Swelling–Deswelling Kinetics of Poly(*N*-isopropylacrylamide) Hydrogels Formed in PEG Solutions

Yucel Dogu, Oguz Okay

Istanbul Technical University, Department of Chemistry, Maslak, 80626 Istanbul, Turkey

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ABSTRACT: A series of poly(*N*-isopropylacrylamide) (PNIPA) hydrogels was prepared by free-radical crosslinking copolymerization of *N*-isopropylacrylamide (NIPA) and *N*,*N*′-methylenebisacrylamide (BAAm) in aqueous solutions of poly(ethylene glycol) of molecular weight 300 g/mol (PEG). The amount of PEG in the polymerization solvent, the crosslinker (BAAm) content, and the gel preparation temperature (T_{prep}) were varied in the gelation experiments. The hydrogels were characterized by the equilibrium swelling and elasticity tests as well as by the measurements of the deswelling–reswelling kinetics of the hydrogels in response to a temperature change between 25 and 48°C. The rate of deswelling of the swollen gel increases while the rate of reswelling of the collapsed gel decreases as the amount of PEG in the polymerization solvent is increased or as the crosslinker content is decreased. The T_{prep} effect on the swelling kinetics of the hydrogels was only observed if the PEG content of the polymerization solvent is less than 20%, which is explained with the screening of H-bonding interactions in concentrated PEG solution. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 37–44, 2005

Key words: hydrogels; macroporous polymers; swelling; modulus

INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNIPA) gel is a typical temperature-sensitive gel exhibiting volume phase transition at approximately 34°C.[1,2] Below this temperature, the gel is swollen and it shrinks as the temperature is raised. The temperature sensitivity of PNIPA gels has attracted great attention in the last years due both to fundamental and technological interests.[3–6] These materials are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators. In these applications, a fast response rate of the hydrogel to the external stimuli is needed. To increase the response rate of PNIPA gels, several techniques were proposed.

1. Submicrometer-sized gel particles:[7] The rate of swelling or shrinking of gels is controlled by diffusion of water molecules through the gel network. This process is slow and even slower near the critical point. Since the rate of response is inversely proportional to the square of the size of the gel,[8] small PNIPA gel particles respond to the external stimuli more quickly than bulk gels.
2. Gels having dangling chains:[9–11] Dangling chains in a gel easily collapse or expand upon an external stimulus because one side of the dangling chain is free.
3. Macroporous PNIPA gels: For a polymer network having an interconnected pore structure, absorption or desorption of water occurs through the pores by convection, which is much faster than the diffusion process that dominates the nonporous gels.

To obtain macroporous structures, a phase separation must occur during the course of the network formation process so that the two-phase structure formed is fixed by the formation of additional crosslinks.[12–14] The extent of phase separation during crosslinking and, thus, the degree of macroporosity of the resulting networks depend on the gel synthesis parameters, such as the temperature, the crosslinker, and the monomer concentrations as well as the amount and the type of the inert diluent (pore-forming agent) present during the network formation process.[14]

The gel preparation temperature T_{prep} is one of the parameters that determines the degree of macroporosity in PNIPA networks. One idea to prepare macroporous PNIPA networks is to start the polymerization of *N*-isopropylacrylamide (NIPA) below the lower critical solution temperature (LCST) of PNIPA and then elevate the temperature above it.[15] Takata et al.[16] showed that a rapid shrinking of PNIPA gels can be

Correspondence to: O. Okay (okayo@itu.edu.tr).

attained by increasing the T_{prep} above LCST due to the increasing degree of spatial gel inhomogeneity. Opposing this, it was reported that decreasing T_{prep} below the freezing point (–18°C) also produces fast responsive PNIPA gels.[17] Xue et al.[18] prepared fast responsive PNIPA gels by using a two-step polymerization method, the initial polymerization being carried out at 20°C, followed by polymerization at –28°C for 24 h. Another method for obtaining the macroporous structure consists of freezing the initial polymerization mixture to a solid monomer matrix;[19,20] polymerization of this frozen matrix leads to a macroporous material called cryogel. In this technique, the monomers and the initiator are concentrated in the unfrozen microzones of the apparently frozen system. The polymerization reactions proceed in these unfrozen microzones and lead to the formation of a polymer network with continuous macroporous channels filled with liquid solvent.[19]

Use of several inert diluents during the crosslinking copolymerization of NIPA and *N*,*N*′-methylenebisacrylamide (BAAm) was also suggested for the preparation of macroporous PNIPA hydrogels. Hydroxypropyl cellulose,[21] acetone,[22] 1,4-dioxane,[23] sucrose,[24] silica particles,[25] inorganic salts,[26] as well as poly(ethylene glycol) (PEG) of various molecular weights[27–30] were used to prepare fast responsive macroporous PNIPA hydrogels. On the other hand, Zhang et al.[31] showed increased degree of porosity in PNIPA gels on rising the crosslinker content. Recently, we have shown that a critical crosslinker (BAAm) concentration is necessary to produce a heterogeneous (macroporous) PNIPA network structure.[32,33] Macroporous PNIPA networks consist of spherical globules called microspheres of 0.1–0.5 μm in diameter aggregated to large, unshaped, discrete clusters with dimensions of a few micrometers.[32] At high BAAm contents, the structure looks like cauliflower, typical for a macroporous network. Changes from homogeneous to heterogeneous gelation result in the formation of fast responsive hydrogels.[32]

The aim of this study was to find out the optimum synthesis parameters of fast-responsive PNIPA hydrogels formed in the presence of PEG of molecular weight 300 g/mol (PEG-300). The hydrogels were synthesized by free-radical crosslinking polymerization of NIPA in the presence of BAAm as crosslinker at an initial monomer concentration of 8 w/v %. PEG-300/water mixtures of various compositions were used as the polymerization solvent and as the pore-forming agent. Two sets of experiments were carried out. In the first set, PEG-300 content of the solvent mixture was varied between 0 and 70 v/v % while the crosslinker (BAAm) concentration was fixed at 1.2 mol %. In the second set, the amount of PEG-300 in the solvent mixture was fixed at 70 v/v % while the BAAm content in the comonomer feed was varied. In addition, gelation experiments at 1.2 mol % BAAm were carried out both below and above the LCST of PNIPA. The gels were characterized by the equilibrium swelling and elasticity tests as well as by their swelling–deswelling kinetics in water. The properties of PNIPA hydrogels formed in PEG-300 were also compared with a PNIPA cryogel formed at –25°C.

EXPERIMENTAL

Materials

NIPA (Aldrich), BAAm (Fluka), ammonium persulfate (APS, Merck), *N*,*N*,*N*′,*N*′- tetramethylethylenediamine (TEMED, Carlo Erba), and PEG-300 (Fluka) were used as received. PNIPA hydrogels were prepared by free radical crosslinking copolymerization of NIPA and BAAm at both 9 and 50°C. It is to be noted that the gel preparation temperature T_{prep} is the temperature of the thermostated bath in which the PNIPA gels are prepared. According to the previous works, the actual reaction temperature deviates from the value of T_{prep} due to the exothermic reaction profiles of the crosslinking copolymerization of NIPA.[34] The polymerization reactions were initiated using 3.5 mM APS and 0.25 v/v % TEMED. The polymerization time was set to 48 h. The initial monomer concentration was also fixed at 0.7*M*. Two sets of experiments were carried out: In the first set, the crosslinker (BAAm) content was fixed at 1.2 mol % (with respect to the monomers), while the PEG content of the PEG–water mixture was varied between 0 and 70 v/v %. In the second set, PEG content was fixed at 70 v/v % while the amount of the crosslinker BAAm was varied between 1.2 and 15 mol %.

To illustrate the synthetic procedure, we give details for the preparation of PNIPA gels in 70 v/v % PEG solutions with 1.2 mol % BAAm as the crosslinker: NIPA (0.792 g), BAAm (0.0126 g), and APS (0.008 g) were first dissolved in a 70% PEG solution in a graduated flask of 10 mL in volume. The solution was purged with nitrogen gas for 20 min. After addition of TEMED (0.025 mL), the volume of the monomer solution was completed to 10 mL with 70% PEG and then, portions of this solution, each about 2 mL, were transferred to glass tubes of 4 mm in diameter. The glass tubes were sealed, immersed in a thermostated bath, and the polymerization was conducted for 48 h. After polymerization, the gels were cut into specimens of equal length (10 mm) and immersed in a large excess of water to wash out any soluble polymers, unreacted monomers, and the initiator.

PNIPA cryogel was prepared by free radical crosslinking copolymerization of NIPA and BAAm in water at –25°C, as described in the literature.[19,20] NIPA (1.337 g) and BAAm (0.006 g) were dissolved in distilled water. After nitrogen bubbling for 15 min,

TEMED (0.013 mL) was added to the monomer solution and then the reaction mixture was taken into a water–ice bath for 2–3 min. After addition of APS (0.0116 g), the reaction mixture was poured into a plastic 5-mL syringe with a closed outlet at the bottom. The plastic syringe was kept at –25°C for 24 h and then the cryogel formed was thawed at room temperature. The cryogel matrix was taken out of the syringe and washed in distilled water.

Equilibrium swelling measurements

The equilibrium swelling measurements were carried out in distilled water at 25°C. To reach the equilibrium degree of swelling, the gels were immersed in water at 25°C at least for 2 weeks. The normalized volume of the equilibrium swollen hydrogels V_{eq} (volume of equilibrium swollen gel/volume of the gel just after preparation) was determined by measuring the diameter of the hydrogel samples by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). V_{eq} was calculated as

$$V_{eq} = (D/D_0)^3$$

where D and D_0 are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively.

Measurements of deswelling and reswelling kinetics

For the deswelling kinetics measurements, the hydrogels equilibrium swollen in water at 25°C were transferred into hot distilled water (48°C). The weight changes of gels were measured gravimetrically after blotting the excess surface water at regular time intervals. For the measurement of the reswelling kinetics of gels, the equilibrium collapsed PNIPA gel samples at 48°C were transferred into water at 25°C. The weight changes of gels were also determined gravimetrically as described above. The water uptake or the water retention was calculated in terms of the relative gel mass, m_{rel}:

$$m_{rel} = \frac{m_t}{m_{sw}}$$

where m_t is the mass of the gel sample at time t and m_{sw} is its swollen mass at 25°C.

Mechanical measurements

Uniaxial compression measurements were performed on gels just after their preparation. All the mechanical measurements were conducted at 25°C. The stress–strain isotherms were measured by using a previously described apparatus.[32] The elastic modulus G_0 was determined from the slope of linear dependence, $f = G_0 (\alpha - \alpha^{-2})$, where f is the force acting per unit cross-sectional area of the undeformed gel specimen and α is the deformation ratio (deformed length/initial length).

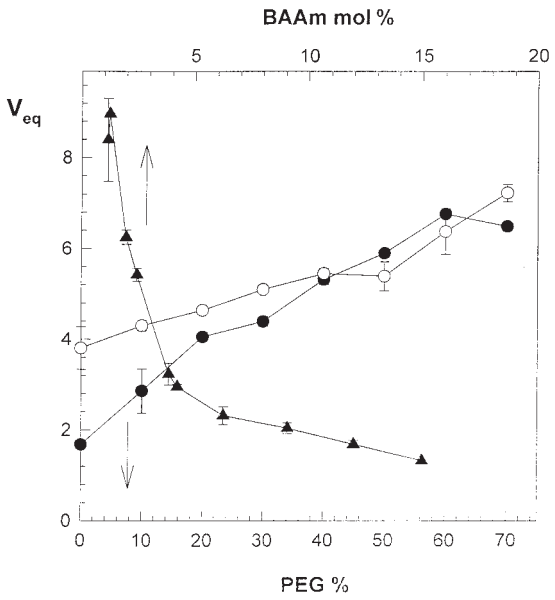

Figure 1 Equilibrium swelling ratio V_{eq} of PNIPA hydrogels shown as a function of the PEG content of the polymerization solvent and BAAm concentration. T_{prep} = 9°C (filled symbols) and 50°C (open symbols).

RESULTS AND DISCUSSION

Characteristics of PNIPA hydrogels

PNIPA hydrogels were first characterized by the equilibrium swelling and elasticity tests. The equilibrium swelling measurements were carried out in water at 25°C. Figure 1 shows the swelling ratio V_{eq} of the hydrogels plotted as functions of the PEG content of the polymerization solvent and the crosslinker (BAAm) concentration. The filled and open symbols represent the swelling data of gels prepared at 9 and 50°C, respectively. The equilibrium swelling ratio of PNIPA hydrogels increases with increasing amounts of PEG-300 present in the gel formation system. Another point shown in Figure 1 is that, if PEG content is less than 40 v/v %, the gels formed at 50°C swell in water much more than those formed at 9°C. However, for PEG contents above 40%, both 9 and 50°C gels exhibit almost the same swelling capacity in water. Figure 1 also shows that, the higher the crosslinker (BAAm) content, the lower the swelling capacity of the resulting hydrogels. This is expected since increasing crosslinker content decreases the mesh size of the gel network so that the hydrogel with a high amount of

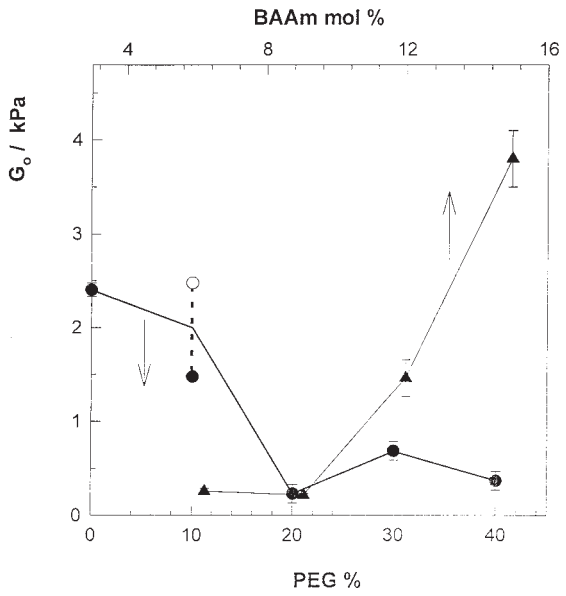

Figure 2 Modulus of elasticity G_0 of PNIPA hydrogels shown as a function of the PEG content of the polymerization solvent and BAAm concentration. Open and filled symbols connected by a dotted line represent the moduli data of the PNIPA gel sample prepared in 10% PEG; one measured from the transparent and the other from the opaque part, respectively.

BAAm absorbs lesser amount of water in the equilibrium swollen state.

Figure 2 shows the modulus of elasticity G_0 of the hydrogels plotted as functions of the PEG and BAAm contents used in the gel preparation. Note that the hydrogels prepared at 50°C as well as those prepared in PEG solutions with more than 40% PEG were too weak to withstand the elasticity tests. Figure 2 shows that the modulus of elasticity decreases with increasing PEG concentration. This is due to the fact that increasing amounts of PEG promote the extent of phase separation during gelation, so that the porosity of the resulting networks increases;[29] increasing porosity on rising the PEG content reduces the mechanical stability of the hydrogels so that the modulus decreases. Indeed, visual appearance of the gel samples supports this explanation. At T_{prep} = 9°C, the gels formed in the absence of PEG were transparent, while those prepared with more than 10% PEG were opaque, indicating existence of phase-separated domains in these samples. Interestingly, PNIPA hydrogels prepared with 10% PEG were partly transparent and opaque; this PEG concentration thus represents a critical concentration for the formation of a macroporous structure. As seen in Figure 2, two moduli data are given for the gel sample formed at 10% PEG; one measured from the transparent part (open symbol) and the other measured from the opaque part (filled symbol). The modulus of elasticity of the opaque part of the gel is lower than that of the transparent part, which is in accord with the above explanation. Another point shown in Figure 2 is that the moduli of gels increases with increasing BAAm concentration, indicating increased stability of the network structure on rising crosslinker content.

Effect of PEG concentration

In this section, the crosslinker (BAAm) content was fixed at 1.2 mol %. T_{prep} was also fixed at 9°C. The amount of PEG-300 in the gel formation system was varied between 0 and 70 v/v %. The hydrogels thus obtained were subjected to swelling and deswelling kinetics measurements. For this purpose, they were first swollen in water at 25°C to their equilibrium state. Thereafter, the swollen gels were immersed in water at 48°C and the deswelling process was monitored by recording the relative gel mass m_{rel} as a function of the time of deswelling. After attaining the equilibrium collapsed state at 48°C, the gels were again immersed in water at 25°C and the reswelling behavior was monitored until the new equilibrium state is obtained.

Typical deswelling–reswelling cycles of PNIPA gels are presented in Figure 3. Filled and open symbols represent data of gels prepared in water and in 10% PEG solution, respectively. It is seen that the deswelling response rate of the swollen gel to an external temperature change from 25 to 48°C occurs much more rapidly than the reswelling response rate of the same gel starting from its collapsed state. The swollen gel attains its equilibrium collapsed state within 10 min, while the reswelling to the same initial swollen

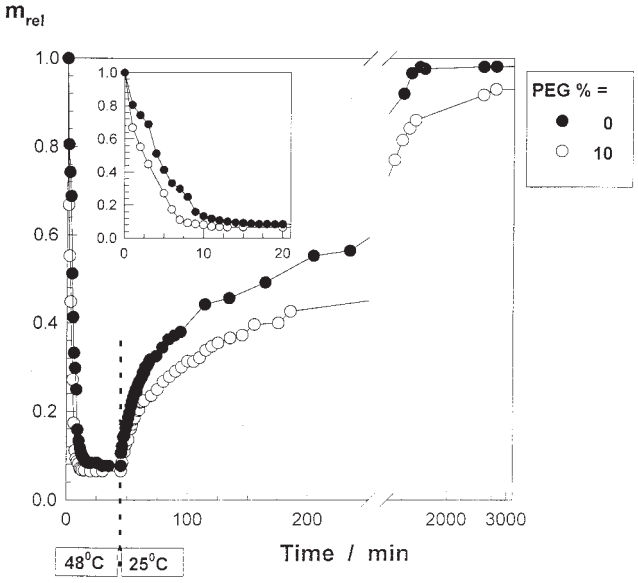

Figure 3 Deswelling–reswelling kinetics of PNIPA hydrogels formed in water and in a 10% PEG solution. The relative gel mass m_{rel} is plotted against the time in minutes. The inset shows the deswelling behavior of gels in the first 20 min.

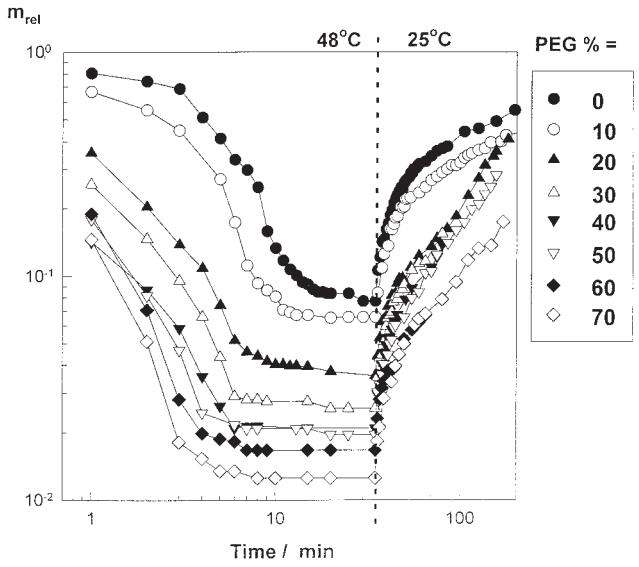

Figure 4 Deswelling–reswelling kinetics of PNIPA hydrogels shown as the variation of the relative gel mass m_{rel} with time. PEG-300 contents used in the hydrogel preparation are indicated.

volume requires a few days. Moreover, addition of PEG-300 in the gel formation system accelerates the deswelling but slows down the reswelling process in water.

The effect of PEG-300 content on the response time of PNIPA gels is illustrated in Figure 4, where the kinetic data of gels recorded between 1 and 200 min are presented. PEG-300 contents used in the hydrogel preparation are also indicated in the figure. PNIPA gel prepared in the absence of PEG-300 reaches the equilibrium collapsed state in 20 min. This time decreases with increasing PEG content and becomes only 4 min at 70 v/v % PEG. Moreover, within the first minute of the deswelling process, PNIPA gel prepared in water loses only 20% of its water content, while this amount increases to 85% in PNIPA gel prepared in 70% PEG. These results can be explained with the action of PEG-300 as a pore-forming agent during the gelation process. The porous structure formed in the presence of PEG-300 allows an easy diffusion of water molecules outside of the gel phase. Since the porosity of the networks increases with the PEG concentration, the deswelling rate of PNIPA hydrogels increases with increasing amounts of PEG used in the hydrogel preparation.

Another point shown in Figure 4 is that, the higher the PEG content, the smaller the mass of PNIPA gels in their equilibrium collapsed state. For example, the mass of the collapsed gel m_{rel} is 10^{-1} and 10^{-2} for gels prepared in water and in 70% PEG, respectively. Thus, the total amount of lost water during deswelling is an increasing function of the PEG content used in the hydrogel preparation. This behavior is also a result of the formation of an interconnected pore structure in PNIPA hydrogels prepared in PEG solutions. In case of nonporous gels, the initial deswelling produces an unswollen skin layer just inside the hydrogel surface, so that the water molecules inside the hydrogel cannot be squeezed out.[35] However, if there are interconnected pore channels inside the hydrogel, water can easily diffuse outside of the gel phase so that the skin layer formed during shrinking does not prevent water diffusion.

Figures 3 and 4 also show that the reswelling process of gels occurs in two steps: a rapid reswelling step continuing for 10^{-1} min followed by a slow reswelling step until the equilibrium swollen state, which needs a few days. Moreover, the increasing concentration of PEG in the gel formation system slows down the response rate of the collapsed gels in cold water. The two-step reswelling profile can be explained with the formation of a two-phase structure during swelling of PNIPA gels. When a collapsed PNIPA gel sample is immersed in cold water, the outer surface of the sample will first be in contact with water molecules so that the collapsed network chains at the gel surface will start to relax. Since the surface area of the collapsed gel is initially large, water absorption by the gel network occurs easily. However, as the gel swells, a two-phase structure will form: one containing solvated network chains at the gel surface and the other containing relatively unswollen network chains in the inner part of the gel sample. Since the surface area of the inner part of the gel becomes smaller with the increasing degree of swelling, the reswelling process slows down after the initial rapid swelling period.

Moreover, the decrease of the reswelling rate of gels with increasing PEG content can be explained with the collapse of the porous structure in PNIPA hydrogels. The collapse of the pores in the PNIPA network can be ascribed to the cohesional forces, when the solvated PNIPA chains are approaching each other due to the loss of water. As reported before,[33] the pores in PNIPA networks with a low crosslink density are unstable and, thus, they disappear in the shrunken state of the gel. As seen in Figure 2, the modulus of elasticity, that is, the effective crosslink density, decreases with increasing PEG content. This suggests that the polymer chains, which are phase separated during the crosslinking reactions in a PEG solution, induce a loose pore structure, which can easily collapse during the shrinking process. Thus, since all the collapsed gel samples at 48°C behave as nonporous materials, the reswelling time increases as the initial gel mass decreases, i.e., as the PEG content increases.

Effect of gel preparation temperature

In this section, gelation experiments reported above were carried out at 50°C instead of 9°C. In Figure 5,

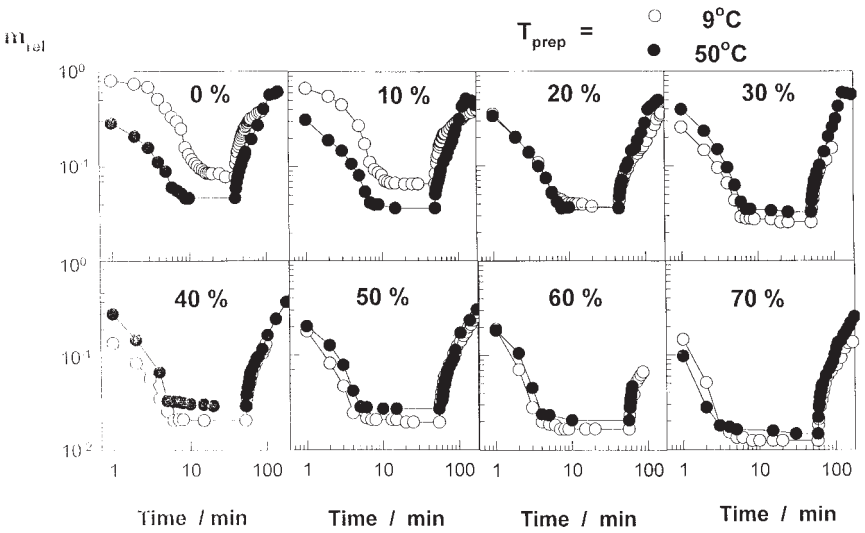

Figure 5 Comparison of deswelling–reswelling behavior of PNIPA hydrogels prepared at 9°C (○) and 50°C (●). PEG-300 contents used in the hydrogel preparation are indicated.

the deswelling–reswelling kinetics of PNIPA gels formed at 50°C (filled symbols) is compared with those formed at 9°C (open symbols). In accord with the previous results, the deswelling response rate becomes faster while the reswelling rate becomes slower as the amount of PEG present in the gel formation system is increased. Moreover, if the PEG content is 20% or more, both 9 and 50°C gels exhibit the same deswelling–reswelling cycles. A difference between the two series of gels appears if the PEG content is less than 20%: In this range of PEG, the gels formed at 50°C show a much more rapid deswelling course than those prepared at 9°C. Also, the reswelling course becomes faster by increasing the gel preparation temperature T_{prep} from 9 to 50°C.

For a temperature–sensitive polymer such as PNIPA, increasing T_{prep} above its LCST will induce a phase separation during the polymerization reactions, so that the gels formed at $T_{prep} > T_{LCST}$ are expected to exhibit a more rapid deswelling–reswelling course than those formed below LCST. This explanation is supported by our gelation experiments conducted in water or in 10% PEG solutions (Figure 5). However, experiments conducted in PEG solutions with more than 10% PEG show no T_{prep} effect on the swelling kinetics of PNIPA gels. This unexpected result can be explained with the equilibrium swelling behavior of PNIPA gels in PEG solutions. As we reported recently,[36,37] if the PEG content in the external solution is above 20%, the temperature does not affect the swelling behavior of PNIPA gels. Thus, the gels become temperature-insensitive in PEG solutions with more than 20% PEG. This is due to the fact that replacing water with PEG in the swelling medium reduces the extent of H-bonding interactions so that the van der Waals interactions dominate the swelling process. Accordingly, if the same PEG solutions are used as the polymerization solvent for NIPA, the growing PNIPA chains during gelation will not be affected from the gel preparation temperature T_{prep}; thus, the hydrogels prepared both at 9 and 50°C will show the same swelling behavior. However, in water or in dilute PEG solutions, H-bonding interactions dominate the swelling process of PNIPA gels and, therefore, they exhibit temperature sensitivity. Thus, if T_{prep} is 50°C, the growing PNIPA chains separate out of the gel phase and lead to the formation of macroporous hydrogels with a high swelling capacity. However, if T_{prep} is 9°C, which is below the LCST of PNIPA, the growing chains remain in the solution phase and result in a less porous hydrogel matrix with a relatively low swelling capacity.

Effect of the crosslinker content

In the previous sections, the concentration of the crosslinker BAAm was fixed at 1.2 mol %. From the literature,[14,31–33] it is well known that the crosslinker content also affects significantly the porosity of the networks. Therefore, in this section, we prepared a series of PNIPA gels with various amounts of the crosslinker BAAm, while T_{prep} and PEG content were fixed at 9°C and 70%, respectively. In Figure 6, the reswelling–deswelling cycles of PNIPA gels with various amounts of BAAm are presented. It is seen that the time to attain the equilibrium collapsed state is 4, 6, and 15 min for gels with 1.2, 3.9, and 9.1 mol % BAAm, respectively. Moreover, the higher the crosslinker content, the higher the mass of the equilibrium collapsed gel at 48°C. Thus, both the deswelling response rate of the hydrogels and the total amount of lost water during deswelling decrease with

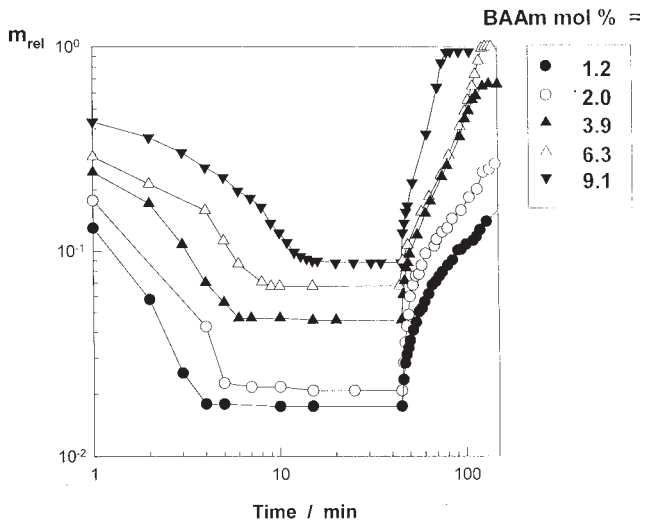

Figure 6 Deswelling–reswelling kinetics of PNIPA hydrogels of various BAAm contents. T_{prep} = 9°C. The crosslinker contents are indicated.

increasing crosslinker content. This is probably due to the reduction in the mesh size of gel on raising the crosslinker content, which slows down the diffusion rate of water molecules out of the gel phase. However, in contrast to the deswelling behavior, the reswelling of gels becomes faster on raising the crosslinker content. Also, the two-step reswelling profile observed at low crosslinker contents becomes a single step as the crosslinker content is increased. These results can be explained with increasing stability of the porous structure in PNIPA hydrogels on raising the crosslinker content, which prevents the collapse of the porous structure during the shrinking process.

Comparison of the response rate of PNIPA hydrogels with that of a PNIPA cryogel

From the above results, one may conclude that a PNIPA hydrogel with the fastest response rate to an external temperature change between 25 to 48°C can be prepared in 70% PEG solution at T_{prep} = 9 or 50°C and in the presence of 1.2% BAAm. The deswelling–reswelling cycle of this gel is replotted in Figure 7 by the filled symbols. To compare the response rate of this gel with PNIPA cryogels, we prepared a PNIPA cryogel at –25°C in ice, as reported in the literature.[19,20] The deswelling–reswelling cycle of this gel is also shown in Figure 7 by the open symbols. It is seen that the cryogel deswells much faster than the gel formed in PEG solution. Their deswelling times are 1 and 4 min, respectively. Moreover, the reswelling of the cryogel also occurs much faster than the PNIPA gel. In contrast to these disadvantages of PNIPA hydrogels formed in PEG solution, they release a much larger amount of water compared to the cryogel. As seen in Figure 7, m_{rel} in the equilibrium collapsed state is 0.01 and 0.3 for the hydrogel and for the cryogel, respectively. Thus, PNIPA hydrogels formed in PEG solutions are suitable in application areas, where the total amount of water released in a long run is important.

CONCLUSIONS

In many gel applications, the swelling and shrinking kinetics are very important. In the present work, we investigated the optimum synthesis parameters for the preparation of fast-responsive PNIPA hydrogels. PEG-300/water mixtures of various compositions were used as the polymerization solvent and as a pore-forming agent during the network formation process. In our experiments, the amount of PEG in the polymerization solvent, the crosslinker (BAAm) content, and the gel preparation temperature (T_{prep}) were varied. The hydrogels were characterized by the equilibrium swelling and elasticity tests as well as by the measurements of the deswelling–reswelling kinetics of the hydrogels in response to a temperature change between 25 and 48°C. The rate of deswelling of the swollen gel increases while the rate of reswelling of the collapsed gel decreases as the amount of PEG in the polymerization solvent is increased or as the crosslinker content is decreased. T_{prep} effect on the swelling kinetics of the hydrogels was only observed if the PEG content of the polymerization solvent was less than 20%, which is explained with the screening of H-bonding interactions in concentrated PEG solution.

Increasing deswelling rate of swollen hydrogels with increasing PEG concentration was explained

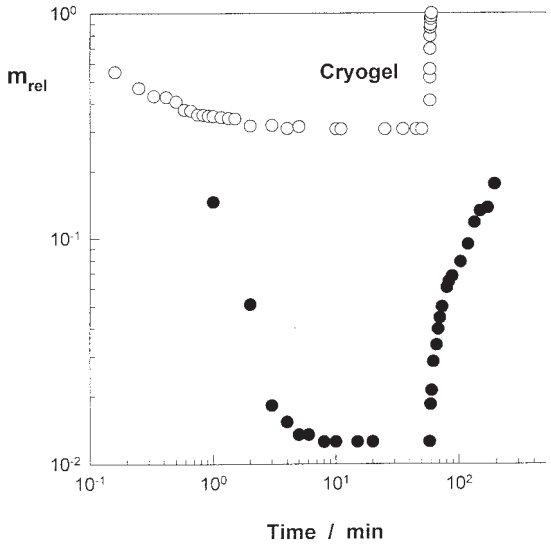

Figure 7 Comparison of deswelling–reswelling kinetics of PNIPA hydrogel formed in 70% PEG solution with that of a PNIPA cryogel prepared at —-25°C.

with the action of PEG-300 as a pore-forming agent during the gelation process. The porous structure formed in the presence of PEG-300 allows an easy diffusion of water molecules outside of the gel phase. Moreover, the decrease of the reswelling rate of gels with increasing PEG content was explained with the collapse of the porous structure in PNIPA hydrogels. Since increasing crosslinker content also increases the stability of the pore structure in PNIPA networks, an enhancement in the reswelling rate of the collapsed gels was observed by raising the crosslinker concentration.

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