Synthesis and Characterization of Porous Poly(*N*-isopropylacrylamide) Hydrogels Prepared in Ethanol–Water Mixtures

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ABSTRACT: Poly(*N*-isopropylacrylamide) (PNIPAM) hydrogels were prepared by free-radical polymerization in different ethanol–water mixtures. A scanning electron microscopy study revealed that the resulting hydrogels were macroporous. The swelling ratios of the resultant hydrogels in water at 20°C followed this order: $X_{0.34} \approx X_{0.68} > X_{0.48} > X_{0.09} > X_{0.04} > X_0$, where X_a denotes a gel prepared in an ethanol–water solvent mixture with an ethanol molar fraction of *a*. Below the lower critical solution temperature, the swelling ratio values of all of the hydrogels gradually decreased with increasing temperature. The complete collapse of the PNIPAM chain of all of these gels occurred at about 38°C, whereas the same was observed at about 35°C for the conventional gel prepared in water. The swelling ratio values of all of the PNIPAM gels with different molar fractions of ethanol at 20°C passed through a minimum in the cononsolvency zone. The deswelling rates of the hydrogels decreased in the following order: $X_{0.34} > X_{0.48} > X_{0.68} > X_{0.09} > X_{0.04} > X_0$. The reswelling rates of these hydrogels decreased in the following order: $X_0 > X_{0.04} \approx X_{0.48} > X_{0.09} \approx X_{0.68} > X_{0.34}$. The freeze-drying process decreased the swelling ratios but increased the deswelling and reswelling properties of the PNIPAM gels. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2422–2429, 2011

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INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNIPAM) homopolymer and its crosslinked gel undergoes a volume-phase transition in water at around 33°C.[1] This temperature is known as its lower critical solution temperature (LCST). PNIPAM also undergoes a volume-phase transition below its LCST because of the variations of composition of water in water-miscible good organic solvents, such as methanol,[2–4] ethanol,[5] tetrahydrofuran,[6–8] dimethyl sulfoxide,[1,7] and *N*,*N*-dimethylformamide.[9,10] This is mainly due to the cononsolvency phenomenon,[11–13] where the mixture of two good solvents behaves as a poor solvent for a linear polymer or its crosslinked gel.

For example, below its LCST, in an ethanol–water mixture, the PNIPAM homopolymer shows a gradual collapse of the coiled chain into a thermodynamically stable globular state in the ethanol molar fraction (x_m) range of 0.0–0.12 because of the onset of cononsolvency.[5] In this range, the stronger interaction between ethanol and water gradually predominates over that of their interactions with pnipam. This interaction is at a maximum in the cononsolvency zone around $x_m = 0.12$–0.21.[5] The globular state of PNIPAM was observed in this cononsolvency zone.[5] With a further increase in the ethanol content in the range $x_m = 0.21$–0.5, the globular state starts redissolving around $x_m = 0.21$ and becomes completely dissolved around $x_m = 0.5$.[5] With a further increase in the ethanol content ($x_m > 0.5$), the solvency (average hydrodynamic radius) of the PNIPAM chain remains almost constant.[5]

In this context, the study of the polymerization (crosslinking) reaction of *N*-isopropylacrylamide (NIPAM) with the crosslinker *N*,*N'*-methylenebisacrylamide (BIS) in a mixture of ethanol and water is very important for understanding the cononsolvency effect on the properties of the formed gel. Zhu and Napper[5] reported the effect of different alcohols, including ethanol, on the conformational changes of PNIPAM macromolecules at interfaces. Tokuyama et al.[14]

TABLE I
Synthesis of PNIPAM Gels in the Presence of Ethanol–Water Mixtures with Different Compositions

	Run[a]							
	X_0	$X_{0.04}$	$X_{0.09}$	$X_{0.16}$	$X_{0.24}$	$X_{0.34}$	$X_{0.48}$	$X_{0.68}$
Ethanol (mL)	—	0.25	0.5	0.75	1.0	0.75	1.0	1.25
Water (mL)	1.25	1.0	0.75	0.5	0.25	0.5	0.25	—
Solution of TEMED (107 mmol/dm^3) in water (mL)	0.5	0.5	0.5	0.5	0.5	—	—	—
Solution of TEMED (107 mmol/dm^3) in ethanol (mL)	—	—	—	—	—	0.5	0.5	0.5
Conversion (%)[b]	95	98	86	69	64	76	69	69
Appearance	Transparent	Translucent	Opaque	Opaque	Opaque	Opaque	Transparent	Transparent
W_s/W_d at 20°C	11.4	14.0	22.0	—	—	32.6	29.0	32.6
W_s/W_d at 40°C	1.8	2.0	2.0	—	—	1.8	2.0	2.2

The polymerization data were as follows: 160 mg of NIPAM, 8 mg of BIS, 0.25 mL of an aqueous APS solution with a concentration of 84 mmol/dm^3, a polymerization temperature of 5°C, and a polymerization time of 12 h.

[a] X_a denotes a gel prepared in an ethanol–water solvent mixture with ethanol molar fraction a.

[b] Determined gravimetrically after drying *in vacuo* at 50°C for 72 h after dialysis.

reported the effects of synthesis solvents, including ethanol, on the swelling and elastic properties of the formed gel and explained the same in terms of the extent of the reaction and the effective crosslinking density. Only Lee and Yen[15] reported the preparation of PNIPAM hydrogels in different ethanol–water mixtures as the synthesis solvents and studied the properties for the gels prepared in ethanol–water mixtures with x_m values of 0.03, 0.07, and 0.12, but they did not report detailed characterization studies of the other prepared gels. Apart from this, so far, to our knowledge, there has been no report of the synthesis of PNIPAM gels in different compositions of an ethanol–water mixtures and the study of their morphology, swelling, deswelling, and reswelling properties. Here, we report the synthesis of a series of PNIPAM gels in different compositions of ethanol–water mixture with x_m values ranging from 0 to 0.68, their morphology as studied by scanning electron microscopy (SEM), the variation of their swelling ratios in water at different temperatures, the variation of their swelling ratios in different compositions of an ethanol–water mixture at 20°C, their deswelling kinetics in water with a swift-changing temperature from 20 to 40°C, and their reswelling kinetics in water at 20°C. Moreover, we report the effect of freeze-drying on the swelling properties of the hydrogels.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAM, Aldrich, St. Louis, Missouri) was purified by recrystallization from *n*-hexane. *N*,*N*′-methylenebisacrylamide (BIS, Aldrich, St. Louis, Missouri), ammonium persulfate (APS, Loba Chemie, Mumbai, India), and *N*,*N*,*N*′,*N*′-tetra-

methylethylenediamine (TEMED, Aldrich, St. Louis, Missouri) were used as received. Ethanol (Saraya Distilliary, Gorakhpur, India) was distilled over ignited calcium oxide. Deionized water was prepared by the redistillation of double-distilled water in an all-glass distillation apparatus.

Synthesis of the PNIPAM hydrogels

Three stock solutions were prepared: (1) a solution of TEMED in water having a concentration of 107 mmol/dm^3, (2) a solution of TEMED in ethanol having a concentration of 107 mmol/dm^3, and (3) a solution of APS in water having a concentration of 84 mmol/dm^3. At first, the required amount (as specified in Table I) of NIPAM, BIS, and TEMED solution and solvents were placed in a small borosilicate glass tube (internal diameter = 6 mm, length = 100 mm) fitted with a rubber septum. Both the pregel mixture (of NIPAM, BIS, and TEMED) and the APS stock solution in water were purged with N$_2$ gas for 30 min. These two mixtures were dipped into an isothermal bath maintained at 5 ± 0.1°C under an N$_2$ atmosphere for 30 min. Then, we added the nitrogen-purged APS stock solution to the pregel mixture through a rubber septum by a degassed syringe, mixed it immediately by tilting the reaction tube up and down, and allowed it to react at 5 ± 0.1°C for 12 h. We cut the prepared gels into small disk-type pieces 3 mm thick with an internal diameter of 6 mm and dipped them into deionized water for dialysis to remove the unreacted chemicals. The water was changed twice a day until the conductance of water used in the dialysis become equal to the freshly distilled deionized water. After the dialysis, the gels were dried *in vacuo* at 50°C for 72 h. The conversion (percentage) was determined gravimetrically.

Surface morphology

The hydrogels were swollen in deionized water at 20°C for 24 h until they reached equilibrium swelling conditions. These equilibrium-swollen gels were freeze-dried *in vacuo* to completely remove the water. The surface morphology of the freeze-dried samples was analyzed with an FEI Quanta 200F scanning electron microscope (Philips, Eindhoven, Netherlands) at an accelerated voltage of 5 kV.

Swelling ratios at different temperatures

The swelling ratios of the different gels at 20, 22.5, 27.5, 30, 32.5, 35, 38, and 40°C were measured gravimetrically. The preweighed dried gels were immersed in deionized water for 24 h at the desired temperature to get the equilibrium-swollen gels. These equilibrium-swollen gels were then taken out, the surface water was soaked with moistened filter paper, and their weights were taken. The swelling ratio (W_s/W_d) was calculated as the ratio of the weight of the equilibrium-swollen gel (W_s) to the weight of the dried gel (W_d).

Swelling ratios in different ethanol–water mixtures at 20°C

The swelling ratios of the different gels in ethanol–water mixtures with x_m values of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.8, and 1.0 at 20°C were measured gravimetrically with the method described previously.

Deswelling kinetics at 40°C

The deswelling kinetics of the equilibrium-swollen gels in water at 40°C of the equilibrium gels obtained after they were immersed in water at 20°C for 24 h were measured gravimetrically. The preweighed equilibrium-swollen gels at 20°C were immersed quickly in the water at 40°C. At definite time intervals, the gels were taken out, the surface water was soaked with moistened filter paper, the weights were taken, and then, the gels were quickly immersed back in water at 40°C. The water retention (%) was calculated as the weight percentage of the water retained by the swollen gel at any definite time t ($W_t - W_d$) with respect to the weight percentage of the water retained by the equilibrium-swollen hydrogel ($W_s - W_d$) at 20°C (where W_t is the weight of the swollen gel at time t).

Reswelling kinetics at 20°C

The reswelling kinetics in water at 20°C of the equilibrium-swollen gels obtained after immersion in water at 40°C for 24 h were measured gravimetri-

cally. The preweighed equilibrium-swollen gels at 40°C were immersed quickly in water at 20°C. At definite time intervals, the gels were taken out, the surface water was soaked with moistened filter paper, their weights were taken, and then, the gels were quickly immersed back in water at 20°C. The water uptake (percentage) was calculated as the weight percentage of water absorbed by the swollen hydrogel at any definite time t ($W_t - W_d$) with respect to the weight percentage of water absorbed by the equilibrium-swollen hydrogel ($W_s - W_d$) at 20°C.

RESULTS AND DISCUSSION

The PNIPAM hydrogel synthesis conditions and their characterization data are included in Table I. The observed yields (percentages) were between 64 and 95%. The appearance of the as-prepared hydrogels changed from transparent (run X_0) through translucent ($X_{0.04}$) to opaque (runs $X_{0.09}$, $X_{0.16}$, $X_{0.24}$, and $X_{0.34}$) and then changed back to transparent (runs $X_{0.48}$ and $X_{0.68}$). The observed transparency of the gels prepared at $x_m = 0$ (run X_0), 0.48 (run $X_{0.48}$), and 0.68 (run $X_{0.68}$) was due to the highly solvated coiled conformation of the PNIPAM chain segment in the gel because of the strong interaction of the solvent–solvent mixtures with the PNIPAM chain segment. On the other hand, the observed opacity of the gels prepared with x_m values of 0.09, 0.16, 0.24, and 0.34 (runs $X_{0.09}$, $X_{0.16}$, $X_{0.24}$, and $X_{0.34}$, respectively) was indicative of the formation of the less solvated aggregated globular PNIPAM chain segment because of the cononsolvency of such ethanol–water mixtures toward the PNIPAM chain segments in the gel. The observed translucency of the gel prepared at $x_m = 0.04$ (run $X_{0.04}$) was due to the intermediate solvency of the PNIPAM chain segment in this solvent composition compared to the gels prepared at $x_m = 0.09$, 0.16, 0.24, and 0.34 (runs $X_{0.09}$, $X_{0.16}$, $X_{0.24}$, and $X_{0.34}$, respectively) and at $x_m = 0$, 0.48, and 0.68 (run X_0, $X_{0.48}$, and $X_{0.68}$, respectively). The gels prepared with x_m values of 0.16 and 0.24 (runs $X_{0.16}$ and $X_{0.24}$, respectively) were very weak in nature. This may have been due to the very fast solid (swollen)-phase polymerization in these solvent compositions due to the cononsolvency phenomena.[16] The very high-viscosity ethanol–water mixture in these two solvent compositions may have also played an important role here.[17]

Figure 1 shows the SEM images of all of the freeze-dried hydrogels. The magnifications of all of the SEM images are 6000×. The gel prepared in water ($x_m = 0$) was macroscopically homogeneous [Fig. 1(a)], as was evident from the absence of any apparently visible pores. The porosities of the gels increased gradually with increasing x_m from 0
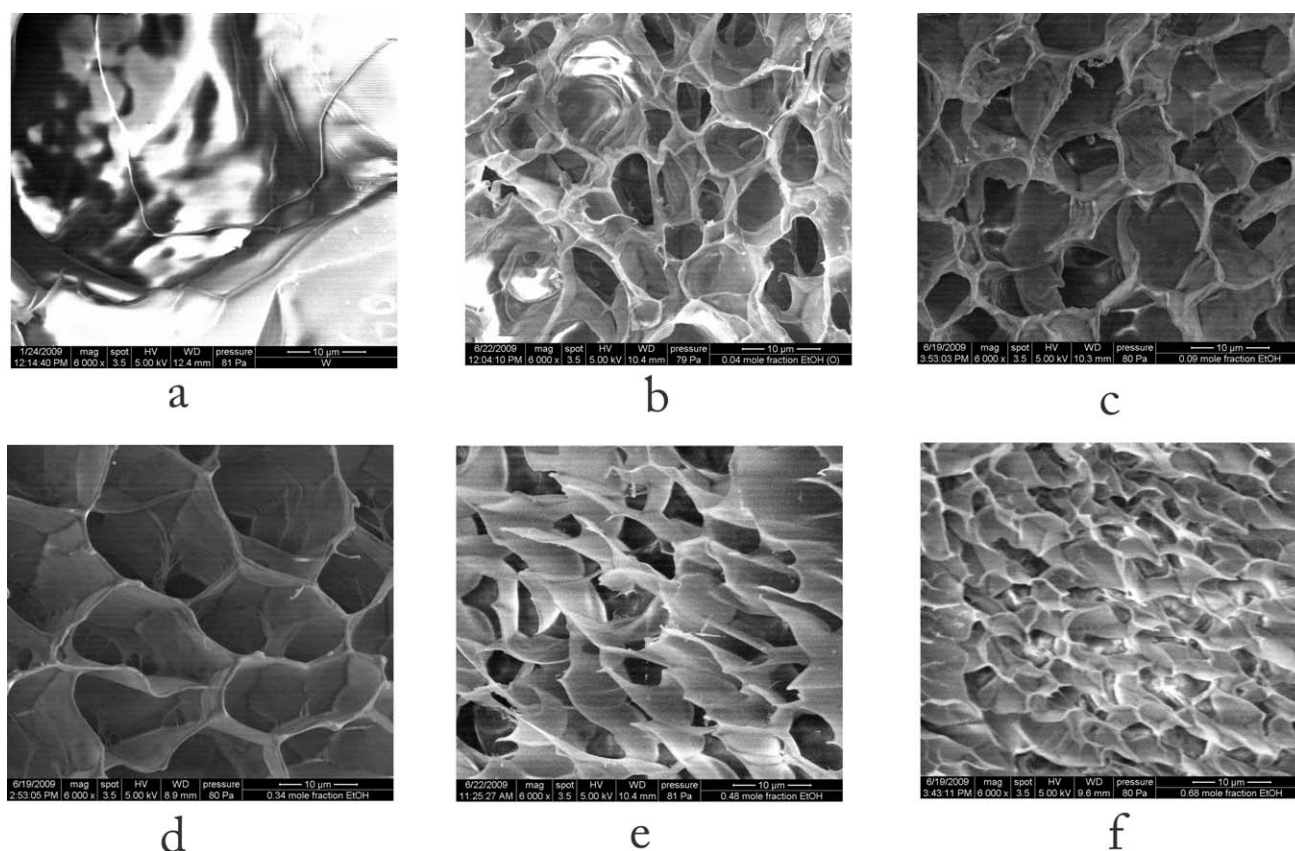
Figure 1 SEM images of the hydrogels synthesized in ethanol–water mixtures with x_m values of (a) 0, (b) 0.04, (c) 0.09, (d) 0.34, (e) 0.48, and (f) 0.68.

[Fig. 1(a), run X_0] to 0.04 [Fig. 1(b), run $X_{0.04}$] to 0.09 [Fig. 1(c), run $X_{0.09}$] in the synthesized solvent mixtures. This was due to (1) the increase in the polymerization rate in the presence of ethanol due to the faster decomposition of the APS initiator[16] and (2) the gradual decrease in the solvency of the PNIPAM chain segment due to the onset of the cononsolvency. With a further increase of the x_m value to 0.34 (run $X_{0.34}$), there was a significant increase in the porosity of the gel [Fig. 1(d)]. This may have been due to the complete collapse of the PNIPAM chain segment into its globular state within the proximity of the cononsolvency zone ($x_m = 0.1$–0.3) during gel formation. However, with a further increase of x_m to 0.48 (run $X_{0.48}$), the resulting gel showed a macroporous morphology with a small pore size [Fig. 1(e)]. This may have been due to the increase in the solvency (redissolution) of the PNIPAM chain segment in the proximity of the ethanol-rich zone ($x_m \geq 0.50$).[5] The morphology of the gel prepared at $x_m = 0.68$ (run $X_{0.68}$) was macroporous [Fig. 1(f)] with a smaller pore size than the gel prepared at $x_m = 0.48$ (run $X_{0.48}$) [Fig. 1(e)] because of the higher solvency of the PNIPAM chain segment in the higher ethanol content medium. Thus, the pore size of the formed gel decreased with increasing ethanol content (x_m) in the range 0.34–0.68. All of these con-

firmed the formation of highly porous structures of the hydrogels prepared in ethanol–water mixtures. Moreover, the pore sizes of the gels passed through a maximum at $x_m = 0.34$ (run $X_{0.34}$) in the cononsolvency zone.

The swelling ratios at different temperatures of all of hydrogels prepared in the different ethanol–water mixtures are shown in Figure 2. Below the volume-phase transition, the equilibrium swelling ratio of the gel prepared in water ($x_m = 0$, run X_0) was smaller than those of all of the other gels prepared in different ethanol–water mixtures (see Fig. 2). This was due to the formation of a macroporous cross-linked gel in the ethanol–water mixture as per discussion in the Synthesis of the PNIPAM Hydrogels section; this eventually led to an increase in the porosity and a water-uptake tendency in the gel. Figure 3 shows the plot of the swelling ratio of the hydrogels in water at 20°C against x_m of the synthesis solvent mixtures (see Table I). The equilibrium swelling ratio of the hydrogels in water at 20°C increased gradually from 11.4 through 14 to 22 with increasing x_m of synthesis solvents from 0 (run X_0) through 0.04 (run $X_{0.04}$) to 0.09 (run $X_{0.09}$), respectively, because of the gradual increase in the porosity of the formed gel in the cononsolvency region. The swelling ratio again increased significantly to
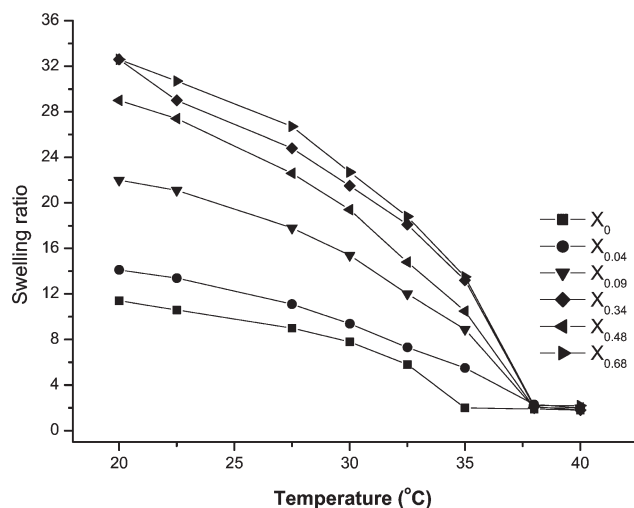
Figure 2 Equilibrium swelling ratios of all the PNIPAM hydrogels in water at 20, 22.5, 27.5, 30, 32.5, 35, 38, and 40°C.

Figure 4 Equilibrium swelling ratios of all the PNIPAM hydrogels in ethanol–water mixtures with x_m values of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.8, and 1.0 at 20°C.

around 32.6 for the gel prepared at $x_m = 0.34$ (run $X_{0.34}$). This was due to the formation of a very less crosslinked (i.e., larger pore size) gel through the solid (swollen)-phase polymerization due to the complete collapse of the PNIPAM chain segment into its globular state within the proximity of the cononsolvency zone ($x_m = 0.1–0.3$; see Figure 3). Then, the swelling ratio decreased slightly to 29 for the gel prepared at $x_m = 0.48$ (run $X_{0.48}$). This was due to the formation of a macroporous gel with a smaller pore size due to the redissolution of the collapsed globular PNIPAM chain segment into its relatively more solvated coiled state at the outside of the cononsolvency zone ($x_m = 0.1–0.3$). The swelling ratio remained almost constant with further increases to $x_m = 0.68$ (run $X_{0.68}$) because of the formation of a similar solvated coiled state of the
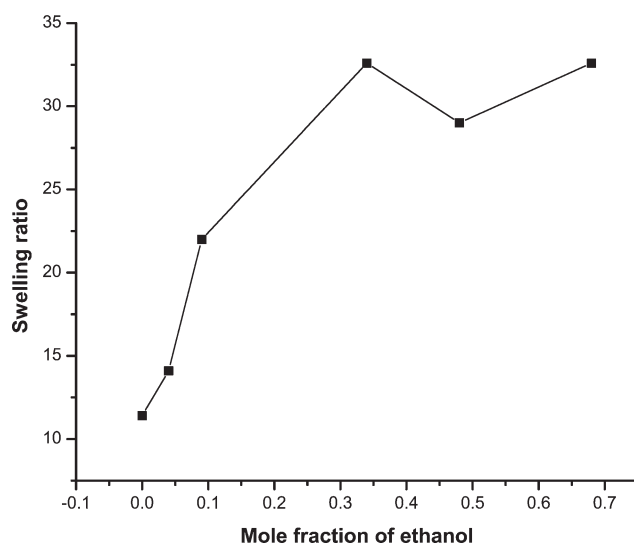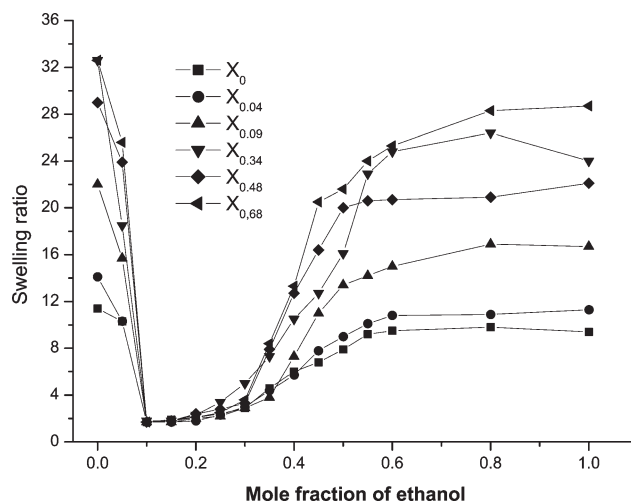

Figure 3 Plot of the swelling ratios of the hydrogels in water at 20°C versus the x_m values of the synthesis solvent.

PNIPAM chain segment, as was observed for the gel prepared at $x_m = 0.48$ (run $X_{0.48}$). In general, the equilibrium swelling ratio in water at 20°C of all of the PNIPAM gels varied in the following order: $X_{0.34} \approx X_{0.68} > X_{0.48} > X_{0.09} > X_{0.04} > X_0$. The swelling ratio in water at 40°C for all of the gels was more or less close to 2 (see Table I and Fig. 2). This was due to the complete collapse of the coiled conformation of the PNIPAM chain segment into its slightly solvated globular form at this temperature. In general, below LCST, the swelling ratio values gradually decreased with increasing temperature because of the release of water due to the gradual collapse of the PNIPAM chain segment in the gel. Similar types of results have also been reported in the literature for mixtures of water and other water-miscible solvent systems.[6,18–22] Moreover, the swelling ratio values of all of the gels except the one prepared in water (run X_0) were at a minimum (ca. 2) at about 38°C, whereas the same for the gel prepared in water (run X_0) was observed around 35°C. This was due to the formation of macroporous crosslinked gels in the ethanol–water mixture.

The changes in the swelling ratio values of all of the PNIPAM gels with different x_m values at 20°C are shown in Figure 4. With x_m increasing from 0 to 0.1, the swelling ratio values of all of the hydrogels decreased sharply because of the onset of the cononsolvency and became almost equal to the minimum value of about 2 around $x_m = 0.1$. After this point, the swelling ratio values of all gels, except the one prepared at $x_m = 0.34$, increased slightly with increasing x_m value from 0.1 to around 0.3, and the observed swelling ratio values were almost same for all of the hydrogels in these solvent compositions. This indicated that the PNIPAM chain segments of
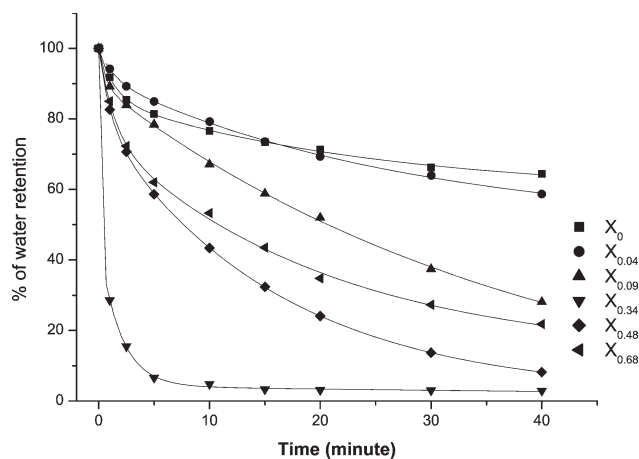
Figure 5 Deswelling kinetics of the PNIPAM hydrogels synthesized in ethanol–water mixtures with x_m values of 0 (run X_0), 0.04 (run $X_{0.04}$), 0.09 (run $X_{0.09}$), 0.34 (run $X_{0.34}$), 0.48 (run $X_{0.48}$), and 0.68 (run $X_{0.68}$).

the collapsed gels in the cononsolvency region were in the same molecular conformational state. Their swelling ratio values increased very slowly because of the very slow redissolution of the aggregated PNIPAM chain segment with increasing ethanol content. Moreover, this behavior was only due to the molecular interaction of the solvent and polymer not to other factors, such as crosslinking density, extent of aggregation of the PNIPAM chain segments, or extent of formation of free PNIPAM chain segments. With the further increase in x_m from 0.3 to 0.6, the swelling ratio values of all of the hydrogels gradually increased, and this reswelling trend was almost like the deswelling trend observed during the onset of the cononsolvency zone ($x_m = 0$–0.1 region). With a further increase in x_m from 0.6 to 1, the swelling ratio values of all of hydrogels almost leveled off. Finally, the observed swelling ratio values of all of the hydrogels in ethanol were lower than that in water. This was due to the lower density or larger molecular volume of ethanol with respect to that of water. In this regard, the PNIPAM hydrogels prepared with an x_m value of 0.34 (run $X_{0.34}$) showed slightly higher swelling ratio values in the ethanol–water mixture range of $x_m = 0.25$–0.3 than the other hydrogels. This again confirmed that the chain conformation of this gel was slightly different than other gels, as mentioned during the discussion of the morphology and swelling ratio values in water at 20°C.

The deswelling rates of all of the hydrogels in water at 40°C are shown in Figure 5. This rate was slowest with the hydrogel prepared in water ($x_m = 0$, run X_0). It gradually increased for the hydrogels prepared in the synthesis solvent containing higher x_m values from 0 to 0.04 to 0.09 (runs X_0, $X_{0.04}$, and $X_{0.09}$, respectively). With a further increase in x_m

from 0.09 to 0.34 (run $X_{0.34}$), the deswelling rate of the resulting hydrogel became drastically fastest. After this, the deswelling rate of the hydrogel prepared at $x_m = 0.48$ (run $X_{0.48}$) significantly decreased and came between those of the gels prepared with x_m values of 0.09 and 0.34 (runs $X_{0.09}$ and $X_{0.34}$, respectively). With a further increase in x_m to 0.68, the obtained hydrogel showed a slower deswelling rate than that prepared with an x_m value of 0.48 (run $X_{0.48}$) of ethanol content but faster than that prepared with an x_m value of 0.09 (run $X_{0.09}$). In general, the deswelling rate depended on the rate of the ejection of water from the polymer matrix. This ejection rate depended on the porosity, the extent of aggregation of the PNIPAM chain segment in the gel, and so on. The larger the porosity was, the faster the deswelling rate was, the higher the extent of aggregation of the PNIPAM chain segment was, and the faster the deswelling rate was. The observed faster deswelling rate with the gel prepared in the x_m range of 0–0.09 (runs X_0, $X_{0.04}$, and $X_{0.09}$, respectively) was due to the formation of a larger pore size crosslinked gel and also to the formation of more aggregated globular PNIPAM chains in the formed gel because of the gradual collapse of the PNIPAM chain segment due to the onset of cononsolvency. The drastically faster deswelling rate of the resulting hydrogel prepared at $x_m = 0.34$ (run $X_{0.34}$) was due to the formation of the macroporous crosslinked gel with a larger pore size and highly aggregated PNIPAM chain segment through the solid (swollen)-state polymerization due to the cononsolvency of the ethanol–water mixtures. The considerably slower deswelling rate of the gel prepared at $x_m = 0.48$ (run $X_{0.48}$) was due to the formation of a relatively smaller pore size macroporous gel containing less aggregated PNIPAM chain segments in the ethanol-rich region ($x_m \geq 0.50$) beyond the cononsolvency zone. The observed slower deswelling rate of the gel prepared at $x_m = 0.68$ (run $X_{0.68}$) with respect to the gel prepared at $x_m = 0.48$ (run $X_{0.48}$) was due to the formation of a macroporous gel containing relatively less aggregated PNIPAM chain segments in the higher ethanol-rich region outside the cononsolvency zone. Its faster deswelling rate with respect to the gel prepared at $x_m = 0.09$ (run $X_{0.09}$) was due to the formation of a relatively larger pore size. These observations also indicated that the aggregation state of the PNIPAM chain segments in the formed gel at $x_m = 0.68$ (run $X_{0.68}$) was between the two gels prepared at $x_m = 0.48$ (run $X_{0.48}$) and $x_m = 0.09$ (run $X_{0.09}$). Thus, the deswelling rate of the hydrogels decreased in the following order: $X_{0.34} > X_{0.48} > X_{0.68} > X_{0.09} > X_{0.04} > X_0$.

The reswelling rates of all of the hydrogels at 20°C are shown in Figure 6. The reswelling rate was fastest with the hydrogel prepared in water ($x_m = 0$,
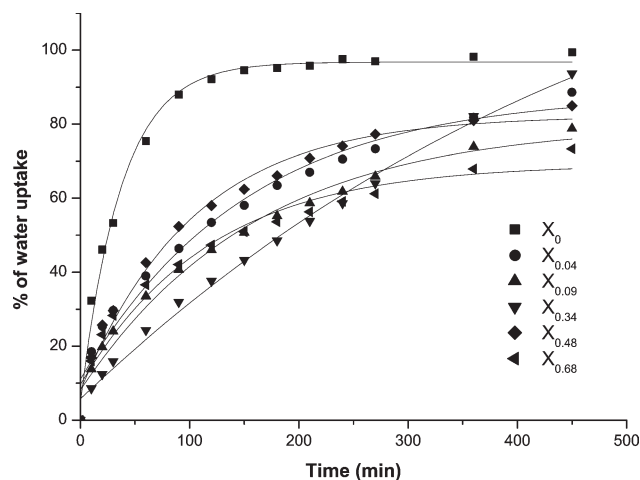
Figure 6 Reswelling kinetics of the PNIPAM hydrogels synthesized in ethanol–water mixtures with x_m values of 0 (run X_0), 0.04 (run $X_{0.04}$), 0.09 (run $X_{0.09}$), 0.34 (run $X_{0.34}$), 0.48 (run $X_{0.48}$), and 0.68 (run $X_{0.68}$).

run X_0) and slowest with the gel prepared at $x_m = 0.34$ (run $X_{0.34}$). It increased slightly and became almost comparable with the gels prepared at $x_m = 0.09$ and 0.68 (runs $X_{0.09}$ and $X_{0.68}$, respectively). It further increased slightly and became almost comparable for the gels prepared at $x_m = 0.04$ and 0.48 (runs $X_{0.04}$ and $X_{0.48}$, respectively). The reswelling rate is generally controlled by the rate of diffusion of water into the polymer matrix. Apart from the porosity, the rate of diffusion depends on the state of the polymer chains in its matrix. The reswelling rate is faster when the polymer chains are in a loosely aggregated coiled structure. The rate is slower when the polymer chains are present in a highly aggregated globular structure. On gradual addition of
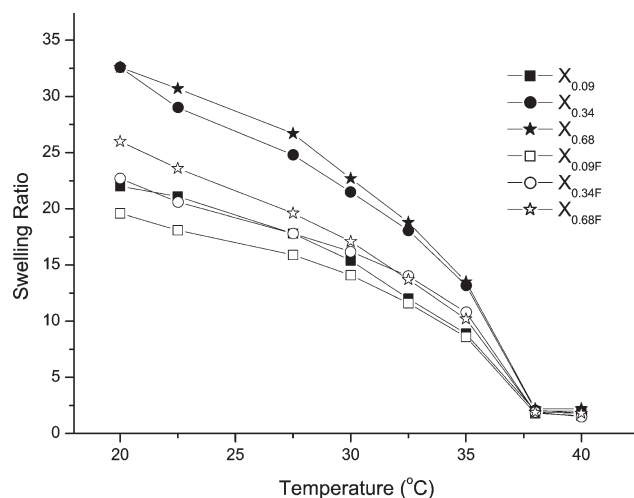

Figure 7 Equilibrium swelling ratios of the PNIPAM hydrogels synthesized in ethanol–water mixtures with x_m values of 0.09 (run $X_{0.09}$), 0.34 (run $X_{0.34}$), and 0.68 (run $X_{0.68}$) in water at 20, 22.5, 27.5, 30, 32.5, 35, 38, and 40°C before and after freeze-drying. The subscript F indicates corresponding freeze-dried samples.
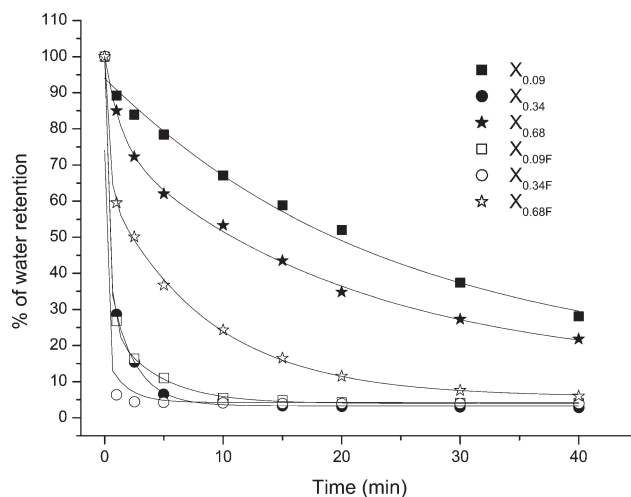

Figure 8 Deswelling kinetics of the PNIPAM hydrogels synthesized in ethanol–water mixtures with x_m values of 0.09 (run $X_{0.09}$), 0.34 (run $X_{0.34}$), and 0.68 (run $X_{0.68}$) before and after freeze-drying. The subscript F indicates corresponding freeze-dried samples.

ethanol to water, because of the onset of the cononsolvency of ethanol–water synthesis solvent mixture toward the PNIPAM chain segment, the coil conformation of the PNIPAM chain segment gradually turned into an aggregated globular state up to around $x_m = 0.1$. Therefore, the observed decrease in the reswelling rate with increasing ethanol content from $x_m = 0$ to 0.04 to 0.09 (runs X_0, $X_{0.04}$, and $X_{0.09}$, respectively) was in conformity with the previous explanation. On further increase of the ethanol content (x_m) from 0.1 to 0.34 (in the cononsolvency zone), the PNIPAM chain segment expectedly presented in the highly aggregated globular state. Therefore, the reswelling rate was slowest with such gels prepared within the proximity of the cononsolvency zone. The observed slowest reswelling rate for the gel prepared at $x_m = 0.34$ (run $X_{0.34}$) was in conformity with the previous explanation. A slight increase in the reswelling rate for the gel prepared at $x_m = 0.48$ (run $X_{0.48}$) was due to the relatively less aggregated PNIPAM chain in the gel formed at the higher ethanol content ($x_m = 0.48$) medium outside the cononsolvency zone because of the higher solvency of the PNIPAM segment. The almost comparable reswelling rates of the gels prepared at $x_m = 0.04$ and 0.48 (runs $X_{0.04}$ and $X_{0.48}$, respectively) may have been due to the similar and highly aggregated globular states of the polymer chains in the gel matrices. The observed faster reswelling rate for the gel prepared at $x_m = 0.68$ (run $X_{0.68}$) was due to the formation of a loosely aggregated (highly solvated) coiled structure of the PNIPAM chain segment in the gel matrix. The almost comparable reswelling rate of this gel with that prepared at $x_m = 0.09$ (run $X_{0.09}$) may have been due to the similar loosely
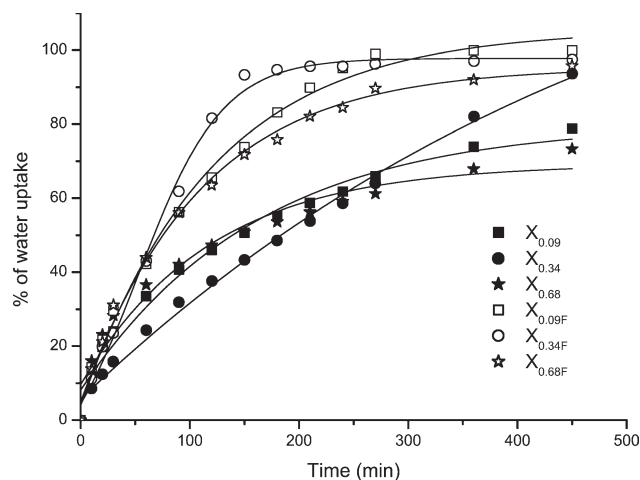
Figure 9 Reswelling kinetics of the PNIPAM hydrogels synthesized in ethanol–water mixtures with x_m values of 0.09 (run $X_{0.09}$), 0.34 (run $X_{0.34}$), and 0.68 (run $X_{0.68}$) before and after freeze-drying. The subscript F indicates corresponding freeze-dried samples.

aggregated coiled structure of the polymer chain in the gel matrix. Thus, the reswelling rates of these hydrogels decreased in the following order: $X_0 > X_{0.04} \approx X_{0.48} > X_{0.09} \approx X_{0.68} > X_{0.34}$.

To study the effect of freeze-drying on the swelling properties, we measured the swelling ratio values of three PNIPAM gels, namely, $X_{0.09}$, $X_{0.34}$, and $X_{0.68}$, after freeze-drying at different temperatures, and the results are shown in Figure 7. It is clear from the figure that in all of the gel samples, there was a decrease in the swelling ratio in all temperatures below the LCST value. This may have been due to the breakage of the cross-linked network of the gel during the freeze-drying process. This view was supported by the faster deswelling rates of these freeze-dried gels in water at 40°C, as shown in Figure 8. Moreover, the increase in the reswelling rate of the corresponding freeze-dried gels in water at 20°C, as shown in Figure 9, also supported this. Thus, the freeze-drying process decreased the swelling ratio but increased the deswelling and reswelling properties of the PNIPAM gels because of the internal breakage of the crosslinked network.

CONCLUSIONS

PNIPAM hydrogels were prepared by free-radical polymerization in different ethanol–water mixtures. SEM study revealed that the resulting hydrogels were macroporous. The swelling ratios of the resulting hydrogels in water at 20°C followed the order: $X_{0.34} \approx X_{0.68} > X_{0.48} > X_{0.09} > X_{0.04} > X_0$. Below the LCST, the swelling ratio values gradually decreased with increasing temperature because of the release of water due to the gradual collapse of the PNIPAM chain segment in the gel. The swelling ratio values of all of the PNIPAM gels with different x_m values

at 20°C passed through a minimum in the cononsolvency zone. Moreover, the swelling ratios of all of the gels in pure water were higher than those observed in ethanol. The deswelling rates of the hydrogels decreased in the following order: $X_{0.34} > X_{0.48} > X_{0.68} > X_{0.09} > X_{0.04} > X_0$. Thus, we systematically varied the deswelling rate of the hydrogels by simply varying the ethanol–water mixture composition used as the synthesis solvent, and the fastest rate occurred when x_m was 0.34. The reswelling rate of these hydrogels decreased in the following order: $X_0 > X_{0.04} \approx X_{0.48} > X_{0.09} \approx X_{0.68} > X_{0.34}$. the freeze-drying process decreased the swelling ratio but increased the deswelling and reswelling properties of PNIPAM gels. All of these swelling, deswelling, and reswelling properties were explained on the basis of the variation of the crosslinking density (porosity), polymer chain and solvent interaction, and chain conformation due to the cononsolvency behavior of the ethanol–water mixture toward the PNIPAM chain segment in the PNIPAM hydrogel and the extent of solution or solid (swollen)-phase polymerization with gradual changes in the composition of the ethanol–water mixture.

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