Colloid Polym Sci (2006) 284: 1038–1048
DOI 10.1007/s00396-006-1478-7

ORIGINAL CONTRIBUTION

Tuncer Çaykara
Eylem Turan

Effect of the amount and type of the crosslinker on the swelling behavior of temperature-sensitive poly(*N-tert*-butylacrylamide-*co*-acrylamide) hydrogels

Received: 20 December 2005
Accepted: 22 February 2006

T. Çaykara (✉) · E. Turan
Department of Chemistry,
Faculty of Art and Science,
Gazi University,
06500 Besevler, Ankara, Turkey
e-mail: caykara@gazi.edu.tr

Abstract Temperature-sensitive poly (*N-tert*-butylacrylamide-*co*-acrylamide) [P(NTBA-*co*-AAm)] hydrogels were synthesized by free-radical copolymerization in a water–methanol mixture using three types of crosslinkers: 1,2-ethyleneglycol dimethacrylate, *N*,*N*-methylenebisacrylamide, and 1,3-butandiol dimethacrylate. These thermosensitive hydrogels were swollen to equilibrium in water at 20°C and examined by gravimetric measurements. The influence of type and content of crosslinkers on the swelling ratio, the polymer–solvent interaction parameter (χ), the average molecular mass between crosslinks $\left(\overline{M}_c\right)$, and the effective crosslinking density (ν_E) of the hydrogels were reported and discussed. The swelling process in water was found to be non-Fickian diffusion. The enthalpy (ΔH) and entropy (ΔS) changes appearing in the χ parameter for the hydrogels were determined by using the Flory–Rehner theory based on the phantom network model of swelling equilibrium. Negative values for ΔH and ΔS indicated that the hydrogels had a negative temperature-sensitive property in water; that is, swelling at a lower temperature and shrinking at a higher temperature. The temperature-reversibility and on–off switching properties of the P(NTBA-*co*-AAm) hydrogels may be considered as good candidates for designing novel drug-delivery systems.

Keywords Poly(*N-tert*-butylacrylamide-*co*-acrylamide) · Thermosensitive · Hydrogel · Crosslinking · Network

Introduction

Temperature-sensitive hydrogels can swell in a solvent at low temperatures but they shrink as the temperature is raised above the phase-transition temperature. These kinds of hydrogels have recently attracted a great deal of research interest because of their rheological and technological importance and potential biomedical applications [1–5]. The phase-transition phenomenon is associated with the temperature dependence of hydrogen bonding and hydrophobic interactions [6, 7]. As the temperature increases, pendant groups of the hydrogel become more mobile, and the hydrophobic groups also become active, causing phase separation at temperatures greater than the phase-transition temperature [8, 9]. Inomata et al. [7] and others [10–12] also suggested that the phase separation of *N*-isopropylacrylamide (NIPA) hydrogel is attributable to the hydrophobic interactions. These authors proposed that the good swelling of the hydrogel at a lower temperature is due to the hydration and water molecules forming cagelike structures around the hydrophobic solutes. As temperature increases, the structure around the hydrophobic groups is destroyed and the hydrophobic groups of polymer chains start to associate; this leads to the phenomenon of phase separation [13].

The chemical modification by copolymerization is a basic route for tuning the phase-transition temperature to a desired value. The incorporation of hydrophilic comonomer leads to an increase in the phase-transition temperature, whereas the incorporation of hydrophobic comonomer leads to a decrease [14]. It is well known that pure poly(NIPA) (PNIPA) exhibits volume phase-transition at approximately 32 °C [7]. However, copolymerization of NIPA with butylmethacrylate, which is a hydrophobic monomer in a feed ratio of 96:4 mol%, gives a phase-transition temperature at 29 °C, while copolymerization with acrylamide, which is a hydrophilic monomer in a similar feed ratio, gives a phase-transition temperature at 35 °C [15]. Öztürk and Okay [16] investigated several series of hydrogels based on *N-tert*-butylacrylamide (NTBA). It was shown that the hydrogels exhibit changes in their phase-transition temperatures as a function of their comonomer composition. Yi et al. [17] showed that the phase-transition temperature of P(NIPA-*co*-NTBA) copolymeric hydrogels decreased with an increasing mole ratio of NTBA in the monomer feed composition.

On the other hand, crosslinking is responsible for the three-dimensional network structures that characterize these materials. The elasticity and swelling properties are attributed to the presence of physical or chemical crosslinks within polymer chains. The level of crosslinking of the hydrogels is also important because the physical states of the hydrogels alter with the changing of the crosslinking level. Ilavsky and Hrouz [18] systematically investigated the effect of the amount of the crosslinking agent *N*,*N*-methylenebisacrylamide (MBAAm) on the properties of poly(acrylamide) (PAAm)-based hydrogels in water/acetone and water/ethanol mixtures. Recently, Xue et al. [19] reported the effect of the nature and amount of crosslinker on the swelling ratio and polymer–water interaction parameter. However, further investigations of the influence of the amount and type of the crosslinker on the properties, especially the phase-transition behavior, responsive dynamics, and network parameters, of the poly(*N-tert*-butylacrylamide-*co*-acrylamide) [P(NTBA-*co*-AAm)] hydrogels have not been reported. Therefore, the aim of this article is to report the findings of a comprehensive and systematic study of the effects of the amount and type of the crosslinker on the swelling properties of the P(NTBA-*co*-AAm) hydrogels. Hydrogels were prepared by free-radical crosslinking copolymerization of NTBA and AAm in the presence of crosslinkers. The phase-transition behavior and network parameters of the P(NTBA-*co*-AAm) hydrogels with different crosslinkers, as well as the temperature dependence of the equilibrium swelling ratio and responsive dynamics, were analyzed.

Experimental procedure

Materials

Monomers NTBA, AAm, the crosslinkers 1,2-ethyleneglycol dimethacrylate (EGDMA), MBAAm, 1,3-butandiol dimethacrylate (BDDMA), initiator ammonium persulfate (APS), and the accelerator *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were purchased from Aldrich Chemical. The chemicals were used as received.

Hydrogel synthesis

P(NTBA-*co*-AAm) hydrogels were synthesized by free-radical crosslinking copolymerization of NTBA and AAm in a methanol–water mixture (1:1 v/v). APS (0.056 M) and TEMED (0.32 M) solutions prepared in deionized water were used as the redox initiator system. The NTBA (0.7 g), AAm (0.3 g), APS (2.0 mL), and crosslinker (mol% of EGDMA or MBAAm or BDDMA at 2.4, 3.0, 3.7, 4.3, and 5.0) were dissolved in methanol (4.0 mL) and the solution was purged with nitrogen gas for 10 min. After the addition of TEMED (2.0 mL), the solution was placed in poly(vinylchloride) straws of 4-mm diameters and about 20-cm lengths. The poly(vinylchloride) straws were sealed and immersed in a thermostated water bath at 20 °C, and the copolymerization was conducted for 24 h. Upon completion of the reaction, the hydrogels were cut into specimens approximately 10 mm in length and immersed in large excess amounts of water at room temperature for at least 72 h. The water was changed every several hours to wash out any unreacted monomers and the initiator. The hydrogel samples were then dried at 50 °C under vacuum to a constant weight. The ratio between the mass of the dried copolymer and the calculated copolymer mass for 100% conversion for these samples was found in the range of 1.08–1.13. An analysis of these values shows both the presence of bound water and the conversion of monomer to polymer to be close to 100%. The cross-linked *N*-substituted acrylamide hydrogels always contain about 10–20 wt.% of bound water, even after several months of drying under vacuum [16].

The volume fraction of polymer network after preparation, ν_{2r}, was calculated as:

$$\nu_{2r} = \left[1 + \frac{\left(\frac{m_r}{m_d} - 1\right)\rho_2}{\rho_1}\right]^{-1} \tag{1}$$

where m_r is the mass of the hydrogel after preparation and m_d is the mass of the hydrogel after drying, ρ_2 and ρ_1 are densities of polymer network and solvent, respectively. The values of ρ_2 and ρ_1 used were 1.10 and 1.0 g/mL, respectively. The density of the polymer network was determined by a pycnometer using acetone as nonsolvent.

Measurement of the swelling ratio and pulsatile kinetics

For the swelling dynamic studies, the hydrogels were immersed in deionized water at 22 °C. At a prescribed time interval, the hydrogels were taken out from the water and weighed after wiping off the excess water from the surface of the hydrogel. The swelling ratio of the hydrogels was defined as follows:

$$SR = \frac{m_t - m_d}{m_d} \qquad (2)$$

where m_d and m_t are the masses of the dry and swollen hydrogels at time t, respectively.

For the temperature-response studies, hydrogels were equilibrated in distilled water at temperatures ranging from 5 to 60 °C. The hydrogels were allowed to swell in distilled water for at least 24 h at each predetermined temperature, controlled up to ±0.1 °C in a constant-temperature water bath (Thermo Haake K10). The gravimetric method was employed to study the hydrogel-swelling ratio. After immersion in distilled water at a predetermined temperature, the hydrogels were removed from the water and blotted with wet filter paper for the removal of excess water from the hydrogel surface; the hydrogels were then weighed. After this weight measurement, the hydrogels were re-equilibrated in distilled water at another predetermined temperature, and their swollen weight was determined. The average values of three measurements were taken for each hydrogel, and the equilibrium swelling ratio q_v was calculated as follows:

$$q_v = \frac{1}{\nu_{2m}} = 1 + \frac{\left(\frac{m_s}{m_d} - 1\right)\rho_2}{\rho_1} \qquad (3)$$

where m_s is the mass of the swollen hydrogel and ν_2m is the volume fraction of the polymer network in the swollen gel at the equilibrium state.

The pulsatile swelling behavior was observed in water with the temperature alternating between 10 and 40 °C. During the pulsatile swelling process, the weight change of the hydrogels was measured at 5-min intervals, and the temperature was switched every 100 min.

Results and discussion

Synthesis of P(NTBA-*co*-AAm) hydrogels

The hydrogels made of NTBA alone were too fragile to handle. Therefore, we added AAm to make copolymers to improve the mechanical property of the hydrogels. P(NTBA-*co*-AAm) hydrogels can also be easily synthesized in methanol–water mixtures. Öztürk and Okay [16] showed that the addition of NTBA 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 NTBA compared to that of AAm monomer, as well as to the different solubilities of the monomers and the corresponding homopolymers [16, 20]. The monomer NTBA and the polymer synthesized from NTBA are insoluble in water but soluble in organic solvents such as *tert*-butanol, methanol, and tetrahydrofolate (THF), whereas PAAm is soluble in water but insoluble in the organic solvents [21, 22]. In this study, we conducted the copolymerization reactions in several solvents including *tert*-butanol, *tert*-butanol–water, THF, THF–water, methanol, and methanol–water mixtures. Reproducible results were obtained in the methanol–water mixture as the polymerization solvent at 22 °C. At the end of polymerization, the hydrogels appear to be translucent with obviously fine opaque domains in the matrix, indicating that their network structure may be heterogeneous and the pore size within the hydrogel is probably relatively large [23]. This may have arisen from the phase separation of the formed P(NTBA-*co*-AAm) chains in the methanol–water mixture.

Swelling kinetics

The kinetic response of hydrogels depends both upon the history of a given hydrogel and its chemical composition, e.g., the swelling kinetics of hydrogels are reported to change with the initial anisotropy of the matrix, as well as with changing the constituent of the matrix, particularly introducing hydrophilic monomers in the parent hydrogels [24]. In addition, the nature and type of the crosslinker directly affects the network structure and thereby greatly influences the swelling behavior of hydrogels [25].

To evaluate the effect of the nature of the crosslinker on the swelling ratio of the P(NTBA-*co*-AAm) hydrogels, three different crosslinkers, namely, EGDMA, MBAAm, and BDDMA, were used. The crosslinker content in the monomer mixture was varied in the range of 2.4–5.0 mol%. The swelling kinetics of the P(NTBA-*co*-AAm) hydrogels with three different crosslinkers measured at 22 °C are shown in Fig. 1. The data show that both the swelling ratio and the swelling rate of all the hydrogels decreased with the increasing amount of the crosslinker. The hydrogels with EGDMA showed the higher swelling ratio when compared with the hydrogels crosslinked with MBAAm or BDDMA. However, the hydrogel with 2.4% EGDMA had an about 2.5 swelling ratio within 200 min, or 3.6 within 480 min, whereas the hydrogel with 5.0% EGDMA had about 2.1 and 3.1 swelling ratios, within the same respective time frames. The swelling experiments of different crosslinked P(NTBA-*co*-AAm) hydrogels indicated that BDDMA crosslinked hydrogels had lower swelling ratio values than those of EGDMA or MBAAm crosslinked hydrogels. This is due to the variation in the reactivity of different crosslinkers. Due to the high-solubility nature of BDDMA, this hydrogel forms a dense three-dimensional structure, which ultimately reduces the mesh size, leading to lower swelling capacity. Whereas the other crosslinkers, EGDMA and MBAAm, are insoluble in aqueous phase, less reactive than BDDMA, and may not form dense three-dimensional structures in the hydrogel, leading to high elastic behavior, thereby increasing the swelling ratio. In addition, due to the employment of methanol in crosslinker solutions, porosity is generated in the hydrogel, which is further responsible for the enhanced swelling ratio. Thus, the order of the swelling capacity of the P(NTBA-*co*-AAm) hydrogels crosslinked by different crosslinkers is noticed as EGDMA > MBAAm > BDDMA.

To determine the nature of water diffusion into the hydrogels, initial swelling data were fitted to the following exponential equation [26]:

$$F = \frac{M_t}{M_\infty} = kt^n \tag{4}$$

where F denotes the fraction of water at time t; M_t and M_∞ represent the amount of solvent diffused into the hydrogel at time t and infinite time (at equilibrium), respectively; k is a constant related to the structure of the network; and the exponent n is a characteristic coefficient of transport. This equation is applied to the initial stages of swelling, and plots of lnF vs lnt yield straight lines to almost a 60% increase in the mass of the hydrogel. The values of the diffusion constant calculated from the slopes of the lines and the k constant values calculated from the intercept, for the P(NTBA-*co*-AAm) hydrogels with various crosslinker content, are listed in Table 1. In Eq. (4), the numerical value of n provides information about the mechanism of swelling kinetics. Alfrey et al. [27] distinguished three classes of diffusion according to the relative rates of diffusion and polymer relaxation. First, Fickian diffusion (n=0.5) is much slower than that of relaxation. In this case, the system is controlled by a diffusion phenomenon. Second, the case II diffusion (n=1.0) process is very fast in corporation with the relaxation process. The controlling step is the velocity of an advancing front, which forms the boundary between a swollen gel and a glassy core. Finally, non-Fickian diffusion (n=0.5–1.0) describes those cases in which the diffusion and relaxation rates are comparable.

A slight variation of the diffusion exponent with crosslinker content is observed, and its value higher than 0.50, indicating the diffusion of water to the interior of all the hydrogels, follows an anomalous mechanism and reveals the existence of certain coupling between molecular diffusion and tension relaxation developed during the swelling of the hydrogels. The highly anomalous behavior of these hydrogels is due to the strong interchain interactions via the formation of hydrogen bonding, leading to a compact structure which would accentuate the anomalous aspects of diffusion, even for a molecule as small as water.

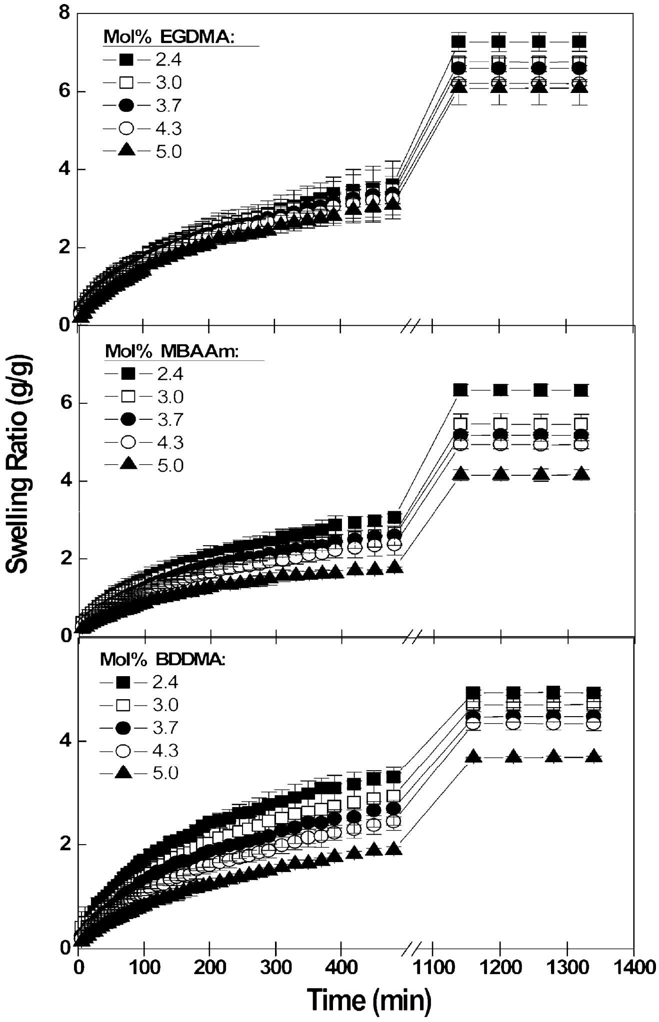

Fig. 1 Swelling kinetics of the P(NTBA-*co*-AAm) hydrogels. The amount and type of the crosslinkers are indicated as the insert. The *curves* show the trend of the data

Table 1 The variation of diffusion parameters with the amount and type of crosslinker in the P(NTBA-*co*-AAm) hydrogels

Crosslinker	Mol% of crosslinker	$k \times 10^2$	n	$D \times 10^7$ cm^2 s^{-1}
EGDMA	2.4	1.52±0.63	0.63±0.01	2.97
	3.0	2.14±0.57	0.57±0.01	2.20
	3.7	2.70±0.52	0.52±0.01	1.36
	4.3	2.91±0.51	0.51±0.01	1.26
	5.0	2.52±0.52	0.52±0.01	1.17
MBAAm	2.4	1.47±0.64	0.64±0.01	2.74
	3.0	2.13±0.57	0.57±0.01	1.91
	3.7	2.87±0.51	0.52±0.01	1.20
	4.3	2.69±0.52	0.52±0.01	1.18
	5.0	2.53±0.51	0.52±0.01	0.94
BDDMA	2.4	2.02±0.67	0.67±0.01	2.63
	3.0	1.81±0.61	0.61±0.01	0.96
	3.7	2.56±0.56	0.56±0.02	0.81
	4.3	2.19±0.57	0.57±0.01	0.77
	5.0	2.83±0.54	054±0.02	0.71

For calculating the diffusion coefficient of water moving through the hydrogels, the following equation was employed [26].

$$D = \pi r^2 \left(\frac{k}{4}\right)^{1/n} \tag{5}$$

where D is the diffusion coefficient of water (cm^2 s^{-1}) and r is the radius of the dry gel.

The D values are also presented in Table 1. The diffusion coefficients, D, of all the hydrogels decreased with an increase of the crosslinker content. This is explained by the restriction of the expansion of the network structure resulting from the increase of the crosslinking density [28–30]. The results also show that the D values for the P(NTBA-*co*-AAm) hydrogels crosslinked by different crosslinkers in water are in the order of EGDMA < MBAAm < BDDMA. This shows that the rate of water penetrating in the hydrogel is highest for the hydrogels with EGDMA during the swelling process.

Network parameters

The key parameters of crosslinked polymeric networks are the molecular masses between crosslinks $\left(\overline{M}_c\right)$ or effective crosslinking density (ν_{E}) for a highly swollen network. Several theories have been proposed to calculate the molecular mass between crosslinks in a polymeric network. However, in the highly swollen state, the constrained junction theory indicates that a real network exhibits properties close to those of the phantom network model [31]. In this study, the experimental $\overline{M}_c$ values were calculated from equilibrium swelling ratios of the hydrogels by using the following Flory–Rehner equation based on the phantom network model [32, 33]:

$$\overline{M}_{cE} = -\frac{(1-2/\phi)V_1\rho_2\nu_{2r}^{2/3}\nu_{2m}^{1/3}}{\left(ln(1-\nu_{2m})+\nu_{2m}+\chi\nu_{2m}^2\right)} \tag{6}$$

where ϕ is the number of branches originating from a crosslink site (ϕ=4), V_1 is the molar volume of the solvent (18 mL/mol), and χ is the polymer–solvent interaction parameter.

The χ parameter can be derived from Eq. (6) by neglecting its elastic term and expanding the entropic term in series. In this manner, the isolation of the χ parameter depends mainly on the mixing contribution, i.e., three terms on the denominator of Eq. (6). Numerically, it is found that the elastic contribution, i.e., the remaining term, has only a slight effect on the derived value of the χ parameter because, in the present system wherein $\nu_{2\mathrm{m}}$ is very small and $\overline{M}_{cE}$ is very large, this is especially true, and Eq. (6) can be reduced as follows to an excellent approximation.

$$ln(1-\nu_{2m})+\nu_{2m}+\chi\nu_{2m}^2 \cong 0 \tag{7}$$

The expansion of the logarithmic series, followed by truncation of term in $\nu_{2m}^4, \nu_{2m}^5, \nu_{2m}^6,$ etc., and rearrangement yields [19].

$$\chi \cong \frac{1}{2} + \frac{\nu_{2m}}{3} \tag{8}$$

Equation (8) neglects the $\overline{M}_{cE}$ dependence of the χ parameter, and therefore, is very approximate. In addition, of course the full implementation of Eq. (6) does allow, in principle, the values of the χ parameter to be <0.50. However, Eq. (8) indicates that $\chi \geq 0.50$ [19]. In fact, the use of Eq. (8) in conjunction with the values of ν_{2m} affords values of χ that lie in close accord with those listed in Table 2. As shown in Table 2, χ parameters of the P(NTBA-*co*-AAm) hydrogels were found in the range of 0.533–0.544, depending on the amount and type of the crosslinker. These values of χ are in good agreement with the value of 0.52 found from the elasticity measurement by Gündoğan and coworkers [34].

After finding the χ parameter for the present system, the $\overline{M}_{cE}$ value can now be evaluated using Eq. (6) together with the experimental ν_{2r} and ν_{2m} values of the hydrogels. The calculation results are collected in Table 2.

The experimental crosslinking density ν_E was calculated via Eq. (9):

$$\nu_E = \frac{\rho_2}{\overline{M}_{cE}} \tag{9}$$

On the other hand, assuming that all crosslinker molecules used in the hydrogel synthesis participate in forming effective crosslinks, theoretical $\overline{M}_c$ values of the hydrogels were calculated by the following equation [10]:

$$\overline{M}_{cT} = \frac{\rho_2 \overline{V}_r}{2X} \tag{10}$$

where X is the crosslinker ratio (mole ratio of crosslinker to NTBA+AAm) and $\overline{V}_r$ is the average molar volume of polymer repeat units. $\overline{V}_r$ can be calculated as:

$$\overline{V}_r = \frac{M_{NTBA} f_{NTBA} + M_{AAm} f_{AAm}}{\rho_2} \tag{11}$$

where M_{NTBA} is the molecular mass of NTBA, f_{NTBA} is the mole fraction of NTBA, M_{AAm} is the molecular mass of AAm, and f_{AAm} is the mole fraction of AAm in the gel system.

Table 2 The variation of network parameters with the amount and type of crosslinker in the P(NTBA-*co*-AAm) hydrogels

Crosslinker	Mol% of crosslinker	χ	$\overline{M}_{cE}\times10^{-2}$ (g/mol)	$\nu_E\times10^4$ (mol/cm^3)
EGDMA	2.4	0.533	71	1.6
	3.0	0.535	58	1.9
	3.7	0.536	54	2.0
	4.3	0.537	46	2.4
	5.0	0.538	45	2.5
MBAAm	2.4	0.537	49	2.2
	3.0	0.541	33	3.3
	3.7	0.543	30	3.9
	4.3	0.544	26	4.4
	5.0	0.550	16	6.8
BDDMA	2.4	0.544	26	4.3
	3.0	0.546	23	4.9
	3.7	0.547	20	5.6
	4.3	0.548	18	6.1
	5.0	0.554	12	9.2

The theoretical crosslinking density ν_T was calculated from the following equation Eq. (12):

$$\nu_T = \frac{\rho_2}{M_{cT}} \tag{12}$$

The relevant experimental parameters of the hydrogels are also given in Table 2. As can be seen from Table 2, the experimental $\overline{M}_c$ values of all the hydrogels decreased with an increasing amount of the crosslinker. However, irrespective of the type of crosslinker, the theoretical $\overline{M}_c$ values of the hydrogels were calculated as 2,200, 1,700, 1,500, 1,200, and 1,000 g mol^{-1}. The experimentally found $\overline{M}_c$ values of all the hydrogels are higher than their theoretically calculated counterparts. The difference between the theoretical and experimental $\overline{M}_c$ values of the hydrogels indicates that a significant fraction of the crosslinkers is wasted during the crosslinking copolymerization, probably due to the cyclization and multiple crosslinking reactions [16]. The high degrees of dilution during the hydrogel preparation, as well as the higher crosslinker reactivity, are mainly responsible for these reactions. In addition, the difference between the theoretical and experimental $\overline{M}_c$ values may also be explained specifying that, due to a number of network imperfections, such as chain loops and dangling ends in polymer chains, the basic assumption of tetrafunctional crosslinks is not satisfactory. All these network imperfections contribute to decreasing the hydrogel elastic response.

On the other hand, it has been proposed that ν_E varies with ν_T according to the following equation Eq. (13) [35]:

$$\nu_E = \alpha + \beta \nu_T \tag{13}$$

where α is the crosslinking coefficient at 0 crosslinker content and β is the efficiency of the crosslinking coefficient. The β and α values of these hydrogels were calculated from the slopes and intercepts of the graph of ν_E against ν_T. The α values for the hydrogels with EGDMA, MBAAm, and BDDMA were found to be 8.12×10^{-5}, 1.34×10^{-5}, and 2.17×10^{-5}, respectively. The value of α is the value of effective crosslinking in the absence of any chemical crosslinker, and this value may arise from physical crosslinking or crosslinking induced when γ-radiation is used in the synthesis [35]. For the synthesis of the P(NTBA-*co*-AAm) hydrogels, the radiation-induced polymerization technique was not used. In this case, it can only be presumed the low α values might arise either from an extraneous form of crosslinking caused by the chain transfer or defects in the network, such as loops, entanglements, or microcrystallite, or, more probably, from the hydrophobic physical interactions present in the hydrogel [35]. For these hydrogels, it is reasonable to assume that strong association should take place though the hydrophobic interaction of the *tert*-butyl groups of the P(NTBA-*co*-AAm) hydrogels. The parameter is a measure of crosslinking efficiently ($\beta = \nu_E/\nu_T$ when α=0) and its magnitude is usually $\beta \leq 1.0$, although one unusual case has been reported, where $\beta \geq 1.0$ [35]. It was also observed that the β values for the P(NTBA-*co*-AAm) hydrogels crosslinked with different amounts of EGDMA, MBAAm, and BDDMA crosslinkers via chemical initiation are 0.164, 0.700, and 0.768, respectively. In this case, 84, 30, and 23% of EGDMA, MBAAm, and BDDMA crosslinkers, respectively, were wasted during the crosslinking copolymerization of NTBA and AAm. In connection with crosslinking efficiently, it has been observed by Mark and Dusek [36] that gel formation in solution is often characterized by low crosslinking efficiency due to the formation of a large number of elastically ineffective dangling ends in the network. In the work of Gündoğan and coworkers [34], who used MBAAm in PNIPA, the crosslinking efficiency was reported in the range of 0.15–0.30. It is not possible to make meaningful comparison of the present network parameters with literature values because such values are scant for thermosensitive hydrogels [35]. In this respect, the finding of this report reveals that BDDMA is more efficient than MBAAm and EGDMA for crosslinking NTBA–AAm copolymers. This conclusion is supported by the data of $\overline{M}_{cE}$ for the hydrogels prepared by three crosslinkers. Table 2 shows that $\overline{M}_{cE}$ values of BDDMA networks are always smaller than the corresponding values when MBAAm and EGDMA are used as the crosslinking agents because $\overline{M}_{cE}$ is used to determine the distance between two successive crosslinks. The smaller value of the hydrogels with BDDMA indicates higher crosslinking density networks. As the crosslinking density increases, the water content of the hydrogels is reduced (see Fig. 1). It was also observed that the β values are less than unity, which is due to the fact that water is a good swelling agent for these hydrogel systems. This is because β is a measure not only of chemical crosslinking but also of physical interactions between the chains when the values are higher than unity [35].

Temperature-dependent swelling behavior

Figure 2 demonstrates the temperature-dependent swelling behavior of the P(NTBA-*co*-AAm) hydrogels crosslinked by different crosslinkers when the temperature of the aqueous media increased from 5 to 60 °C. The data show that all the hydrogels, regardless of the amount and type of crosslinkers, had similar swelling behaviors as a function of temperature, and the phase-transition temperatures of these hydrogels lay in the vicinity of 20–25 °C. This effect could be expected in that the temperature sensitivity of the P(NTBA-*co*-AAm) hydrogels was attributed to the dissociation of ordered water molecules surrounding hydrophobic *tert*-butyl groups in the hydrogel. It is also observed that the P(NTBA-*co*-AAm) hydrogels exhibit a negative temperature-sensitive property; that is, swelling at a lower temperature and shrinking at a higher temperature. Under

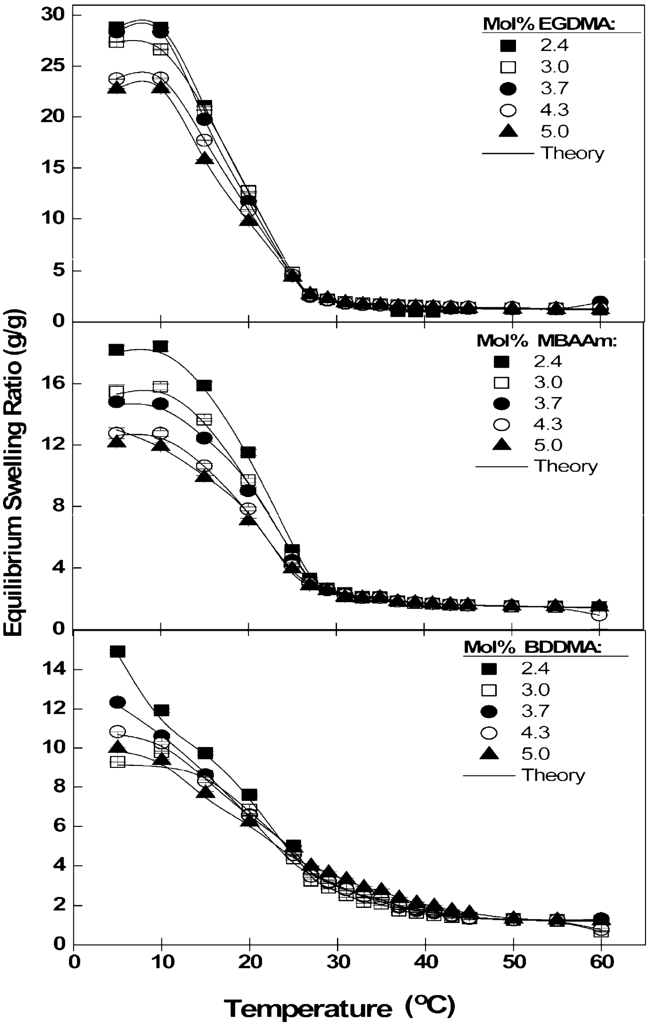

Fig. 2 Equilibrium swelling ratios of the P(NTBA-*co*-AAm) hydrogels in water shown as a function of temperature. The *solid curve* was calculated using Eqs. (6) and (16). The amount and type of the crosslinkers are indicated as the insert

an equilibrium condition, all the P(NTBA-*co*-AAm) hydrogels show increasing swelling at lower temperatures, but they deswell above their phase-transition temperatures because of the aggregation of the network chains. When the external temperature is increased from 5 °C toward the phase-transition temperature, the swelling ratio or water content inside the P(NTBA-*co*-AAm) hydrogels decreases slowly during the shrinkage, and the water release rate is controlled mainly by the collective diffusion of the hydrogel. Even though the phase-transition temperatures of the P(NTBA-*co*-AAm) hydrogels were virtually not affected by the amount and type of crosslinkers, the data in Fig. 2 show also that, at a temperature below the phase-transition temperature (e.g., 10 °C), the equilibrium swelling ratios of these hydrogels were significantly reduced from the hydrogel with 2.4 mol% crosslinker to the hydrogel with 5.0 mol% crosslinker, and the magnitude of the negative swelling slope below the phase-transition temperature also decreased from the hydrogel with 2.4 mol% crosslinker to the hydrogel with 5.0 mol% crosslinker. It is believed that an increase in the amount of crosslinker from 2.4 to 5.0 mol% would reduce the free volume within the hydrogel network structure, in which water would reside during swelling.

There was no obvious effect of the amount and type of crosslinker on the swelling ratio of the P(NTBA-*co*-AAm) hydrogels at temperatures above their the phase-transition temperatures. This suggests that, regardless of the amount and type of crosslinkers, all P(NTBA-*co*-AAm) hydrogels would collapse into similar collapsed structures at a temperature above their the phase-transition temperatures.

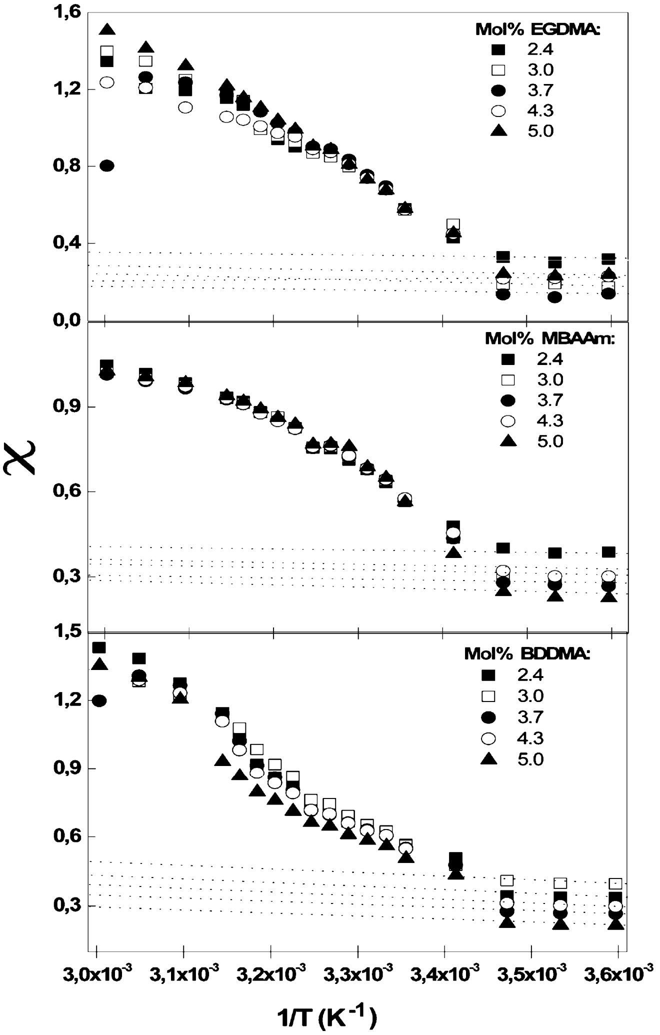

Fig. 3 Variation of the polymer–solvent interaction parameter χ of the P(NTBA-*co*-AAm) hydrogel–water systems with the inverse temperature $1/T$. The amount and type of the crosslinkers are indicated as the insert

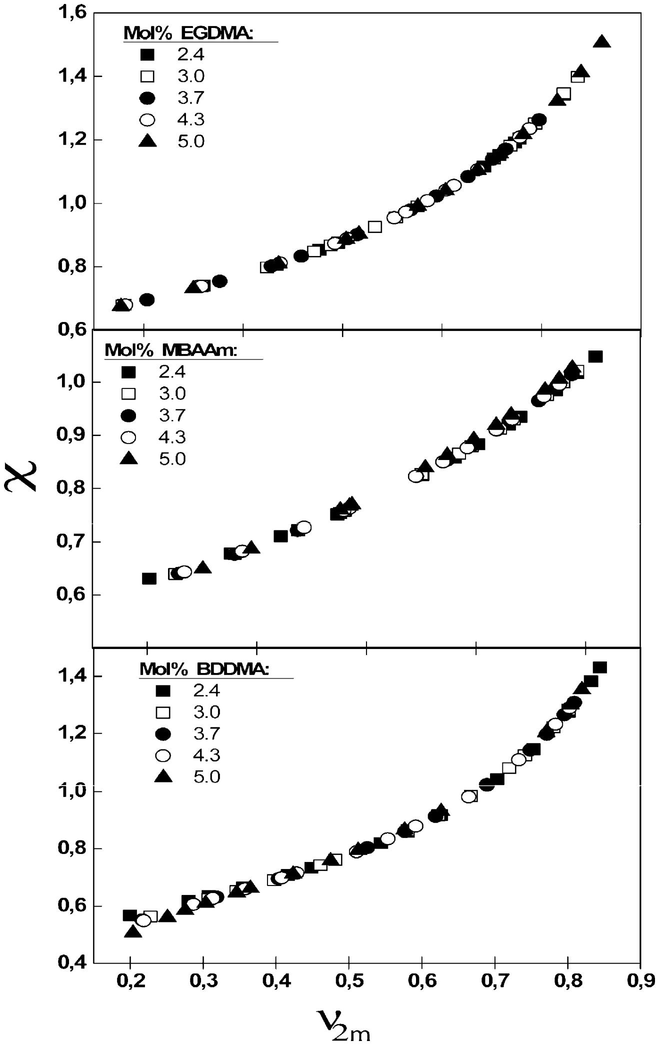

Fig. 4 Variation of the polymer–solvent interaction parameter χ of the P(NTBA-*co*-AAm) hydrogel–water systems with the polymer volume fraction ν_{2m}. The amount and type of the crosslinkers are indicated as the insert

Table 3 The variation of enthalpy and entropy in χ parameter with the amount and type of crosslinker in the P(NTBA-*co*-AAm) hydrogels

Crosslinker	Mol% of crosslinker	ΔH (J/mol)	ΔS (J/mol K)
EGDMA	2.4	−662±96	−4.9±0.3
	3.0	−838±41	−4.5±0.2
	3.7	−386±84	−2.5±0.3
	4.3	−638±91	−4.2±0.4
	5.0	−639±50	−4.3±0.2
MBAAm	2.4	−951±99	−6.6±0.4
	3.0	−1,253±17	−6.9±0.6
	3.7	−850±22	−5.3±0.1
	4.3	−1,254±89	−7.1±0.3
	5.0	−1,246±10	−7.1±0.4
BDDMA	2.4	−1,378±67	−7.7±0.2
	3.0	−1,375±37	−8.2±0.1
	3.7	−1,387±50	−7.2±0.2
	4.3	−1,364±35	−7.4±0.1
	5.0	1,371±54	−8.3±0.2

Polymer–solvent interaction parameter

One of the basic structural parameters of crosslinked polymeric networks is the polymer–solvent interaction parameter (χ). It is well known that this parameter depends on temperature and, for many systems, also on composition. In poor solvents, $\chi \geq 0.7$ and the equilibrium swelling ratio is not affected at temperature variations. For good solvents, $\chi \leq 0.5$; however, because of increasing polymer–solvent interactions, the equilibrium swelling ratio is shifted to higher values [32, 37]. The χ parameter is expressed as a series expansion in powers of $\nu_{2\mathrm{m}}$ [38],

$$\chi = \chi_1 + \chi_2 \nu_{2m} + \chi_3 \nu_{2m}^2 \tag{14}$$

where the coefficients χ_1, χ_2, and χ_3 are the functions of temperature and the molecular characteristics of the polymer–solvent system. For high swelling ratios, $\nu_{2\mathrm{m}}$ dependence of χ can be neglected, as defined by Eq. (15). In this case, χ reduces to χ_1 and the following equation can be obtained for χ_1 [32]:

$$\chi_1 = \frac{\Delta H - T\Delta S}{RT} \tag{15}$$

where ΔH and ΔS are the changes in the enthalpy and entropy during the swelling of crosslinked polymer in a solvent, respectively. By using Eq. (8), χ parameters of the hydrogels were calculated from $\nu_{2\mathrm{m}}$ values at each temperature. The variation of χ parameter with $1/T$ and $\nu_{2\mathrm{m}}$ for the P(NTBA-*co*-AAm) hydrogels are given in Figs. 3 and 4, respectively. Figure 3 shows that at low temperatures, i.e., at high swelling ratios, the dependence of χ parameter on $1/T$ is linear. This indicates that the enthalpy and the entropy contributions to the interaction parameter are constant and χ parameter equals χ_1 in this range of temperatures [Eq. (15)] [16]. The dashed lines in Fig. 3 are the linear regression lines obtained from the low temperature range of the data points. The slope and the intercept of these lines give the ΔH and ΔS values appearing in the χ_1 parameter of the P(NTBA-*co*-AAm) network–water system. The calculation results of ΔH and ΔS values of these hydrogels are given in Table 3. As can be seen from Table 3, the signs of both quantities are negative for all the hydrogels. The negative values for ΔH and ΔS indicate that the P(NTAB-*co*-AAm) hydrogels show a negative temperature-sensitive property in water; that is, swelling at a lower temperature and shrinking at a higher temperature. Almost constant ΔS values and changing ΔH values with the variation of the amount

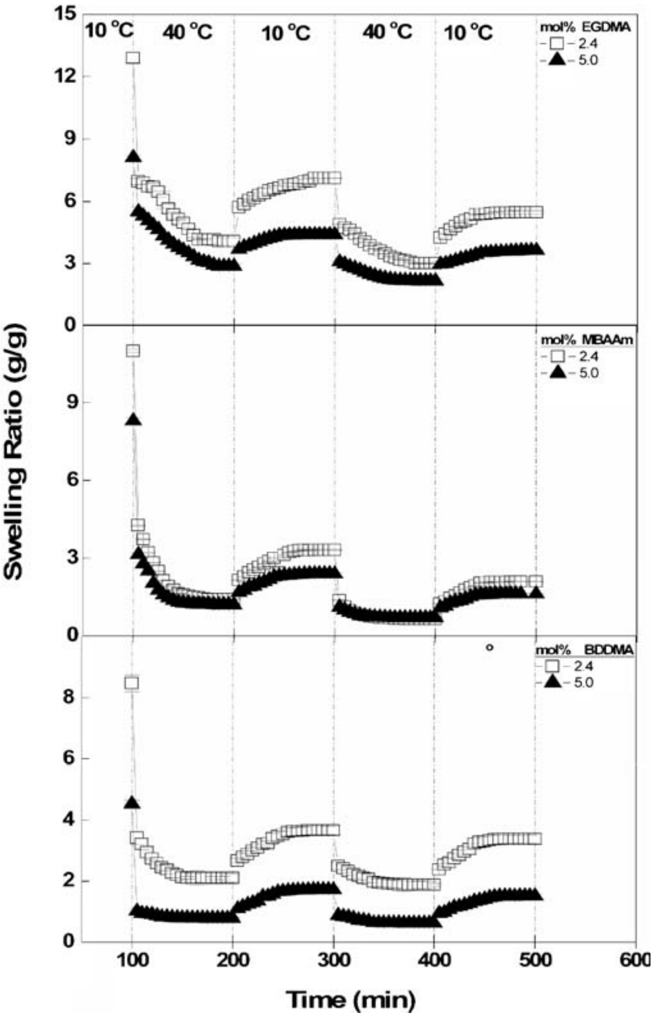

Fig. 5 Pulsatile temperature-dependent swelling behavior of the P(NTBA-*co*-AAm) hydrogels. The amount and type of the crosslinkers are indicated as the insert

and type of crosslinker indicate that the polymer–solvent interactions are mainly controlled by the enthalpy factor.

Nonlinear regression analyses of the data, χ, ν_{2m}, and T for all P(NTBA-*co*-AAm) hydrogels gave the following relationship for the dependence of χ on ν_{2m} and T [16]:

$$\chi = \chi_1 + \left(a - \frac{b}{T}\right)\nu_{2m} + \left(c - \frac{d}{T}\right)\nu_{2m}^2 \tag{16}$$

The equilibrium swelling ratios of the P(NTBA-*co*-AAm) hydrogels calculated using Eqs. (6) and (16) are shown in Fig. 2 as the solid curve plotted as a function of the temperature. It is clearly seen that, after taking into account the sensitive dependence of the χ parameter on both ν_{2m} and T, the prediction of the Flory–Rehner theory provides a satisfactory agreement to the experimental swelling data.

Pulsatile swelling behavior

The pulsatile swelling behavior of the P(NTBA-*co*-AAm) hydrogels with three different crosslinkers was observed in temperatures alternating between 10 and 40 °C, as shown in Fig. 5. The swelling ratio of the hydrogels with temperature changes was measured every 5 min, as temperature was switched every 100 min. The swelling–deswelling cycles were repeated for 10 h without observing any deformation in their shapes. Also, their swelling processes are proved to be repeatable with temperature changes. The hydrogels with 2.4 mol% crosslinkers respond to temperature change more rapidly than the hydrogels with 5.0 mol% crosslinkers. These results are in agreement with those obtained by the fast swelling behavior of the hydrogels with 2.4 mol% crosslinkers. On the other hand, the data also showed that all of the hydrogels had a small swelling–deswelling range. As the phase-transition temperature of these hydrogels is around 25 °C, when the swollen hydrogel is immersed in the 40 °C water, the surface of the hydrogel immediately dehydrates to form the hydrophobic skin layer, which blocks the inner water flow out of the hydrogel. When the hydrogel is immersed in 10 °C water again, the water molecules also first hydrate with the surface of the hydrogel. Therefore, the hydration–dehydration change occurs on the surface of the hydrogel in a brief time, and it causes the small swelling and deswelling range. In addition, the inspection of Fig. 5 also showed a clear decrease in the swelling ratios with each cycle. Some irreversible steps are included in this system. This may be explained by various heterogeneous structures, such as a polymer-rich phase and a solvent-rich phase, which were created during the posttreatment at 40 °C. The diffusion rate is controlled by collective diffusion coefficient and hydrogel morphology. The resulting heterogeneous structure acts as a barrier for further water uptake and prevents water transfer from the aqueous medium to the inner part of the hydrogel.

Acknowledgement This work was supported by the State Planning Organization (Devlet Planlama Teskilati), contact grant number 2003K 120470-31.

References

1. Schild HG (1992) Prog Polym Sci 17:163
2. Kokufuta E (1993) Adv Polym Sci 110:157
3. Okano T (1993) Adv Polym Sci 110:179
4. Chen G, Hoffman AS (1995) Macromol Rapid Commun 16:175
5. Saito S, Konno M, Inomata H (1993) Adv Polym Sci 11:207
6. Feil H, Bae YH, Feijen J, Kim SW (1993) Macromolecules 26:2416
7. Inomata H, Goto S, Saito S (1990) Macromolecules 23:4887
8. Tokuhiro T, Amiya T, Mamada A, Tanaka T (1991) Macromolecules 24:2936
9. Bokias G, Hourdet D, Iliopoulos I, Staikos G, Audebert R (1997) Macromolecules 30:8293
10. Ulbrich K, Kopecek J (1979) J Polym Sci Polym Symp 66:209
11. Tanaka T, Touhara H, Nakanishi K, Watanabe N (1984) J Chem Phys 80:5170
12. Nakanishi K, Ikari K, Okazaki S, Touhara H (1984) J Chem Phys 80:1656
13. Zhang XZ, Wu DQ, Chu CC (2003) J Polym Sci B Polym Phys 41:582
14. Mueller KF (1992) Polymer 33:3470
15. Kaneko Y, Yoshida R, Sakai K, Sakurai Y, Okano T (1995) J Membr Sci 13:101
16. Öztürk V, Okay O (2002) Polymer 43:5017
17. Yi YD, Oh KS, Bae YC (1997) Polymer 38:3471
18. Ilavsky M, Hrouz J (1982) Polym Bull 8:387
19. Xue W, Champ S, Huglin MB (2001) Polymer 42:3665
20. Cavell EAS, Gilson IT (1968) Macromol Chem 119:153
21. Kilic S, Baysal BM (1986) J Macromol Sci Rev C26:483
22. Özmen MM, Okay O (2003) Eur Polym J 39:877
23. Wu XS, Hoffman AS, Yager P (1992) J Polym Sci A Polym Chem 30:2121
24. Biren D, Kabra BG, Gehrke SH (1992) Polymer 33:554
25. Bajpai SK (2001) J Appl Polym Sci 80:2782

26. Korsmeyer RW, Peppas NA (1983) Controlled release delivery systems. Marcel Dekker, New York, p 173
27. Alfrey T, Gurnee EF, Lloyd WG (1966) J Polym Sci C Polym Symp 12:249
28. Ruiz J, Cadiz V (2001) Polymer 42:6347
29. Peniche C, Cohen ME, Vazquez B, San Roman J (1997) Polymer 38:5977
30. Bhardwaj YK, Kumar V, Sabharwal S (2003) J Appl Polym Sci 88:730
31. Erbil C, Aras S, Uyanik N (1999) J Polym Sci A Polym Chem 37:1847
32. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca
33. Mark JE, Erman B (1988) Rubberlike elasticity a molecular primer. Wiley, New York
34. Gündoğan N, Melekaslan D, Okay O (2002) Macromolecules 35:5616
35. Champ S, Xue W, Huglin MB (2001) Polymer 42:6439
36. Mark JE, Dusek K (1992) Adv Polym Sci 44:1
37. Şen M, Güven O (1998) Polymer 39:1165
38. Erman B, Flory PJ (1986) Macromolecules 19:2342