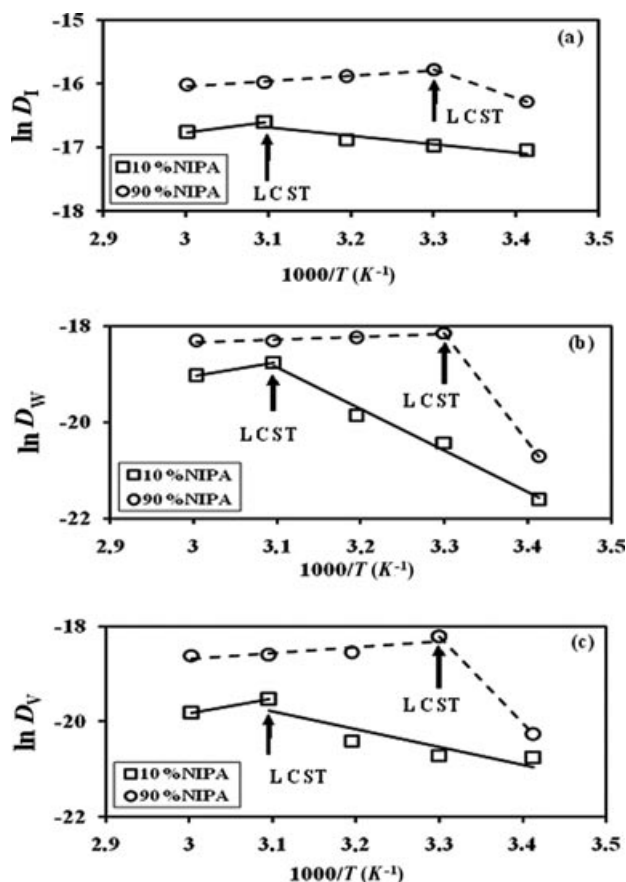


FIGURE 7. Linear regressions of desorption diffusion coefficients versus temperature measured by (a) fluorescence, (b) gravimetric, and (c) volumetric techniques for 10% and 90% NIPA content copolymers, respectively.

the copolymer at a molecular level. However, volumetric and gravimetric measurements provide the information of the macroscopic (i.e., bulk) behavior of the copolymer. According to the above-presented argument, one may suggest that chain segments move faster than the bulk polymeric material itself during the drying process.

On the other hand, the behavior of the desorption coefficients (D_I , D_W , and D_V) versus T predicts that $D - T$ relation may obey the following Arrhenius law:

$$D = D_0 \exp(-\Delta E/kT) \quad (25)$$

where ΔE is the energy of drying, k is Boltzmann's constant, and D_0 is the desorption coefficient at $T = \infty$ for each technique. The logarithmic form of Eq. (25) is presented in Figs. 7a, 7b, and 7c for the data

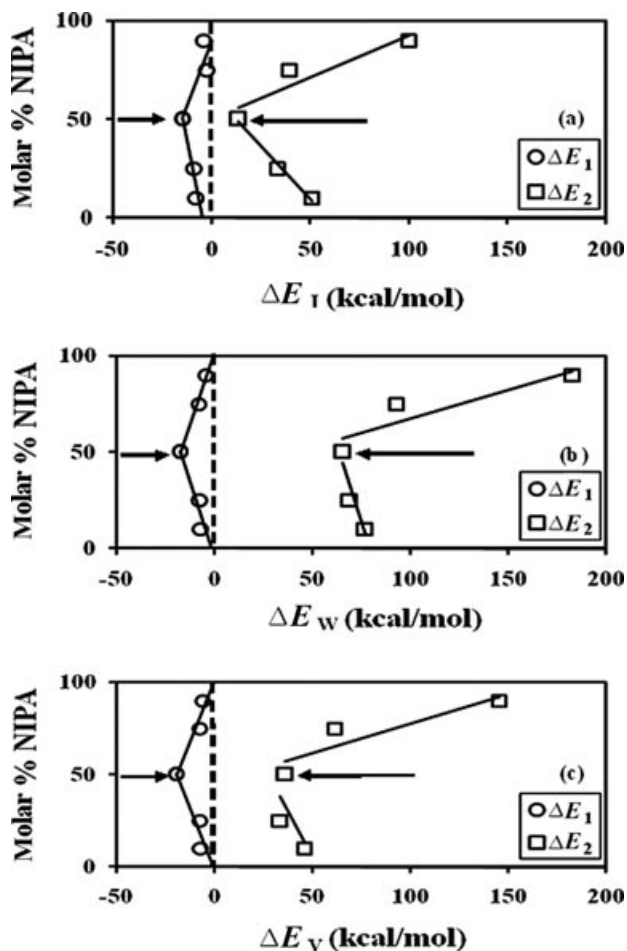


FIGURE 8. Molar percentage of NIPA monomer content versus drying energies measured by (a) fluorescence, (b) gravimetric, and (c) volumetric techniques, respectively.

obtained by fluorescence, gravimetric, and volumetric techniques, respectively, from which ΔE values are produced and listed in Table II. Here ΔE_1 and ΔE_2 are energies defined as below LCST and above LCST, respectively, where it is seen that ΔE_1 and ΔE_2 decreased up to 50% of NIPA content and then increased as shown in Fig. 8. Comparing Fig. 8 with Fig. 6 and realizing the position of the arrows at the 50% of NIPA content, which presents the critical value for the LCST at which the lowest energy need is predicted for drying. Otherwise, copolymer needs higher energies for the drying due to the extended version of NIPA chains, that is, breakdown of the hydrophobicity. It must also be noticed that energies are exothermic (ΔE_1) and endothermic (ΔE_2), below and above LCST, during the drying processes for the copolymer system.

TABLE II
Energy for Various Molar Percentages of NIPA Monomer Content during the Drying Process by Fluorescence, Gravimetric, and Volumetric Techniques

Molar % NIPA	ΔE_I (kJ/mol)		ΔE_W (kJ/mol)		ΔE_V (kJ/mol)	
	1	2	1	2	1	2
10	-7.6	50.7	-6.6	77.3	-6.6	45.9
25	-8.7	33.3	-7.4	69.3	-7.4	33.6
50	-14.8	13.5	-17.5	65.7	-19.4	36.2
75	-2.3	39.1	-8.1	92.9	-7.5	61.5
90	-3.6	99.7	-4.4	183.2	-6.1	145.6
100	Opaque		-3.1	185.3	-5.2	150.0

Conclusions

This work has presented a novel fluorescence method for the study of the drying kinetics of poly(NIPA-co-AAc) copolymer in various AAC and NIPA monomer contents. The desorption coefficient, D , for the drying process has been calculated with a moving boundary diffusion model combined with the Stern–Volmer kinetics. We have been able to indicate that temperature-induced drying caused by LCST provides higher D values for the poly(NIPA-co-AAc) copolymer system. It is understood that LCST gives lower values above the critical NIPA monomer content (50% NIPA) by approaching its original value, where the energy requirement is the minimum for drying. It is believed that in the future the fluorescence method together with the proposed diffusion model can be used for studying drying processes as well as swelling of hybrid polymeric gels.

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References

- Harmathy, T. Z. *Ind Eng Chem Fund* 1969, 8, 92.
- Mikhailov, M. D. *Int J Heat Mass Transfer* 1975, 18, 797.
- Scherer, W. G. *J Non-Cryst Solids* 1989, 107, 135.
- Scherer, W. G. *J Non-Cryst Solids* 1989, 109, 183.
- Scherer, W. G. *J Non-Cryst Solids* 1992, 363, 147–148.
- Scherer, W. G. *J Non-Cryst Solids* 1989, 109, 171.
- Jomma, W.; Aregba, W.; Puiggali, J. R.; Quintard, M. *Drying* 1991, 9, 110.
- Roques, M. A.; Zagrouba, F.; Sobral, P. D. *Drying Technol* 1994, 12(6), 1245.
- Derdour, L.; Desmorieux, H.; Andrieu, J. *Drying Technol* 2000, 18(1–2), 237.
- Kemp, I. C.; Fyhr, B. C.; Laurent, S.; Roques, M. A.; Groenewold, C. E.; Tsotsas, E.; Sereno, A. A.; Bonazzi, C. B.; Bimbenet, J. J. *Drying Technol* 2001, 19(1), 15.
- Coumans, W. J. *Chem Eng Process* 2000, 39, 53.
- Wallqvist, A.; Gallicchio, E.; Levy, R. M. *J Phys Chem B* 2001, 105, 6745.
- Bastide, J.; Duoplessix, S.; Picot, C.; Candau, S. J. *Macromolecules* 1984, 17(1), 83.
- Peters, A.; Candau, S. J. *Macromolecules* 1988, 21, 2278.
- Zirinyi, M.; Rosta, J.; Horkay, F. *Macromolecules* 1993, 26, 3097.
- Horie, K.; Mita, I.; Kawabata, J.; Nakahama, S.; Hirao, A.; Yamazaki, N. *Polym J* 1980, 12, 319.
- Kara, S.; Pekcan, Ö. *J Appl Polym Sci* 2001, 80, 1898.
- Kara, S.; Pekcan, Ö. *J Appl Polym Sci* 2001, 82, 1944.
- Aktaş, D. K.; Evingür, G. A.; Pekcan, Ö. *J Macromol Sci, Part B: Phys* 2007, 46, 581.
- Evingür, G. A.; Aktaş, D. K.; Pekcan, Ö. *Chem Eng Process: Process Intensif* 2009, 48, 600.
- Tanaka, T.; Sato, E.; Hirokawa, Y.; Hirotsu, S.; Peetermans, J. *Phys Rev Lett* 1985, 55, 2455.
- Schild, H. G. *Progr Polym Sci* 1992, 17, 163.
- Feil, H.; Bae, Y. H.; Feijen, J.; Kim, S. W. *Macromolecules* 1993, 26, 2496.
- Lin, S. Y.; Chen, K. S.; Chu, L. R. *Polymer* 1999, 40, 6307.
- Shirota, H.; Ohkawa, K.; Kuwabara, N.; Endo, N.; Horie, K. *Macromol Chem Phys* 2000, 201(16), 2210.
- Lee, W.; Yeh, Y. *Eur Polym J* 2005, 41, 2488.
- Birks, J. B. *Photophysics of aromatic molecules*; Wiley-Interscience: New York, 1971.
- Crank, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford, UK, 1975.
- Evingür, G. A.; Aktaş, D. K.; Pekcan, Ö. *Phase Transitions* 2009, 82(1), 53.