

# Temperature sensitive poly(*N-t*-butylacrylamide-*co*-acrylamide) hydrogels: synthesis and swelling behavior

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Received 21 March 2002; received in revised form 4 June 2002; accepted 5 June 2002

## Abstract

A series of temperature sensitive hydrogels was prepared by free-radical crosslinking copolymerization of *N-t*-butylacrylamide (TBA) and acrylamide in methanol. *N,N'*-methylenebis(acrylamide) was used as the crosslinker. It was shown that the swelling behavior of the hydrogels can be controlled by changing the amount of TBA units in the network chains. Hydrogels immersed in dimethylsulfoxide (DMSO)–water mixtures exhibited reentrant swelling behavior, in which the gels first deswell then reswell if the DMSO content of the solvent mixture is continuously increased. In water over the temperature range of 2–64 °C, hydrogels with less than 40% TBA by mole were in a swollen state while those with TBA contents higher than 60% were in a collapsed state. Hydrogels with 40–60% TBA exhibited swelling–deswelling transition in water depending on the temperature. The temperature interval for the deswelling transition of 60% TBA gel was found to be in the range from 10 to 28 °C, while for the 40% TBA gel, the deswelling started at about 20 °C and continued until the onset of the hydrolysis of the network chains at around 64 °C. It was shown that the Flory–Rehner theory of swelling equilibrium provides a satisfactory agreement to the experimental swelling data of the hydrogels, provided that the sensitive dependence of the  $\chi$  parameter on both temperature and polymer concentration is taken into account. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* *N-t*-butylacrylamide; Acrylamide; Temperature sensitive hydrogels

## 1. Introduction

Certain polymers are soluble in water at low temperature but become insoluble as the temperature rises above the lower critical solution temperature (LCST). Such temperature sensitive polymer–solvent systems have received considerable attention due both to fundamental and technological interests [1]. The temperature sensitivity of polymer solutions or polymeric gels is associated with the temperature dependence of hydrogen bonding and hydrophobic interactions [2]. At lower temperatures, water molecules in the vicinity of hydrophobic polymer chains are highly hydrogen bonded. Since these hydrogen bonding interactions lower the free energy of mixing considerably, the polymer chains dissolve or swell in water at low temperatures. At higher temperatures, the hydrogen bonds weaken; at the same time, the tendency of the system to minimize the contact between water and hydrophobic surfaces, i.e. the hydrophobic interaction increases [3]. As

a result, on heating a polymer solution or a polymer gel, a transition from swollen to collapsed state occurs at a critical temperature. For example, polyacrylamide (PAAm) gel exhibits temperature independent swelling behavior. However, if one of the amide hydrogens of the repeat unit is replaced with the hydrophobic *N*-isopropyl group, the resulting material, poly(*N*-isopropylacrylamide) (PNIPA), becomes temperature sensitive and exhibits volume phase transition at approximately its LCST, i.e. at 34 °C [4,5]. Below this temperature, the gel is swollen and it shrinks as the temperature is raised.

The modification of the LCST of temperature sensitive polymer solutions or gels is of primary interest. A decrease in the LCST can be achieved by increasing the hydrophobicity of the network chains [1]. Liu and Zhu investigated several series of linear copolymers based on *N*-substituted acrylamides [6]. It was shown that the copolymers exhibit changes in their LCST's as a function of their comonomer composition. With increasing content of *N-t*-butylacrylamide (TBA) from 20 to 60 mol%, the LCST of TBA/*N,N*-dimethylacrylamide copolymers decreases from 80 to 20 °C. Seker and Ellis showed that the length of the alkyl group on poly(*N*-alkylacrylamide)s

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has significant effect on the gel swelling [7]. Larger alkyl chains produced dramatic decrease in the gel transition temperature. Yi et al. showed that the volume transition temperature of *N*-isopropylacrylamide (NIPA)/TBA copolymer gel particles decreases with increasing mole ratio of TBA in the monomer feed composition [8,9].

The aim of this work was to prepare a series of well-characterized temperature sensitive hydrogels based on TBA and AAm exhibiting various LCST's. Synthesis and swelling behavior of such copolymer gels have not been reported before. Hydrogels were prepared by free-radical crosslinking copolymerization of TBA and AAm in the presence of *N,N'*-methylenebis(acrylamide) (BAAm) as the crosslinker. By preliminary experiments, methanol was found to be the most suitable solvent for the copolymerization. As will be shown below, several series of hydrogels were prepared exhibiting temperature sensitivity in water and, reentrant swelling phenomena in solvent mixtures.

## 2. Experimental

### 2.1. Materials

Acrylamide (AAm, Merck) was crystallized from acetone/ethanol mixture (70/30 by volume) below 30 °C. TBA (Fluka), BAAm (Merck), and 2,2'-azobisisobutyronitrile (AIBN, Merck) were used as received. In the swelling experiments, distilled and deionized water and reagent-grade solvents dimethylsulfoxide (DMSO), ethylene glycol, *iso*-butanol, tetrahydrofuran (THF), acetone, methanol, ethanol, and 2-propanol were used without further purification.

### 2.2. Synthesis of hydrogels

Free-radical crosslinking copolymerization was carried out in methanol, as the polymerization solvent, at 60 °C in the presence of 1 mol% AIBN (with respect to the monomers) as initiator. Both the crosslinker ratio (mole ratio of the crosslinker BAAm to the monomers AAm and TBA) and the total monomer concentration were fixed at 1/80 and 20 w/v%, respectively, whereas the TBA content of the monomer mixture was varied from 0 to 100 mol%. To illustrate the synthetic procedure, we give details for the preparation of the hydrogel with 60 mol% TBA in the monomer feed composition:

TBA (1.457 g), AAm (0.543 g), BAAm (0.0368 g), and AIBN (0.0314 g) were dissolved in methanol to give a total volume of 10 ml. After bubbling nitrogen for 15 min, the solution was poured into several glass tubes of about 5 mm internal diameters and about 20 cm long. The glass tubes were then sealed, immersed in a thermostated water bath at 60 °C and the polymerization was conducted for 1 day. Homologous series of hydrogels were prepared in this way

allowing systematic variation of the TBA content of the monomer mixture.

After polymerization, the reaction was stopped by cooling the reaction mixture in an ice-water bath. The crude hydrogels, 5 mm in diameter, were freed from the glass tubes and they were cut into samples of about 10 mm length. Each sample was placed in an excess of water, and water was replaced many times. The hydrogels after extraction were carefully deswollen in acetone. The hydrogel samples were then dried at room temperature under vacuum to constant weight. Dilution degree of the hydrogels after preparation  $q_F$  was calculated as

$$q_F = \frac{m_0}{m_{\text{dry}}} \quad (1)$$

where  $m_0$  and  $m_{\text{dry}}$  are the weights of the hydrogel after preparation and after drying, respectively.  $q_F$  of the hydrogels with 20–100 mol% TBA contents was found to be  $2.8 \pm 0.2$ , compared to its theoretical value of 5.0 calculated from the initial monomer concentration (20 w/v%) in the feed and assuming that the monomer conversions are complete after the crosslinking copolymerization. The discrepancy between the experimental and theoretical  $q_F$  values is probably due to the evaporation of the polymerization solvent methanol during the sample preparation.

### 2.3. Copolymer network composition

Two independent techniques were used to determine the composition of poly(TBA-*co*-AAm) copolymer networks. First, the TBA content of dried copolymers was estimated from IR spectra. The IR spectra of the samples in KBr pellets were recorded on a Perkin–Elmer 983 spectrophotometer. A typical spectrum of poly(TBA-*co*-AAm) copolymers is shown in Fig. 1. The characteristic absorption

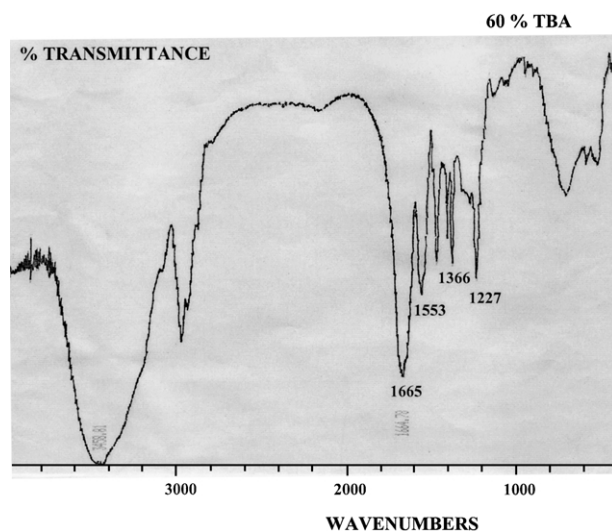


Fig. 1. IR spectrum of a poly(TBA-*co*-AAm) network with 60 mol% TBA in the KBr pellet.

peaks of TBA units are shown at 1227 and 1366  $\text{cm}^{-1}$  due to the  $-\text{C}(\text{CH}_3)_3$  group. The intensity of the peak at 1227  $\text{cm}^{-1}$  was normalized using C=O stretching peak of both AAm and TBA units at 1665  $\text{cm}^{-1}$ . The calculation of the absorbances at 1227 and 1665  $\text{cm}^{-1}$  ( $A_{1227}$  and  $A_{1665}$ , respectively) was performed using the base-line method [10, 11]. In order to quantify the results, a calibration curve was prepared using polymer samples prepared by mixing linear PAAm and poly(TBA) homopolymers in predetermined mole ratio.

Second, elemental microanalysis (EM) results of the network samples were used to estimate their chemical composition. The C, H, and N analysis were performed on a Carlo Erba 1106 elemental analyzer. The interpretation of the microanalysis results was, however, complicated due to the bound water in the polymer samples. It was found that the homopolymers or copolymers of TBA always contain about 10 wt% water, even after several months of drying at room temperature under vacuum. Therefore, two unknowns existed for each copolymer sample, namely their TBA and water contents. Let  $w$  be the weight fraction of water in the dried copolymer, C and N contents can be calculated using the equations

$$\text{C}\% = \left( \frac{3/F_2 + 4}{\bar{M}_r} \right) \times 1200 \quad (2a)$$

$$\text{N}\% = \frac{1}{F_2 \bar{M}_r} \times 1400 \quad (2b)$$

where  $\bar{M}_r$  is the molecular weight of the repeat unit (TBA + AAm + bound water), i.e.

$$\bar{M}_r = (56 + 71/F_2)/(1 - w) \quad (2c)$$

Fitting Eqs. (2a)–(2c) to the observed EM data allowed calculations of the two unknowns  $F_2$  and  $w$ .

Proton nuclear magnetic resonance,  $^1\text{H}$  NMR spectra were obtained with a Bruker 200 MHz spectrometer. For these measurements, linear poly(TBA-co-AAm) copolymers were prepared under the same reaction condition as the hydrogels except that BAAm crosslinker was not used. Water, DMSO, methanol, and acetone were used as the solvents for copolymers having 0, 20–40, 60–80, and 100 mol% TBA, respectively.

#### 2.4. Swelling measurements

Swelling measurements were carried out in various solvents. After crosslinking copolymerization, the initial diameters of the gel samples  $D_0$  were measured by a calibrated digital compass. Then, each sample was placed in an excess of solvent or solvent mixture at a given temperature. In order to reach the equilibrium degree of swelling, the hydrogels were immersed in solvents for at least 2 weeks during which solvent was replaced every other day; the swelling equilibrium was tested by weighing the samples, or by measuring their diameters. To achieve good

precision, three measurements were carried out on samples of different length taken from the same gel.

The equilibrium volume swelling ratio of the hydrogels with respect to the after preparation state  $V/V_0$  (volume of swollen gel/volume of the gel after preparation) was determined by measuring the diameter of the hydrogel samples by a calibrated digital compass.  $V/V_0$  was calculated as

$$V/V_0 = \left( \frac{D}{D_0} \right)^3 \quad (3)$$

where  $D$  is the diameter of hydrogels after equilibrium swelling in solvent. The standard deviations of the measured swelling ratios were less than 10% of the mean.

#### 2.5. Mechanical measurements

Uniaxial compression measurements were performed on hydrogels after their preparation. All the mechanical measurements were conducted in a thermostated room of  $21 \pm 0.1$  °C. The stress–strain isotherms were measured by using an apparatus described before [12]. The elastic modulus  $G$  was determined from the slope of linear dependence [13]

$$f = G(\alpha - \alpha^{-2}) \quad (4)$$

where  $f$  is the force acting per unit cross-sectional area of the undeformed gel specimen, and  $\alpha$  is the deformation ratio (deformed length/initial length).

### 3. Results and discussion

In order to obtain hydrogels of a fixed crosslink density but differing in polymer composition, free-radical crosslinking copolymerization of TBA, AAm, and BAAm was conducted at a fixed crosslinker ratio (1/80) and initial monomer concentration (20 w/v%) but at various TBA contents. Preliminary experiments showed that the addition of TBA in the monomer mixture decreases the rate of the reactions significantly. This is due to the lower propagation rate constant of the growing radicals with the vinyl group of TBA compared to that of AAm monomer [14], as well as due to the different solubilities of the monomers and the corresponding homopolymers. The monomer TBA and the polymer derived from TBA are insoluble in water but soluble in organic solvents such as methanol, THF, or DMSO, whereas PAAm is soluble in water but insoluble in the organic solvents [15]. In our experiments, we first conducted the crosslinking copolymerization reactions in several solvents including THF, THF/water mixtures, DMSO, DMSO/water mixtures, methanol and methanol/water mixtures. Reproducible results and complete monomer conversions were obtained in methanol as the polymerization solvent at 60 °C using AIBN as the initiator.

The comonomer feed compositions containing higher than 20 mol% TBA led to the formation of transparent gels. If the TBA content in the feed is equal or less than 20 mol%, white or opaque gels were obtained, indicating that a micro phase separation takes place during the gel formation process in methanol.

### 3.1. Composition of the network chains

$^1\text{H}$  NMR spectra were recorded from solutions of linear poly(TBA-co-AAm) copolymers, which were prepared under the same reaction condition as the hydrogels except that the BAAM crosslinker was not used. NMR spectra of the copolymers with 0–60 mol% TBA are shown in Fig. 2. The NMR signal at 1.26 ppm corresponds to the protons of the *t*-butyl group of TBA units and the signals at 1.44 and 2.08 ppm to the protons of  $\text{CH}_2$  and CH groups of the polymer backbone. It is seen that the peak intensity at 1.26 ppm increases continuously as the TBA content in the monomer feed composition increases. However, due to the absence of a characteristic peak for AAm units, NMR spectra cannot be used for quantitative characterization of the polymer chains. Therefore, IR and EM techniques were used to estimate the composition of the network chains.

By the IR technique, the ratio of the absorbances of the copolymers at  $1227\text{--}1665\text{ cm}^{-1}$  together with a calibration curve prepared by mixing PAAm and poly(TBA) homopolymers allowed calculation of TBA mole fraction  $F_2$  in the copolymers. By the EM technique, Eqs. (2a)–(2c) were fitted to the observed chemical composition of dried copolymers giving  $F_2$  and the water content  $w$  of the samples. Table 1 shows the measured elemental composition of some dried poly(TBA-co-AAm) copolymers together with the fit results. It is seen that the poly(TBA-co-AAm) copolymers after constant weight drying at room temperature still contain water of about 2–16 wt%. Existence of residual water of about 10 wt% was reported before in dried PAAm gels [11]. This is probably due to the hydrogen bonds of water with the AAm units of the network chains. According to Table 1, the residual water content decreases with increasing TBA content in the monomer feed composition, probably due to the simultaneous increase of the hydrophobicity of the hydrogels. Table 1 also shows that the calculation results provide good agreement with the observed values.

In Fig. 3, the TBA mole fraction in the network chains  $F_2$  evaluated by IR (open symbols) and EM techniques (filled symbols) is shown as a function of the TBA mole fraction in the feed  $f_2$ . The dotted straight line represents the relation  $F_2 = f_2$ . It is seen that the compositions of the network chains are very close to the original monomer compositions in the feed prior to crosslinking copolymerization.

### 3.2. Crosslink density of the hydrogels

The effective crosslink density of the hydrogels was

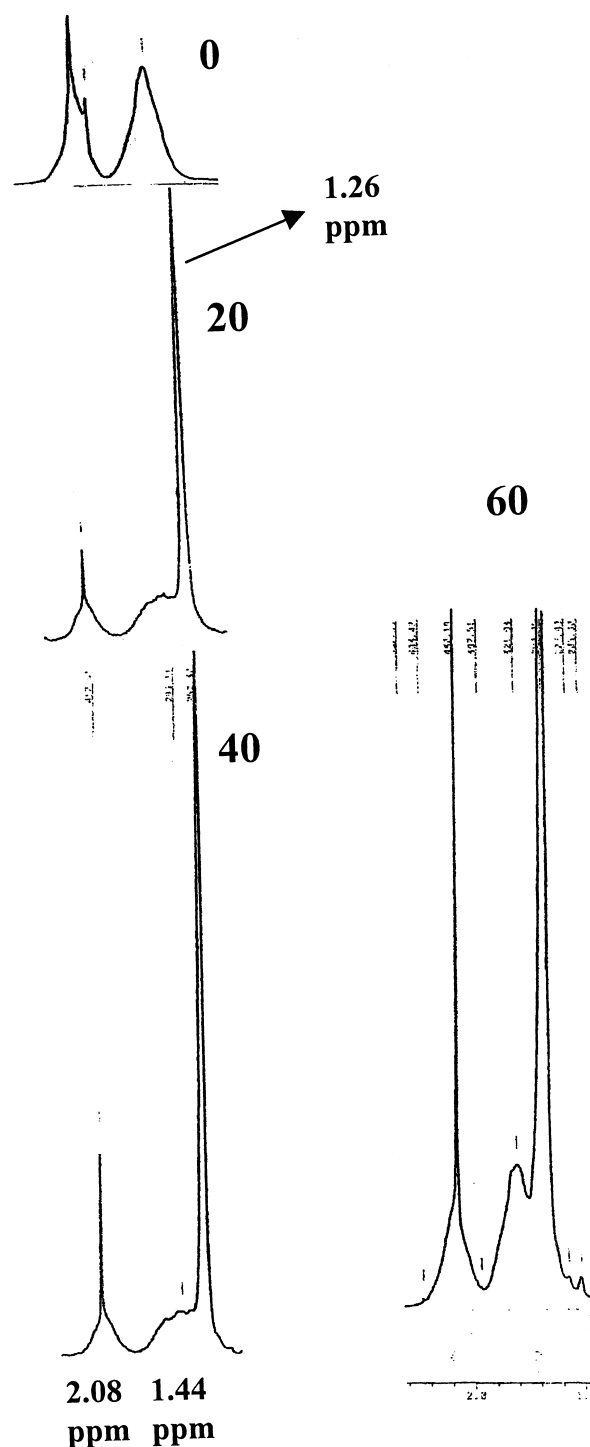


Fig. 2.  $^1\text{H}$  NMR spectra of poly(TBA-co-AAm) copolymers at room temperature showing the NMR signals of interest. TBA contents in mol% are indicated in the figure.

estimated from compression–strain tests carried out on hydrogels after their preparation. Measurements on hydrogel samples with 20–100 mol% TBA yield an elastic modulus  $G = 10.7 \pm 0.6$  kPa. The constancy of the elastic moduli of the hydrogels is expected due to the fixed crosslinker ratio in the feed (80 moles TBA + AAm per

Table 1  
Elemental microanalysis results of AAm/TBA copolymer networks

$10^2 f_2$	$10^2 F_2$	$w$	C%		H%		N%	
			Found	Calculated	Found	Calculated	Found	Calculated
20	24	0.10	50.7	50.7 (55.5)	8.8	8.5 (8.0)	15.0	15.0 (17.0)
40	48	0.16	50.9	50.9 (59.1)	8.9	9.3 (8.8)	12.1	12.1 (15.0)
60	67	0.09	57.1	57.1 (62.0)	9.9	9.7 (9.4)	11.8	11.8 (13.4)
80	94	0.08	60.1	60.1 (64.3)	10.2	10.2 (9.8)	10.4	10.4 (12.1)
100	100	0.02	64.9	64.8 (66.1)	11.1	10.3 (10.2)	10.0	10.8 (11.0)

$f_2$  = mole fraction of TBA in the initial comonomer mixture.  $F_2$  = mole fraction of TBA in the network chains.  $w$  = weight fraction of water in the dried polymers.  $F_2$  and  $w$  were calculated by fitting Eqs. (2a)–(2c) to the observed C and N contents. The standard deviations in the  $F_2$  and  $w$  values were less than 10% of the mean. The values in parenthesis are C, H, N calculation results for  $F_2 = f_2$  and  $w = 0$ .

mole of the crosslinker BAAM) and due to the fixed initial monomer concentration (20 w/v%). For a homogeneous affine network of Gaussian chains, the elastic modulus after the gel preparation  $G$  relates to the network crosslink density through the equation [13,16]

$$G = \frac{\rho}{\bar{M}_c} RT \nu_2^0 \quad (5)$$

where  $\rho$  is the polymer density,  $\bar{M}_c$  the molecular weight of the network chains,  $\nu_2^0$  the volume fraction of crosslinked polymer after the gel preparation,  $R$  and  $T$  are in their usual meanings.  $\nu_2^0$  relates to the dilution degree after the gel preparation  $q_F$  through the equation

$$\nu_2^0 = \left(1 + \frac{(q_F - 1)\rho}{d_1}\right)^{-1} \quad (6)$$

where  $d_1$  is the solvent (methanol) density. Using the value

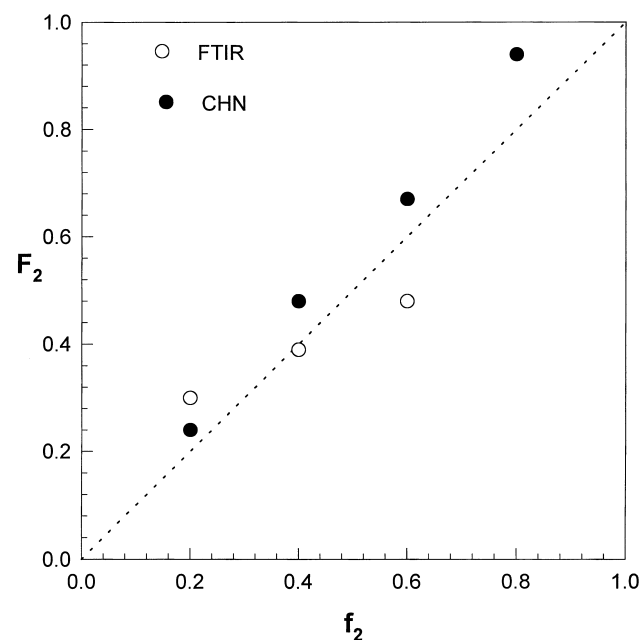


Fig. 3. The TBA mole fraction in the network  $F_2$  evaluated by IR (open symbols) and by EM techniques (filled symbols) shown as a function of the TBA mole fraction in the feed  $f_2$ . The dotted line represents the relation  $F_2 = f_2$ .

of  $q_F = 2.8 \pm 0.2$  found by experiments and assuming that  $d_1 = 0.795$  g/ml, and  $\rho = 1.35$  g/ml (the density of PAAm),  $\nu_2^0$  value of the hydrogels was calculated as  $0.25 \pm 0.02$ . Solution of Eq. (5) for  $\bar{M}_c$  then yields  $75\,000 \pm 8000$  g/mol. If one assumes that all the BAAM molecules form effective crosslinks in the final network, chemical value of  $\bar{M}_c$  can be calculated from the crosslinker ratio 1/80 as 4000 g/mol. Comparison of the effective and chemical  $\bar{M}_c$  values indicates that only one BAAM molecule forms effective crosslinks out of 20 molecules, i.e. about 95% of BAAM are wasted, probably due to the cyclization and multiple crosslinking reactions [17]. Such a high extent of cyclization was also reported for the free-radical crosslinking copolymerization of AAm [18].

### 3.3. Swelling behavior of hydrogels

Equilibrium swelling degrees of the hydrogels were first determined at room temperature ( $21 \pm 1$  °C). In Fig. 4, the equilibrium swelling ratios ( $V/V_0$ ) of the hydrogels in various solvents are plotted against the amount of TBA in the network chains. Water, alcohols of various alkyl lengths, ethylene glycol, DMSO, THF, and acetone were used as the solvents in the swelling experiments. If the amount of TBA is less than 60 mol%, water, DMSO, and ethylene glycol are good solvents for the hydrogels. In these solvents, the gel volume decreases continuously as the TBA content increases. Conversely, the gel volume in *iso*-butanol, acetone or THF increases steadily with increasing TBA content. The swelling curves obtained in methanol, ethanol, or 2-propanol exhibit maxima at 60–80 mol% TBA, indicating that these are good solvents for these hydrogels. Fig. 4 also shows that, as the TBA content increases, the gel swells in alcohols having larger alkyl chains.

In Fig. 5, the swelling ratios  $V/V_0$  of the hydrogels in DMSO–water mixtures are shown as a function of the DMSO content of the solvent mixture. Hydrogels with  $\leq 20$  mol% TBA remain in the swollen state over the entire range of the solvent composition. At higher TBA contents, the hydrogel exhibits reentrant swelling transition, i.e. the gel first deswells and then reswells as the DMSO content in the external solvent mixture continuously increases. The

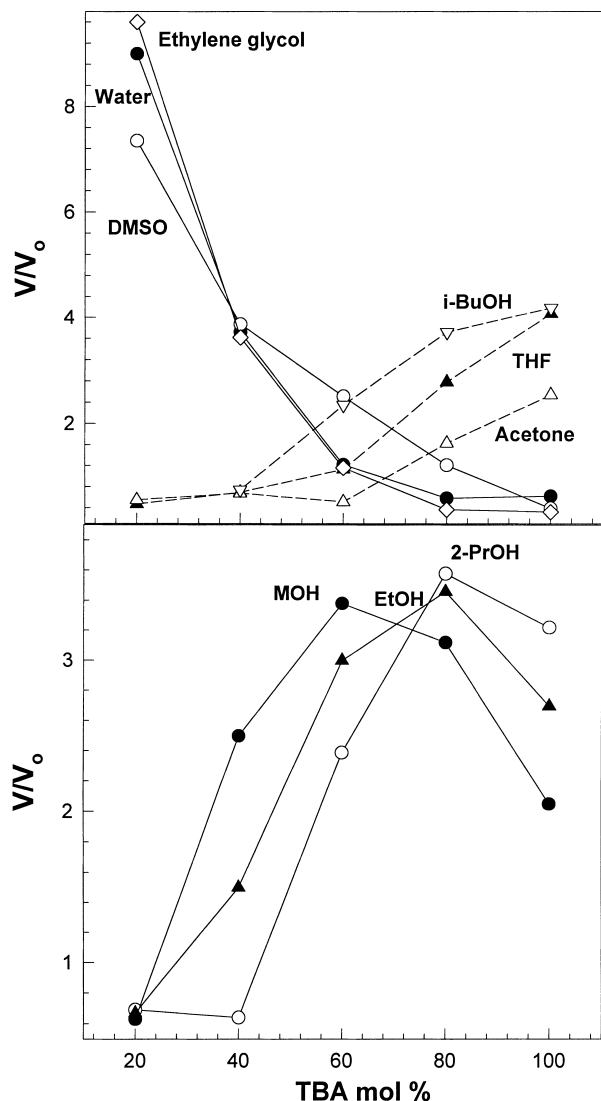


Fig. 4. The equilibrium volume swelling ratios of the hydrogels  $V/V_0$  in various solvents shown as a function of their TBA contents. The solvents used in the swelling experiments are indicated in the figure. MOH = methanol, EtOH = ethanol, 2-PrOH = 2-propanol, *i*-BOH = *iso*-butanol.

magnitude of the reentrant swelling transition is greatest in the hydrogel with 40 mol% TBA, which has a minimum volume in 60/40 (v/v) DMSO–water mixture. At TBA contents higher than 40 mol%, the volume changes are less dramatic due to the small volumes of the hydrogels in water.

Since the reentrant phenomenon is not observable in PAAm gels or in gels containing less than 40 mol% TBA, the existence of *t*-butyl groups is responsible for the reentrant transition behavior of the hydrogels in DMSO–water mixtures. As seen in Fig. 4, increasing amount of TBA of the network chains decreases the swelling capacity of the hydrogels in water. This indicates that the hydrophobic *t*-butyl group decreases the attractive interactions between water and the polymer segments. As a result, water, in mixture with DMSO, is attracted more strongly by the DMSO molecules so that the attractive

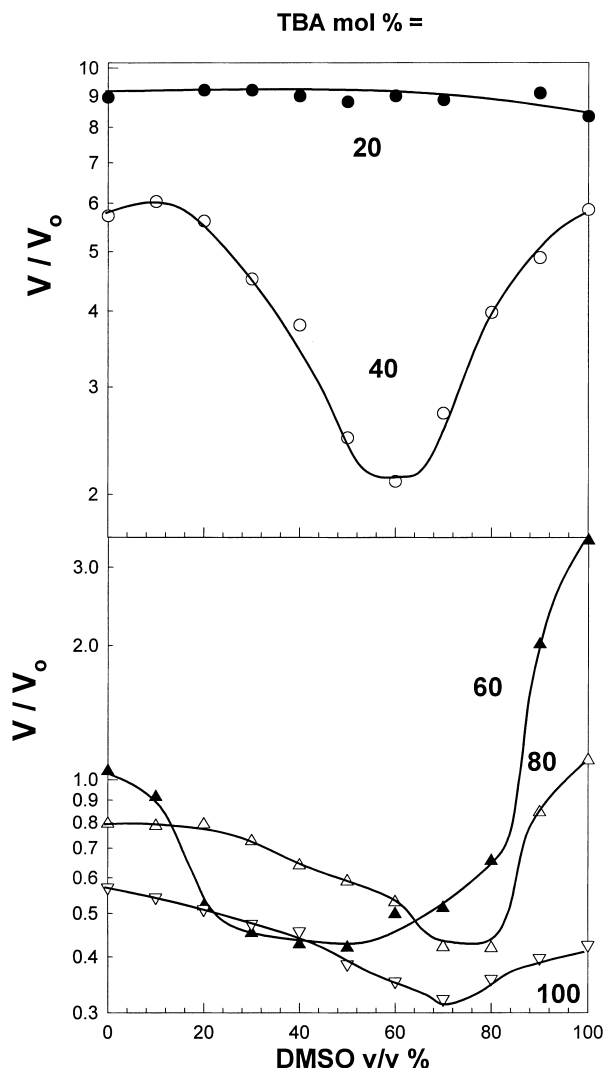


Fig. 5. The equilibrium volume swelling ratios of the hydrogels  $V/V_0$  in DMSO–water mixtures shown as a function of the DMSO content (in vol%) of the solvent mixture. The TBA contents of the hydrogels are indicated in the figure.

water–DMSO interactions dominate over the water–hydrogel and DMSO–hydrogel interactions. This has a consequence that the addition of water to DMSO or DMSO to water results in the deswelling of the gel and the appearance of the reentrant phenomena. It must be pointed out that the PNIPA hydrogels immersed in methanol–water, ethanol–water, DMSO–water, or poly(ethylene glycol)–water mixtures also exhibit reentrant phase transitions [19–23].

### 3.4. Temperature sensitive swelling of hydrogels

In Fig. 6, the equilibrium swelling degrees of the hydrogels in water  $V/V_0$  are plotted as a function of temperature for hydrogels of five different compositions. Over the temperature interval 2–64 °C, hydrogels with equal or less than 20 mol% TBA are in a swollen state

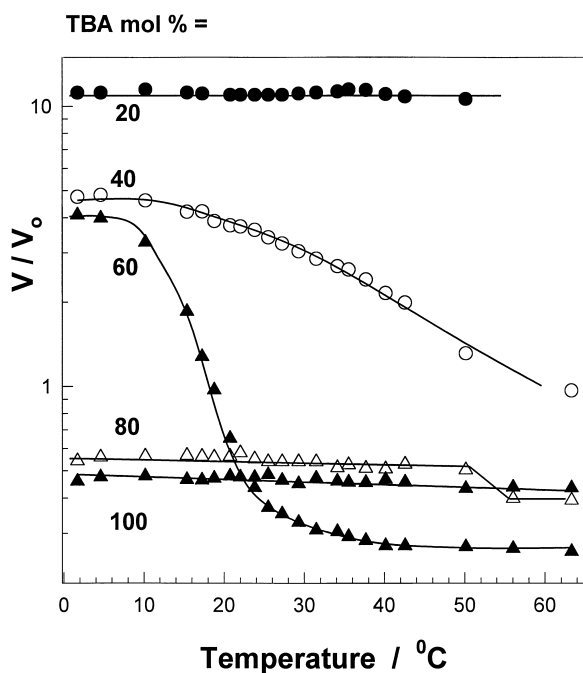


Fig. 6. The equilibrium volume swelling ratios of the hydrogels  $V/V_0$  in water shown as a function of the temperature. The TBA contents of the hydrogels are indicated in the figure.

whereas those with higher than 60 mol% TBA are in a collapsed state. On heating from 2 to 64 °C, the hydrogels containing 40 and 60 mol% TBA show transition from swollen to collapsed state, which is reflected in decreasing swelling degrees. One can also see that increasing TBA content results in shifting of the transition temperature interval in which the deswelling transition takes place. While for the 60% TBA gel, the temperature interval for the deswelling transition is in the range from 10 to 28 °C, for the 40% TBA gel, the deswelling starts at around 20 °C and continues until 64 °C. Further increase of the temperature results, however, in the reswelling of the 40% TBA gel. This unusual feature is shown in Fig. 7. In these experiments, water temperature was first increased from 2 to 80 °C and then decreased again to 2 °C. It is seen that, if the hydrogels are in a collapsed state, the swelling curves obtained during the heating process can also be reproduced during the cooling process. However, for the hydrogels in a swollen state, i.e. those with 20 and 40 mol% TBA, the volume of the gels starts to increase at temperatures higher than 50 °C and thereafter, the gels remain in the swollen state over the entire range of temperatures. This behavior of the gels can be explained with the hydrolysis of the network chains at elevated temperature. Since charged groups are produced by hydrolysis, these groups may lead to the increased swelling ratios of the hydrogels, as shown in Fig. 7. Similar to the *iso*-propyl group in PNIPAA gels [24], one may expect that the *t*-butyl group stabilizes the amide carbon of TBA against the hydrolysis. Therefore, the hydrolysis of AAm units seems to be responsible for the observed swelling behavior of the hydrogels at high temperature.

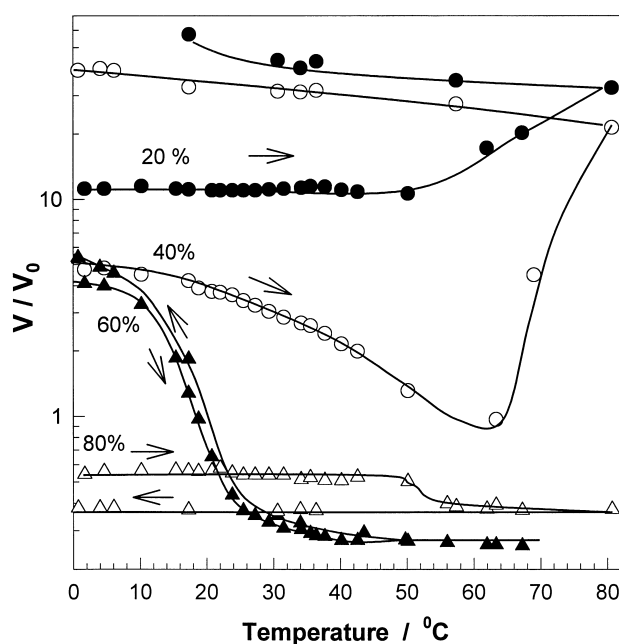


Fig. 7. The equilibrium volume swelling ratios of the hydrogels  $V/V_0$  in water shown as a function of the temperature. The TBA contents of the hydrogels are indicated in the figure. The arrows show the direction of the measurements.

### 3.5. Interaction parameter of poly(TBA-co-AAm) copolymer network–water system

In the following paragraphs, the temperature sensitive swelling behavior of the hydrogels was analyzed within the framework of the Flory–Rehner theory of swelling equilibrium. According to the Flory–Rehner theory, the osmotic pressure  $\pi$  of a non-ionic gel is the sum of two contributions [16]

$$\pi = \pi_{\text{mix}} + \pi_{\text{el}} \quad (7)$$

where  $\pi_{\text{mix}}$  and  $\pi_{\text{el}}$  are the osmotic pressures due to polymer–solvent mixing and due to deformation of network chains to a more elongated state, respectively. Osmotic pressure  $\pi$  of a gel determines whether the gel tends to expand or to shrink. When non-zero,  $\pi$  provides a driving force for gel volume change. Solvent moves into or out of the gel until  $\pi$  is zero, i.e. until the forces acting on the gel are balanced.

The osmotic pressure due to polymer–solvent mixing,  $\pi_{\text{mix}}$ , is satisfactorily represented by a Flory–Huggins type expression of the form [16]

$$\pi_{\text{mix}} = -\frac{RT}{V_1} \left( \ln(1 - \nu_2) + \nu_2 + \chi \nu_2^2 \right) \quad (8)$$

provided that the polymer–solvent interaction parameter  $\chi$  is expressed as a series expansion in powers of the crosslinked polymer volume fraction  $\nu_2$ , i.e. [25]

$$\chi = \chi_1 + \chi_2 \nu_2 + \chi_3 \nu_2^2 + \dots \quad (9)$$

where the coefficients  $\chi_1, \chi_2, \chi_3, \dots$  are functions of

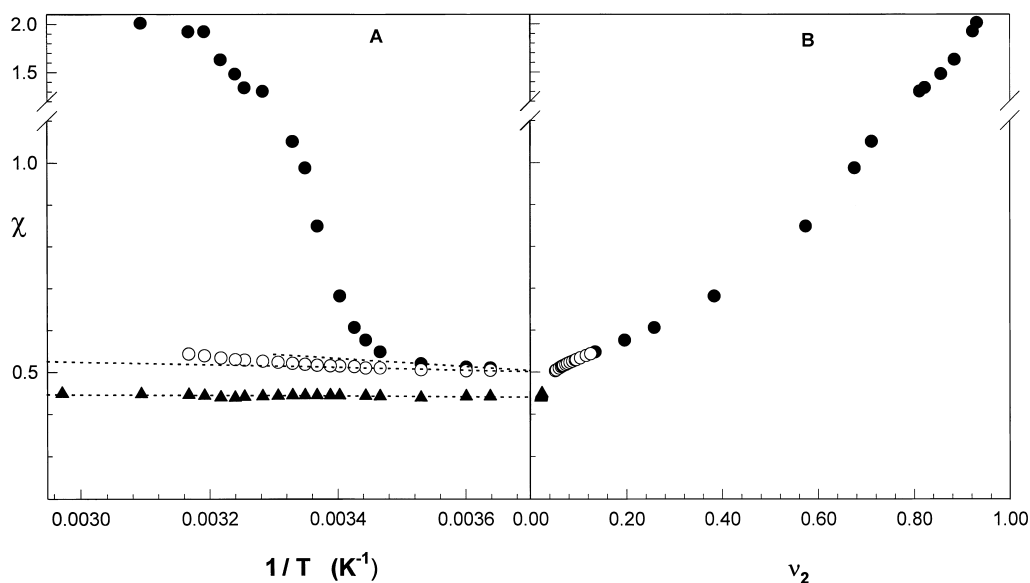


Fig. 8. The polymer–solvent interaction parameter  $\chi$  for the poly(TBA-co-AAm) copolymer network–water system shown as functions of the inverse temperature  $1/T$  (A) and the polymer concentration  $v_2$  (B). TBA content of the hydrogels are 20 (▲), 40 (○), and 60 mol% (●).

temperature and the molecular characteristics of the polymer–solvent system. Note that  $V_1$  in Eq. (8) is the molar volume of segment and, the polymer volume fraction  $v_2$  relates to the experimentally determined swelling ratios  $V/V_0$  through the equation:

$$v_2 = \frac{v_2^0}{V/V_0} \quad (10)$$

To describe the elastic contribution  $\pi_{el}$ , we will use here the simplest affine network model to describe the behavior of gels obeying the Gaussian statistics [16]:

$$\pi_{el} = -RT \frac{\rho}{M_c} \left( (v_2)^{1/3} (v_2^0)^{2/3} - v_2/2 \right) \quad (11)$$

Substituting Eqs. (8) and (11) into Eq. (7) and putting  $\pi = 0$ , one obtains the following well-known equation

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + \frac{\rho}{M_c} V_1 \left( (v_2)^{1/3} (v_2^0)^{2/3} - v_2/2 \right) = 0 \quad (12)$$

describing the condition of equilibrium swelling in gels. In the Flory–Rehner theory represented by Eq. (12), the mechanism of phase transitions in gels is incorporated into the polymer–solvent interaction parameter  $\chi$ . For large swelling ratios, we can neglect  $v_2$  dependence of  $\chi$  defined by Eq. (9). Thus, at high swelling ratios  $\chi$  reduces to  $\chi_1$ , and it is given by [16]

$$\chi_1 = \frac{\Delta G}{RT} = \frac{\Delta H - T\Delta S}{RT} \quad (13)$$

where  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  are the changes in the free energy, enthalpy, and entropy during the formation of polymer–solvent contact from polymer–polymer and solvent–solvent contacts, respectively.

Using the experimentally determined swelling ratios of the hydrogels in water (Fig. 6) together with  $\bar{M}_c = 75\,000$  g/mol found from the elasticity measurements,  $\rho = 1.35$  g/ml,  $v_2^0 = 0.25$ , and  $V_1 = 18$  ml/mol, we calculated  $\chi$  parameter values at each temperature and polymer volume fraction  $v_2$  by use of Eq. (12). The results of the calculations are given in Fig. 8(A) and (B) plotted as functions of  $1/T$  and  $v_2$ , respectively, for the hydrogels with 20, 40, and 60 mol% TBA. Fig. 8(A) shows that at low temperatures, i.e. at high swelling ratios the dependence of  $\chi$  on  $1/T$  is linear. This indicates that the enthalpy and the entropy contributions to the interaction parameter are constant and  $\chi$  equals to  $\chi_1$  in this range of concentration and temperature (Eq. (13)). The dotted lines in Fig. 8(A) are the linear regression lines calculated from the low temperature portion of the data points. The slope and the intercept at  $1/T = 0$  of these lines give the  $\Delta H$  and  $\Delta S$  values appearing in the  $\chi_1$  parameter of poly(TBA-co-AAm) copolymer network–water system (Eq. (13)). The calculation results of  $\Delta H$  and  $\Delta S$  are collected in Table 2 together with the values reported for the PNIPA–water system [5]. It is seen that the signs of both quantities are negative for all the hydrogels. Since

Table 2  
Enthalpy and entropy changes appearing in the  $\chi$  parameter for the poly(TBA-co-AAm)–water systems

TBA (mol%)	$\Delta H$ (J/mol)	$\Delta S$ (J/mol K)
20	$-70 (\pm 28)$	$-3.9 (\pm 0.1)$
40	$-274 (\pm 67)$	$-5.2 (\pm 0.2)$
60	$-790 (\pm 125)$	$-7.1 (\pm 0.5)$
PNIPA	$-7829^a$	$-27.1^a$

For comparison, the values reported for the PNIPA–water system are also given [5].

<sup>a</sup> Values given in Ref. [5]. They were converted into mole basis.



polymer–solvent systems possessing the LCST are characterized by negative values of both  $\Delta H$  and  $\Delta S$ , the results indicate that all the TBA hydrogels studied here have LCST's. Moreover, the absolute values of both  $\Delta H$  and  $\Delta S$  increase with increasing amount of TBA indicating that the temperature sensitivity of the hydrogels increases with increasing TBA content. However, comparison with the reported values of  $\Delta H$  and  $\Delta S$  for the PNIPA–water system shows that the temperature dependence of the present hydrogels is weaker than that of the PNIPA hydrogel, probably due to the temperature independent swelling behavior of AAm segments of the network chains.

As the polymer concentration increases,  $\chi$  vs  $1/T$  curves deviate from linearity and this deviation is greatest for the 60% TBA gel (Fig. 8). The deviation from linearity indicates that  $\Delta H$  and  $\Delta S$  become concentration dependent as  $\nu_2$  increases. Least squares analysis of the data points  $\chi$ ,  $\nu_2$ , and  $T$  for the 60% TBA gel gave the following relationship for the dependence of  $\chi$  on  $\nu_2$ , and  $T$ :

$$\chi = \chi_1 + \left(4.22 - \frac{1170}{T}\right)\nu_2 + \left(10.5 - \frac{2972}{T}\right)\nu_2^2 \quad (14)$$

The swelling ratios of the 60% TBA gel calculated using Eqs. (12) and (14) are shown in Fig. 9 as the solid curve plotted as a function of the temperature. For comparison, the experimental data points are also given in the figure by the symbols. It is seen that, after taking into account

the sensitive dependence of the  $\chi$  parameter on both temperature and polymer concentration, the prediction of the Flory–Rehner theory provides a satisfactory agreement to the experimental data. Using the functional form of the  $\chi$  parameter given by Eq. (14), one can also predict the effect of the ionic groups on the temperature dependent swelling behavior of the 60% TBA gel. In case of ionic gels, an additional osmotic pressure term should be added into the right-hand side of Eq. (7) due to the non-uniform distribution of mobile counterions between the gel and the solution. For slightly charged gels, this osmotic pressure of counter ions,  $\pi_{\text{ion}}$ , is given by [16]

$$\pi_{\text{ion}} = RTf\nu_2 \quad (15)$$

where  $f$  is the effective charge density, i.e. the mole fraction of the charged units in the network chains. Calculation results for the 60% TBA gel having various charge densities  $f$  are shown in Fig. 9 as the dashed curves. In certain ranges of temperature, calculations gave three roots for the swelling ratios, corresponding to the stable, unstable, and metastable states of the gel and thus, predict a discontinuous phase transition [2]. In these cases, the phase transition temperatures and the polymer concentrations in the co-existing phases were determined by using the Maxwell construction. The dotted lines in Fig. 9 represent phase transition regions. It is seen that the theory predicts a first order volume phase transition, provided that the hydrogel contains charged groups. The critical temperatures are 18.4, 21.7, and 28.0 °C for the hydrogels having 0.2, 0.3, and 1.0% charged units, respectively. Experiments are in progress to prove this prediction.

#### 4. Conclusions

The following conclusions were drawn from the experimental data:

1. Methanol is the best solvent for obtaining temperature sensitive hydrogels based on TBA and AAm. It was shown that the composition of the network chains is very close to the original monomer composition in the feed prior to crosslinking copolymerization.
2. The elastic moduli of the hydrogels prepared at a crosslinker ratio of 1/80 and at an initial monomer composition of 20 w/v% are in the range of  $10.7 \pm 0.6$  kPa. This indicates that only 5% of the crosslinker BAAM form effective crosslinks in the final network.
3. The swelling behavior of the hydrogels can be controlled by changing the amount of TBA units in the network chains. As the TBA content of the hydrogel increases, the gel swells in alcohols having larger alkyl chains. If the amount of TBA is 40% or more, hydrogels exhibit reentrant swelling behavior in DMSO–water mixtures, in which the gels first deswell then reswell if the DMSO

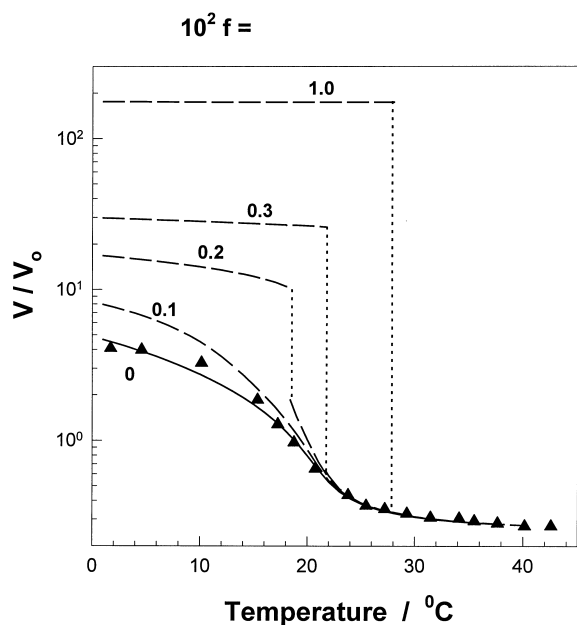


Fig. 9. The equilibrium volume swelling ratios of the hydrogels  $V/V_0$  in water shown as a function of the temperature. The experimental data points for the non-ionic poly(TBA-co-AAm) copolymer network with 60% TBA are shown by symbols. The solid curve was calculated using Eqs. (12) and (14). The dashed curves were calculated for the ionic gels. The ionic group contents  $f$  used in the calculations are indicated in the figure. The dotted lines represent the phase transition regions.

- content of the solvent mixture is continuously increased.
- In water over the temperature range of 2–64 °C, hydrogels with less than 40% TBA by mole are in a swollen state while those with TBA contents higher than 60% are in a collapsed state. Hydrogels with 40–60% TBA exhibit swelling–deswelling transition in water depending on the temperature. The temperature interval for the deswelling transition of 60% TBA gel is in the range from 10 to 28 °C, while for the 40% TBA gel, the deswelling starts at about 20 °C and continues until the onset of its hydrolysis at around 64 °C.
  - The Flory–Rehner theory provides a satisfactory agreement to the experimental swelling data of the hydrogels, provided that the sensitive dependence of the  $\chi$  parameter on both temperature and polymer concentration is taken into account.

### Acknowledgments

Work was supported by Istanbul Technical University Research Fund.

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