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Preparation of Macroporous Acrylamide-based Hydrogels: Cryogelation under Isothermal Conditions

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Macroporous hydrogels based on acrylamide, as well as on 2-acrylamido-2-methylpropane sulfonic acid monomers, were prepared using N,N'-methylenebis(acrylamide) crosslinker in frozen aqueous solutions. The cryogelation reactions at temperatures as low as -25°C were carried out isothermally by use of two techniques. First, after addition of the polymerization initiator into the reaction solution, the system was immediately cooled down to -196°C using liquid nitrogen and then, the system was immersed into a thermostate at the desired subzero temperature T_{prep} . It was found that the precooling of the reaction system before the onset of the reactions provides formation of superfast responsive hydrogels at temperatures close to the freezing point of water. The precooling step however destroyed the regularity of the pores in the hydrogel networks. As a second technique to achieve isothermal cryogelation, hydroquinone as the polymerization inhibitor was included into the reaction solution. It was shown that, the addition of hydroquinone produces more monodisperse and smaller pores. The hydrogels obtained by both techniques exhibit size-independent superfast swelling behavior in response to the external stimuli.

Keywords: macroporous hydrogels; freezing; swelling; response rate

1 Introduction

Responsive hydrogels are soft and smart materials, capable of changing volume in response to specific external stimuli, such as the temperature, solvent quality, pH, electric field, etc (1). These properties of the hydrogels received considerable interest and, a large number of hydrogel based devices have been proposed, including artificial organs, actuators, and on-off switches. However, the application of hydrogels is limited due to their slow rate of response, as well as due to their lack of mechanical strength. In order to increase the response rate of hydrogels, several techniques were proposed, such as reducing the size of the gel particles (2), creating dangling chains on the gel samples (3), or, constructing an interconnected pore structure within the hydrogel matrices (4).

Hydrogels with a macroporous structure are usually prepared by a reaction-induced phase separation technique (4, 5). In this technique, an inert diluent is used as a pore forming agent during the gel formation process. Phase separation before or after the macroscopic gel point leads to the formation of polymer domains of various sizes. The

interstices between these domains after the completion of the reactions constitute the porous structure of the hydrogels. The sizes of the pores in these materials vary from a few nanometers up to micrometers. The macroporous hydrogels formed by phase separation are, however, mechanically weak and they exhibit brittle properties. Further, since a large amount of crosslinker has to be used to induce a phase separation during gelation, the network chains do not behave like flexible polymer chains sensitive to the external stimuli.

Another technique is the cryogelation technique, in which the polymerization-crosslinking reactions are conducted in apparently frozen reaction solutions (6–10). During freezing of the monomer solution, the monomers expelled from the ice concentrate within the channels between the ice crystals, so that the reactions only take place in these unfrozen liquid channels. After polymerization and, after melting of ice, a porous material is produced whose microstructure is a negative replica of the ice formed. The advantage of these so-called “cryogels” compared to the macroporous hydrogels obtained by phase separation is their high mechanical stability. They are very tough, and can withstand high levels of deformations, such as elongation and torsion; they can also be squeezed under mechanical force to drain out their solvent content (11). The improved mechanical properties of cryogels originate from the high monomer content of the

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unfrozen liquid channels of the reaction system. Thus, after polymerization, the gel channels with high polymer content are perfect materials for building the pore walls. Recently, we have shown that by conducting the copolymerization-crosslinking reactions below -8°C , hydrogels based on acrylamide (AAM) as well as on 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) monomers with superfast swelling properties could be obtained (11–14).

N,N'-methylenebis(acrylamide) (BAAM) was the crosslinker used in the hydrogel preparation. A typical SEM image of such materials in their dried states is shown in Figure 1 illustrating their honeycomb morphology, which significantly differs from macroporous gel networks obtained by phase separation mechanism. The network structure shown in Figure 1 is due to the freezing of the free water in the gel causing the network chains to gather and condense so that a heterogeneous network forms after removing the ice.

Our previous work showed the variation of the hydrogel properties such as the elasticity, degree of swelling and morphology depending on the synthesis parameters (11–13). The main experimental parameter in the preparation of such hydrogels was found to be the gel preparation temperature T_{prep} , which is the temperature of the thermostated bath in which the reactions were carried out. To obtain macroporous networks, the reaction system should be in an apparently frozen state at the temperature T_{prep} . However, since the polymerization initiator should be added into the monomer solution before freezing the reaction system, i.e., at 0°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} . For example, at $T_{prep} = -18^{\circ}\text{C}$, 1.5 mL of an aqueous 5 w/v% solution of AAM and BAAM in a glass tube of 4 mm in diameter freezes in 15 min, while the onset of gelation at a crosslinker ratio of 1/80 occurs within 20 min. Thus, gelation reactions occur non-isothermally during the cooling period from 0 to -18°C . Moreover, the

lower the gel preparation temperature T_{prep} , the shorter the time period until the freezing temperature of the reaction solution is reached. This means that the experimental parameter T_{prep} actually corresponds to the freezing rate of the reaction system. One may expect that, conducting gelation reactions under isothermal conditions would facilitate homogeneous nucleation of ice crystals so that the polymer network formed will exhibit monodisperse pores (15). Furthermore, isothermal gelation would also provide formation of porous structures at a temperature close to the freezing point of the reaction system.

The aim of the present work was to conduct the cryopolymerization reactions under isothermal conditions. Here, we applied two strategies: First, after addition of the initiator into the reaction solution, the system was immediately cooled down to -196°C using liquid nitrogen and then, the system was immersed into a thermostate at the desired T_{prep} value. The reactions before reaching T_{prep} were too slow so that a near isothermal condition can be provided. Second, hydroquinone as the polymerization inhibitor was included into the reaction solution. By adjusting the hydroquinone concentration in the reaction system, the onset of gelation can be shifted beyond the thermal equilibration point of the reaction solution with the surrounding thermostate. Two different reaction systems were investigated, namely AAM-BAAM and AMPS-BAAM comonomer pairs in aqueous solutions. Both systems were previously investigated under non-isothermal conditions (11, 12). As will be seen below, the pre-cooling step of the reaction solution in liquid nitrogen provides formation of macroporous networks at much higher subzero temperatures while the addition of hydroquinone produces more monodisperse and smaller pores. The hydrogels obtained by both techniques exhibit size-independent superfast swelling behavior in response to the external stimuli.

2 Experimental

2.1 Materials

Acrylamide (AAM, Merck), N,N'-methylenebis(acrylamide) (BAAM, Merck), ammonium persulfate (APS, Merck), N,N,N',N'-tetramethylethylenediamine (TEMED, Merck), and hydroquinone (Merck) were used as received. 2-acrylamido-2-methylpropane sulfonic acid (AMPS- H^+ , Merck) was crystallized from the boiling methanol. It was neutralized with NaOH and a stock solution was prepared containing 0.966 M AMPS. Stock solutions of APS and TEMED were prepared by dissolving 0.16 g APS and 0.50 mL TEMED, each in 20 mL of distilled water. Stock solutions of BAAM and hydroquinone were prepared by dissolving 0.132 g BAAM and 0.05 g hydroquinone each in 10 mL of distilled water.

Hydrogels were prepared by free-radical crosslinking copolymerization of AAM or AMPS monomers with

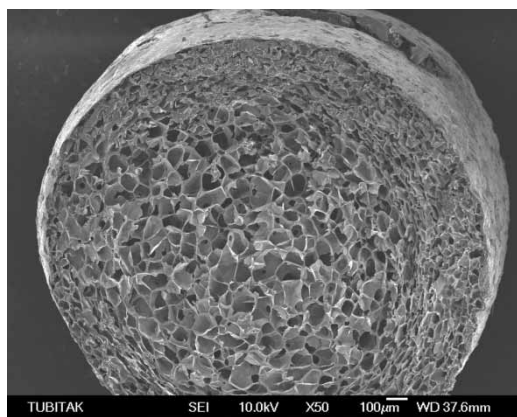


Fig. 1. SEM of PAAm networks prepared by cryogelation at $T_{prep} = -18^{\circ}\text{C}$, as described in Ref. (11). Initial monomer concentration = 3 w/v%. The crosslinker ratio $X = 1/80$. The scaling bar is 100 μm . Magnification = $\times 50$.

BAAm as a crosslinker in aqueous solutions. The initial concentration of the monomer and the crosslinker was 5 w/v%. The crosslinker ratio X , the molar ratio of the crosslinker BAAm to the monomer AAm or AMPS were fixed at 1/80, and 1/6, for polyacrylamide (PAAm) and poly(AMPS) (PAMPS) hydrogels, respectively. Thus, the synthesis conditions were identical as described previously (11, 12). The reaction time was set to 24 h. APS (3.51 mM) and TEMED (0.25 mL/100 mL reaction solution) were used as the redox initiator system.

As mentioned in the Introduction, two strategies were used to conduct isothermal cryogelation reactions. First, after addition of the APS initiator at 0°C, the reaction solution was immediately immersed in liquid nitrogen (−196°C) for 30 min before transferring into a thermostated bath at the desired subzero temperature T_{prep} . Second, hydroquinone was included into the reaction mixture to delay the onset of the reactions. The gelation reactions were carried out in the presence of various amounts of hydroquinone. To illustrate the synthetic procedure, we give details for the preparation of PAAm hydrogels in the presence of 0.2 w/w% hydroquinone (with respect to the mass of the monomer) and at a gel preparation temperature $T_{prep} = -18^\circ\text{C}$:

0.4868 g AAm, stock solutions of BAAm (1 mL), TEMED (1 mL), hydroquinone (0.2 mL), and distilled water (6.8 mL) were first mixed in a graduated flask of 10 mL in volume. The solution was cooled to 0°C in an ice-water bath, purged with nitrogen gas for 20 min and then, APS stock solution (1 mL) was added. Portions of this solution, each 1.5 mL, were transferred to glass tubes of about 4 mm in diameter, the glass tubes were sealed, immersed in a thermostated bath at $T_{prep} = -18^\circ\text{C}$ and the polymerization was conducted for one day. After polymerization, the gels were cut into specimens of approximately 10 mm in length and immersed in a large excess of water to wash out any soluble polymers, unreacted monomers and the initiator.

2.2 Methods

The gel fractions after the polymerization were determined by the extraction of the hydrogels in an excess of water and then drying the insoluble polymer to a constant mass. The details about the gravimetric determination of the conversions were given elsewhere (16). The gelation time during the cryogelation reactions was determined as the midpoint between the last time at which a soluble polymer was obtained and that at which the polymer was not soluble in water. For the equilibrium swelling measurements, hydrogel samples after preparation in the form of rods of 4 mm in diameter and about 10 mm length, were placed in an excess of water at room temperature ($21 \pm 0.5^\circ\text{C}$). 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 carefully deswollen in a series of water-acetone mixtures with increasing acetone contents. This solvent exchange process facilitated final drying of the hydrogel samples. They were then washed several times with acetone and dried at 80°C to a constant weight. The normalized volume swelling ratio V_{eq} of the hydrogels with respect to the state after preparation was calculated as:

$$V_{eq} = (D_w/D_0)^3 \quad (1a)$$

where D_w and D_0 are the diameters of the gel sample after equilibrium swelling in water and just after its preparation, respectively. The equilibrium volume and the equilibrium weight swelling ratios of the hydrogels, q_v and q_w , respectively, were calculated as:

$$q_v = (D_w/D_{dry})^3 \quad (1b)$$

$$q_w = (m_w/m_{dry}) \quad (1c)$$

where D_{dry} is the diameter of dry gels, m_w and m_{dry} are the weight of gels after equilibrium swelling in water and after drying, respectively.

For the deswelling kinetics measurements, the equilibrium swollen hydrogel samples in water were immersed in acetone at 21°C. The weight changes of gels were measured gravimetrically after blotting the excess surface solvent at regular time intervals. For the measurement of the swelling kinetics of gels, the collapsed gel samples in acetone were transferred into water at 21°C. The weight changes of gels were also determined gravimetrically as described above. The results were interpreted in terms of the relative weight swelling ratio $m_{rel} = m/m_w$, where m is the mass of the gel sample at time t .

Uniaxial compression measurements were performed on equilibrium swollen gels in water. All the mechanical measurements were conducted in a thermostated room of $21 \pm 0.5^\circ\text{C}$. The stress-strain isotherms were measured by using an apparatus previously described (5). The elastic modulus G was determined from the slope of linear dependence (17):

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

where f is the force acting per unit cross-sectional area of the undeformed gel specimen, and λ is the deformation ratio (deformed length/initial length).

For the texture determination of dry hydrogels, scanning electron microscopy studies were carried out at various magnifications between 50 and 300 times (Jeol JSM 6335F Field Emission SEM). Prior to the measurements, network samples were sputter-coated with gold for 3 min using a

Sputter-coater S150 B Edwards instrument. The texture of the hydrogels was also investigated under XSZ single Zoom microscope using the image analyzing system Image-Pro Plus.

3 Results and Discussion

3.1 Effect of Precooling of the Reaction Solution before Cryogelation

The gelation reactions of AMPS and BAAM were conducted in aqueous solutions at various temperatures T_{prep} between -25 and 20°C . To illustrate the effect of precooling, the hydrogels were prepared both with and without precooling of the reaction solutions. The hydrogels thus obtained are called as I-gels (isothermal gels), and N-gels (usual gels), respectively. After one day of the reaction time, gravimetric measurements showed that the gel fraction is higher than 85% for all the networks prepared in this study. Thus, reducing T_{prep} below the bulk freezing temperature of the reaction system does not decrease the amount of the cross-linked polymer in the crude hydrogels.

In the range of T_{prep} between -8 and -2°C , the precooling step prior to the gelation reactions significantly affected the properties and the microstructure of the hydrogels. For example, the images denoted by (A) and (B) in Figure 2 were taken from equilibrium swollen N- and I-gel samples,

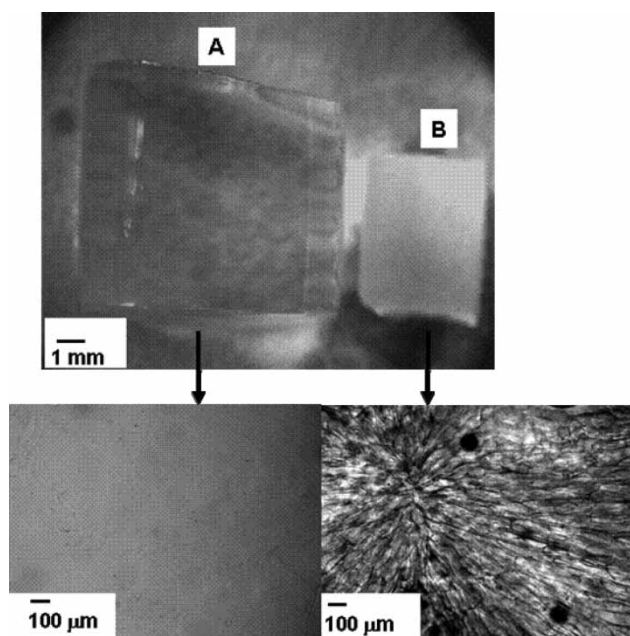


Fig. 2. Images of swollen PAMPS gel samples taken from the optical microscope. The gels were prepared without (A) and with precooling of the reaction solution (B). $T_{prep} = -2^\circ\text{C}$, $X = 1/6$. The scaling bars are 1 mm and 100 μm for the upper and lower figures. The initial diameters of the gel samples were 4.3 mm. In their swollen states, the diameters were 9.80 mm (A) and 4.65 mm (B).

respectively, both prepared at $T_{prep} = -2^\circ\text{C}$. Although the initial diameters of both gel samples after their preparation were the same (4.3 mm), the swollen volume of N-gel is about 10-fold larger than the volume of I-gel. Further, the N-gel was transparent, while the I-gel was opaque, both after preparation and after equilibrium swelling in water. The magnified images of the equilibrium swollen gel samples taken from the optical microscope also illustrate the structural differences between the two gel samples (Figure 2). While the N-gel is homogeneous in the swollen state, the I-gel exhibits a discontinuous morphology consisting of solvent and gel domains.

In Figure 3, the equilibrium volume swelling ratio V_{eq} and the modulus of elasticity G of swollen hydrogels are shown as a function of the gel preparation temperature T_{prep} . Filled and open symbols represent data points obtained from I- and N-gels, respectively. Above a critical gel preparation temperature T_f , shown in the figure by the dotted vertical lines, both N- and I-gels exhibit a high swelling ratio of the order of 10^1 and a low modulus of elasticity of less than 1 kPa. In this range of T_{prep} , the hydrogels obtained were transparent and appeared homogeneous to the eye. The swelling capacity of the hydrogels rapidly decreases and the modulus of elasticity rapidly increases as T_{prep} is decreased below T_f . The hydrogels obtained below T_f were opaque, indicating that these gels are heterogeneous with separate domains in a spatial scale of submicrometer to micrometer. Figure 3 also shows that, the T_f values are $-9 \pm 1^\circ\text{C}$, and $-1 \pm 1^\circ\text{C}$, for N- and I-gels, respectively. This indicates that the precooling of the reaction solution shifts T_f to a temperature close to the freezing point of water. Another point shown in Figure 3 is that the elastic modulus of I-gels prepared below -10°C is much lower than that of N-gels. This is an indication of the reduced rate of the crosslinking reactions during the formation of I-gels. Thus, the network build-up process seems to take place mainly during the

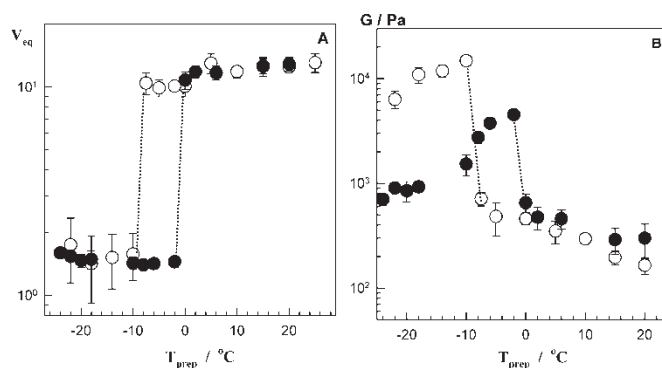


Fig. 3. The equilibrium volume swelling ratio V_{rel} and the elastic modulus G of equilibrium swollen PAMPS hydrogels shown as a function of the gel preparation temperature T_{prep} . Filled and open symbols represent data obtained from I- and N-gels, respectively. $X = 1/6$. The dotted lines represent the temperatures T_f below which the hydrogels become opaque.

non-isothermal period between 0°C and T_{prep} , so that the I-gels prepared with precooling exhibit a lower modulus of elasticity than the N-gels.

Figure 4 shows SEM images of PAMPS networks prepared at various T_{prep} with (left column) and without precooling (right column) of the reaction solution. It is seen that, below T_f , the network samples obtained without precooling exhibit polyhedral pores of sizes 10^1 mm. However, the regularity of the pores was destroyed if a pre-cooling step is included into the synthesis procedure. Similar results were also obtained for the AAm-BAAm copolymerization system. Macroporous PAAm networks also exhibited a collapsed structure after introduction of the pre-cooling step. One may expect that, the collapsed pore structure of dried I-gels is due to their low modulus of elasticity (Figure 3). Since the polymer matrix is mechanically weak, it collapses during drying of the hydrogels so that the pore structure partially disappears. However, as T_{prep} approaches to T_f , the pores in the network became more visible in the SEM images, indicating that the extent of the

pore collapse decreases due to the increasing elastic modulus of I-gels. At or above $T_{\text{prep}} = -8^{\circ}\text{C}$, the networks obtained without precooling were non-porous, while those obtained with precooling exhibited a porous structure up to $T_{\text{prep}} = 0^{\circ}\text{C}$. Thus, the pre-cooling step prior to the gelation reactions provides formation of porosity in the gel network at temperatures close to the freezing point of the reaction system.

Swelling and deswelling kinetics of both N-and I-gels prepared at various temperatures were investigated in water and in acetone, respectively. Both gels prepared below T_f exhibited fast response rate against the solvent changes, as reported previously (11). However, distinct differences were observed in the hydrogel samples prepared between $T_{\text{prep}} = -8$ and -2°C . For example, the swelling-deswelling cycles of I-and N-gels formed at $T_{\text{prep}} = -2^{\circ}\text{C}$ are shown in Figure 5A by the filled and open circles, respectively. Here, the relative weight swelling ratio m_{rel} (mass of gel at time t /mass of equilibrium swollen gel in water) is plotted against the time of deswelling in acetone and re-swelling in water. The I-gel deswells in acetone within 15 min while it re-swells in water within 1 min to attain its original mass. The deswelling-swelling cycles of I-gel samples were repeated many times without a change in the behavior shown in the figure. Further, the cycles were also reproduced using I-gel samples of various sizes. In contrast to the fast responsive behavior of the I-gel, the N-gel formed at the same temperature was too weak in its swollen state to withstand the volume changes; during the first deswelling process in acetone, it was broken into several pieces so that a cycle cannot be completed. The time period during which the gel sample breaks down during deswelling is shown in the figure by the arrow. To compare the re-swelling behavior of both I-and N- gels formed at $T_{\text{prep}} = -2^{\circ}\text{C}$, we investigated the swelling of the gels in water starting from their dry states. The results are shown in Figure 5B in terms

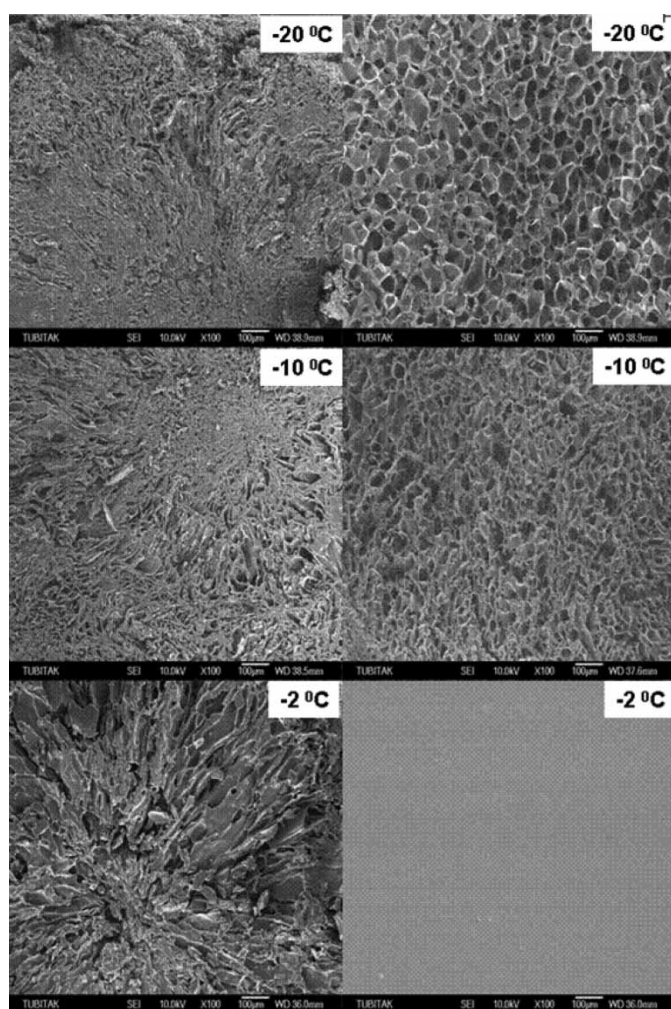


Fig. 4. SEM of PAMPS networks prepared with (left column) and without precooling (right column). The gel preparation temperatures T_{prep} are indicated in the Figures $X = 1/6$. The scaling bars are $100\ \mu\text{m}$. Magnification = $\times 100$.

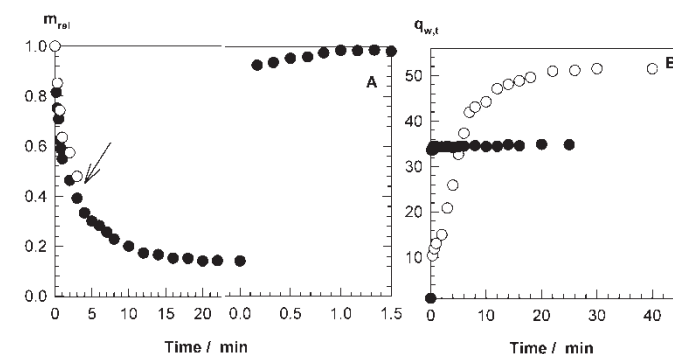


Fig. 5. (A) The relative weight swelling ratio m_{rel} of PAMPS hydrogels obtained at $T_{\text{prep}} = -2^{\circ}\text{C}$ shown as a function of the time of deswelling in acetone and re-swelling in water. Filled and open circles represent m_{rel} data of I-and N-gels, respectively. N-gel breaks down during deswelling as indicated by the arrow; (B) The weight swelling ratio $q_{w,t}$ (mass of gel at time t /mass of dry network) of I-gel (filled symbols) and N-gel (open symbols) plotted against the deswelling and swelling times in acetone and water, respectively. $T_{\text{prep}} = -2^{\circ}\text{C}$. $X = 1/6$.

of the weight swelling ratio $q_{w,t}$ (mass of gel at time t /mass of dry network) of the I-gel (filled symbols) and the N-gel (open symbols) plotted against the swelling time in water. The times to attain the equilibrium states in water are 0.2 min and 20 min for I- and N-gel samples, respectively. The results clearly show the fast responsive behavior of the hydrogels created using the precooling step of the gelation reactions.

3.2 Effect of Inhibition of the Reaction Solution before the Cryogelation

Another approach to conduct the cryogelation reactions under isothermal conditions is the polymerization in the presence of a polymerization inhibitor. In the preliminary experiments, hydroquinone (Hq) was found to be an effective inhibitor for the polymerization-crosslinking reactions of acrylamide-based monomers. In Figure 6, the gelation times in AMPS/BAAm and AAm/BAAm copolymerization systems at $T_{prep} = -22$ and -18°C , respectively, are plotted against the Hq content of the reaction solutions. The dotted horizontal lines represent the freezing times. It is seen that, for both cryogelation systems, the gel point is shifted towards longer reaction times as the amount of Hq is increased. At a Hq concentration of 0.3%, no gel formation was observed in AAm/BAAm copolymerization indicating that Hq is more effective for this gelation system.

The swelling characteristics of both PAAm and PAMPS hydrogels remained unchanged by the addition of Hq up to 0.3%. However, as seen in Figure 7, the elastic moduli of swollen PAMPS and PAAm hydrogels decrease with the addition of 0.1% Hq but then, they remain constant as the Hq content is further increased. The relatively higher modulus of PAMPS hydrogels compared to PAAm hydrogels is due to the higher crosslinker ratio X used in the preparation of the former hydrogels (1/6 vs. 1/80). Figure 8 shows typical SEM images of PAMPS networks prepared at $T_{prep} = -22^\circ\text{C}$ with and without addition of Hq inhibitor. From several SEM images, the average diameter of the pores was calculated as $45 \pm 5 \mu\text{m}$, which was independent on the

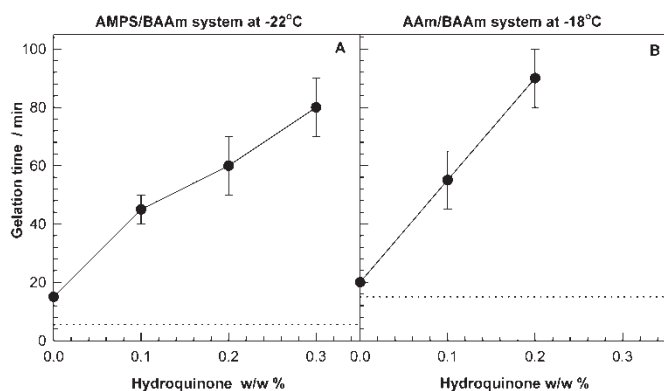


Fig. 6. The gelation times plotted against the hydroquinone (Hq) content of the reaction solutions. The dotted horizontal lines indicate the freezing times.

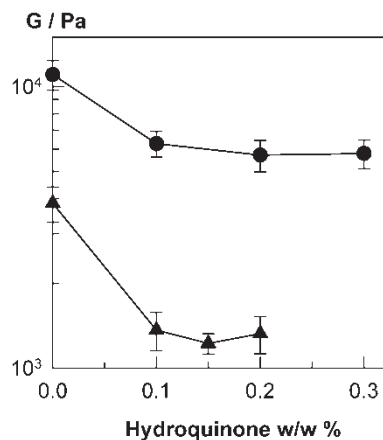


Fig. 7. The elastic modulus G of equilibrium swollen hydrogels shown as a function of the hydroquinone (Hq) concentration. The circles and the triangles are data points obtained from PAMPS and PAAm hydrogels, respectively.

Hq content of the reaction solution. Both the size and the shape of the pores remained unchanged while the regularity of the pore structure in PAMPS networks slightly increased with the addition of Hq.

In Figures 9A and 9B, the images taken from the optical microscope are shown for swollen PAAm hydrogels prepared at $T_{prep} = -18^\circ\text{C}$, without and with 0.2% Hq, respectively. It is seen that the size of the pores in the swollen hydrogels decreases and the pores become more regular if Hq is used in the gel preparation. In Figures 9C and 9D, SEM images of dried PAAm hydrogels prepared with and without Hq, respectively, are shown. The pore size of PAAm networks also decreases in the presence of Hq inhibitor. From several SEM images, the average diameter of the pores was calculated as $35 \pm 11 \mu\text{m}$ and $12 \pm 4 \mu\text{m}$ for 0 and 0.2% Hq, respectively. The decrease in the pore size of PAAm networks indicates decreasing size of the ice crystals formed during the cryogelation reactions. Thus, the addition of Hq provides homogeneous nucleation of ice crystals so that the number of crystals increases while their size decreases, leading to the formation of small pores in

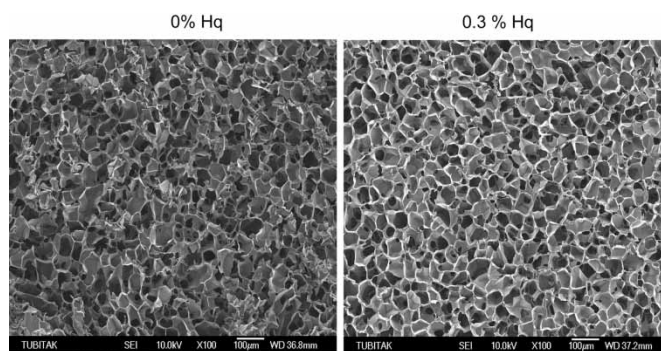


Fig. 8. SEM of PAMPS networks formed at $T_{prep} = -22^\circ\text{C}$ with and without hydroquinone inhibitor. $X = 1/6$. The scaling bars are 100 μm . Magnification = $\times 100$.

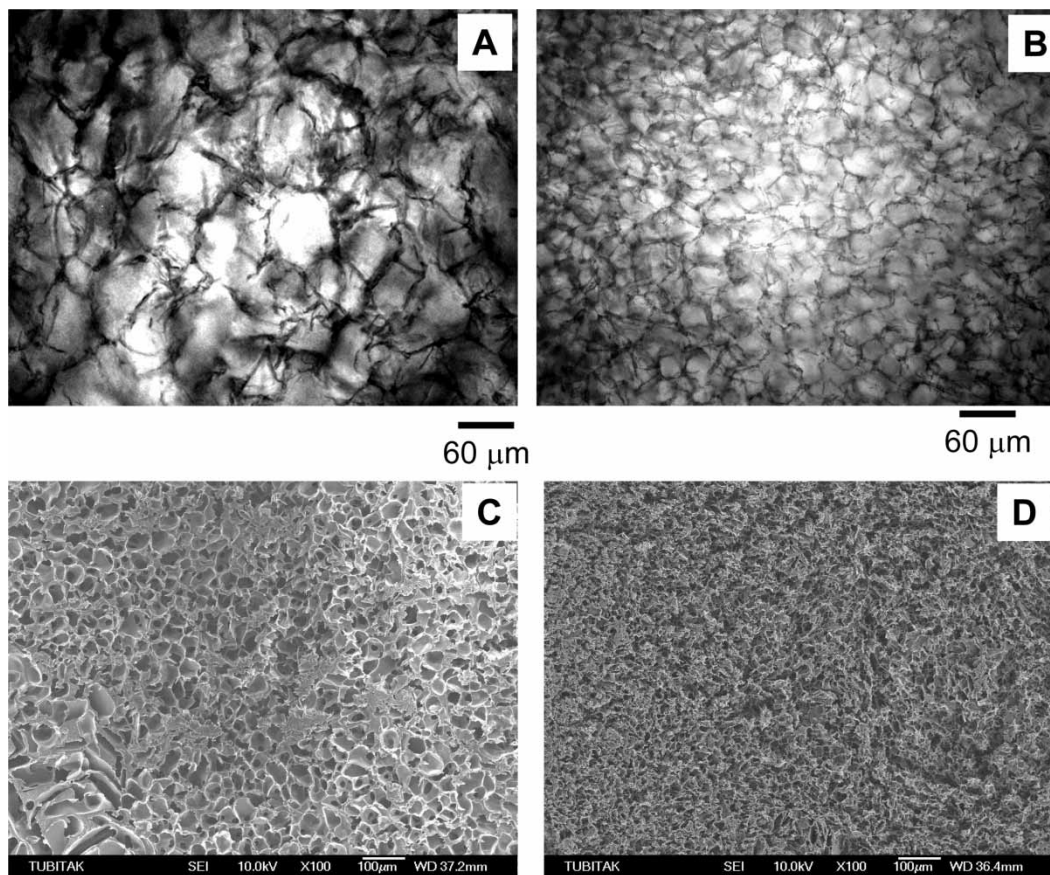


Fig. 9. (A) and (B): Images taken from the optical microscope for PAAm hydrogels in their swollen states. (C) and (D): SEM images of dried PAAm hydrogels. Hq = 0 (A, C) and 0.2 w/w % (B, D). $T_{prep} = -18^{\circ}\text{C}$, $X = 1/80$.

the final material. Such a decrease in the pore size was not observed in PAMPS hydrogels. This is probably due to the fact that gelation in AMPS/BAAM reaction system already occurs beyond the freezing point, even in the absence of Hq (Figure 6A). During the formation of PAAm hydrogels, however, gel point is close to the freezing point of the reaction system so that the effect of Hq addition becomes more dominant.

The swelling and deswelling kinetics of both hydrogels were also investigated as a function of Hq concentration. No substantial change in the response rate of the hydrogels was observed. The swelling-deswelling cycle of the hydrogel samples was similar to the cycle of the I-gel shown in Figure 5. One should also notice the difference in the swelling and deswelling profiles of the hydrogels prepared at temperatures below T_f . As seen in Figure 5, while the hydrogels immersed in water swell almost immediately, their deswelling in acetone occurs relatively slowly. During deswelling, the hydrogel first loses over 50% water content in only 1 min. Then, it undergoes a relatively slow desorption of water until equilibrium is attained; this time for this slower stage being about 10 min (Figure 5). Such a deswelling behavior was also observed before in AAm-based cryogels (11), and needs some comments.

For both PAAm and PAMPS hydrogels prepared below T_f , the equilibrium weight swelling ratios are much larger than the equilibrium volume swelling ratios. For example, in Figure 10A, the weight swelling ratio q_w (mass of

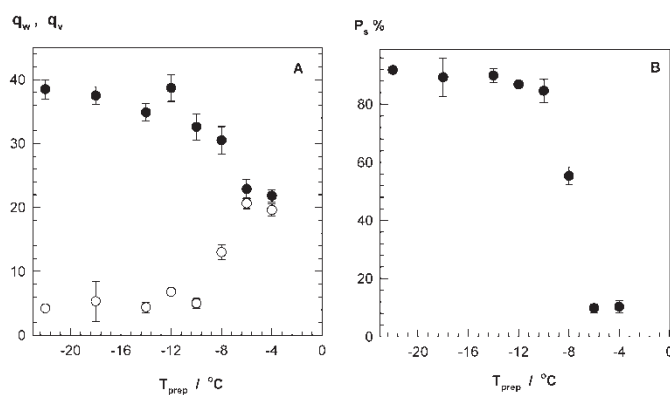


Fig. 10. (A) The equilibrium weight (q_w , filled symbols) and the equilibrium volume swelling ratios (q_v , open symbols) of PAAm hydrogels prepared in the presence of 0.2 w/w % Hq shown as a function of the gel preparation temperature T_{prep} . $X = 1/80$; (B) The swollen state porosity P_s plotted against the gel preparation temperature T_{prep} .

swollen gel/mass of dry gel) and the volume swelling ratio q_v (volume of swollen gel/volume of dry gel) of PAAm hydrogels prepared in the presence of 0.2% Hq are plotted against the gel preparation temperature T_{prep} . It is seen that, below T_f , q_w is about 10-fold larger than q_v . From the weight and volume swelling ratios, the swollen state porosity of the hydrogels P_s can be estimated using Equation (3):

$$P_s = 1 - q_v[1 + (q_w - 1)d_2/d_1]^{-1} \quad (3)$$

where d_1 and d_2 are the densities of solvent (water) and polymer, respectively. Assuming that $d_1 = 1$ g/mL and $d_2 = 1.35$ g/mL, the swollen state porosities P_s calculated using Equation (3) are shown in Figure 9B plotted against T_{prep} . The swollen state porosities are about 90% for all the low temperature gels. This means that the swelling or deswelling of the hydrogels occurs as the replacement of one solvent in the pores of the gel network with another one, accompanied by the stretching or shrinking of the network chains to assume equilibrium conformation with the solvent. Since water is a good solvent for PAAm chains, as well as due to the strong hydrogen bonding interactions between water and AAm segments of the network chains, filling of the pores with water occurs immediately. However, since acetone forms weak hydrogen bonds with the AAm units, replacement of water molecules bound to the pore walls with acetone molecules occurs more slowly. As a consequence, swelling response rate of collapsed gel occurs much more rapidly than the reswelling response rate of the same gel starting from its swollen state.

4 Conclusions

The cryogelation reactions of both AMPS/BAAm and AAm/BAAm systems were carried out isothermally by use of two techniques. First, after addition of the initiator into the reaction solution, the system was immediately cooled down to -196°C using liquid nitrogen and then, the system was immersed into a thermostat at the desired T_{prep} value. It was found that the precooling of the reaction system before the onset of the reactions provides formation of superfast responsive hydrogels at temperatures close to the freezing point of water. The precooling step however destroyed the regularity of the pores in the hydrogels due to their low moduli of elasticity. As a second technique to achieve isothermal cryogelation, hydroquinone as the polymerization

inhibitor was included into the reaction solution. By adjusting the hydroquinone concentration in the reaction system, the onset of gelation can be shifted beyond the thermal equilibration point of the reaction solution with the surrounding thermostat. It was shown that, the addition of hydroquinone produces more monodisperse and smaller pores. The hydrogels obtained by both techniques exhibit size-independent superfast swelling behavior in response to the external stimuli.

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