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Formation of macroporous poly(acrylamide) hydrogels in DMSO/water mixture: Transition from cryogelation to phase separation copolymerization

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ABSTRACT

Poly(acrylamide) hydrogels were prepared by free-radical crosslinking copolymerization of acrylamide and *N*,*N*′-methylenebis(acrylamide) at −18 °C in aqueous DMSO solutions of various composition. The hydrogels formed in the solvent mixture with less than 25% DMSO by volume have irregular large pores of about 10^1 μm in diameter, typical for macroporous networks created by the cryogelation technique. Non-porous hydrogels were obtained in solutions containing 25% DMSO, while at larger DMSO contents, the structure of the hydrogel networks consists of aggregates of microspheres, which looks as cauliflowers, typical for a macroporous network formed by reaction-induced phase separation mechanism. Swelling measurements show that fast responsive PAAm hydrogels can be obtained as the DMSO content in the mixed solvent is decreased or increased starting from 25 v/v%. The results were interpreted as the transition from cryogelation to the phase separation copolymerization due to the marked freezing point depression of the solvent mixture as well as due to the action of the mixed solvent as a poor solvating diluent at −18 °C. It was also shown that the initial temperature of the cryogelation reactions in water strongly affects the hydrogel properties. Hydrogels formed at an initial temperature T_{ini} of 0 °C were very tough and can be compressed up to about 100% strain without any crack development while those formed at T_{ini} = 21 °C were fragile.

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1. Introduction

Hydrophilic gels called hydrogels are hydrophilic polymer networks swollen in water. They exhibit drastic volume changes in response to specific external stimuli, such as the temperature, solvent quality, pH, and electric field [1,2]. These properties of hydrogels received considerable interest in the last three decades. They are useful materials for drug delivery systems, artificial organs, separation operations in biotechnology, processing of agricultural products, on–off switches, sensors, and actuators. Despite this fact and considerable research in this field, the design and control of hydrogel-based devices still present some problems since a number of network properties are inversely coupled. For example, decreasing the degree of crosslinking of hydrogels in order to increase their mesh size ("molecular porosity") results in their accelerated chemical degradation. Further, loosely crosslinked hydrogels are soft and fragile materials when handled in the swollen state; typically, they exhibit moduli of elasticity in the order of kilopascals and fracture energy in the range of 10^{-1}–10^0 J/m^2, much smaller than the fracture energy of rubbers [3]. The poor mechanical performance of highly swollen hydrogels limits their technological applications. A fast response of hydrogels to the external stimuli is also a requirement in many application areas of these materials. However, the kinetics of hydrogel volume change involves absorbing or desorbing solvent by the polymer network, which is a diffusive process. This process is slow

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and even slower near the critical point. Increasing the response rate of hydrogels has been one of the challenging problems in the last 25 years.

A widely used approach to obtain fast-responsive hydrogels is to create voids (pores) inside the hydrogel matrix, so that the response rate becomes a function of the microstructure rather than the size or the shape of the gel samples. 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 non-porous hydrogels. There are two basic techniques to obtain crosslinked polymers with a macroporous structure. The first technique, called reaction-induced phase separation, involves the free-radical crosslinking copolymerization of the monomer-crosslinker mixture in the presence of an inert diluent, which is soluble in the monomer mixture [4–7]. In order to obtain macroporous structures, a phase separation must occur during the course of the gelation process so that the two-phase structure formed is fixed by the formation of additional crosslinks. After the polymerization, the diluent is removed from the network, leaving a porous structure within the highly crosslinked polymer network. Another technique to create a macroporous network structure is the use of inert templates in the preparation of hydrogels. By this technique, the polymer formation reactions are carried out in the presence of templates; a macroporous structure in the final hydrogel matrix appears after extraction of template materials. For example, by the cryogelation technique, the polymer formation reactions are carried out below the bulk freezing temperature of the reaction system [8]. Thus, the essential feature of such reaction systems is that the monomers and the initiator are concentrated in the unfrozen microzones of the apparently frozen system. The polymerization and crosslinking reactions proceed in the unfrozen microzones of the reaction system. A macroporous structure in the final material appears due to the existence of ice crystals acting as a template for the formation of the pores [9–15].

Here, we describe, for the first time based on our knowledge, the change of the formation mechanism of the porous structures in hydrogels from cryogelation to phase separation polymerization by simply varying an experimental parameter. By conducting the crosslinking polymerization of acrylamide in aqueous DMSO solutions, we were able to manipulate the porosity formation mechanism through the amount of DMSO present in the reaction system. DMSO is a polyfunctional molecule with a highly polar S=O group and two hydrophobic CH_3 groups. Its polar site can interact with water forming strong hydrogen bonds, and its non-polar sites can cause effects of hydrophobic hydration and hydrophobic association of DMSO molecules. Therefore, aqueous solutions of DMSO display interesting intermediate behavior not seen in either neat solvent and depart strongly from ideal behavior [16–18]. For example, Fig. 1 shows the freezing point of aqueous DMSO solutions plotted against the DMSO content. It is seen that DMSO–water mixtures exhibit a marked freezing point depression. In the present work, the gelation reactions were carried out at −18 °C. As seen in Fig. 1, the reaction system will freeze at −18 °C if the DMSO content is less than about 30 v/v%. Indeed, we observed formation of macroporous structures below 25 v/v% DMSO due to the cryogelation mechanism. However, at higher DMSO contents, materials with cauliflower morphology were obtained indicating that the porosity is induced by phase separation mechanism. This paper describes the transition condition from one to another mechanism by simply varying the mixed solvent composition. Most hydrogels, particularly macroporous hydrogels, are known to suffer from the lack of mechanical toughness. Here, we also report formation conditions of macroporous hydrogels with a high degree of toughness by adjusting the initial temperature of the crosslinking polymerization at −18 °C.

2. Experimental

2.1. Materials

Acrylamide (AAm), *N*,*N*′-methylenebis(acrylamide) (BAAm), ammonium persulfate (APS), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), and dimethyl sulfoxide (DMSO), all from Merck, Germany, were used as received. Stock solutions of APS and TEMED were prepared by dissolving 0.24 g APS and 0.50 mL TEMED each in 20 mL of distilled water. Poly(acrylamide) (PAAm) hydrogels were prepared by free-radical crosslinking copolymerization of AAm and BAAm in DMSO–water mixtures of various composition. To obtain macroporous structures, the gel preparation temperature T_{prep} was set to −18 °C. Control experiments were carried out similarly, except that T_{prep} was 22 °C. The initial concentration of the monomers (AAm + BAAm) as well as the crosslinker ratio *X*, that is, the mole ratio of the crosslinker BAAm to the monomer AAm, were fixed at 0.15 g/mL and 1/80, respectively. The reaction time was also set to 24 h. APS (5.26 mM) and

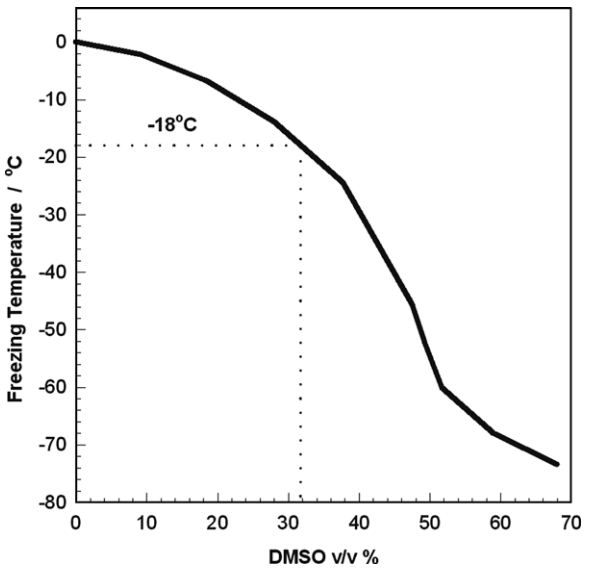

Fig. 1. Freezing temperature of aqueous DMSO solutions shown as a function of their DMSO content by volume percent. Data were taken from [16,17].

TEMED (0.25 mL/100 mL reaction solution) were used as the redox initiator system. The following example illustrates the synthetic procedure for hydrogels prepared in 50 v/v% DMSO/water mixture: 1.46 g AAm, 0.0396 g BAAm, water (3 mL), DMSO (5 mL), and TEMED stock solution (1 mL) were first mixed in a graduated flask of 10 mL in volume. The solution was purged with nitrogen gas for 10 min at 21 °C and then APS stock solution (1 mL) was added. The solution was transferred to a plastic syringe of 4.4 mm in diameter, immersed in a thermostated bath at T_{prep}, and the polymerization was conducted for one day. After polymerization, the syringe was taken out of the bath and the gel rod was removed from the syringe. The gel was cut into specimens of approximately 10 mm in length and immersed in a large excess of water at 21 °C to wash out any soluble polymers, unreacted monomers, and the initiator. In order to obtain PAAm networks, the equilibrium swollen gel samples were taken out of water and immersed in acetone followed by drying under vacuum at 40 °C.

2.2. Gel fraction measurements

For the gel fraction measurements, the hydrogel samples were extracted with water at least for one month. For this purpose, each hydrogel sample was placed in an excess of water at 21 °C and water was replaced several times. The gel fraction W_g was calculated as

$$W_g = \frac{m_{dry}}{m_o c_M} \quad (1)$$

where m_{dry} and m_o are the weights of the gel samples after drying and just after preparation, respectively, and c_M is the initial monomer concentration (0.15 g/mL).

2.3. Swelling measurements

For the swelling measurements, the hydrogel samples after preparation in the form of rods of 4.4 mm in diameter and about 10 mm length were placed in an excess of water at 21 ± 0.5 °C. In order to reach swelling equilibrium, the hydrogels were immersed in water for at least two weeks replacing the water every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples by using an image analyzing system consisting of a microscope (XSZ single Zoom microscope), a CDD digital camera (TK 1381 EG), and a PC with the data analyzing system Image-Pro Plus. The swelling equilibrium was also tested by weighing the gel samples. Thereafter, the hydrogel samples equilibrium swollen in water were dried as described above to constant weight. The equilibrium volume and the equilibrium weight swelling ratios of the hydrogels, q_v and q_w, respectively, were calculated as

$$q_v = (D_w/D_{dry})^3 \quad (2)$$

$$q_w = m_w/m_{dry} \quad (3)$$

where D_w and D_{dry} are the diameters of the equilibrium swollen and dry gels, respectively, m_w and m_{dry} are the weights of gels after equilibrium swelling in water and after drying, respectively.

For the measurement of the deswelling times of gels, the equilibrium swollen hydrogel samples in water were immersed in acetone at 21 °C. The volume changes of gels were measured in situ by following the diameter of the samples under microscope using the image analyzing system. For the measurement of the swelling times of gels, the collapsed gel samples in acetone were transferred into water at 21 °C. The diameter changes of gels were also determined as described above. The normalized swelling ratio V_{rel} at a given swelling time t was calculated as

$$V_{rel} = (D/D_w)^3 \quad (4)$$

where D is the diameter of the gel sample at time t.

2.4. Elasticity tests

Uniaxial compression measurements were performed on equilibrium swollen gels in water. All the mechanical measurements were conducted in a thermostated room of 21 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus previously described [19,20]. Briefly, a cylindrical gel sample of 4–8 mm in diameter and 7–15 mm in length was placed on a digital balance (Sartorius BP221S, readability and reproducibility: 0.1 mg). A load was transmitted vertically to the gel through a rod fitted with a PTFE end-plate. The compressional force acting on the gel was calculated from the reading of the balance. The resulting deformation was measured after 20 s of relaxation by using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of 10^{-3} mm. The measurements were conducted up to about 15% compression. From the repeated measurements, the standard deviations in the modulus value were less than 3%. The elastic modulus G was determined from the slope of linear dependence [21],

$$f = G(\alpha - \alpha^{-2}) \quad (5)$$

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).

2.5. Texture determination

For the texture determination of dried hydrogels, scanning electron microscopy studies were carried out at various magnifications between 50 and 3000 times (Jeol JSM 6335F Field Emission SEM). Prior to the measurements, network samples were sputter-coated with gold for 3 min using Sputter-coater S150 B Edwards instrument.

3. Results and discussion

We discuss the results of our experiments in two subsections. In the first subsection, development of a macroporous structure in poly(acrylamide) (PAAm) hydrogels depending on the mixed solvent composition is discussed. In the second subsection, the possibility of obtaining tough PAAm hydrogels is discussed and experimental observations are interpreted.

3.1. Porosity formation

Crosslinking copolymerization of AAm/BAAm comonomer system was carried out at −18 °C in aqueous DMSO solutions. Control reactions were carried out at 22 °C. If the DMSO content is more than 60 v/v% in the solvent mixture, no gel formation was observed at −18 °C. Fig. 2 shows the weight fraction of gel W_g and the modulus of elasticity of swollen hydrogels G plotted as a function of DMSO% of the reaction solution. Filled and open symbols are the results of measurements on gels prepared at −18 and 22 °C, respectively. Independent of the gelation temperature, the gel fraction W_g, that is the conversion of monomer to the crosslinked polymer, is almost complete up to about 25 v/v% DMSO, whereas it slightly decreases as the DMSO% is further increased. Complete monomer conversion even at −18 °C is due to the high monomer concentration in the unfrozen reaction zones of the apparently frozen reaction system [13,14]. Thus, when the reaction solution is cooled down to −18 °C, solvent freezes while the solutes (AAm, BAAm, APS, and TEMED) expelled from the solvent crystals accumulate in the liquid phase, in which the reactions proceed. It seems that the decrease of the rate constants of polymerization and crosslinking reactions at −18 °C is compensated by the increased monomer concentration in the reaction zones so that the gel fraction is unaffected by T_{prep}. Similar to the gel fraction results, the elastic behavior of gels is almost independent of temperature in the range of 0 to 25 v/v% DMSO (Fig. 2B). In this range, the gels exhibit an elastic modulus of about 20 kPa. As the DMSO content is further increased, the elastic modulus of low temperature gels rapidly decreases and approaches to 10^2 Pa at 60 v/v% DMSO.

Fig. 3A and B shows the equilibrium weight (q_w) and volume swelling ratios (q_v) of the hydrogels prepared at −18 and 22 °C, respectively, plotted against the DMSO content of the reaction solution. For the room temperature gels, both q_w and q_v are equal and slightly increasing function of DMSO%. However, low temperature gels exhibit non-monotonic volume swelling behavior with a maximum appearing at about 20 v/v% DMSO at which q_v becomes equal to q_w. The relative values of q_w and q_v of gels provide information about their internal structure in the swollen state. This is due to the fact that the weight swelling ratio includes the solvent locating in both pores and in the polymer region of the gel, while, assuming isotropic swelling, the volume swelling only includes the solvent in the polymer region. Thus, the larger the difference between q_w and q_v, the larger the amount of solvent in the pores, i.e., the larger the total volume of pores. From the weight and volume swelling ratios of PAAm hydrogels, their swollen state porosities P_s can be estimated using Eq. (5):

$$P_s\ \% = \left(1 - \frac{q_v}{1 + (q_w - 1)d_2/d_1}\right) \times 10^2 \qquad (6)$$

where d_1 and d_2 are the densities of the swelling agent (water) and the polymer, respectively. Assuming that d_1 = 1.0 g/mL and d_2 = 1.35 g/mL, the swollen state porosities P_s were calculated and are shown in Fig. 3C and D plotted against DMSO% for gels prepared at −18 and 22 °C, respectively. The gels formed at room temperature exhibit negligible porosities in the swollen state while those formed at −18 °C are porous outside of the range of about 15 to 25 v/v% DMSO. The swollen state porosity increases as the DMSO content is decreased or increased from 15 to 25 v/v%.

To visualize the pores in PAAm hydrogels, the network samples were investigated by scanning electron microscopy (SEM). As expected, the entire room temperature gel networks were non-porous. Fig. 4 shows SEM images of the network samples prepared at −18 °C in DMSO/water mixture of various compositions, as indicated in the figure. In accord with Fig. 3C, the gels prepared in 25 v/v% DMSO exhibit glass-like fracture surfaces at the dry state but without pronounced microstructure. However, the gels

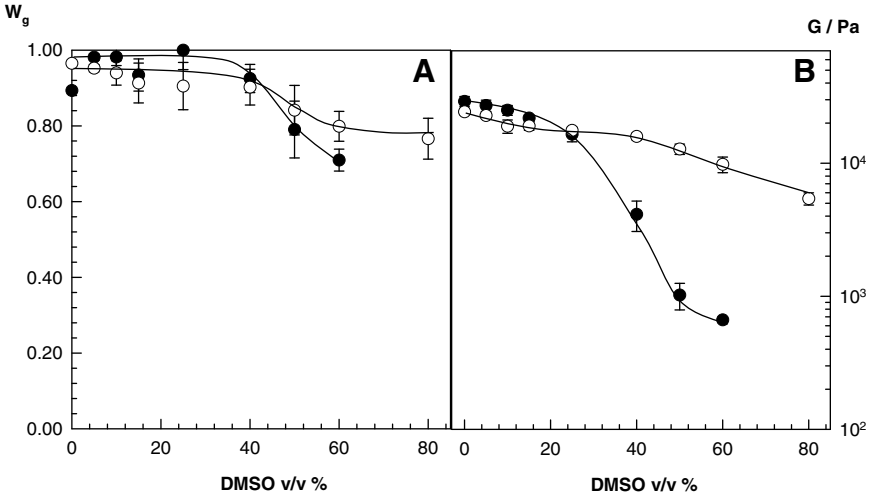

Fig. 2. The weight fraction of gel W_g (A) and the modulus of elasticity of swollen hydrogels G (B) plotted as a function of DMSO% of the reaction solution. Filled and open symbols are the results of measurements on hydrogels prepared at −18 and 22 °C, respectively. The curves only show the trend of data.

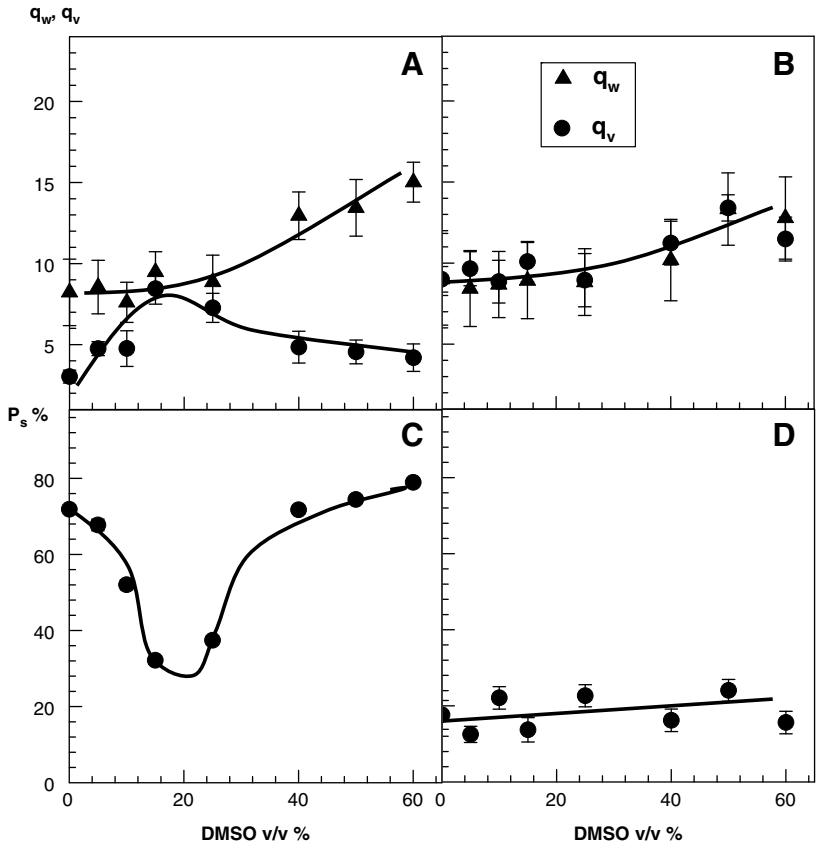

Fig. 3. The equilibrium weight (q_w, triangles) and volume swelling ratios (q_v, circles) of PAAm hydrogels plotted against the DMSO content of the reaction solution. T_{prep} = −18 (A) and 22 °C (B). The swollen state porosities P_s calculated using Eq. (6) shown as a function of DMSO% for the hydrogels prepared at T_{prep} = −18 (C) and 22 °C (D). The curves only show the trend of data.

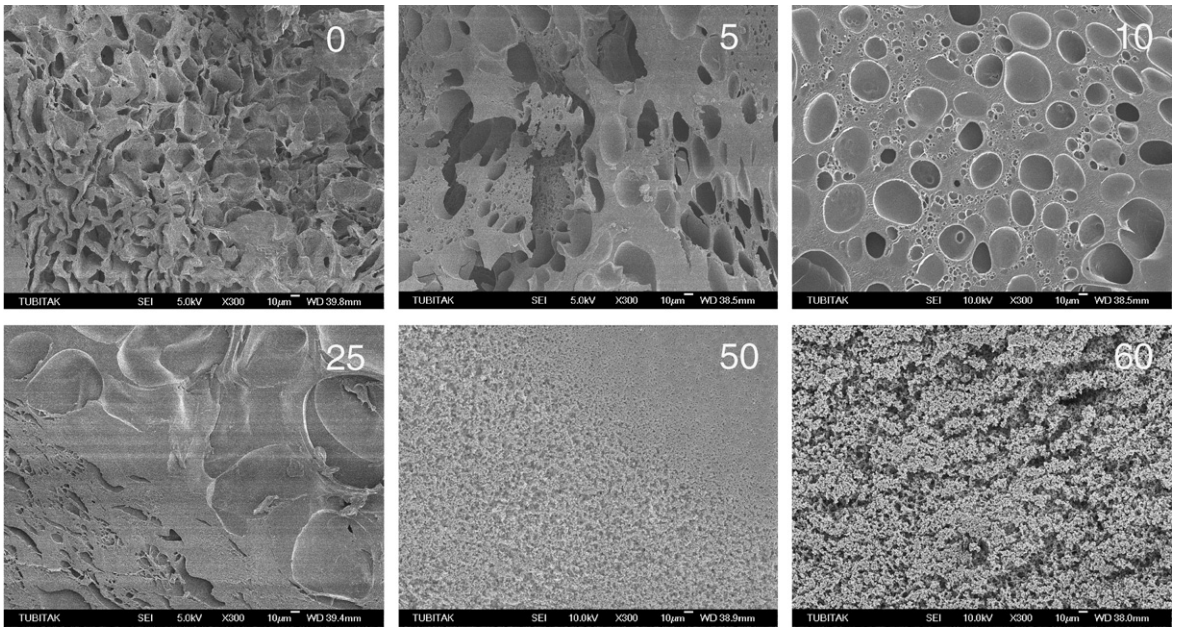

Fig. 4. SEM images of PAAm network samples prepared at −18 °C in DMSO/water mixture of various compositions. DMSO v/v% in the mixed solvent is indicated in the pictures. Magnification = 300×. Scaling bars are 10 μm.

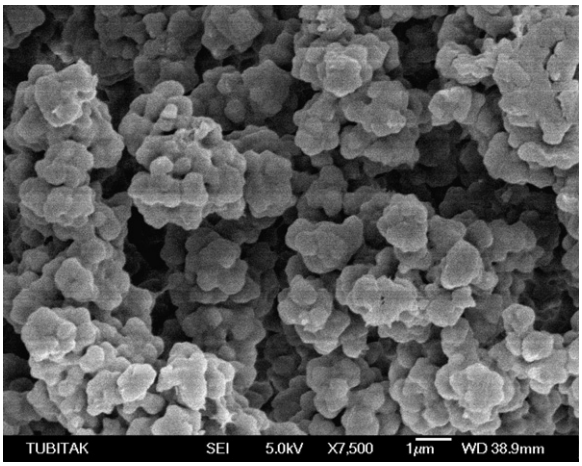

Fig. 5. SEM image of the network sample prepared at −18 °C in an aqueous DMSO solution containing 60 v/v% DMSO. Magnification = 7500×. Scaling bar is 1 μm.

formed below or above 25 v/v% DMSO have a porous structure; those formed below 25 v/v% DMSO have irregular large pores of about 10^1 μm in diameter, typical for macroporous networks created by the cryogelation technique [13]. However, those obtained above 25 v/v% DMSO have relatively small pores. Fig. 5 shows the SEM image of −18 °C gel prepared in 60 v/v% DMSO at a larger magnification than in Fig. 4. The morphology consists of aggregates of 3–5 μm dimensions of well-defined microspheres. Two generation of pores building the microstructure of the gel network can be seen from the SEM image; one submicrometer-sized pores between the microspheres and the other micrometer-sized pores between the aggregates. The microspheres are about 0.1–0.5 μm in diameter. Thus, the structure of the networks formed above 25 v/v% DMSO looks like cauliflowers, typical for a macroporous copolymer network formed by reaction-induced phase separation mechanism [5].

Fig. 6 compares the response rate of the hydrogels prepared at −18 °C (filled symbols) and at 22 °C (open symbols). Here, the normalized gel volume V_{rel} (volume of gel at time t/equilibrium swollen volume in water) is plotted against the time t of deswelling in acetone and re-swelling in water. Both the swelling and deswelling rates of −18 °C gels prepared in water or in 50 v/v% DMSO solution are much faster than those prepared at 22 °C. The low temperature gel attains its equilibrium collapsed and equilibrium swollen states within 5–10 min, while the conventional gel requires 60 and 300 min to attain the equilibrium states in acetone and in water, respectively. The semilogarithmic plots in Fig. 7 show the relative volume V_{rel} of low temperature gels prepared in aqueous DMSO solution of various compositions plotted against the swelling time in water. It is seen that the time to attain the equilibrium swollen gel state increases, that is, the response rate decreases as the DMSO content is increased up to 25 v/v% (Fig. 7A); at this DMSO concentration, the response rate of the low temperature gel is almost equal to that of the room temperature gels. Further increase in the DMSO% again increases the response rate of the hydrogels (Fig. 8B). Similar findings were also observed during the deswelling processes of the hydrogels in acetone. Since creation of pores inside the hydrogel matrix increases its response rate, these results are in accord with the microscopic observation of the network structures reported above. Thus, fast responsive PAAm hydrogels form as the DMSO content in the mixed solvent is decreased or increased starting from 25 v/v%.

Our experimental results are consistent with the following scenario: As reported in the literature, macroporous structures by the cryogelation mechanism start to appear at polymerization temperatures about 8 °C below the freezing point of the reaction system [13–15]. Thus, to obtain macroporous PAAm gels at −18 °C, the freezing

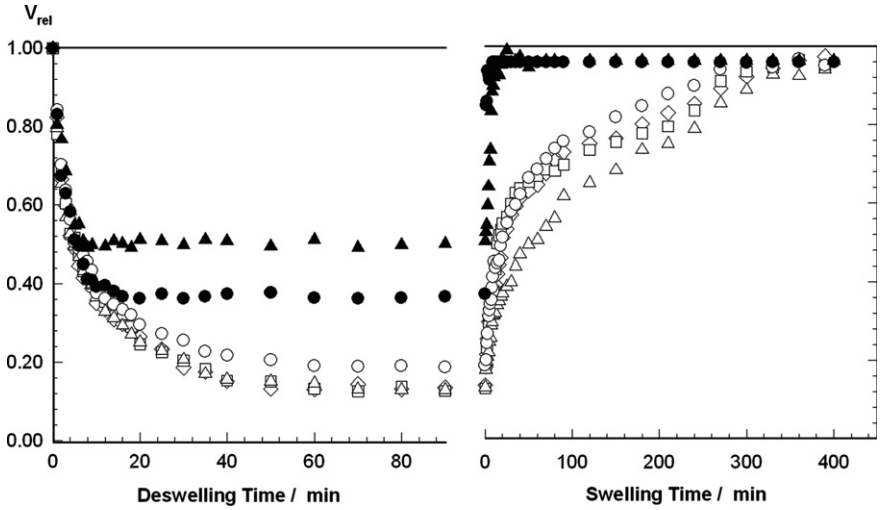

Fig. 6. Deswelling and swelling kinetics of PAAm hydrogels in acetone and in water, respectively, shown as the variation of the gel volume V_{rel} with the time of deswelling or re-swelling. T_{prep} = 22 °C, DMSO v/v% = 0 (○), 25 (◇), 40 (□), and 60 (△). T_{prep} = −18 °C, DMSO v/v% = 0 (●), 50 (▲).

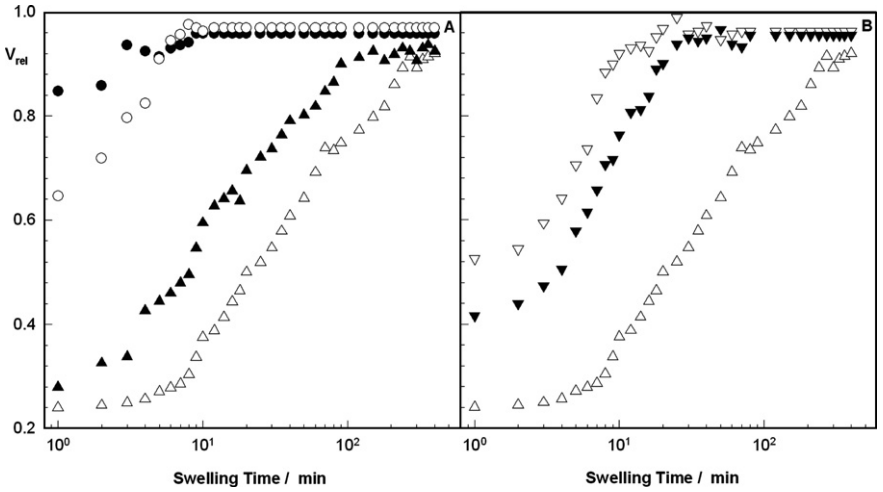

Fig. 7. Swelling kinetics of PAAm hydrogels in water shown as the variation of the gel volume V_{rel} with the time of swelling. $T_{prep} = -18$ °C. DMSO v/v% = 0 (●), 5 (○), 10 (▲), 25 (△), 40 (▼), and (▽). (A) and (B) show the DMSO ranges between 0 and 25, and 25 and 50 v/v%, respectively.

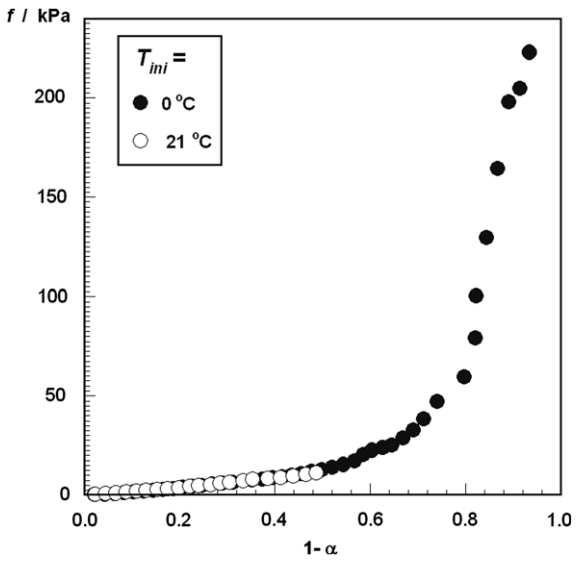

Fig. 8. Stress–strain data of PAAm hydrogels prepared in water at $T_{prep} = -18$ °C as the dependence of f on fractional deformation $1 - \alpha$. The initial temperature of polymerization T_{ini} is indicated. The hydrogel samples subjected to the mechanical tests up to complete compression were 16 mm in diameter and about 10 mm in length.

point of the reaction solution should be −10 °C, which corresponds to a DMSO concentration of 23 v/v% (Fig. 1). Accordingly, at DMSO contents below 23 v/v%, porous structures in PAAm hydrogels should form due to the cryogelation where the solvent crystals in the reaction system act as a template. Indeed, SEM images of the gel networks formed below 25 v/v% DMSO are typical for those of the cryogels.

At larger DMSO contents, one would expect formation of non-porous hydrogels due to the fact that the reaction system is unfrozen at −18 °C (Fig. 1). In contrast, however, only gels formed around 25 v/v% DMSO were found to be non-porous while at larger DMSO contents, macroporous hydrogels with cauliflower morphology were obtained. Thus, formation of macroporous PAAm hydrogels in this range of DMSO should be a result of a phase separation process with the action of DMSO/water mixture as an inert diluent. To explore the condition of phase separation during the reactions, we investigated the swelling capacity of the hydrogels in the mixed solvents at −18 °C. We found that the gels are in a collapsed state in aqueous DMSO solutions containing more than 30 v/v% DMSO indicating that the mixed solvent is a poor solvating diluent for PAAm at −18 °C. Indeed, recent work also shows that DMSO/water mixture of 1:1 by volume is a poor solvent for PAAm at subzero temperatures [22]. Thus, the polymer chains formed during the reaction at subzero temperatures undergo a deswelling transition, which is responsible for the formation of macroporous hydrogels in the mixed solvent containing more than 25 v/v% DMSO.

3.2. Effect of the initial temperature of polymerization

In the previous section, macroporous PAAm hydrogels were prepared by setting the gel preparation temperature T_{prep} to −18 °C. However, T_{prep} is the temperature of the thermostated bath in which the reactions were carried out. Since the polymerization initiator APS was added into the monomer solution before the freezing of the reaction system, i.e., at 21 °C, the polymerization and crosslinking reactions proceed non-isothermally from the moment of the initiator addition to the moment when the temperature of the reaction system reaches to T_{prep}. In this section, we investigated the effect of the initial temperature of the polymerization (T_{ini}) on the hydrogel properties. Experiments were carried out at $T_{prep} = -18$ °C and under the same experimental conditions as described above, except that the initiator APS was added to the reaction system at $T_{ini} = 0$ and 21 °C. The reactions were conducted both in water (cryogelation) and in aqueous DMSO solution with 60 v/v% DMSO (phase separated polymerization).

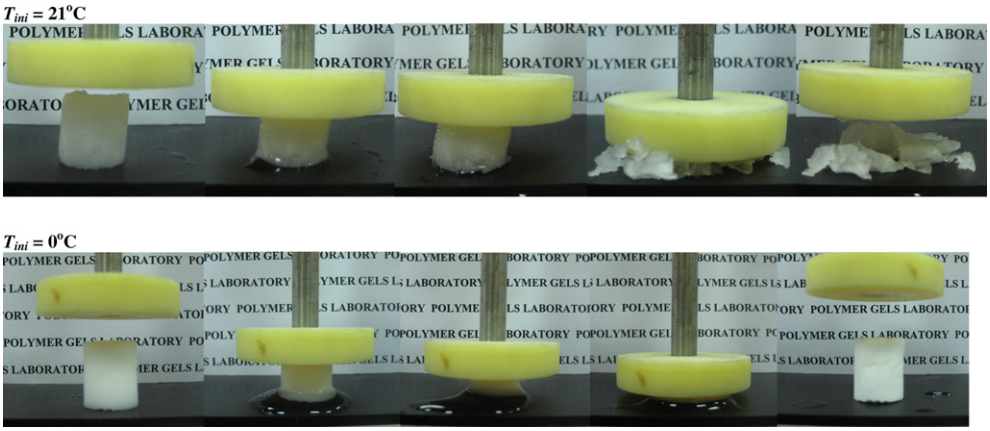

Fig. 9. Photographs of PAAm hydrogels formed at −18 °C during the compression tests. T_{ini} = 21 °C (upper panel) and 0 °C (bottom panel).

Not surprisingly, the hydrogels prepared in 60 v/v% DMSO exhibited similar properties independent on the initial temperature T_{ini}. This is due to the fact that the reaction system remains unfrozen during the crosslinking reactions and the extent of phase separation does not change much depending on the cooling rate. However, significant changes in the hydrogel properties were observed when the reactions were conducted in water. Decreasing T_{ini} from 21 to 0 °C decreased the modulus of elasticity of the swollen hydrogels from 30 to 13 kPa. Further, an important improvement in the degree of toughness of the hydrogels was observed by decreasing the initial temperature T_{ini}. Hydrogels formed at T_{ini} = 0 °C were very tough and can be compressed up to about 100% strain without any crack development while those formed at T_{ini} = 21 °C were fragile. This behavior is shown in Fig. 8 where the stress f is plotted against the fractional deformation (deformed length/initial length, $1-\alpha$) for gels formed using an initial temperature T_{ini} of 0 °C (filled symbols) and 21 °C (open symbols). Although the gels prepared at T_{ini} = 21 °C broke at a stress of 11 kPa and a strain of about 50%, those prepared at T_{ini} = 0 °C did not break even at a strain of more than 98%. Photographs in Fig. 9 also demonstrate how the hydrogel sample prepared at T_{ini} = 0 °C sustains a high compression. As shown in the upper panel of Fig. 9, the swollen gel prepared using T_{ini} = 21 °C fractured under relatively low deformation suggesting that cracks develop easily in the gel. However, those obtained at T_{ini} = 0 °C remain mechanically stable up to complete compression (bottom panel of Fig. 9). Important point is that, as the gel is squeezed under the piston, the gel releases all its water so that it can completely be compressed. After the release of the load and after the addition of water, the sample immediately recovers its original shape.

Fig. 10 shows SEM images of the gel networks prepared in water and at T_{ini} = 0 °C (left) and 21 °C (right). It is seen that decreasing the initial temperature of cryogelation decreases the size of the pores in the network. At the same time, the pore walls become thinner and a second generation of pores starts to appear with decreasing the initial polymerization temperature from 21 to 0 °C.

As the initial polymerization temperature is decreased, a longer period of the reactions takes place in the frozen state, which slows down the crosslinking reactions and leads to a twofold decrease in the elastic modulus of the hydrogels. Thus, the flexibility of the polymer making the

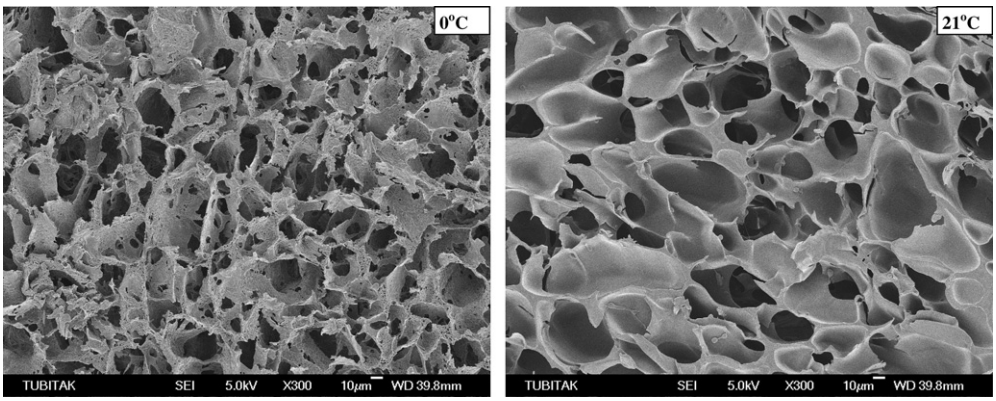

Fig. 10. SEM images of PAAm network samples prepared at −18 °C in water. The initial temperature T_{ini} is indicated. Magnification = 300×. Scaling bars are 10 μm.

pore walls increases by decreasing T_{ini} so that the hydrogel becomes mechanically stable even at very large deformation ratios. Further, formation of relatively thin pore walls and the existence of a second generation of pores within the pore walls may also contribute the stability of the materials formed at a lower initial polymerization temperature.

4. Conclusions

Free-radical crosslinking copolymerization of AAm/BAAm comonomers was carried out at −18 °C in aqueous DMSO solution of various compositions. PAAm hydrogels formed in the mixed solvent with less than 25 v/v% DMSO have irregular large pores of about 10^1 μm in diameter, typical for macroporous networks created by the cryogelation technique. Non-porous hydrogels were obtained in solutions with 25 v/v% DMSO. At larger DMSO contents, the structure of the hydrogel networks consists of aggregates of microspheres, which look like cauliflowers, typical for a macroporous network formed by reaction-induced phase separation mechanism. Swelling measurements show that fast responsive PAAm hydrogels can be obtained as the DMSO content in the mixed solvent is decreased or increased starting from 25 v/v%. The results were interpreted as the transition from cryogelation to the phase separation polymerization due to the marked freezing point depression of the solvent mixture as well as due to the action of the mixed solvent as a poor solvating diluent at −18 °C. It was also shown that the initial temperature of the cryogelation reactions in water strongly affects the hydrogel properties. Hydrogels formed at an initial temperature T_{ini} of 0 °C were very tough and can be compressed up to about 100% strain without any crack development while those formed at T_{ini} = 21 °C were fragile and broke at a strain of about 50%. Experiments are in progress to obtain fast responsive tough PAAm hydrogel beads by inverse suspension polymerization technique.

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