

Superfast responsive ionic hydrogels with controllable pore size

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Abstract

A series of strong polyelectrolyte hydrogels was prepared from the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as the monomer and *N,N'*-methylene(bis)acrylamide (BAAm) as a crosslinker in aqueous solutions. The gel preparation temperature (T_{prep}) was varied between -22 and 25 °C. It was found that the swelling properties and the elastic behavior of the hydrogels drastically change at $T_{\text{prep}} = -8$ °C. The hydrogels prepared below -8 °C exhibit a discontinuous morphology consisting of polyhedral pores of sizes 30 – 50 μm , while those formed at higher temperatures have a non-porous structure. The pore size of the networks increased by decreasing the charge density of the hydrogels, while addition of low molecular weight salts into the gelation system reduced the size of the pores. Calculations based on the equilibrium between the ice and unfrozen gel phases in the reaction system at low temperatures explain the results of observations. It was also shown that the hydrogels formed below -8 °C exhibit superfast swelling properties as well as reversible swelling–deswelling cycles in water and acetone.

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1. Introduction

Responsive hydrogels are smart materials, capable of changing volume and/or shape in response to specific external stimuli, such as the temperature, solvent quality, pH, electric field, etc. [1]. Depending on the design of the hydrogel matrices, this volume change may occur continuously over a range of stimulus values, or, discontinuously at a critical stimulus level. These properties of the hydrogels received considerable interest in last three decades and, a large number of hydrogel based devices have been proposed, including artificial organs, actuators, and on–off switches [2,3]. However, the practical design and control of these devices still present some problems. In particular, hydrogel based devices are limited in their response rate by diffusion processes, which are slow and even slower near the critical point [4]. In addition, the durability of the hydrogel based devices requires a good mechanical performance of gels in their swollen state. Polymer gels

under interest are, however, soft and fragile when handled in the swollen state.

Recently, we introduced a novel concept to design hydrogels that stiffen upon swelling in good solvents [5,6]. The concept was to utilize the properties of highly inhomogeneous ionic hydrogels consisting of regions of high polymer concentration (microgels [7]) connected through the network chains locating in dilute regions. Since the network chains in the dilute phase are highly stretched, the gels exhibited stiffened properties at their swollen state due to the non-Gaussian elasticity. The gels were prepared by free-radical crosslinking copolymerization of the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomer with *N,N'*-methylenebis (acrylamide) (BAAm) crosslinker at 5 °C in dilute aqueous solutions. It was shown that, as the gel swells starting from its preparation state, the modulus of elasticity increases from 10^2 to 10^3 Pa [5]. Using this route, although the mechanical properties of swollen hydrogels were improved, their response rate against the external stimuli was too slow for practical applications.

It occurred to us that, by conducting the copolymerization-crosslinking reactions below -8 °C, one could obtain poly(AMPS) (PAMPS) hydrogels with superfast swelling properties. This was achieved by using gelation reactions

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occurring in the apparently frozen reaction system, which allowed for the formation of a bicontinuous morphology in PAMPS networks. The morphology of the networks consists of polyhedral pores and the network chains building the pore walls. In the following, we also show that the size of the pores in the networks could be regulated using the gel preparation parameters.

2. Experimental section

2.1. Materials

Acrylamide (AAm, Merck), *N,N'*-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), *N,N,N',N'*-tetramethylethylenediamine (TEMED, Merck), and sodium chloride (Merck) were used as received. 2-acrylamido-2-methylpropane sulfonic acid (AMPS- H^+ , Merck) was crystallized from 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 solution of BAAm was prepared by dissolving 0.75 g of BAAm in 50 mL of distilled water.

Poly(2-acrylamido-2-methylpropane sulfonic acid sodium salt) (PAMPS) hydrogels were prepared by free-radical crosslinking copolymerization of AMPS with BAAm in aqueous solution at various temperatures (T_{prep}) between -22 and 25 °C. 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. The initial concentration of the monomer (AMPS + BAAm) was fixed at 5 w/v%. The crosslinker (BAAm) content in the monomer mixture was also fixed at 17 mol%. Typically, stock solutions of AMPS (1.99 mL), BAAm (4.03 mL), TEMED (1 mL) were first mixed in a graduated flask of 10 mL in volume and the volume of the solution was completed to 9 mL with distilled water. The solution was cooled to 0 °C in 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 4 mm in diameter, the glass tubes were sealed, immersed in a thermostated bath at T_{prep} and the polymerization was conducted for 1 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. The hydrogels after extraction 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 40 °C under vacuum to constant weight.

Gelation reactions using AMPS and AAm monomer mixtures at $T_{\text{prep}} = -22$ °C were carried out by using the

same procedure described above. In this set of experiments, the crosslinker (BAAm) content of the monomer mixture was set to 3 mol%.

2.2. Methods

The monomer conversions and 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 constant mass. The details about the gravimetric determination of the conversions were given elsewhere [8,9]. For the equilibrium swelling measurements, PAMPS hydrogels after preparation in the form of rods of 4 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at room temperature (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. 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 $V_{\text{eq}} = (D/D_0)^3$, where D and D_0 are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively.

For the swelling kinetics measurements, the dry PAMPS networks were first immersed in water at 21 °C. The weight changes of gels were measured gravimetrically after blotting the excess surface water at regular time intervals. For the measurement of the deswelling kinetics of gels, the equilibrium swollen PAMPS gel samples in water were transferred into acetone at 21 °C. The weight changes of gels were also determined gravimetrically as described above. The results were interpreted in terms of the weight swelling ratio $q_w = m/m_{\text{dry}}$, where m is the mass of the gel sample at time t and m_{dry} is its dry mass.

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 [9]. 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 sample weight loss during the measurements due to water evaporation was found to be negligible. The elastic modulus G was determined from the slope of linear dependence [10], $f = G(\lambda - \lambda^{-2})$, 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 dried hydrogels, scanning electron microscopy studies were carried out at magnifications of 50–300 times (Jeol 5600 LV). Prior to the measurements, network samples were sputter-coated with gold for 3 min using Emscope SC-500 instrument.

3. Results and discussion

PAMPS hydrogels were prepared at 5 w/v% initial monomer concentration. The crosslinker (BAAM) content in the monomer mixture was set to 17 mol%. The gel preparation temperature, T_{prep} , was varied between -22 and 25 °C. It should be noted that T_{prep} is the temperature of the thermostated bath in which the reactions were carried out. Since the addition of the initiator APS into the monomer solution occurred at 0 °C, the reactions proceed non-isothermally from the moment of the APS addition to the moment when the temperature of the reaction system reaches to T_{prep} . In order to obtain reproducible heating, cooling, or freezing patterns, the reaction mixtures of the same volume and shape were used. The time period between the APS addition and the transfer of the reaction system into the thermostat was also accurately controlled. After 1 day of the reaction time, gravimetric measurements [9] showed that the product of the fractional monomer conversion and 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 crosslinked polymer in the crude hydrogels.

Results of the equilibrium swelling and elasticity measurements are collected in Fig. 1, which shows the equilibrium volume swelling ratio V_{eq} (filled symbols) and the elastic modulus G (open symbols) of the equilibrium swollen hydrogels plotted against the gel preparation temperature T_{prep} . Depending on T_{prep} , two different regimes can be seen from the figure. At $T_{\text{prep}} = -8$ °C or above, the gels exhibit relatively high swelling ratios V_{eq} of the order of 10^1 and low moduli of elasticity G in the range of 10^2 – 10^3 Pa. However, decrease of T_{prep} below -8 °C results in a 10-fold decrease in the swelling ratio and about 10-fold increase in the elastic modulus of gels. Moreover, the gels formed at or above -8 °C were transparent while those formed at lower temperatures were opaque, indicating that these gels have separate domains in a spatial scale of submicrometer to micrometer. Thus, the hydrogel properties drastically change as T_{prep} is decreased below -8 °C.

The morphologies of dried gel samples were observed by

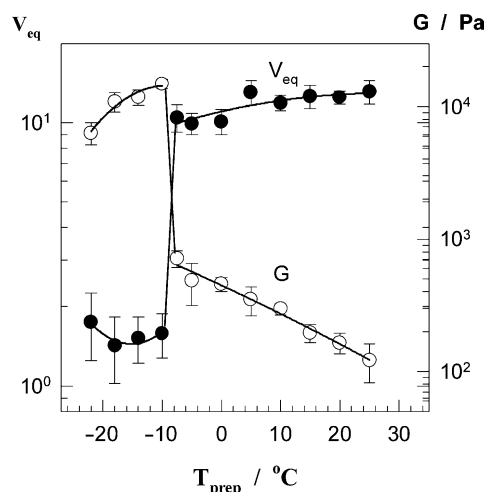


Fig. 1. Volume swelling ratio V_{eq} (filled symbols) and the elastic modulus G (open symbols) of equilibrium swollen PAMPS hydrogels shown as a function of the gel preparation temperature T_{prep} .

scanning electron microscopy (SEM). SEM analysis of PAMPS networks formed below -8 °C revealed the presence of bicontinuous morphologies. In the scanning electron micrograph in Fig. 2(A), the microstructure of the network formed at $T_{\text{prep}} = -22$ °C is given and Fig. 2(B) shows the magnified observation of the pores in the same network. Although the geometry and size of the pores are quite irregular, one can identify from Fig. 2(A) regular assembly of polyhedral pores forming junctions with angles of about 120° . This type of a microstructure is distinctly different from the macroporous networks formed by the reaction-induced phase separation mechanism, where the structure looks like cauliflowers and consists of aggregates of various sizes [11]. Fig. 3 shows SEM images of PAMPS networks formed at various T_{prep} between -22 and -8 °C. All the polymer samples formed below -8 °C have a porous structure with pore sizes of 30 – 50 μm while those formed at or above -8 °C exhibit a continuous morphology. At -10 °C, the pore walls seem to be too weak so that they are more or less fused together to form large aggregates. Comparison of Figs. 1 and 3 indicates that the drastic change of the network microstructure between $T_{\text{prep}} = -8$ and -10 °C is reflected by the swelling and elasticity tests with decreasing swelling ratio and increasing modulus of elasticity.

PAMPS hydrogels formed at various T_{prep} were subjected to swelling and deswelling processes in water and in acetone, respectively. For this purpose, the dry polymer was first immersed in water and the weight change of gel was determined as a function of the swelling time. After reaching the equilibrium state in water, the swollen hydrogel was immersed in acetone and the deswelling process was monitored by recording the weight decrease with time. In order to check the durability of the gel sample against the volume changes, this swelling–deswelling cycle was repeated twice. Typical results are shown in Fig. 4(A)

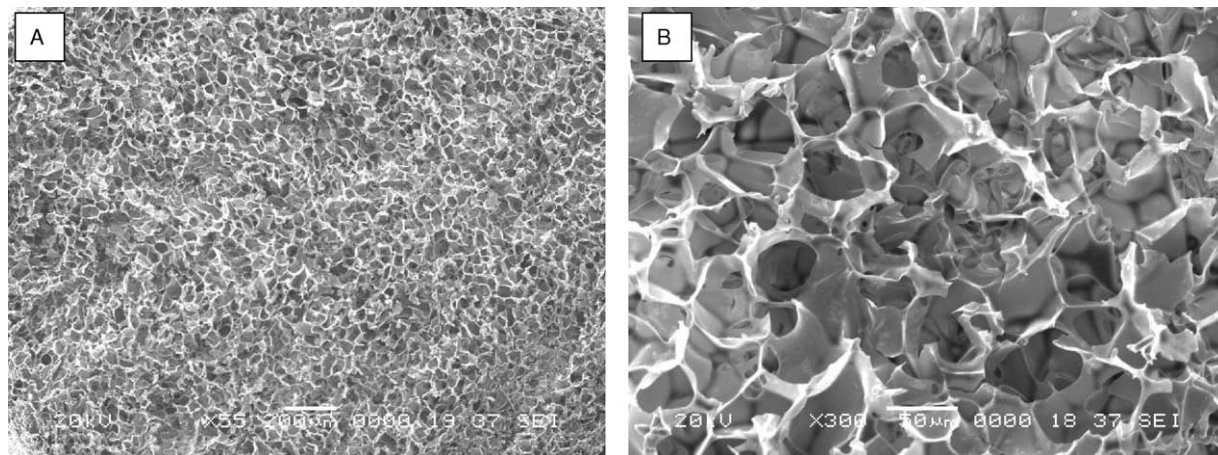


Fig. 2. SEM of PAMPS networks formed at $T_{\text{prep}} = -22$ °C. The scaling bars are 200 μm (A) and 50 μm (B). Magnification = 55 \times (A) and 300 \times (B).

where the swelling ratio q_w is plotted against the time of swelling or deswelling. Completely reversible swelling–deswelling cycles were obtained using gel samples prepared below -8 °C. However, those formed at higher temperatures were too soft in their swollen states in water; during the first deswelling process in acetone, they were broken into several pieces so that a cycle cannot be completed. Fig. 4(B) shows the initial stages of swelling and deswelling processes of gels in water and in acetone, respectively. Gels

formed below -8 °C attain their equilibrium swollen and equilibrium collapsed volumes in less than 30 s and in 5–10 min, respectively, while those formed at higher temperatures require about 1 h to reach their equilibrium state in water (Fig. 4(A)). The accelerating swelling and deswelling rates below $T_{\text{prep}} = -8$ °C is due to the formation of a porous structure in PAMPS networks, which increases their internal surface area so that the contact area between the solvent and the polymer increases.

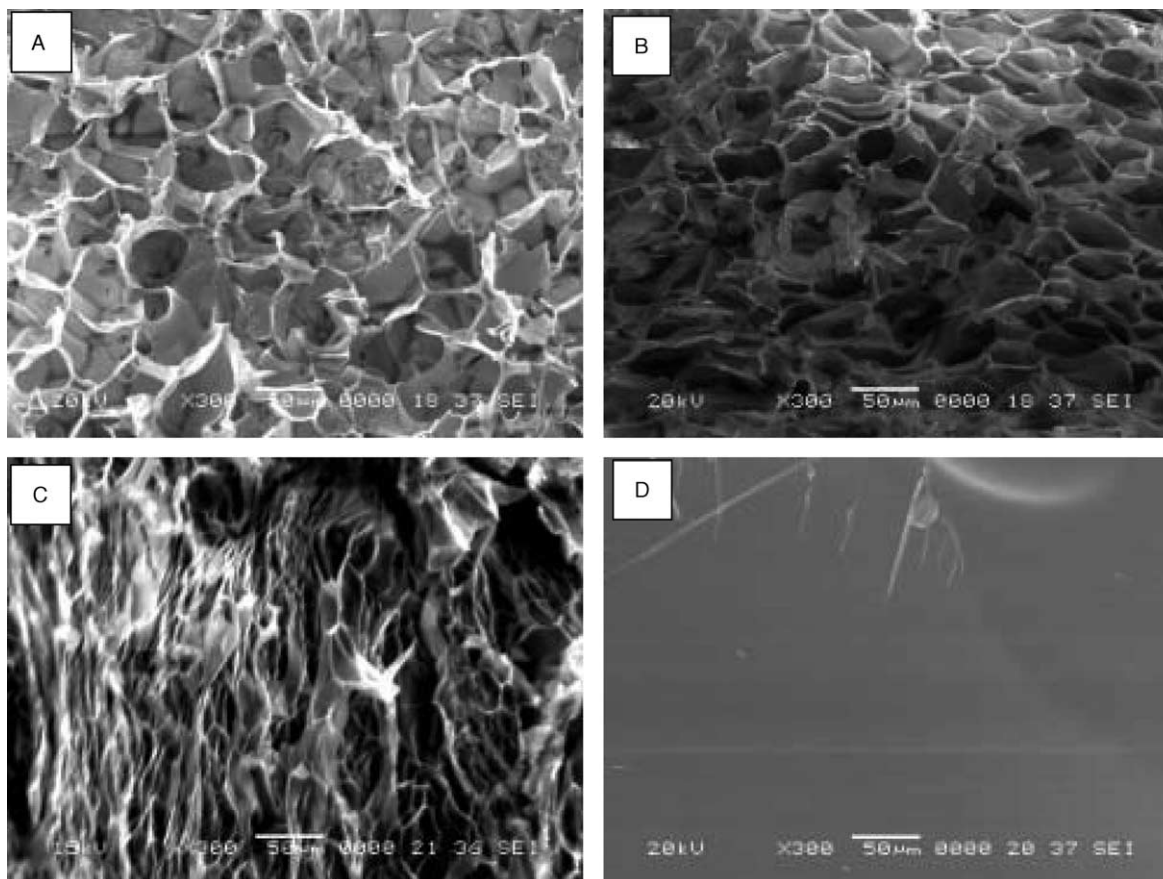


Fig. 3. SEM of PAMPS networks formed at $T_{\text{prep}} = -22$ (A), -18 (B), -10 (C), and -8 °C (D). The scaling bar is 50 μm .

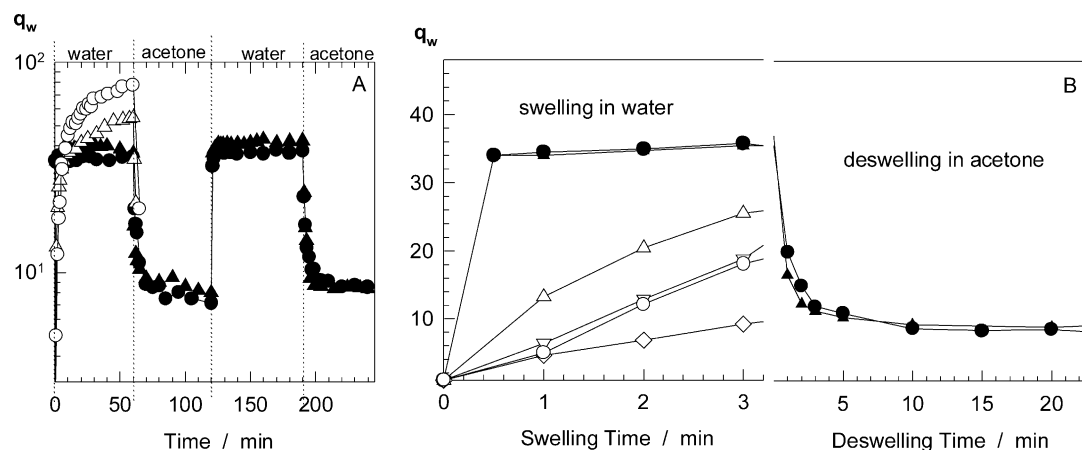


Fig. 4. (A) Swelling and deswelling kinetics of PAMPS hydrogels in water and in acetone, respectively, shown as the variation of the weight swelling ratio q_w with the time of swelling or deswelling. (B) The initial period of swelling and deswelling processes of the hydrogels. $T_{\text{prep}} = -22$ (●), -18 (▲), -8 (◇), 0 (△), 15 (▽), and 25 °C (○).

Thus, decreasing T_{prep} below -8 °C results in the formation of superfast responsive PAMPS hydrogels, which are also stable against the volume changes. In contrast to these improvements in the hydrogel properties, they exhibit relatively low swelling ratios compared to the conventional ionic hydrogels.

The occurrence of the polymerization and crosslinking reactions below the freezing point of water as well as formation of a heterogeneous network structure can be explained with the presence of unfrozen regions in the apparently frozen reaction system, in which the reactions proceed. It is known that, even when cooled below the bulk freezing temperature, some water in aqueous solutions remains unfrozen [12–14]. The amount of unfrozen water depends on the temperature as well as on the amount and type of the solute in the solution. Lozinsky and co-workers investigated polymerization reactions conducted below the freezing point of water [15–18]. 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 reactions only proceed in these unfrozen zones and leads to the formation of a polymer network with macroporous channels [15]. Such materials are called cryogels. Cryogels formed from dilute aqueous solutions of gelatin, poly(vinyl alcohol), chitosan, as well as from crosslinking copolymerization of AAm and BAAM exhibit interconnected systems of macropores and sponge-like morphology [15,16]. Thus, in these cryogelation systems, although there is no phase separation during the course of the network formation, the frozen zones (ice crystals) of the reaction system act as template during gelation, which is removed from the gel by thawing leading to a porous structure [15]. The reason why water in aqueous solutions does not freeze at below the bulk freezing temperature is attributed, in the main, to the freezing point depression of the water due to the solutes [13]. Although the usual solute concentrations can lower the freezing point by

only a few degrees, once ice is present, the effect is enhanced. This is because solutes are excluded from the ice structure and become more concentrated in the remaining unfrozen regions. Thus, as water freezes (crystallizes), the solute concentration in the liquid phase rises continuously so that successively greater osmotic pressure is required to keep the liquid phase in equilibrium with the pure ice phase.

To quantify our results, we assume that only pure water freezes out of the reaction solution when it is cooled to its freezing point. Further, since the unfrozen solution phase of the reaction system becomes the gel phase forming the pore walls after polymerization, it is also assumed that the gel is in thermodynamic equilibrium with the ice crystals. The equilibrium condition between the ice and gel phases at the freezing temperature T_f is that the chemical potentials of pure ice (μ_1^{ice}) and of water in the gel (μ_1^{gel}) must be equal. (μ_1^{gel}) in the gel phase is $\mu_1^{\text{gel}} = \mu_1^0 + RT_f \ln a_A$, where μ_1^0 is the chemical potential of pure liquid water and a_A is the activity of water in the gel. Equating μ_1^{ice} and μ_1^{gel} at the freezing point T_f and, since $\mu_1^{\text{ice}} - \mu_1^0$ equals the molar Gibbs free energy change for melting of ice, one obtains:

$$\ln a_A = \frac{\Delta H_m}{R} \left(\frac{1}{T_f^0} - \frac{1}{T_f} \right) \quad (1)$$

where ΔH_m is the molar enthalpy of fusion of pure ice, T_f^0 is the normal freezing point of pure water, and R is the gas constant. The Flory–Rehner theory including the ideal Donnan equilibria gives the following relation between the activity of a solvent in gel and the gel parameters [19]:

$$\ln a_A = \ln(1 - v_2) + v_2 + \chi v_2^2 + v_e V_1 \left[v_2^{1/3} (v_2^0)^{2/3} - 0.5v_2 \right] - f v_2 \quad (2)$$

where v_2 is the volume fraction of polymer in the gel, χ is the polymer–solvent interaction parameter, v_e is the effective crosslink density of the network, V_1 is the molar volume of solvent, v_2^0 is the volume fraction of polymer network after

gel preparation, and f is the effective charge density, i.e. the fraction of charged units in the network chains that are effective in gel swelling. Substituting Eq. (2) into Eq. (1), one may calculate the freezing temperature T_f of water confined in a network of polymer chains as a function of the network parameters. Since $v_2^0 = v_2$ after the gel preparation, Eqs. (1) and (2) yield

$$\frac{1}{T_f} = \frac{1}{T_f^0} - \frac{R}{\Delta H_m} [\ln(1 - v_2) + v_2 + \chi v_2^2 + 0.5v_e V_1 v_2 - f v_2] \quad (3)$$

Note that v_2 and v_e in Eq. (3) are the polymer volume fraction and the effective crosslink density in the unfrozen microzones of the reaction system after polymerization. In the following, the polymer concentration in the unfrozen zones is given in terms of c , mass of polymer in 100 mL of solution, which is related to v_2 by:

$$c = v_2 \rho 10^2 \quad (4)$$

where ρ is the polymer density. Further, assuming complete monomer conversion, the volume fraction of ice in the reaction system f_{ice} can be calculated as

$$f_{ice} = 1 - \frac{c_0}{c} \quad (5)$$

where c_0 is the initial monomer concentration, which was 5 w/v% in our experiments. For the following calculations, the system specific parameters used were: $T_f^0 = 273.15$ K, $\Delta H_m = 6.01$ kJ/mol, $\chi = 0.480$ [20], $V_1 = 18.0$ g/mL, and $\rho = 1.35$ g/mL [21]. The estimation of the effective crosslink density v_e of PAMPS gels from their moduli data is difficult due to the complex character of heterogeneous networks during their deformation process. However, for a homogeneous network of Gaussian chains, the modulus G relates to the network crosslink density through the equation [10]:

$$G = v_e RT (v_{2,eq})^{1/3} (v_2^0)^{2/3} \quad (6)$$

where $v_{2,eq}$ is the polymer volume fraction in the equilibrium swollen hydrogel, i.e. $v_{2,eq} = v_2^0 / V_{eq}$ and T is the temperature at the modulus measurements (294 K). For the PAMPS gel formed at $T_{prep} = -8$ °C, the values $G = 712 \pm 100$ Pa, $V_{eq} = 10.5 \pm 1.3$ and $v_2^0 = 0.037$ found by experiments yield $v_e = 17 \pm 3$ mol/m³, which was used for the simulations. However, respective calculations for various crosslink densities v_e showed that the effect of gel elasticity on the freezing point depression is negligible. Therefore, following results are valid for both gels and solutions of high molecular weight polymers in equilibrium with ice.

In Fig. 5, the polymer concentration c in the unfrozen gel phase in equilibrium with pure ice and the volume fraction of ice in the system f_{ice} are shown as a function of the freezing temperature T_f . Calculations were for various

charge densities f indicated in the figure. Assuming complete ionization of the AMPS units, the curves with $f=1$ correspond to the behavior of PAMPS gels just after their preparation. Let us first consider the freezing temperature $T_f = -22$ °C for which $c = 30.6\%$ and $f_{ice} = 0.84$. This indicates that, at $T_{prep} = -22$ °C, water freezes and separates out of the gel phase until the polymer concentration in the gel rises to 30.6%. After complete conversions, f_{ice} equals 0.84 indicating that 84% of the reaction system consists of ice crystals acting as template in forming of pores. Similarly, at $T_{prep} = -10$ and -5 °C, the critical polymer concentrations are 13.5 and 6.7% while ice fractions are 0.63 and 0.25, respectively. Thus, the lower the T_{prep} , the higher the polymer concentration in the reaction zones and the larger the ice fraction. Fig. 5(B) also shows that the reaction system with $f=1$ does not freeze ($f_{ice}=0$) if $T_{prep} = -3.8$ °C or above. As the temperature drops below -3.8 °C, the amount of ice in the system increases first steeply up to about $T_{prep} = -10$ °C, and subsequently increases gradually.

The simulation results explain the existence of unfrozen regions in ice at temperatures about 20 °C below the freezing temperature and thus, explain the occurrence of gelation reactions at such low temperatures. Moreover, the decrease of the rate constants of polymerization and crosslinking reactions at low temperatures seems to be compensated by the increased polymer concentration in the reaction zones so that the monomer conversions and the gel fractions are unaffected from T_{prep} . The decreased swelling ratios of gels formed at low temperature can also be explained with the high polymer concentration in the reaction zones. Although the initial monomer concentration in our experiments was set to 5%, the actual concentration in the reaction zones is expected to be much higher (Fig. 5). Previous work shows that, increasing monomer concentration causes the polymer chains to entangle so that the network formed in a concentrated solution can swell less than that formed in a dilute solution [22]. As a consequence, the equilibrium swelling capacities of the gels formed at $T_{prep} < -8$ °C are much smaller than those of the standard hydrogels.

Calculation results also suggest that the polymer concentration in the gel phase should be larger, that is the pore walls should be thinner and the size of the pores should be larger as T_{prep} is decreased. However, SEM analysis of the network samples formed at various T_{prep} did not show these dependences. Also, why a porous structure in PAMPS networks does not start to develop at $T_{prep} = -3.8$ °C cannot be explained using the simulations. These discrepancies may partially be attributed to the non-equilibrium effects during freezing [13]. The concentrated unfrozen polymer solutions at low temperatures have high viscosities, that may slow down the equilibration of water and the growth of ice crystals to an extent that stops freezing. Moreover, the initial non-isothermal reaction period between 0 °C (APS addition) and T_{prep} (equilibration of the reaction system with

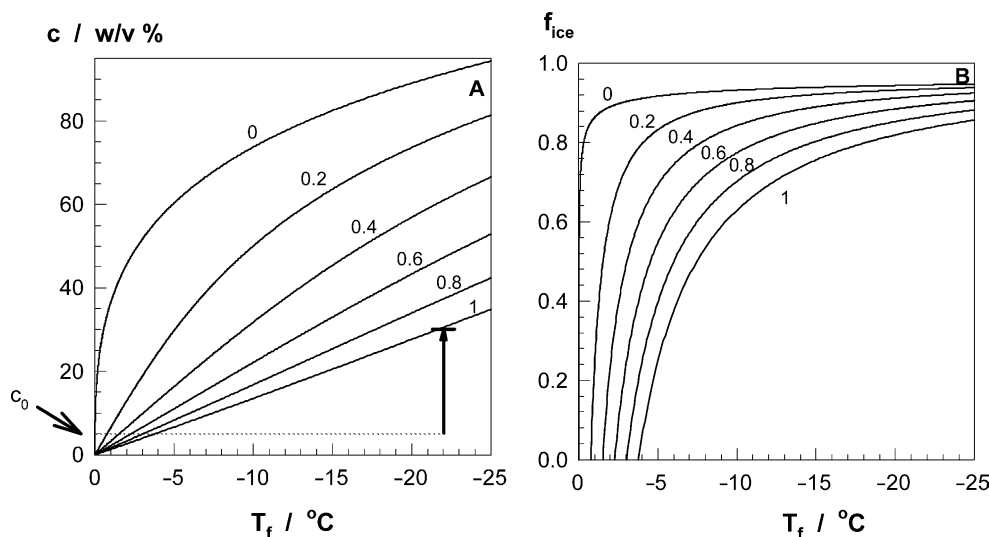


Fig. 5. Polymer concentration c in the unfrozen gel phase in equilibrium with pure ice and the volume fraction of ice in the system f_{ice} shown as a function of the freezing temperature T_f . Calculations were for various charge densities f indicated in the figure. c_0 is the initial monomer concentration (5%). The up arrow illustrates the increase of the polymer concentration of the gel phase during the reactions up to the value of $c = 30.6\%$.

the thermostated bath) may also be responsible for the observed deviations from the theory. Indeed, we observed that the time needed for the bulk freezing of the reaction system strongly depends on T_{prep} . For example, the reaction mixtures at $T_{prep} = -22^\circ\text{C}$ became apparently frozen within 4–5 min while those at $T_{prep} = -5^\circ\text{C}$ required more than 1 h for freezing. Compared to these freezing times, the gelation time recorded using the falling ball technique [23] was found to be 5 min at 0°C . Thus, one may expect that gelation and gel growth reactions at $T_{prep} = -5^\circ\text{C}$ mainly occur before the onset of bulk freezing of the system, while the reactions at $T_{prep} = -22^\circ\text{C}$ mainly occur in the unfrozen microzones. Therefore, we may conclude that the variation of the cooling rate depending on T_{prep} is responsible for the appearance of porous structures at temperatures much below the bulk freezing point of the reaction system. The abrupt decrease in V_{eq} between -8 and -10°C is also an indication that the actual cryogelation reactions start below this temperature range.

The formation of polyhedral pores in gels may be explained as follows: Water molecules in crosslinked hydrophilic polymers are known to exist in three states [24,25]: (1) Free water in the middle of the mesh of the network, (2) bound water adjacent to the network chains, and (3) film water adsorbed on the bound water layer. Freezing of free water and the growth of ice crystals thus formed may lead to the deformation of the polymer network by stretching the hydrated network chains around the ice crystals. Although the polymer elasticity allows easy deformation of the network chains, the high viscosity of the system may slow down the growth of the crystals. As a consequence, one may expect formation of ice crystals in the mesh of polymer network separated by swollen polymer chains. Moreover, the total surface energy of ice crystals is minimized by coming the crystals together, forming four ice

crystals in contact with angles of 120° where the forces of interfacial tension balance.

Calculation results predict that a decrease in the charge density f of the network chains would increase the volume fraction of ice in the reaction system so that the pores in the final hydrogels would be larger (Fig. 5). In order to check this point, we conducted the gelation reactions using AMPS and AAm monomer mixtures of various compositions. The crosslinker content was 3 mol% and T_{prep} was set to -22°C . Fig. 6 shows SEM images of the networks formed at various ionic comonomer (AMPS) levels. At 70 and 90 mol% AMPS (Fig. 6(A) and (B)), the morphologies are similar to those of PAMPS gels formed at -22°C . At 0 mol% AMPS, shown in Fig. 6(C) and (D) at two different magnifications, the network consists of spherical pores of sizes 100–150 μm , much larger than those in PAMPS networks. In addition to these large pores, small pores of size 20–30 μm also exist in this network, which were formed probably during the non-isothermal period of the reaction. The equilibrium swelling ratios V_{eq} of the hydrogels are shown in Fig. 7(A) as a function of the AMPS content. The swelling ratio V_{eq} of the non-ionic gel in water is about unity indicating very high polymer concentration in the unfrozen zones of the reaction system. Increasing AMPS content also increases the swelling capacity of gels. This is due to the decrease of the polymer concentration in the reaction zones (Fig. 5) as well as due to the increasing number of counterions (Na^+) in gels creating an osmotic pressure that swells the gel. Swelling–deswelling kinetics measurements showed that the rate of response of the hydrogels does not change with the AMPS contents and, all the hydrogels exhibit reversible swelling–deswelling cycles against the external solvent change.

In addition to the charge density effect, the presence of low molecular weight salts should also affect significantly

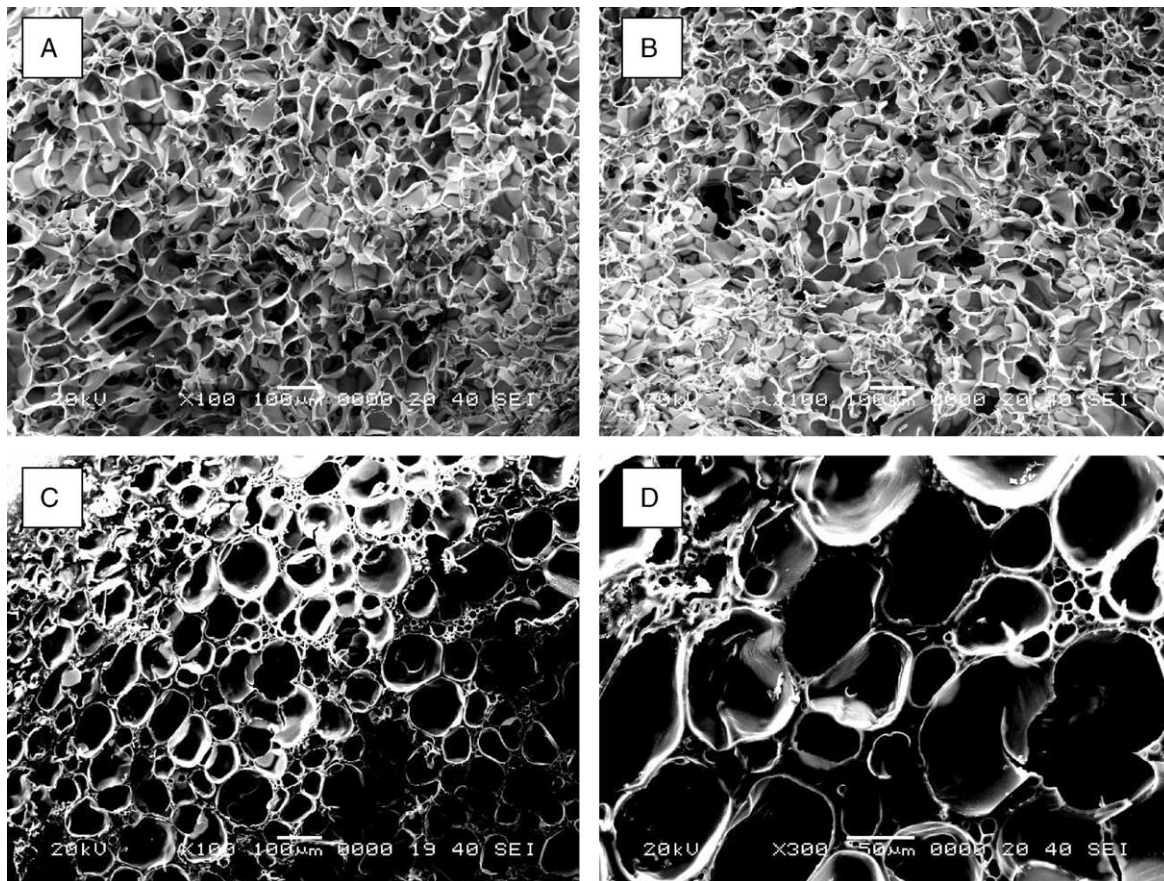


Fig. 6. SEM of AMPS–AAm networks formed at $T_{\text{prep}} = -22^\circ\text{C}$. AMPS mol% = 70 (A), 90 (B), and 0 (C). The scaling bars are 100 μm . Magnification = 100 \times . Picture D is a magnified version of C with a scaling bar of 50 μm .

the microstructure of the hydrogels. Addition of salts into the reaction system should decrease further the bulk freezing temperature so that the volume of the non-frozen solution will increase. This would lead to the formation of hydrogels with smaller pores. Preliminary experiments showed that, as the NaCl content in the reaction mixture

is increased from 0 to 10 w/v%, the bulk freezing times of AMPS–BAAm reaction mixtures at $T_{\text{prep}} = -22^\circ\text{C}$ increased from 5 to 35 min while their gelation times at 0°C remained constant (5 ± 1 min). We prepared PAMPS networks with 17 mol% BAAM and in the presence of various amounts of NaCl. T_{prep} was fixed at -22°C .

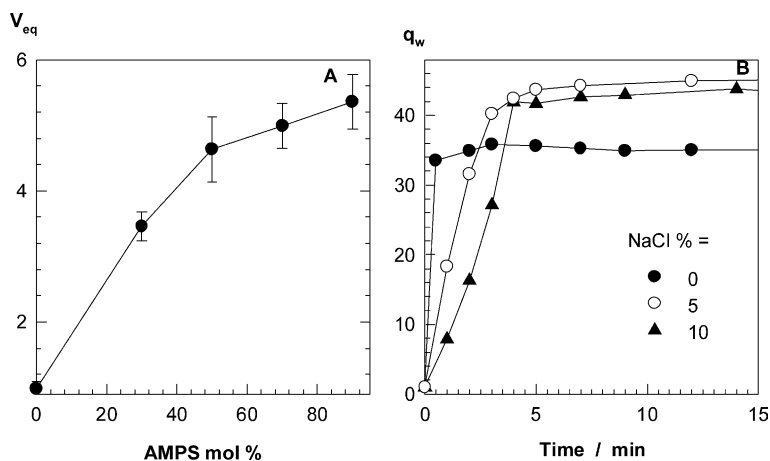


Fig. 7. (A) Equilibrium swelling ratios V_{eq} of the hydrogels shown as a function of the AMPS content. The crosslinker content = 3 mol%. $T_{\text{prep}} = -22^\circ\text{C}$. (B) Initial swelling period of PAMPS networks shown as the dependence of the weight swelling ratio q_w on the swelling time. NaCl contents of the reaction mixtures are indicated. The crosslinker content = 17 mol%. $T_{\text{prep}} = -22^\circ\text{C}$.

Fig. 7(B) shows the initial swelling period of the networks in water. The SEM images shown in Fig. 8 were from PAMPS networks prepared in the presence of 0 (A), 5 (B) and 10 w/v% NaCl (C). As the salt content in the reaction mixture is increased, the pore size decreases from 30–50 to 10–20 μm . Thus, the pore size of PAMPS hydrogels can be reduced by adding NaCl into the polymerization system. Although the gels formed in the presence of NaCl were also stable against the volume changes, their swelling time in water increased from less than 30 s to 5 min with decreasing size of the pores (Fig. 7(B)).

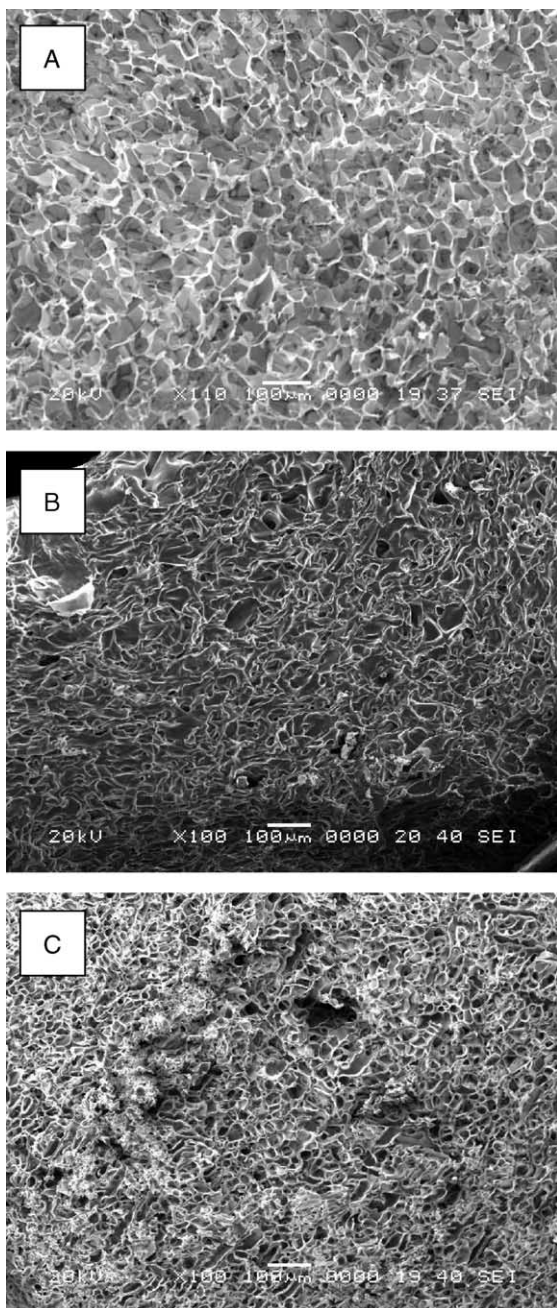


Fig. 8. SEM of PAMPS hydrogels prepared in the presence of 0 (A), 5 (B), and 10 w/v% NaCl (C). The crosslinker content = 17 mol%. $T_{\text{prep}} = -22\text{ }^{\circ}\text{C}$. The scaling bar is 100 μm .

4. Conclusions

In many gel applications, the swelling and deswelling kinetics are very important. Here, we have shown that by conducting the polymerization-crosslinking reactions below $-8\text{ }^{\circ}\text{C}$, one could obtain macroporous PAMPS hydrogels exhibiting superfast swelling properties. It was found that the hydrogels prepared below $-8\text{ }^{\circ}\text{C}$ exhibit a discontinuous morphology consisting of polyhedral pores of sizes 30–50 μm , while those formed at higher temperatures have a non-porous structure. The microstructure of the hydrogels formed at low temperatures was distinctly different from the macroporous networks formed by the reaction-induced phase separation mechanism, where the structure looks like cauliflowers and consists of aggregates of various sizes. We also presented a strategy to regulate the pore size of the gels formed below the bulk freezing temperature of the reaction system. The pore size of the networks increased by decreasing the charge density of the hydrogels, while addition of low molecular weight salts into the gelation system reduced the size of the pores. Calculations based on the equilibrium between ice and unfrozen gel phases in the reaction system at low temperatures explain the results of our observations.

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