Synthesis and Network Parameters of Hydrophobic Poly(*N*-[3-(dimethylaminopropyl)]methacrylamide-*co*-lauryl acrylate) Hydrogels

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ABSTRACT: Hydrophobic poly(*N*-[3-(dimethylaminopropyl)]methacrylamide-*co*-lauryl acrylate) [P(DMAPMA-*co*-LA)] hydrogels with different LA content were synthesized by free-radical crosslinking copolymerization of corresponding monomers in water by using *N,N*-methylenebis(acrylamide) as the crosslinker, ammonium persulfate as the initiator, and *N,N,N′,N′*-tetramethylethylenediamine as the activator. The swelling equilibrium of the hydrogels was investigated as a function of temperature and hydrophobic comonomer content in pure water. An interesting feature of the swelling behavior of the P(DMAPMA-*co*-LA) hydrogels with low LA content was the reshrinking phase transition where the hydrogels swell once and collapse as temperature was varied in the range of 30–40°C. The average molecular mass between crosslinks ($\overline{M}_c$) and polymer–solvent interaction parameter (χ) of the hydrogels were calculated from equilibrium swelling values. 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. The positive values for ΔH and ΔS indicated that the hydrogels had a positive temperature-sensitive property in water, that is, swelling at a higher temperature and shrinking at a lower temperature. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4159–4166, 2006

Key words: poly(*N*-[3-(dimethylaminopropyl)]methacrylamide-*co*-lauryl acrylate); hydrophobic hydrogels; crosslinking; networks

INTRODUCTION

The swelling property of a hydrogel can generally be attributed to the effects of the repulsion and attraction of functional groups attached to the hydrogel. The repulsion and attraction can arise from a combination of four noncovalent interactions: electrostatic, hydrophobic, van der Waals, and hydrogen bonding.[1] In this case, hydrophobic interactions can induce physical crosslinking that affects the hydrogel swelling behavior. Compared with chemical crosslinking, physical crosslinking arising from hydrophobic association is sensitive to the external environment, and the hydrogel pore sizes are reversibly capable of accommodating a solute and inhibiting its diffusion. Hence, these hydrogels can be expected to act as smart materials in controlled or targeted drug release.[2,3] However, it is necessary to understand the relationship between the hydrophobic microstructure and the macroscopic properties of hydrogels.

The copolymer hydrogel prepared from hydrophilic and hydrophobic monomers exhibits different mechanical and structural characteristics from those of homopolymeric (totally hydrophilic) hydrogel.[4] Here, the hydrophobic part tends to form the crystal domain, which acts as a barrier for water flow in the hydrogel. That is, the mobility of water in hydrogel will be much influenced by introducing hydrophobic groups.

Poly(*N*-isopropylacrylamide) (PNIPA) hydrogel is a well known temperature-sensitive hydrogel exhibiting swelling or deswelling transition at about 34°C in water.[5] Moreover, an unusual feature of the swelling behavior of PNIPA hydrogels is a reentrant phenomenon where the hydrogels collapse once and reswell, as a particular external condition is varied monotonically.[6]

Poly(*N*-[3-(dimethylaminopropyl)]methacrylamide) (PDMAPMA) forms swollen hydrogels of crosslinked species because of the presence of both hydrophilic amide groups and hydrophobic dimethylaminopropyl groups in its side chains. PDMAPMA is temperature sensitive, and a dramatic swelling transition occurs at the upper critical solution temperature (UCST) of PDMAPMA, 32–36°C in water.[7] Above this temperature, PDMAPMA is swollen, hydrated, and hydrophilic, whereas below the UCST, hydrogel shrinks and forms a collapsed, dehydrated, and hydrophobic state be-

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cause of the breakdown of the delicate hydrophilic/hydrophobic balance in the network structure.

In this study, hydrophobic poly(*N*-[3-(dimethylaminopropyl)]methacrylamide-*co*-lauryl acrylate) [P(DMAPMA-*co*-LA)] hydrogels were synthesized. The effects of initial crosslinker concentration and hydrophobic content on the swelling behavior and phase transition temperature of these hydrogels were investigated. As will be shown, P(DMAPMA-*co*-LA) hydrogels in water exhibit a reshrinking transition behavior at low hydrophobic group (LA) contents, whereas for LA contents higher than a certain value, the hydrogels almost remain in the deswollen state over the entire range of temperature. The average molecular mass between crosslinks ($\overline{M}_c$) and polymer–solvent interaction parameter (χ) of the hydrogels were calculated from equilibrium swelling values. Enthalpy and entropy changes appearing in the χ parameter for the P(DMAPMA-*co*-LA)–water system were also determined.

EXPERIMENTAL

Materials

Monomers *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMA), lauryl acrylate (LA), the crosslinker *N*,*N*-methylenebisacrylamide (MBAAm), the initiator ammonium persulfate (APS), the accelerator *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were purchased from Aldrich Chemical and used as received.

Hydrogel synthesis

P(DMAPMA-*co*-LA) hydrogels were prepared by the free-radical crosslinking copolymerization of the DMAPMA and LA in aqueous solution at 22°C for 24 h in the presence of predetermined concentrations of the MBAAm crosslinking agent. APS (0.056*M*) and TEMED (0.064*M*) were used as the redox initiator system. The hydrogels were prepared as two sets; in first set, the initial monomer concentration was fixed at 0.9*M*, while the amount of the crosslinker MBAAm was varied between at 6.5 and 12.2 mol %; in second set, the crosslinker amount was fixed at 9.3 mol %, while the amount of LA was changed from 12.5 to 41.7 mol %.

To illustrate the synthesis procedure, we give details for the preparation of the hydrogels with various LA content.

The solutions containing DMAPMA (0.7 mL), MBAAm (0.1350 g), APS (1.0 mL), TEMED (0.4 mL), and LA (0.10, 0.20, 0.30, 0.40, and 0.50 mL) were prepared in 4.0 mL of water. After bubbling nitrogen for 15 min, these solutions were placed in poly(vinylchloride) straws of 4 mm diameters and about 20 cm long. The poly(vinylcloride) straws were sealed and immersed in a thermostated water bath at 20°C, and the polymerization was conducted for 24 h. Upon completion of the reaction, the hydrogels were cut into specimens of ~10 mm in length and immersed in large excess of water to wash out any unreacted monomers and the initiator. The hydrogel samples were then dried at 50°C under vacuum to constant weight. The ratio between mass of dried copolymer and calculated copolymer mass for 100% conversion for these samples was found in the range of 1.01–1.11. An analysis of these values shows both the presence of bound water and conversion of monomer to polymer to be close to 100%. The crosslinked N-substituted acrylamide polymers always contain about 5–15 wt % water, even after several months of drying under vacuum.[8]

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

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

where m_r is the mass of the hydrogel after preparation, m_d is the mass of the dry hydrogel, ρ_2 and ρ_1 are densities of polymer network and solvent, respectively. The values ρ_2 and ρ_1 used were 1.2 and 1.0 g/mL, respectively. The density of polymer network was determined by a pycnometer using acetone as nonsolvent. On the other hand, ν_{2r} can also be calculated from initial monomer concentration of monomers C_0 (mol mL^{-1}) as follows[8]:

$$v_{2r} = C_0\overline{V}_r \tag{2}$$

where $\overline{V}_r$ is the average molar volume of polymer repeat units. $\overline{V}_r$ can be calculated as:

$$\overline{V}_r = \frac{M_{\mathrm{DMAPMA}}f_{\mathrm{DMAPMA}} + M_{\mathrm{LA}}f_{\mathrm{LA}}}{\rho_2} \tag{3}$$

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

The theoretical values of ν_{2r} calculated from eq. (2) are shown in Figure 1 as open symbols together with the experimentally determined ν_{2r} values (filled symbols). As shown in this figure, the experimental ν_{2r} values are larger than the theoretical ones because of the presence of bound water in the hydrogel. Hence, the theoretical ν_{2r} values were used for further calculations.

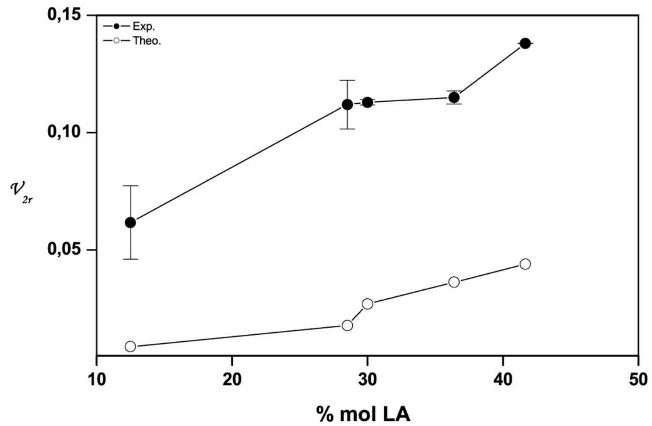

Figure 1 Variation of v_{2r} with the mole percentage of LA. v_{2r} values experimentally and theoretically determined are indicated in the figure.

Determination of swelling kinetics

The swelling kinetics of the P(DMAPMA-*co*-LA) hydrogels were measured gravimetrically. The dried samples were placed in distilled water at 22°C and removed from water at regular time intervals. After the water on the surfaces of the hydrogels was wiped off with moistened filter paper, the weights of the hydrogels were recorded. The swelling ratio was defined as follows:

$$\mathrm{SR} = \frac{m_t - m_d}{m_d} \tag{4}$$

where m_t is the mass of the swollen hydrogels at time t.

Determination of equilibrium swelling ratio

For the temperature-response studies, hydrogels were equilibrated in distilled water at temperatures ranging from 10 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). 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 on the hydrogel surface; they 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 was calculated as follows:

$$q_v = \left[1 + \frac{(m_s/m_d - 1)\rho_2}{\rho_1}\right] \tag{5}$$

where m_s is the mass of the swollen hydrogel at the equilibrium state.

RESULTS AND DISCUSSION

Synthesis and spectral characterization

The crosslinker concentration and the monomer ratios are two important variables affected on swelling capacity of hydrogels. To obtain hydrogels of a fixed crosslink density but differing in polymer composition, free-radical crosslinking copolymerization of DMAPMA, LA, and MBAAm was conducted at a fixed crosslinker ratio (10.4 mol % MBAAm) and initial monomer concentration (0.9*M*) but at various LA contents. The persulfate initiator is decomposed under heating to generate sulfate anion-radical. The radical abstracts hydrogen from TEMED to form the radical on the TEMED. So, this persulfate-TEMED redox system results in active centers on the monomers to radically initiate copolymerization of DMAPMA and LA. Since a crosslinking agent, e.g., MBAAm, is presented in the system, the copolymer comprises a crosslinked structure.

For determination of the relative amount of LA in the hydrogels, FTIR spectroscopy was used. The spectra of dried copolymers were shown in Figure 2. The characteristic absorption bands of DMAPMA units were observed at ~1650 and ~1530 cm^{-1} due to the C═O stretch and N—H vibration, respectively. The area of the band at 1530 cm^{-1} was normalized using CH_2 stretching band of both DMAPMA and LA units at ~2860 cm^{-1}. The calculation of the band areas at 1530 and 2860 cm^{-1} (A_{1530}/A_{2860}) was performed using baseline method.[8,9] The variation of normalized band ratios versus the mol % of LA was shown in Figure 3. The normalized band ratios indicated that the mol % of LA in synthesized copolymers increased with increasing LA content in the initial monomer mixture. This behavior was attributed to the formation of random copolymers.

Dynamic swelling kinetics

The swelling kinetic curves of the hydrogels with different MBAAm content are given in Figure 4. The data of this figure showed that both the swelling ratio and the swelling rate decreased with increasing amount of the crosslinker.

Before the swelling process, there existed strong intermolecular and/or polymer–polymer interactions, such as hydrogen bonds and hydrophobic interactions, in the dried hydrogel samples, which remained in a glassy state. In this case, their glass transition temperature (T_g) is higher than the room temperature.[10] This also suggests that a glassy inner core might exist in a hydrogel having a higher crosslinking

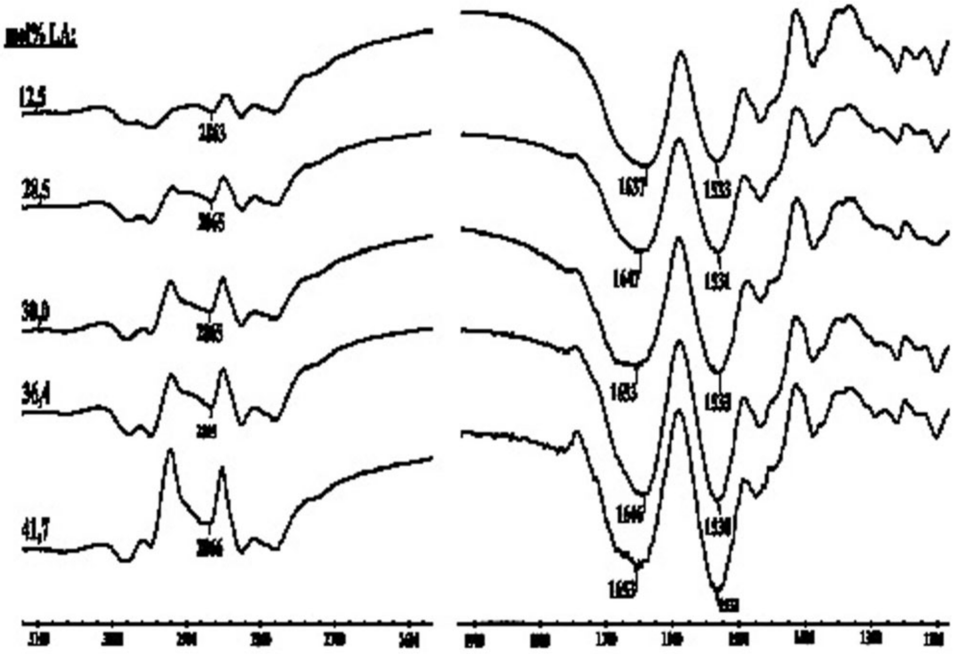

Figure 2 FTIR spectra of the P(DMAPMA-*co*-LA) hydrogels. LA contents are indicated in the figure.

level, because the high crosslinking may lead to strong such interactions. Therefore, the hydrogels having a high crosslinking level, such as the hydrogels with 10.4% and 12.2% MBAAm, might have glassy cores, which would lead to a significant reduction in the rate of water absorption, and the rate of reduction in water absorption would depend on the disappearing rate of the core upon swelling. As a result, with increasing amount of MBAAm, the swelling ratio of the hydrogels reduced because of dense three-dimensional structure formed at the high crosslinker concentration.

To determine the nature of water diffusion into hydrogels, initial swelling data were fitted to the following exponential equation[11]:

$$F = \frac{M_t}{M_\infty} = kt^n \tag{7}$$

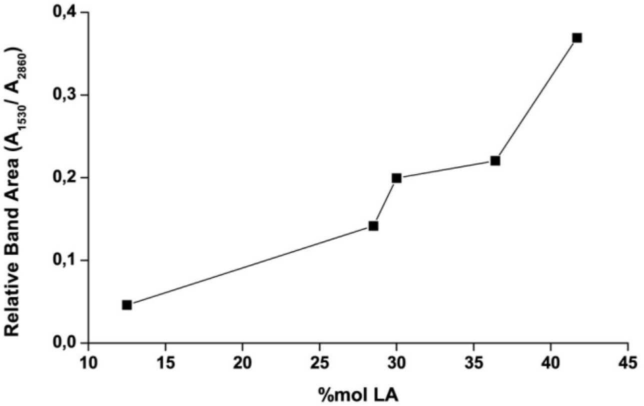

Figure 3 Variation of normalized band area ratios (A_{1530} /A_{2860}) with mole percentage of LA.

where F denotes the amount of water fraction at time t, M_t and M_∞ represent the amount of water absorbed by the hydrogel at time t and at equilibrium, k is a characteristic constant of the hydrogel, and n is a characteristic exponent of the mode of transport of the penetrate. The constants n and k were calculated from the slopes and intercepts of the graph of a double logarithmic F versus t plots for hydrogels with various MBAAm content in water. These results are shown in Table I. In the eq. (7), the numerical value n provides information about the mechanism of swelling kinetics. For the first case, $n = 0.5$, corresponding to a Fickian diffusion, the rate of diffusion is much lower than the

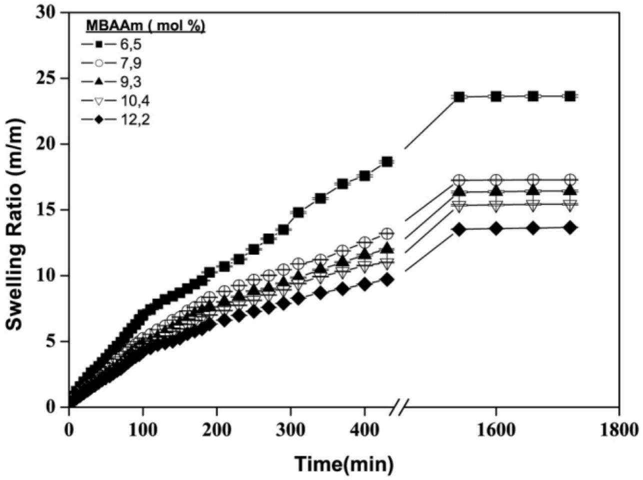

Figure 4 Swelling kinetics of P(DMAPMA-*co*-LA) hydrogels with different MBAAm content in water at 25°C. Experimental data are shown as symbols.

TABLE I
Kinetic Parameters of the P(DMAPMA-co-LA) Hydrogels

MBAAm (mol %)	k (10^2)	n	D (10^6 cm^2 s^{-1})
6.45	9.51	0.73 ± 0.01	3.11
7.87	8.72	0.75 ± 0.01	2.64
9.3	8.99	0.76 ± 0.02	2.35
10.4	8.06	0.78 ± 0.01	2.23
12.2	5.26	0.86 ± 0.01	1.47

rate of relaxation and for the second, $n = 1$, the diffusion is very fast, contrary to the rate of relaxation, and the third case corresponds to an anomalous diffusion with n values lying between 0.5 and 1.

A slight variation of diffusion exponent with MBAAm content is observed, and its value higher than 0.50, indicating 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 swelling of the hydrogels. The highly anomalous behavior of these hydrogels is due to the regularity of the chain and strong interchain interactions via the formation of hydrogen bonding, leading to a compact structure that would accentuate the anomalous aspects of diffusion even for a molecule as small as water.

For calculating diffusion coefficient of water moving through the P(DMAPMA-*co*-LA) hydrogels, the following equation was employed.[11]

$$D = \pi r^2 \left(\frac{k}{4}\right)^{1/n} \tag{8}$$

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 I. The diffusion coefficients D decreased with an increase of MBAAm content in the hydrogel. This is explained by the restriction of the expansion of the network structure resulting from the increase of the crosslinking density.

Molecular mass between crosslinks

Several theories for calculating the molecular mass between crosslinks ($\overline{M}_c$) in polymer networks have been proposed. In the highly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the phantom network model. In this study, the experimental $\overline{M}_c$ values were calculated from equilibrium swelling ratios of the hydrogels by using the following equation based on the phantom network model[12,13]:

$$\overline{M}_c(\text{Expt}) = -\frac{(1 - 2/\phi)V_1\rho_2 \text{v}_{2\text{r}}^{2/3}\text{v}_{2\text{m}}^{1/3}}{(\ln(1 - \text{v}_{2\text{m}}) + \text{v}_{2\text{m}} + \chi \text{v}_{2\text{m}}^2)} \tag{9}$$

where ϕ is the functionality of the crosslinks ($\phi = 4$), V_1 is the molar volume of the solvent (18 mL/mol), $\text{v}_{2\text{m}}$ is the volume fraction of the polymer network in the swollen gel at the equilibrium state, and χ is the polymer solvent interaction parameter. The $\text{v}_{2\text{m}}$ values were calculated from the following expression valid at swelling equilibrium.

$$\text{v}_{2\text{m}} = \frac{1}{q_v} \tag{10}$$

χ parameter can be derived from eq. (9) by neglecting its elastic term and expanding the entropic term in series. In that manner, isolation of χ parameter depends mainly on the mixing contribution, i.e., three terms on the denominator of eq. (9) Numerically, it is found that the elastic contribution, i.e., remaining term, has only a slight effect on the derived value of χ parameter. This is especially true in the present system wherein $\text{v}_{2\text{m}}$ is very small and $\overline{M}_c$ is very large, and eq. (9) can be reduced as follows to an excellent approximation:

$$\ln(1 - \text{v}_{2\text{m}}) + \text{v}_{2\text{m}} + \chi \text{v}_{2\text{m}}^2 \cong 0 \tag{11}$$

Expansion of the logarithmic series, followed by truncation of term in $\text{v}_{2\text{m}}^4$ $\text{v}_{2\text{m}}^5$, $\text{v}_{2\text{m}}^6$, etc. and rearrangement yields[14]

$$\chi \cong \frac{1}{2} + \frac{\text{v}_{2\text{m}}}{3} \tag{12}$$

Equation (12) neglects the $\overline{M}_c$ dependence of the χ parameter and therefore very approximate. In addition, of course full implementation of eq. (9) does allow in principle the values of χ parameter to be <0.50. However, eq. (12) indicates that $\chi \geq 0.50$.[14] In fact, use of eq. (12) in conjunction with the values of $\text{v}_{2\text{m}}$ affords values of χ that lie in close accord with those listed in Table II.

On the other hand, assuming that all MBAAm 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[15]:

$$\overline{M}_c(\text{Theo}) = \frac{\rho_2 \overline{V}_r}{2X} \tag{13}$$

where X is the crosslinker ratio (mole ratio of MBAAm to DMAPMA + LA). The relevant experimental and theoretical parameters of the hydrogels were collected in Table II. As can be seen from Table II, the experimental $\overline{M}_c$ values of the hydrogels decreased from 34

TABLE II
The Characteristic Data of the P(DMAPMA-*co*-LA) Hydrogels

MBAAm (mol %)	X (10^2)	ν_{2m} (10^2)	χ	$\overline{M}_c$ (Theo) (g mol^{-1})	$\overline{M}_c$ (Expt) (10^{-4} g mol^{-1})
6.5	6.9	3.40	0.512	1100	34
7.9	8.5	4.65	0.516	880	21
9.3	10.3	4.83	0.517	720	20
10.4	11.6	5.13	0.517	620	19
12.2	13.8	5.76	0.519	570	16

× 10^4 to 16 × 10^4 g/mol with increasing amount of MBAAm, ranging from 6.5 to 12.2%. The experimentally found $\overline{M}_c$ values of the hydrogel with 6.5% MBAAm is 309 times higher than its theoretically calculated counterpart. This value decreased to 278 and 280 when 9.3% and 12.2% MBAAm was used in the hydrogel preparation, respectively. The difference between the theoretical and experimental $\overline{M}_c$ values of the hydrogels indicates that a significant fraction of the crosslinker MBAAm is wasted during the crosslinking copolymerization, probably because of the cyclization and multiple crosslinking reactions.[15] The high degree of dilution during the hydrogel preparation as well as the higher crosslinker reactivity is mainly responsible for these reactions.

Effect of temperature on swelling equilibrium

A brief resume on the reasons for swelling and shrinking behaviors in PDMAPMA hydrogel will be useful for the following discussion. The PDMAPMA has the hydrophilic nature because of the C═O and N—H groups, the hydrogen bonding ability of these groups being instrumental in stabilizing a coil conformation above the upper critical solution temperature (UCST), which means that polymer–water interactions predominate over polymer–polymer interactions. On the other hand, the pendant $(CH_3)_2N(CH_2)_3$ group and the CH_2CCH_3 backbone are hydrophobic in nature, the hydrophobic groups being exposed to form aggregates below the UCST. This forces the polymer chain into a globule conformation in which polymer–polymer interactions are dominant. However, the volume phase transition results from a change in the balance between various types of interaction, especially hydrogen bonding and hydrophobic interactions.

Figure 5 illustrates the temperature dependence of the equilibrium swelling ratio of P(DMAPMA-*co*-LA) hydrogels with different MBAAm content in water when the temperature increased from 10 to 60°C. The data show that all the hydrogels, regardless of the amount of the MBAAm, had almost similar swelling behaviors as a function of temperature. The equilibrium volume swelling ratio of the hydrogels first unchanged up to 28°C and, then increased drastically at between 28 and 35°C (at phase transition temperature range) and remained almost constant (swelling) at between 35 and 40°C and then again decreased slowly up to 60°C (reshrinking). The data in Figure 5 clearly show also that the equilibrium swelling ratios of these hydrogels decreased 85% at 10°C and 80% at 60°C with increasing amount of MBAAm from 6.5% to 12.2%. It is believed that an increase in the level of crosslinking agent would reduce the free volume within the hydrogel network structure in which water would reside during swelling and would also lead to the reduction of pore size of the corresponding hydrogels, which in turn reduced the water holding capacity because of the decreased pore volume.

The effects of the hydrophobic LA content on the equilibrium swelling ratios of the hydrogels are shown in Figure 6. As shown in Figure 6, the P(DMAPMA-*co*-LA) hydrogels exhibited both swelling and deswelling transitions as the external bath temperature was continuously varied. At 32–38°C temperature range, the maximum equilibrium swelling ratio was observed for all hydrogel systems. In this case, the P(DMAPMA-*co*-LA) hydrogels exhibited reshrinking conformational transitions at about 40°C, depending on LA content in the hydrogel. In contrast to the

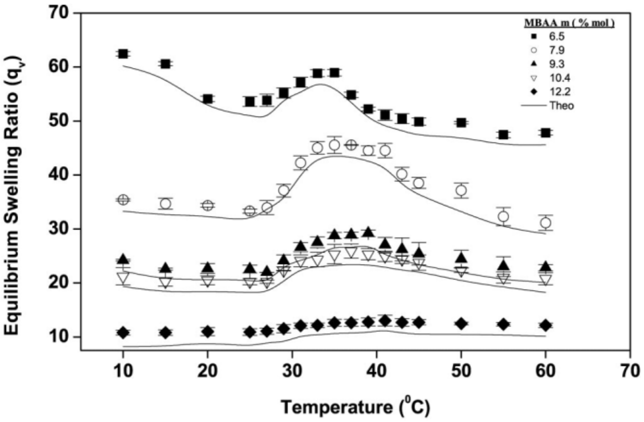

Figure 5 Variation of equilibrium swelling ratio of P(DMAPMA-*co*-LA) hydrogels with different MBAAm content as function of temperature in water. Experimental data are shown as symbols. The solid curves were calculated using eqs. (9) and (16).

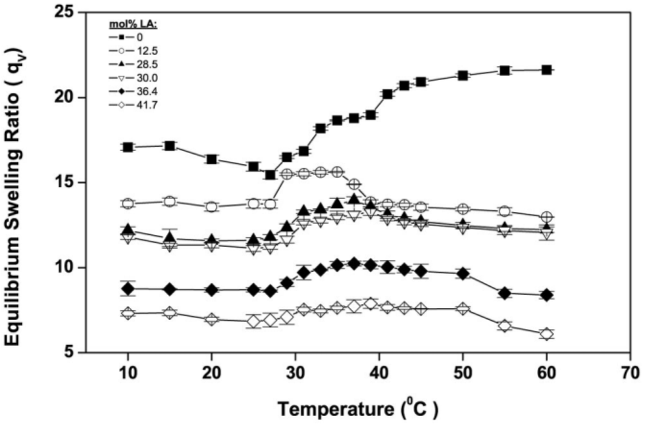

Figure 6 Variation of equilibrium swelling ratio of P(DMAPMA-*co*-LA) hydrogels with different LA content as function of temperature in water. Experimental data are shown as symbols.

P(DMAPMA-*co*-LA) hydrogels, PDMAPMA hydrogel had the UCST at about 34°C. This behavior also demonstrates that the LA units on the network chains are responsible for the observed reshrinking phenomena of the P(DMAPMA-*co*-LA) hydrogels. On the other hand, the deswelling transition of the P(DMAPMA-*co*-LA) hydrogels shifts toward higher temperatures as the LA content is increased. The swelling process of these hydrogels is controlled by the incorporation of a second monomer with hydrophobic character. The maximum hydration degree and diffusion of swelling agent into a hydrogel, as well as the organization of water molecules in the hydrogel, will change depending on the chemical composition and the distribution of the hydrophobic monomeric units along the macromolecular chains.[16] Generally, the equilibrium swelling ratio of a hydrogel is decreased by incorporating a hydrophobic comonomer. For example, when a highly hydrophobic acrylate, 2-ethylhexyl acrylate, was incorporated into 2-hydroxyethyl methacrylate, the equilibrium swelling ratio decreased.[16] In this study, the swelling ratio of the P(DMAPMA-*co*-LA) hydrogels was also decreased 50% at 10°C and 54% at 60°C with increasing amount of LA from 6.5% to 12.2%, indicating that hydrophobic association is formed in the hydrogels. Micellar-like hydrophobic domains, which act as physical crosslinkers to restrain the swelling of the hydrogel networks, arise from hydrophobic side groups dangling on the hydrogel networks. The illustration of hydrophobic interactions in this system is shown in Figure 7. From these considerations, it can be expected that long range hydrophobic interaction requires higher energy to cause aggregation. With the LA content higher than 30.0 mol %, the equilibrium swelling ratios of the hydrogels changed little with the increasing temperature. In this case, physical crosslinking obtains saturation. As a result, it is apparent that the equilibrium swelling ratio of the P(DMAPMA-*co*-LA) hydrogels can be controlled by incorporating more hydrophobic units such as LA in the hydrogel system.

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. The χ parameter is expressed as a series expansion in powers of ν_{2m},[17]

$$\chi = \chi_1 + \chi_2 v_{2m} + \chi_3 v_{2m}^2 + \cdots \qquad (14)$$

where the coefficient χ_1, χ_2, and χ_3 are the functions of temperature and the molecular characteristics of the polymer–solvent system. For high swelling ratio, ν_{2m} 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 it[12]:

$$\chi_1 = \frac{\Delta H - T\Delta S}{RT} \qquad (15)$$

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. (12), χ parameters of the hydrogels were calculated from ν_{2m} values at each temperature. The variation of χ parameter with $1/T$ for the P(DMAPMA-*co*-LA) hydrogels is given in Figure 8. As can be seen from Figure 8, except the reshrinking temperature, at low and high temperatures or low swelling ratios, χ parameter is almost independent from temperature changes. This indicates that the enthalpy and the entropy contribution to the χ parameter are constant.

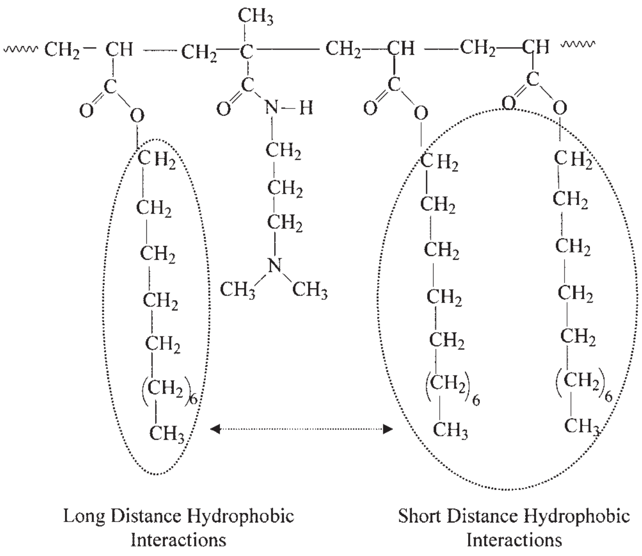

Figure 7 The possible hydrophobic interactions in P(DMAPMA-*co*-LA) hydrogels.

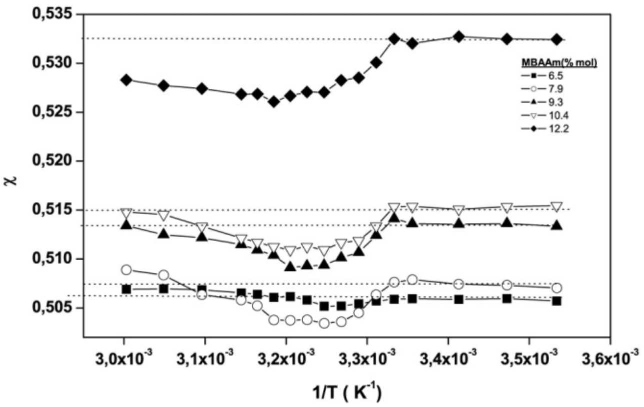

Figure 8 Variation of χ parameter for P(DMAPMA-*co*-LA)–water system as a function of inverse temperature. The mol % of MBAAm is indicated as the insert.

In this case, χ equals to χ_1 in this swelling ratio and temperature ranges.[18] The dashed lines in Figure 8 are the linear regression lines obtained from the high temperature range of the data points.

ΔH and ΔS values appearing in the χ_1 parameter were determined from the slope and intercept of these lines. ΔH and ΔS values of the hydrogels are given in Table III. As can be seen from Table III, the signs of the both quantities are positive for all the hydrogels. The positive values for ΔH and ΔS indicate that the P(DMAPMA-*co*-LA) hydrogels show a positive temperature-sensitive property in water. On the other hand, the ΔH and ΔS values reported for PNIPA–water and poly(*N*-t-butylacrylamide-*co*-acrylamide) [P(TBA-*co*-AAm)] systems are negative.[18] In this case, polymer–solvent systems possessing the LCST are characterized by negative values of both ΔH and ΔS. However, the results indicate that all the P(DMAPMA-*co*-LA) hydrogels studied here have UCSTs because of the positive ΔH and ΔS values. Almost constant ΔS values and changing ΔH values with the variation of the amount of crosslinker indicate that formation of polymer–solvent interactions is mainly controlled enthalpy factor. Moreover, the ΔH values increase with increasing amount of MBAAm increasing that the temperature sensitivity of the P(DMAPMA-*co*-LA) hydrogels increases with increasing MBAAm content.

TABLE III
Enthalpy and Entropy Changes Appearing in the χ Parameter for the P(DMAPMA-*co*-LA) Hydrogels

MBAAm (mol %)	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})
6.5	−2.493	0.514
7.9	0.700	0.504
9.3	3.869	0.499
10.4	4.835	0.497
12.2	13.410	0.485

TABLE IV
Coefficients for the Dependence of χ on ν_{2m} and Temperature

MBAAm (mol %)	χ_1	a	b	c	d
6.5	0.498	0.436	0.001	0.112	0.100
7.9	0.492	0.538	0.001	0.123	0.100
9.3	0.490	0.661	0.413	−2.200	0.122
10.4	0.494	0.430	0.001	0.129	0.100
12.2	0.496	0.377	0.099	0.144	0.100

Nonlinear regression analyses of the data, χ, ν_{2m}, and T for all P(DMAPMA-*co*-LA) hydrogels hydrogels gave the following relationship for the dependence of χ on ν_{2m} and T^{18}:

$$\chi = \chi_1 + \left(a - \frac{b}{T}\right)\mathrm{v}_{2m} + \left(\mathrm{c} - \frac{\mathrm{d}}{\mathrm{T}}\right)\mathrm{v}_{2m}^2 \qquad (16)$$

The coefficients for each hydrogel are given in Table IV. The theoretical equilibrium swelling ratios of the hydrogels calculated using eqs. (9) and (16) are shown in Figure 5 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 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.

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