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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Superfast Responsive Ionic Hydrogels: Effect of the Monomer Concentration

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**To cite this Article** Ozmen, M. Murat and Okay, Oguz(2006) 'Superfast Responsive Ionic Hydrogels: Effect of the Monomer Concentration', Journal of Macromolecular Science, Part A, 43: 8, 1215 – 1225

**To link to this Article:** DOI: 10.1080/10601320600737393

**URL:** <http://dx.doi.org/10.1080/10601320600737393>

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# Superfast Responsive Ionic Hydrogels: Effect of the Monomer Concentration

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*A series of strong polyelectrolyte gels were prepared in aqueous solution, using the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as the monomer and N,N'-methylene(bis)acrylamide (BAAm) as a crosslinker. The gels were both prepared below ( $-22^{\circ}\text{C}$ ) and above ( $25^{\circ}\text{C}$ ) the bulk freezing temperature of the water, producing cryogels and hydrogels, respectively. The crosslinker (BAAm) content was set at 17 mol%, while the initial monomer concentration  $C_0$  was varied over a wide range. It was found that, at  $-22^{\circ}\text{C}$ , a macroscopic network starts to form at an initial monomer concentration of as low as 0.1 w/v%. In contrast to the conventional hydrogels formed at  $25^{\circ}\text{C}$ , the cryogels have a discontinuous morphology consisting of polyhedral pores of sizes  $10^0$ – $10^2$   $\mu\text{m}$ . The cryogels exhibit superfast swelling properties, as well as reversible swelling–deswelling cycles in water and acetone. An increase in the initial monomer concentration from 2.5 to 10% further increases the response rate of the cryogels due to the simultaneous increase of the porosity of the networks.*

**Keywords** macroporous gels, ionic hydrogels, freezing, swelling, response rate

## 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, etc. (1). Such materials are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators (2, 3). In these applications, a fast response rate of the hydrogel to the external stimuli is needed. In addition, the durability of the hydrogel based devices requires good mechanical performance of gels in their swollen state. However, polymer gels under interest are soft and fragile when handled in the swollen state. Moreover, they are limited in their response rate by diffusion processes, which are slow and even slower near the critical point (4).

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.

Received January 2006; Accepted February 2006.

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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 (5). The low modulus of elasticity of poly(AMPS) (PAMPS) hydrogels even at crosslinker (BAAm) contents as high as 50% suggested that the dense regions of gel mainly consists of agglomerates of BAAm molecules. 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.

One of the techniques to increase the response rate of hydrogels is to create an interconnected pore structure within the hydrogel network (8). We have shown that by conducting the copolymerization-crosslinking reactions below  $-8^\circ\text{C}$ , PAMPS hydrogels with superfast swelling properties could be obtained (9). This was achieved by using gelation reactions occurring in the apparently frozen reaction system, which allowed for the formation of a bicontinuous morphology in PAMPS networks. In this report, we will show that, in addition to the polymerization temperature, the initial monomer concentration is also an important parameter in the design of highly crosslinked macroporous PAMPS networks with superfast responsive properties. Using the experimental technique described below, we were able to prepare ionic hydrogels with a two-phase morphology which absorbed large quantities of water within one minute.

## Experimental

### Materials

N,N'-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and N,N,N',N'-tetramethylethylenediamine (TEMED, Merck) were used as received. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS- $\text{H}^+$ , 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 both APS (0.16 g) and TEMED (0.50 ml) 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 two different temperatures ( $T_{\text{prep}}$ ), namely at  $-22^\circ\text{C}$  and  $25^\circ\text{C}$ . APS (3.51 mM) and TEMED (0.25 mL/100 mL reaction solution) were used as the redox initiator system. The reaction time was set to 24 h. The crosslinker (BAAm) content in the monomer mixture was also fixed at 17 mol%. The initial concentration of the monomers (AMPS + BAAm), denoted by  $C_o$ , was varied between 0.1 and 10 w/v%. To illustrate the synthetic procedure, we give details for the preparation of PAMPS gels at  $C_o = 5\%$ . Stock solutions of AMPS (1.99 mL), BAAm (4.03 mL), and 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  $0^\circ\text{C}$  in an ice-water bath, purged with nitrogen gas for 20 min and then, APS stock solution (1 mL) was added. A portion of this solution was poured into a plastic syringe of 12 mm in diameter with a closed outlet at the bottom, and the polymerization was conducted for one day at  $-22^\circ\text{C}$  or at  $25^\circ\text{C}$ .

## Methods

The gel fraction  $W_g$  after the polymerization was determined by the extraction of the gels in distilled water. For this purpose, the gel matrix after polymerization was taken out of the syringe and immersed in a large excess of distilled water to wash out any soluble polymers, unreacted monomers and the initiator. The gels 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 gel samples (10). They were then washed several times with acetone and dried at 40°C under vacuum to constant weight. The gel fraction  $W_g$  was calculated as  $W_g = m_g/m_m$ , where  $m_g$  and  $m_m$  are the weights of extracted dry gel and of the initial monomer (AMPS + BAAM), respectively.

For the equilibrium swelling measurements, PAMPS gels after preparation in the form of rods of 12 mm in diameter were cut into samples of about 15 mm length. Then, each sample was placed in an excess of water at  $21 \pm 0.5^\circ\text{C}$ . In order to reach swelling equilibrium, the gel samples 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 samples by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm) as well as by weighing the gel samples. Then, they were dried, as described above, at 40°C under vacuum to constant weight. The equilibrium volume and weight swelling ratios of the gels,  $q_v$  and  $q_w$  respectively, were calculated as follows:

$$q_v = (D/D_{dry})^3 \quad (1a)$$

$$q_w = m/m_{dry} \quad (1b)$$

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

For the swelling kinetics measurements, PAMPS gels just after their preparation 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 relative gel masses  $m_{rel} = m_t/m_0$ , where  $m_t$  is the weight of the gel sample at time  $t$  and  $m_0$  is its weight just after preparation.

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 (11). Briefly, a cylindrical gel sample of about 12 mm in diameter and 15–20 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 sec 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 (12),  $f = G(\lambda - \lambda^{-2})$ , where  $f$  is the force

acting per unit cross-sectional area of the undeformed gel specimen, and  $\lambda$  is the deformation ratio (deformed length/initial length).

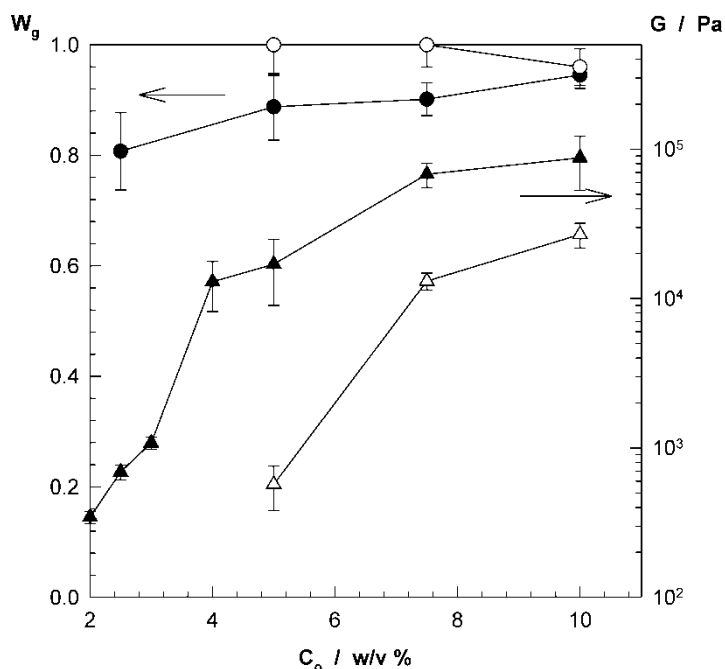
For the texture determination of the dried gels, scanning electron microscopy studies were carried out at magnifications of 30 to 300 times (Jeol 5600 LV). Prior to the measurements, network samples were sputter-coated with gold for 3 min, using an Emscope SC-500 instrument.

## Results and Discussion

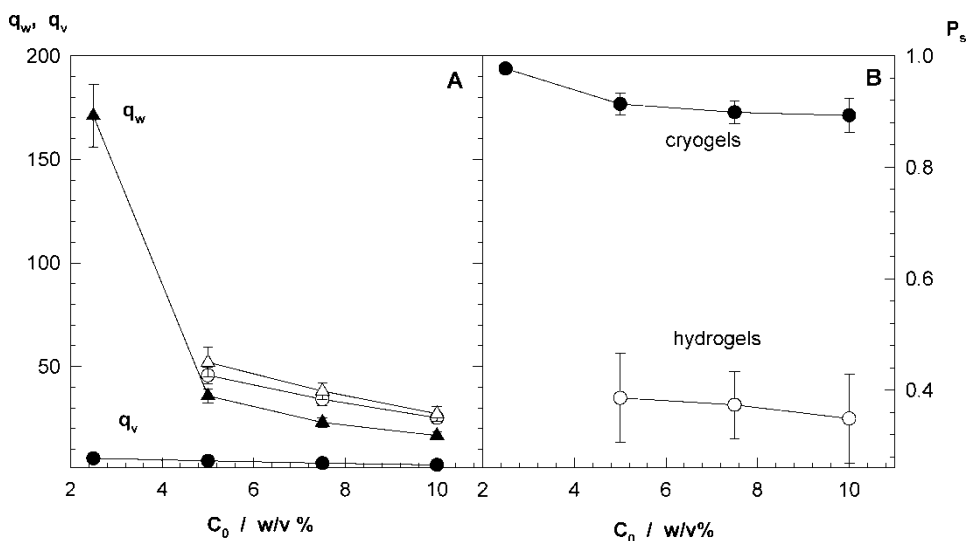
PAMPS gels were prepared both at  $T_{prep} = -22^\circ\text{C}$  and  $25^\circ\text{C}$ , which were designated as cryogels and conventional hydrogels, respectively. It should be noted that the gel preparation temperature  $T_{prep}$  is the temperature of the thermostated bath in which the reactions were carried out. Since the addition of the initiator APS into the monomer solution occurred at  $0^\circ\text{C}$ , 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 or freezing patterns, the reaction mixtures of the same volume were used. The time period between the APS addition and the transfer of the reaction system into the thermostat was also accurately controlled. In our experiments, the crosslinker (BAAm) content was set to 17 mol% while the initial monomer concentration  $C_o$  was varied over a wide range. After one day of the reaction time at  $-22^\circ\text{C}$ , gravimetric measurements showed formation of an insoluble polymer network even at  $C_o = 0.1\%$ . However, gelation reactions conducted at  $25^\circ\text{C}$  required at least an initial monomer concentration of 5% to obtain a crosslinked polymer. Thus, the critical monomer concentration for the onset of gelation is much lower in the cryogels compared to the conventional hydrogels. These results suggest that reducing  $T_{prep}$  below the bulk freezing temperature of the reaction system accelerates the intermolecular crosslinking reactions. This finding is in accord with the observations of Lozinsky (13). He found that, in acrylamide–BAAm copolymerization, the critical concentration for gelation at  $-10^\circ\text{C}$  is twice as low as that at  $20^\circ\text{C}$ .

Figure 1 shows the weight fraction of gel  $W_g$  and the modulus of elasticity of swollen gels  $G$  plotted against the initial monomer concentration  $C_o$ . Filled and open symbols represent data obtained from the cryogels and the hydrogels, respectively. Since the cryogels formed below  $C_o = 2.5\%$  were too weak to withstand the characterization tests, only data in the range of  $C_o = 2.5\text{--}10\%$  are shown in Figure 1. The gel fraction  $W_g$  is higher than 80% for all the networks prepared in this study, indicating the high efficiency of the crosslinking reactions, even at  $-22^\circ\text{C}$ .  $W_g$  of cryogels increases from 0.8 to unity with increasing monomer concentration, while a complete conversion of the monomers to the crosslinked polymer was obtained for all the hydrogels. The moduli of elasticity  $G$  of gels are in the range of  $10^2\text{--}10^5$  Pa. As expected,  $G$  is an increasing function of  $C_o$  due to the simultaneous increase of the concentration of the network chains. Figure 1 also shows that the cryogels exhibit larger moduli than the corresponding hydrogels.

In Figure 2A, the equilibrium weight ( $q_w$ ) and the volume swelling ratios ( $q_v$ ) of the cryogels (filled symbols) and the hydrogels (open symbols), measured using separate techniques, are shown as a function of the monomer concentration  $C_o$ . The  $q_w$  and  $q_v$  data are shown in the Figure by triangles and circles, respectively. For the hydrogels, both  $q_w$  and  $q_v$  equal to  $49 \pm 3$  at  $C_o = 5\%$ , are a slightly decreasing function of the monomer concentration. However, for the cryogels, the weight swelling ratio  $q_w$  is much larger than the volume swelling ratio  $q_v$  and, the difference between  $q_w$  and  $q_v$  is increasing with



**Figure 1.** The gel fraction  $W_g$  (circles) and the elastic modulus  $G$  (triangles) of equilibrium swollen PAMPS cryogels (filled symbols) and hydrogels (open symbols) shown as a function of the initial monomer concentration  $C_0$ .



**Figure 2.** (A) The equilibrium weight ( $q_w$ ) and volume swelling ratios ( $q_v$ ) of the cryogels (filled symbols) and the hydrogels (open symbols) shown as a function of the monomer concentration  $C_0$ .  $q_w$  and  $q_v$  data are shown by triangles and circles, respectively; (B) The swollen state porosity  $P_s$  of the cryogels (filled symbols) and the hydrogels (open symbols), calculated using Equation (2), shown as a function of the monomer concentration  $C_0$ .

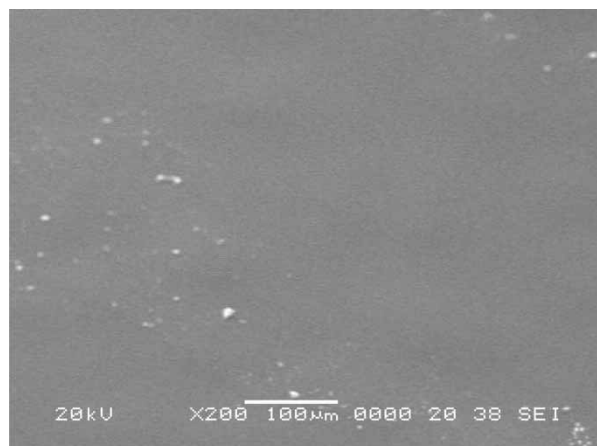
decreasing  $C_o$ ; at  $C_o = 2.5\%$ , cryogel swells about 30-fold more by weight than by volume. The relative values of the weight and the volume swelling ratios of the networks provide information about the internal structure of porous networks in their swollen state (8). During the swelling process, the pores inside the network are rapidly filled with the solvent; at the same time, the polymer region takes up solvent from the environment whose extent depends on the attractive force between the solvent molecules and polymer segments. Thus, two separate processes govern the swelling of porous networks (8): a) solvation of network chains, b) filling of the pores by the solvent. The equilibrium weight swelling ratio  $q_w$  includes the amount of solvent taken by both of these processes, i.e.,  $q_w$  includes the solvent in the gel as well as in the pore regions of the network. Thus, both the solvation and filling processes are responsible for the  $q_w$  values of the networks. On the contrary, if we assume isotropic swelling, that is the volume of the pores remains constant upon swelling, volume swelling ratio  $q_v$  of porous networks is caused by solvation of the network chains, i.e., by the first process. Thus,  $q_v$  only includes the amount of solvent taken by the gel portion of the network. Accordingly, the higher the difference between  $q_w$  and  $q_v$ , the higher is the volume of the pores in the network sample. The swollen state porosity of the networks  $P_s$  can be calculated from the swelling ratios using the Equation (2) (8, 14, 15):

$$P_s = 1 - q_v[1 + (q_w - 1)d_2/d_1]^{-1} \quad (2)$$

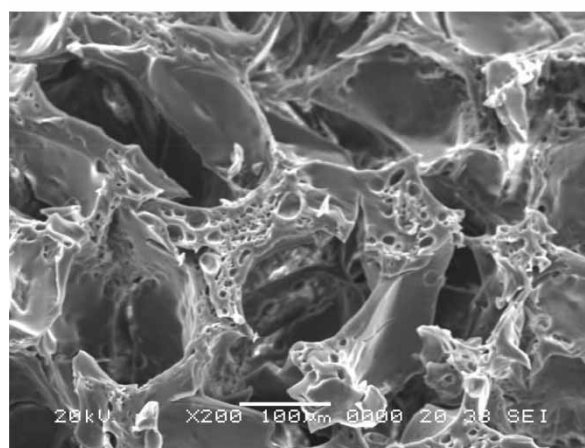
where  $d_1$  and  $d_2$  are the densities of solvent (water) and polymer, respectively. Assuming that  $d_1 = 1 \text{ g/mL}$  and  $d_2 = 1.44 \text{ g/mL}$ , we calculated swollen state porosities  $P_s$  of the networks by use of Equation (2). The results are given in Figure 2B as a function of the monomer concentration  $C_o$ . For the cryogels, the swollen state porosity  $P_s$  is close to 100% at  $C_o = 2.5\%$  and is slightly decreasing with the monomer concentration. However, swollen state porosities of the hydrogels are considerable lower than those of the cryogels.

The morphologies of dried gel samples were observed by scanning electron microscopy (SEM). SEM analysis of the dried hydrogels revealed the presence of a continuous morphology, independent of the monomer concentration. This is also illustrated in Figure 3A, where the SEM image of a dried hydrogel network formed at  $C_o = 5\%$  is shown at a magnification of 200 times. It seems that the pores existing in the swollen hydrogels totally collapse during their drying process. However, a bicontinuous morphology was observed in all SEM pictures of the cryogels. In the scanning electron micrograph in Figure 3B, the microstructure of the dried cryogel formed at  $C_o = 10\%$  is given. One can identify regular assembly of polyhedral large pores of sizes  $10^2 \mu\text{m}$  together with small pores of sizes  $10^1 \mu\text{m}$  locating in the walls of the large pores.

The formation of pores in the cryogels can be explained with the action of ice as a pore-forming agent during their formation processes. Lozinsky and coworkers investigated polymerization reactions conducted below the freezing point of water (13, 16–20). The essential feature of such reaction systems is that the monomers and the initiator are concentrated in the unfrozen micro-zones 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 (13). Thus, in these cryo-gelation 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. The latter steps lead to a porous structure (13). The reason why water in aqueous solutions does not freeze at below the bulk freezing temperature is



(A)



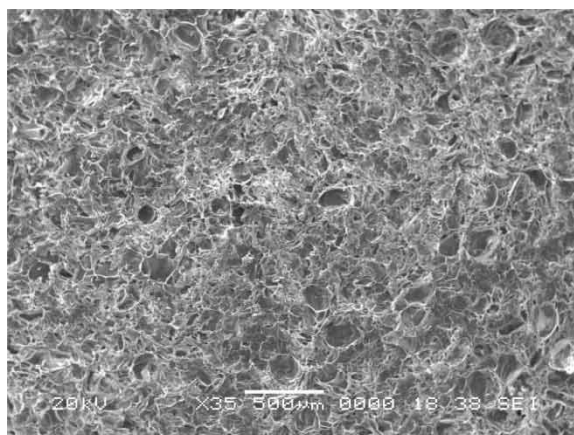
(B)

**Figure 3.** SEM of PAMPS networks formed at  $T_{prep} = 25^{\circ}\text{C}$  (A) and  $-22^{\circ}\text{C}$  (B).  $C_o = 5$  (A) and  $10\text{ w/v}\%$  (B). The scaling bar is  $100\ \mu\text{m}$ . Magnification = 200.

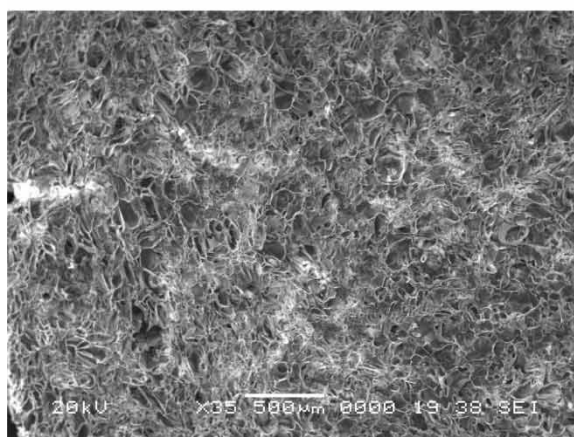
attributed, in the main, to the freezing point depression of the water due to the solutes (21). Recently, we calculated that the amount of unfrozen liquid phase constitutes about 20% of the apparently frozen reaction system at  $T_{prep} = -22^{\circ}\text{C}$  (9). This indicates that the polymerization reactions only proceeds in this unfrozen liquid phase, while the remaining part of the system, about 80% of the whole reaction volume, forms the voids (pores) in the final material. The pores of sizes  $10^2\ \mu\text{m}$  shown in Figure 3B appear after removing the ice phase from the cryogel by thawing. Moreover, the small pores of sizes  $10^1\ \mu\text{m}$  probably form due to the small ice crystals separated from the reaction zones during the initial non-isothermal reaction period between  $0^{\circ}\text{C}$  (APS addition) and  $T_{prep}$ .

Figure 4 shows SEM images of dried cryogels formed at various monomer concentrations  $C_o$  between 2.5 and 10%. All the polymer samples have a porous structure with pore sizes of  $10^0$ – $10^2\ \mu\text{m}$ . The higher the initial monomer concentration, the larger the pores and the thicker the pore walls. It is also seen that the pores become increasingly regular as the monomer concentration is increased. One may expect that, at a low

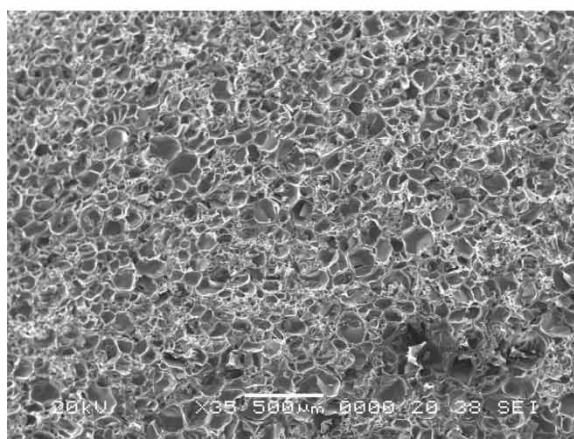




(A)



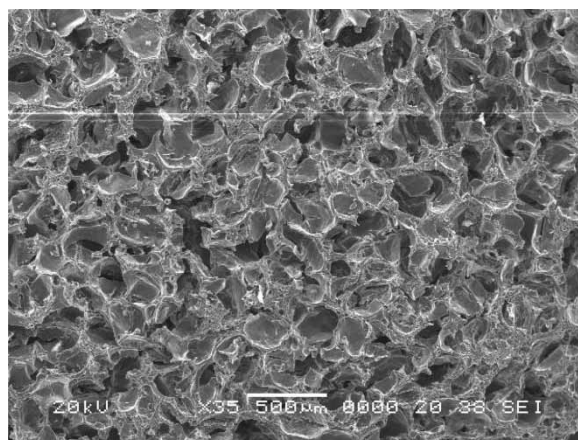
(B)



(C)

**Figure 4.** SEM of PAMPS networks formed at  $T_{prep} = -22^{\circ}\text{C}$ .  $C_o = 2.5$  (A), 5 (B), 7.5 (C), and 10 w/v% (D). The scaling bars are 500  $\mu\text{m}$ . Magnification = 35.

(continued)



(D)

Figure 4. Continued.

monomer concentration, the pore walls are too weak so that the pores are more or less fused together to form irregular aggregates (22, 23).

PAMPS hydrogels and cryogels formed at various  $C_o$  were subjected to swelling and deswelling processes in water and in acetone, respectively. For this purpose, the gel samples after preparation were 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 gels were 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 at least twice. Typical results are shown in Figures 5A and 5B for the cryogels and the hydrogels, respectively. Here, the relative gel mass  $m_{rel}$  is plotted against the time of swelling or deswelling. The initial monomer concentrations  $C_o$  are indicated in

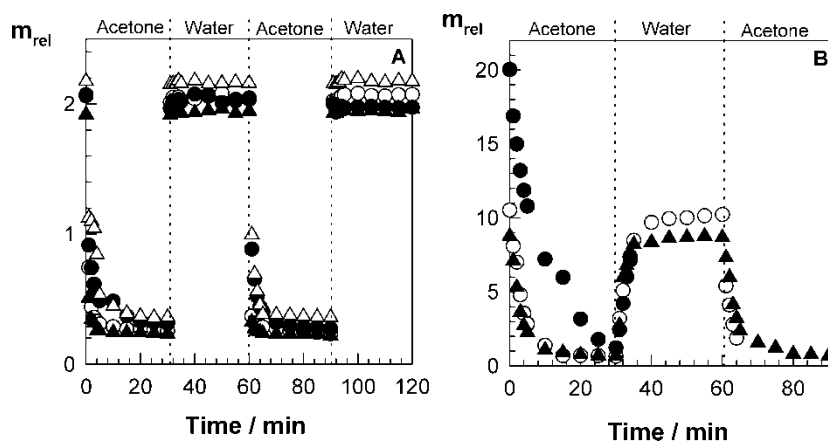
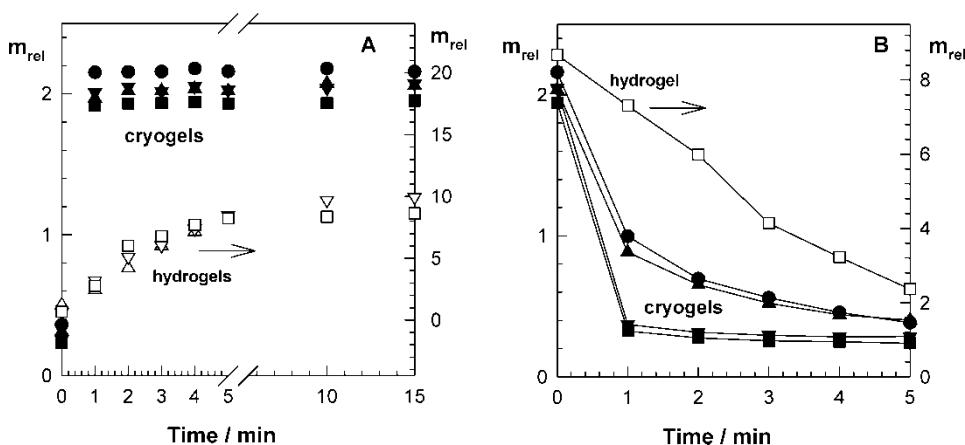


Figure 5. Swelling and deswelling kinetics of the cryogels (A) and the hydrogels (B) in water and in acetone, respectively, shown as the variation of the relative gel mass  $m_{rel}$  with the time of swelling or deswelling.  $C_o = 2.5$  ( $\Delta$ ), 5 ( $\bullet$ ), 7.5 ( $\circ$ ), and 10 w/v% ( $\blacktriangle$ ).

Figure 5. Completely reversible swelling–deswelling cycles were obtained using cryogel samples formed between  $C_o = 2.5$  and 10%. However, hydrogels formed below  $C_o = 10\%$  were too soft in their swollen states in water; during the first or second deswelling processes in acetone, they were broken into several pieces so that a cycle cannot be completed. Figures 6A and 6B show the initial stages of swelling and deswelling processes of gels in water and in acetone, respectively. Filled and open symbols are data obtained from cryogels and hydrogels, respectively. It is seen that the swelling response rate of the collapsed cryogel to a solvent quality change from acetone to water occurs much more rapidly than the response rate of the collapsed hydrogel (Figure 6A). The collapsed cryogels attain their equilibrium states in water in less than 1 min, while the hydrogels require about 10 min to reach their equilibrium states. Further, the deswelling of the cryogels in acetone also occurs much faster than the hydrogels (Figure 6B). The accelerating swelling and deswelling rates of cryogels 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. Thus, the drastic difference of the network microstructure between the cryogels and hydrogels shown in Figure 3 is reflected by the dynamic swelling tests of the gel samples. The two-phase morphology created in the gel network provides a mechanical stability against the volume changes as well as superfast responsive properties. Figure 6B also shows that the cryogels formed above 5% monomer concentration deswells in acetone much more rapidly than the cryogels formed in more dilute solutions. These results can be explained with increasing porosity of cryogels with the initial monomer concentration  $C_o$ . The porous structure in cryogels formed at  $C_o \geq 5\%$  allows an easy diffusion of water molecules outside of the gel phase.

## Conclusions

PAMPS gels were prepared both below ( $-22^\circ\text{C}$ ) and above ( $25^\circ\text{C}$ ) the bulk freezing temperature of the polymerization solvent water, which are called cryogels and the hydrogels, respectively. The initial monomer concentration  $C_o$  used in the gel preparation



**Figure 6.** The initial period of swelling and deswelling processes of the cryogels (filled symbols) and the hydrogels (open symbols) in water and in acetone, respectively.  $C_o = 2.5$  ( $\bullet$ ,  $\circ$ ), 5 ( $\blacktriangle$ ,  $\triangle$ ), 7.5 ( $\blacktriangledown$ ,  $\triangledown$ ), and 10 w/v% ( $\blacksquare$ ,  $\square$ ).

was varied over a wide range. The critical monomer concentration for the onset of gelation was found to be much lower in the cryogels compared to the conventional hydrogels. The cryogels have a discontinuous morphology consisting of polyhedral pores of sizes  $10^0$ – $10^2$   $\mu\text{m}$ . They also exhibit superfast swelling properties as well as reversible swelling–deswelling cycles in water and in acetone. An increase in the initial monomer concentration from 2.5 to 10% further increases the response rate of the cryogels due to the simultaneous increase of the porosity of the cryogel networks.

### Acknowledgment

Work was supported by the Scientific and Technical Research Council of Turkey (TUBITAK), TBAG–105T246.

### References

1. Shibayama, M. and Tanaka, T. (1993) *Adv. Polym. Sci.*, 109: 1.
2. Suzuki, M. and Hirasa, O. (1993) *Adv. Polym. Sci.*, 110: 241.
3. Santulli, C., Patel, S.I., Jeronimidis, G., Davis, F.J., and Mitchell, G.R. (2005) *Smart Mater. Struct.*, 14: 434.
4. Tanaka, T. and Fillmore, D.J. (1979) *J. Chem. Phys.*, 70: 1214.
5. Ozmen, M.M. and Okay, O. (2004) *Polym Bull.*, 52: 83.
6. Gundogan, N., Melekaslan, D., and Okay, O. (2002) *Macromolecules*, 35: 5616.
7. Funke, W., Okay, O., and Joos-Muller, B. (1998) *Adv. Polym. Sci.*, 136: 139.
8. Okay, O. (2000) *Prog. Polym. Sci.*, 25: 711.
9. Ozmen, M.M. and Okay, O. (2005) *Polymer*, 46: 8119.
10. Durmaz, S. and Okay, O. (2000) *Polymer*, 41: 3693.
11. Sayil, C. and Okay, O. (2001) *Polymer*, 42: 7639.
12. Treloar, L.R.G. (1975) *The Physics of Rubber Elasticity*; University Press: Oxford.
13. Lozinsky, V.I. (2002) *Russ Chem. Rev.*, 71: 489.
14. Okay, O. (1988) *Angew Makromol. Chem.*, 157: 1.
15. Okay, O. (1987) *Angew Makromol. Chem.*, 153: 125.
16. Lozinsky, V.I., Plieva, F.M., Galaev, I.Y., and Mattiasson, B. (2002) *Bioseparation*, 10: 163.
17. Arvidsson, P., Plieva, F.M., Lozinsky, V.I., Galaev, I.Y., and Mattiasson, B. (2003) *J. Chromatogr.*, A986: 275.
18. Lozinsky, V.I., Ivanov, R.V., Kalinina, E.V., Timofeeva, G.I., and Khokhlov, A.R. (2001) *Macromol. Rapid. Commun.*, 22: 1441.
19. Ivanov, R.V., Babushkina, T.A., and Lozinsky, V.I. (2005) *Polymer Science, Series A*, 47: 791.
20. Lozinsky, V.I., Kalinina, E.V., Grinberg, V.Y., Chupov, V.V., and Plate, N.A. (1997) *Polymer Science, Series A*, 39: 1300.
21. Wolfe, J., Bryant, G., and Koster, K.L. (2002) *Cryo-Letters*, 23: 157.
22. Okay, O., Soner, E., Gungor, A., and Balkas, T.I. (1985) *J. Appl. Polym. Sci.*, 30: 2065.
23. Okay, O. (1986) *J. Appl. Polym. Sci.*, 32: 5533.