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# Preparation of macroporous poly(acrylamide) hydrogels in DMSO/water mixture at subzero temperatures

**M. Murat Ozmen[1], M. Valentina Dinu[2], and Oguz Okay[1] (✉)**

[1] Istanbul Technical University, Department of Chemistry, Maslak, 34469 Istanbul, Turkey
[2] "Petru Poni" Institute of Macromolecular Chemistry, Functional Polymers Department, Iasi, Romania
E-mail: okayo@itu.edu.tr; Fax: +90-2122856386

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## Summary

The copolymerization reactions of acrylamide and N,N'-methylenebis(acrylamide) were carried out in DMSO/water mixture (1:1 by volume) at various temperatures $T_{prep}$ between -18 and 22°C. Scanning electron microscopy analysis of the networks revealed the presence of porous morphologies. All the network samples formed at or below 0°C have relatively small pores with sizes about $10^0$ μm. In this range of $T_{prep}$, the pore size only slightly increases with the temperature. As the temperature is increased above 0°C, both the average pore size and the degree of polydispersity of the pores rapidly increase. Between $T_{prep}$ = 0 and 13°C, the microstructure gradually changes from networks having relatively small pores to those exhibiting regular assembly of polyhedral large pores of about $10^1$ μm in sizes. The formation of the porous structure at or below 0°C is as a result of the cooling-induced phase separation mechanism, while the large polyhedral pores in the networks prepared at higher temperatures form during the freeze-dry process of the hydrogels after preparation.

## Introduction

Macroporous crosslinked polymers are most efficient materials for many separation processes and therefore, they are widely used as starting material for ion exchange resins and as specific sorbents. Such materials are mainly produced by reaction-induced phase separation technique, which involves the copolymerization of the monomer-crosslinker mixture in the presence of an inert diluent [1-3]. Depending on the thermodynamic parameters of the reaction system, the inert diluent phase separates before or after the onset of macrogelation, leading to the formation of domains of various sizes. After polymerization, the diluent removed from the network leaves a porous structure within the highly crosslinked polymer particles. The inert diluent thus acts as a pore forming agent, and plays an important role in the design of the pore structure of crosslinked materials. The disadvantage of the reaction-induced phase separation technique is however twofold. First, the polymers usually have a broad pore size distribution ranging from a few nanometers to tens of micrometers. Second, the porous materials obtained exhibit poor mechanical performance such as very low

fracture toughness so that they were very difficult to handle in applications requiring significant applied stress or strain.

An alternative approach to obtain macroporous polymers with better mechanical performance is the cryogelation technique. As is well known, in sea ice, pure hexagonal ice crystals are formed and the various impurities, e.g., salts, biological organisms, etc. are expelled from the forming ice and entrapped within the liquid channels between the ice crystals. This natural principle was used by Lozinsky et al. for the preparation of porous gels [4]. As in nature, during the freezing of a monomer solution, the monomers expelled from the ice concentrate within the channels between the ice crystals, so that the polymerization reactions only take place in these unfrozen liquid channels [4-8]. After polymerization and, after melting of ice, a porous material is produced whose microstructure is a negative replica of the ice formed. Recently, we have shown that by conducting the copolymerization-crosslinking reactions below –8°C, macroporous hydrogels based on acrylamide (AAm) as well as 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomers with superfast swelling properties could be obtained [9-11]. This was achieved by using gelation reactions occurring in the apparently frozen reaction system, which allowed for the formation of a heterogeneous morphology in polymer networks. It was shown that the free water freezing in the gel causes the network chains to gather and condense so that a heterogeneous network forms after removing the ice. The polymer network maintains a honeycomb structure upon drying. Further, due to the high polymer concentration in the pore walls of these materials, they were very tough and could withstand high levels of deformation such as elongation, bending, and compression.

To examine the effect of solvent type on the shape and size of the pores, our aim in this study was to conduct the low temperature polymerization reactions of AAm in dimethyl sulfoxide (DMSO) instead of water. Since the freezing point of DMSO is 18°C, one could obtain a larger range of porosities in DMSO as the polymerization solvent. However, preliminary experiments showed no gelation at temperatures 5°C or below and over the range of the initial monomer concentration between 5 and 20 w/v %. In contrast, in 1:1 DMSO/water mixture (all by volume), gelation occurred even at -18°C and, the hydrogels obtained were opaque indicating formation of porous structures. These experimental findings motivated us to explore the formation mechanism of porous structures in poly(acrylamide) (PAAm) hydrogels in 1:1 DMSO/water mixture. The copolymerization – crosslinking reactions of AAm monomer and N,N'-methylenebis(acrylamide) (BAAm) crosslinker were carried out at various temperatures between -18 and 22°C. As will be seen below, remarkably different porous structures were obtained by varying the temperature which is accounted for by the change of the formation mechanism of the pores in the hydrogels.

## Experimental section

### *Materials and Methods*

Acrylamide (AAm, Merck), N,N'-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), N,N,N',N'-tetramethylethylenediamine (TEMED, Merck), dimethyl sulfoxide (DMSO, Merck) were used as received. Stock solutions of APS and TEMED were prepared by dissolving 0.25 g APS and 0.50 mL TEMED each in 20 mL of distilled water. PAAm hydrogels were prepared by free-

radical crosslinking copolymerization of AAm with BAAm in DMSO/water mixture (1:1 v/v) at various temperatures ($T_{prep}$) between -18°C and 22°C. The initial concentration of the monomers (AAm + BAAm), denoted by $c_M$, as well as the crosslinker ratio $X$, the mole ratio of the crosslinker BAAm to the monomer AAm, were fixed at 0.15 g/mL and 1/80, respectively. The reaction time was set to 24 h. APS (5.26 mM) and TEMED (0.25 mL / 100 mL reaction solution) were used as the redox initiator system. The following example illustrates the synthetic procedure applied throughout this work:

1.4604 g AAm, 0.0396 g BAAm, water (3 mL), DMSO (5 mL), and TEMED stock solution (1 mL) were first mixed in a graduated flask of 10 mL in volume. The solution was purged with nitrogen gas for 10 min and then, APS stock solution (1 mL) was added. The solution was transferred to a plastic syringe (or to a glass tube) of about 4 mm in diameter, it was sealed by parafilm, immersed in a thermostated bath at $T_{prep}$ and the polymerization was conducted for one day. After polymerization, the syringe was taken out of the bath and the gel rod was removed from the syringe. The gel was cut into specimens of approximately 10 mm in length and immersed in a large excess of water at 21 ± 0.5°C to wash out any soluble polymers, unreacted monomers and the initiator. In order to obtain PAAm networks, the equilibrium swollen gel samples were taken out of water and immersed in liquid nitrogen for 1 min before they were freeze-dried at -40°C and 76 mm Hg.

It should be mentioned that, since the addition of the initiator APS into the monomer solution occurred at room temperature (21°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 cooling patterns, the reaction mixtures of the same volume and shape were used. Moreover, the type of the reactor (plastic syringe or glass tube) did not influence the hydrogel properties.

*Differential scanning calorimetry (DSC) measurements*

DSC measurements were performed on a Perkin-Elmer Diamond differential scanning calorimeter under a nitrogen flow (20 mL/min). Hydrogel samples equilibrium swollen in 1:1 DMSO/water mixture were placed in the aluminum sample pan of the instrument. The pan was sealed and weighed. Then, it was held within the instrument at -50°C for two hours and then heated to room temperature with a scanning rate of 1°C/min.

*Gel fraction measurements*

For the gel fraction measurements, the hydrogel samples were extracted with water at least for one month. For this purpose, each hydrogel sample was placed in an excess of water at 21 ± 0.5°C and water was replaced several times. The gel fraction $W_g$ was calculated as:

$$W_g = \frac{m_{dry}}{m_o\, c_M} \qquad (\mathbf{1})$$

where $m_{dry}$ and $m_o$ are the weights of the gel samples after drying and just after preparation, respectively.

*Swelling measurements*

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

$$q_v = \left(D_w / D_{dry}\right)^3 \tag{2}$$

$$q_w = m_w / m_{dry} \tag{3}$$

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

For the swelling tests of PAAm hydrogels in 1:1 DMSO/water mixture, gel samples prepared at 22°C were used. The cylindrical gel samples of 4 mm in diameter and about 5 mm in length were first swollen in water until equilibrium is reached. Then, to obtain gels at various initial polymer concentrations $c_P$, equilibrium swollen gels were placed in sealed 50 mL vials at room temperature to evaporate a desired amount of the gel solvent. This procedure ensured uniformity of the network concentration throughout the gel sample [12]. At various evaporation times between a few minutes and a few months, the diameters $D_i$ of partially swollen gels were measured, from which their polymer concentration $c_P$ (in g/mL) was calculated as

$$c_P = \frac{c_M}{\left(D_i / D_o\right)^3} \tag{4}$$

where $D_o$ is the diameter of the gel just after preparation. In this way, a series of hydrogel samples with $c_P$ between 0.05 and 0.30 g/mL were obtained. The gel samples were then immersed in 1:1 DMSO/water mixture at -18°C and its relative volume swelling ratio $V_{rel}$ (volume of swollen gel/volume of gel after preparation) was calculated as

$$V_{rel} = \left(\frac{D_S}{D_o}\right)^3 \tag{5}$$

where $D_S$ is the diameter of the gel samples in 1:1 DMSO/water mixture. The swelling measurements were conducted at various temperatures by gradually changing the temperature of DMSO/water solution from -18°C up to 22°C and then back again to -18°C. To reach swelling equilibrium, the hydrogels were immersed in DMSO/water mixture for at least 2 days at each temperature.

For the measurement of the deswelling times of gels, the equilibrium swollen hydrogel samples in water were immersed in acetone at 21°C. The volume changes of

gels were measured in-situ by following the diameter of the samples under microscope using the image analyzing system. For the measurement of the swelling times of gels, the collapsed gel samples in acetone were transferred into water at 21°C. The diameter changes of gels were also determined as described above.

*Elasticity tests*

Uniaxial compression measurements were performed on gels just after preparation and 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 [13]. 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 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 elastic modulus G was determined from the slope of linear dependence [14],

$$f = G\left(\lambda - \lambda^{-2}\right) \qquad (\mathbf{6})$$

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).

*Texture determination*

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

## Results and discussion

*Characteristics of macroporous PAAm hydrogels*

As mentioned in the Introduction, no gelation was observed during the copolymerization of AAm and BAAm in DMSO at or below 5°C. However, in DMSO/water mixture with a 1:1 volume ratio, PAAm hydrogels were obtained over the whole range of temperature $T_{prep}$ studied. Table 1 shows the observed state of the hydrogels formed in DMSO/water by the naked eye at various $T_{prep}$ and initial monomer concentration $c_M$. As $T_{prep}$ is decreased or, $c_M$ is increased, the hydrogels became opaque indicating the appearance of heterogeneities. At $c_M \geq 0.15$ g/mL, heterogeneous hydrogels could be obtained over a wide range of temperature up to about 13°C. For the following experiments, $c_M$ was kept constant at 0.15 g/mL.

**Table 1.** Appearance of PAAm hydrogels formed in DMSO/water (1:1. v/v) at various temperatures $T_{prep}$ and initial monomer concentrations $c_M$. vO = very opaque, O = opaque, sO = slightly opaque, T = transparent.

| $T_{prep}$ (°C) / $c_M$ (g/mL) | -18 | -10 | 0 | 5 | 13 | 22 |
|---|---|---|---|---|---|---|
| **0.05** | O | T | T | T | T | T |
| **0.10** | O | O | O | O | T | T |
| **0.15** | vO | vO | O | O | sO | T |
| **0.20** | vO | vO | O | O | sO | T |

The gelation experiments in 1:1 DMSO/water mixture were carried out at temperatures $T_{prep}$ between -18 and 22°C. Fig. 1A shows the gel fraction $W_g$ and the moduli of elasticity of the hydrogels just after preparation $G_o$ and after equilibrium swelling in water $G$ plotted against $T_{prep}$. The gel fraction is above 80% and is almost independent of the polymerization temperature. Thus, the conversion of monomer to the crosslinked polymer is almost complete even at very low subzero temperatures. In contrast, however, the elastic modulus of the hydrogels rapidly decreases as $T_{prep}$ is decreased. The hydrogel formed at room temperature exhibit an elastic modulus around 10 kPa which decreases continuously as $T_{prep}$ is decreased and becomes less than 1 kPa at -18°C. Swelling slightly decreases the modulus of elasticity due to the decreasing concentration of the elastically effective network chains in the hydrogels.

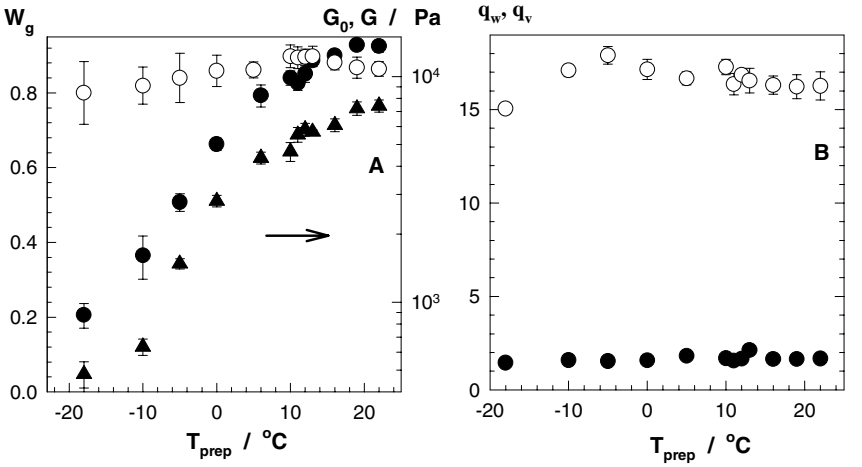


**Figure 1. (A)** The gel fraction $W_g$ (○) and the moduli of elasticity of the hydrogels just after preparation $G_o$ (●) and after equilibrium swelling in water $G$ (▲) shown as a function of $T_{prep}$. **(B)** equilibrium weight $q_w$ (○) and the equilibrium volume swelling ratio $q_v$ (●) of the hydrogels shown as a function of $T_{prep}$.

In Fig. 1B, the equilibrium weight $q_w$ (open symbols) and the equilibrium volume swelling ratios $q_v$ (filled symbols) of the hydrogels are shown as a function of the temperature $T_{prep}$. For all the hydrogels, whether transparent or opaque in appearance,

$q_w$ and $q_v$ equal to 16.6 ± 0.7 and 1.7 ± 0.2, respectively, independent of $T_{prep}$. The relative values of the weight and the volume swelling ratios of the hydrogels are known to provide information about their internal structure in the swollen state [1,2]. During the swelling of heterogeneous gels, the pores inside the network are rapidly filled with the solvent; at the same time, the polymer region takes up solvent from the environment. Thus, two separate processes govern the swelling of porous networks: i) solvation of network chains, and ii) 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 while the volume swelling ratio $q_v$ of porous networks is mainly 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. From the weight and volume swelling ratios of hydrogels, the swollen state porosity of the networks $P_s$ can be estimated using the equation [2]:

$$P_s = 1 - q_v\left[1 + (q_w - 1)\rho / d_1\right]^{-1} \qquad (\mathbf{7})$$

where $d_1$ and $\rho$ are the densities of solvent (water) and polymer, respectively. Assuming that $d_1$ = 1 g/mL and $\rho$ = 1.35 g/mL [15], swollen state porosities $P_s$ of the entire hydrogels were calculated as 92%.

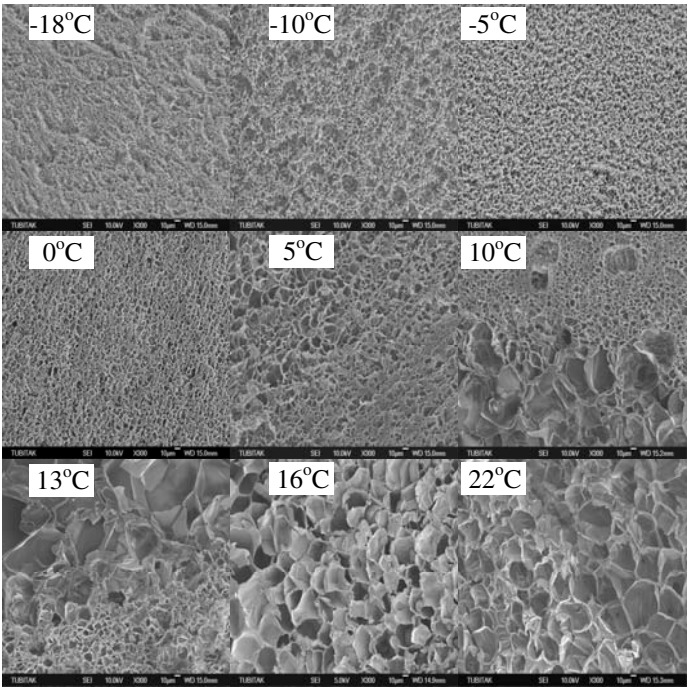


**Figure 2.** SEM of PAAm networks obtained at various $T_{prep}$ indicated. The scaling bars are 10 μm. Magnification = x300. $c_M$ = 0.15 g/mL.

To visualize the pores in the hydrogels, the morphologies of dried gel samples were observed by scanning electron microscopy (SEM). SEM analysis of the networks

formed between 22 and –18°C revealed the presence of heterogeneous morphologies. In the scanning electron micrographs in Figure 2, the microstructure of the networks formed at various $T_{prep}$ is shown. By measuring the sizes of at least 50 pores, the average pore sizes were calculated, and are shown in Figure 3 plotted against $T_{prep}$. Note that the length of the error bars in the figure represents the degree of polydispersity of the pores. All the polymer samples formed at or below 0°C have relatively small pores with sizes about $10^0$ μm. In this range of $T_{prep}$, the pore size only slightly increases with the temperature. As the temperature is increased above 0°C, both the average pore size and the degree of polydispersity of the pores rapidly increase, as seen in Figures 2 and 3. Further, between $T_{prep}$ = 0 and 13°C, two generations of pores can be seen in Figure 2, indicating that the microstructure gradually changes from networks having relatively small pores to those exhibiting regular assembly of polyhedral large pores of about $10^1$ μm in size.

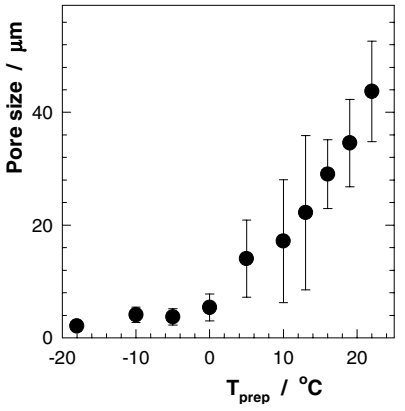


**Figure 3.** Average pore size of PAAm networks shown as a function of $T_{prep}$. The length of the error bars represents the degree of the polydispersity of the pores. The pore sizes were measured from SEM images at various magnifications between 50 and 3000 times.

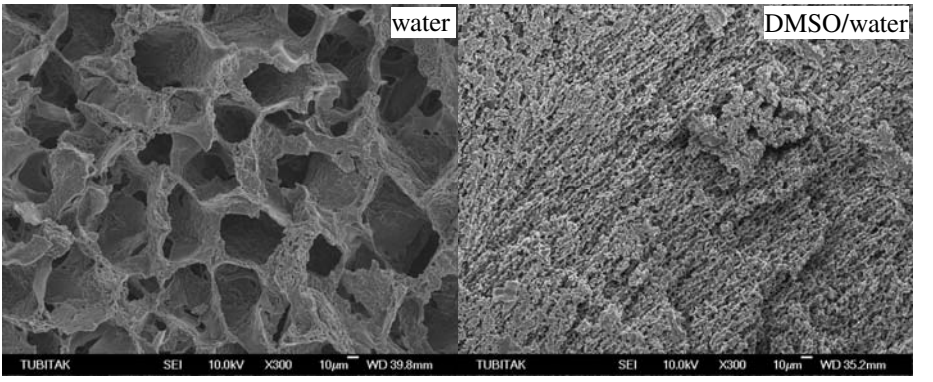


**Figure 4.** SEM of PAAm networks formed at -18°C in water (left) and in 1:1 DMSO/water mixture (right). Scaling bars are 10 μm. Magnification = x300. Characteristics of the hydrogels formed in water: $q_w$ = 14.8, $q_v$ = 3.6, and $P_s$ = 82%.

It should be noted that the morphologies of the present hydrogels are distinctly different from those obtained using water as the polymerization solvent [9]. For example, SEM images shown in Figure 4 were taken from dried PAAm gel samples

formed in water (left) and in 1:1 DMSO/water (right). Both hydrogels were prepared at $T_{prep}$ = -18°C and at an initial monomer concentration of 0.15 g/mL. The hydrogel formed in water has very large pores of about $10^2$ μm while that obtained in DMSO/water exhibits pores about two orders of magnitude smaller than in the former hydrogel. Thus, the presence of DMSO during gelation drastically reduces the pore size in PAAm networks.

*Formation mechanism of macroporous structures*

To answer the question, how the porosity in PAAm network forms over the whole range of the temperature $T_{prep}$, we should first note that the DMSO/water mixtures exhibit a marked freezing point depression due to the formation of stable DMSO/water complexes [16]. By simply adding DMSO to water, freezing point of the resulting mixture is lowered and becomes -52°C at a volume ratio of 1:1 [17]. However, since free water molecules in the mixture may freeze during polymerization and thus, after thawing, may produce pores inside the gel network, DSC measurements were conducted using hydrogel samples swollen in 1:1 DMSO/water mixture. For this purpose, the samples were first cooled down to -50°C and then, they were heated up to the room temperature. No peak in the DSC scans was observed indicating that the crosslinking polymerization reactions of AAm in 1:1 DMSO/water proceed in an unfrozen state.

Thus, formation of macroporous PAAm hydrogels in DMSO/water should be a result of a phase separation process. To explore the condition of phase separation during the reactions, we investigated the swelling capacity of the hydrogels in the reaction solution, i.e., in 1:1 DMSO/water mixture, at various temperatures. As explained in detail earlier [2,3], a phase separation occurs during gelation, if the gel formed cannot absorb all the available reaction solution; in other words, if the swelling capacity of the gel is less than the amount of the DMSO/water mixture present in the system. Thus, let $V_{rel}$ be the equilibrium volume swelling ratio of the hydrogel in the reaction solution (volume of equilibrium swollen gel / volume of gel after preparation), if $V_{rel} \geq 1$, only one phase exists in the reaction system because the gel absorbs all the reaction solution available. A phase separation during gelation requires the condition $V_{rel} < 1$ so that a part of the reaction solvent separates out of the gel phase.

Figure 5 shows $V_{rel}$ of the hydrogels in 1:1 DMSO/water mixture at various initial polymer concentrations $c_P$ plotted against the swelling temperature $T_{swell}$. The direction of the temperature change is indicated in the figures by the arrows. The critical condition for a phase separation is denoted by the dotted horizontal lines. It is seen that the initial polymer concentration $c_P$ in the hydrogels and thus, the direction of the temperature change significantly affect the swelling capacity of the hydrogels. If $c_P$ is above 0.10 g/mL, DMSO/water mixture is a poor solvent for PAAm at low temperatures, so that the hydrogel shrinks, while increasing temperature results in gel swelling. It should be noted that such a strong temperature-dependent swelling behavior of PAAm gels in DMSO/water mixture has not been observed before. The published data show weak temperature dependence due to the low polymer concentration of the hydrogels used in the swelling tests ($c_P$ = 0.01 – 0.05 g/mL) [18]. Figure 5 clearly shows that the polymer concentration in PAAm-DMSO-water ternary system is critical for the observation of deswelling transition at subzero temperatures and, is also responsible for the formation of macroporous hydrogels.

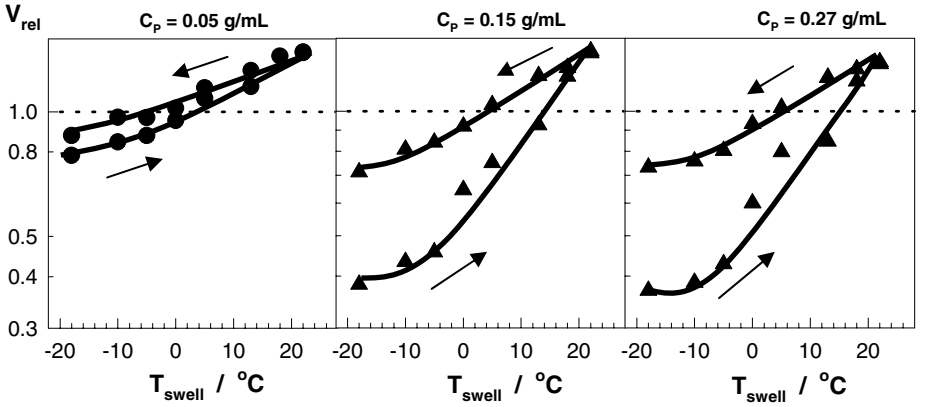


**Figure 5.** Volume swelling ratio $V_{rel}$ of PAAm hydrogels in 1:1 DMSO/water mixture at various $c_P$ plotted against the swelling temperature $T_{swell}$. The direction of the temperature change is indicated by the arrows. The critical condition for a phase separation is denoted by the dotted horizontal lines.

At the polymer concentration of the gelation reactions, namely at $c_p$ = 0.15 g/mL, the gels are in a collapsed state below 0°C, indicating that the polymer network formed below 0°C cannot absorb all the reaction solution so that a solution will separate from the gel phase. Thus, the porous structure with relatively small pores formed below 0°C is a result of the cooling-induced phase separation mechanism. As the temperature is increased, the gel volume $V_{rel}$ rapidly increases (Figure 5). The hydrogels are in a swollen state if the temperature is above 14°C, so that a phase separation cannot occur during gelation. These results are in agreement with the visual appearance of the hydrogel samples formed in this range of temperature (Table 1) indicating that the samples are nonporous after their preparation. Thus, the large polyhedral pores seen in the SEM pictures should be a result of the freeze-dry process of the hydrogels after their preparation. To check this point, all the PAAm hydrogels were prepared again under the same condition as given in the Experimental Part except that, the gel samples were not freeze-dried. The samples swollen in water were first immersed in acetone, a poor solvent for the polymer, and then, they were dried at room temperature under vacuum. While the networks formed at or below 0°C exhibited the same morphologies, those formed above 0°C were homogeneous, as evidenced from the SEM images. Thus, we may conclude that the porous structure formed by the freeze-dry process as well as by phase separation at temperatures above 0°C is too weak so that it collapses during drying.

Further, drastic differences in the morphologies of PAAm networks prepared in water and in DMSO/water (Figure 4) can be explained as a result of two different mechanisms governing the formation process of pores. Water is apparently frozen at -18°C so that the porous structure forms due to the presence of ice acting as a template. At the same temperature but in DMSO/water mixture, however, phase separation is responsible for the formation of pores so that the pores are much smaller in size.

*Swelling – deswelling behavior of hydrogels*

PAAm hydrogels formed at various $T_{prep}$ were subjected to swelling and deswelling processes in water and in acetone, respectively. For this purpose, equilibrium swollen

gel in water was first immersed in acetone and the volume change of gel was determined as a function of the deswelling time. After reaching the equilibrium state in acetone, the gel was immersed in water and the re-swelling process was monitored by recording the volume increase with time. The measurements were carried out by on-line monitoring of the diameter of the gel samples under an optical microscope coupled with an automatic image analyzing system. Typical results are shown in Figure 6A where the normalized gel volume $V/V_w$ (gel volume at time $t$ / equilibrium swollen gel volume in water) is plotted against the time of deswelling or swelling. The hydrogels formed at or below 0°C exhibit a larger gel volume in acetone, indicating the stability of the pores; one may expect that, in such networks, water in the pores is exchanged with acetone during deswelling so that the pore volume remains almost preserved. In contrast, however, since the porous structure of the networks prepared at higher temperatures collapses during the deswelling process in acetone, these hydrogels exhibit lower equilibrium volumes. PAAm hydrogels formed at or below 0°C attained their equilibrium collapsed and equilibrium swollen volumes in 20 min and in 40 min, respectively, while those formed at higher temperatures required about 6 h to reach their equilibrium state in water.

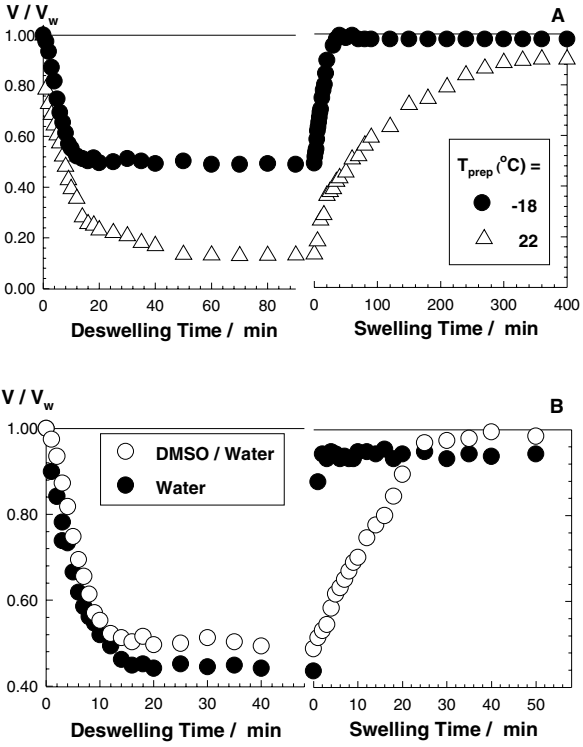


**Figure 6.** Deswelling and swelling kinetics of PAAm hydrogels in acetone and in water, respectively, shown as the variation of the normalized gel volume $V/V_w$ with the time of swelling or deswelling. (**A**): PAAm gels formed in DMSO/water at two different temperatures indicated in the figure. (**B**): PAAm gels formed in water and in DMSO/water at -18°C. $c_M$ = 0.15 g/mL, X = 1/80.

The accelerating swelling rate at low temperatures is due to the stable pore structure of PAAm networks, which increases their internal surface area so that the contact area between the solvent and the polymer increases. Thus, decreasing $T_{prep}$ below 0°C results in the formation of fast responsive PAAm hydrogels. It must be noted, however, if one compares the swelling rates of these hydrogels with the

corresponding cryogels, the latter exhibit much faster swelling rates. For example, Figure 6B shows the deswelling-swelling behavior of PAAm gel samples formed in water (filled symbols) and in 1:1 DMSO/water (open symbols). Both hydrogels were prepared at $T_{prep}$ = -18°C and at an initial monomer concentration of 0.15 g/mL. It is seen that, if water is used as the polymerization solvent, swelling rate is much faster (Swelling times 1 min compared to 40 min). Thus, the response rate of the hydrogels formed by cryogelation is much faster that the hydrogels obtained in DMSO/water mixture by phase separation technique.

## Conclusions

PAAm hydrogels were prepared in 1:1 DMSO/water mixture at various $T_{prep}$ between -18 and 22°C. All the network samples formed at or below 0°C have relatively small pores with sizes about $10^0$ μm. As the temperature is increased above 0°C, both the average pore size and the degree of polydispersity of the pores rapidly increase. The formation of the porous structure at or below 0°C is as a result of the cooling-induced phase separation mechanism, while the large pores of the networks prepared at higher temperatures appear during the freeze-dry process of the hydrogels.

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