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Macroporous poly(N-isopropylacrylamide) networks

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Summary

Effects of the gel preparation temperature T_{prep} and the initial monomer concentration c on the swelling and the porosity properties of poly(N-isopropylacrylamide) (PNIPA) networks are described. PNIPA networks were prepared by free-radical crosslinking copolymerization of N-isopropylacrylamide and N,N'-methylene(bis)acrylamide (BAAm) in aqueous solutions. The crosslinker (BAAm) concentration in the initial monomer mixture was kept constant at 30 wt %. It was shown that macroporous PNIPA networks with a stable porous structure can be prepared at $T_{prep} = 22.5^0$C and at an initial monomer concentration c > 5 w/v %. The PNIPA networks contain pores of about 0.1 μm in radius, corresponding to the interstices between the microspheres. The experimental data also show collapse of the porous structure in PNIPA networks formed at higher temperatures.

Introduction

Poly(N-isopropylacrylamide) (PNIPA) gel is a typical temperature sensitive gel exhibiting volume phase transition at approximately its lower critical solution temperature (LCST), i.e., at 34^0C [1,2]. Below this temperature, the gel is swollen and it shrinks as the temperature is raised. The temperature sensitivity of PNIPA gels has attracted great attention in the last years due both to fundamental and technological interests [3-7]. These materials are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators. In these applications, a fast response rate of the hydrogel to the external stimuli is needed. One of the techniques to increase the response rate of PNIPA is to create an interconnected pore structure within the hydrogel network [8].
Recently, we have shown that macroporous PNIPA networks can be prepared if a large amount of the crosslinker N,N'-methylene(bis)acrylamide (BAAm) is used during the hydrogel preparation [9]. Using this technique, we were able to prepare highly crosslinked macroporous PNIPA networks absorbing large quantities of water within one minute [9].
In this report, we will show that, in addition to the crosslinker content, the gel preparation temperature and the initial monomer concentration are also important parameters in the design of highly crosslinked macroporous PNIPA networks.

Experimental

Network preparation

PNIPA gels were prepared by free-radical crosslinking copolymerization of N-isopropylacrylamide (NIPA) and BAAm in aqueous solutions. The crosslinker (BAAm) concentration in the initial monomer mixture was kept constant at 30 wt %. The reactions were carried out in glass tubes of 5 mm internal diameter and about 10 cm long. The polymerization reactions were initiated using 3.5 mM ammonium persulfate and 0.24 (v/v) % N,N,N',N'-tetramethylethylenediamine (with respect to the reaction solution). The polymerization time was set to one day. Details of the preparation conditions are described before [9]. After polymerization, the gels in the form of rods of 5 mm in diameter 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 dried under vacuum to constant weight.

Characterization

Monomer conversions and the gel fractions were determined as described previously [9]. The results showed that the monomer conversions for all the gel samples are higher than 100 % due to the bounded water in the network samples, in accord with our previous work [9]. The weight and the volume swelling ratios of PNIPA networks were determined in distilled water at 20^0C using separate techniques. For the weight swelling ratio measurements, dry PNIPA network samples were immersed in vials filled with distilled water. The vials were set in a temperature-controlled bath of 20 ± 0.1 ^{0}C. In order to reach the equilibrium degree of swelling, the gels were immersed in water at least for three weeks. The mass of the swollen gels was measured on an analytical balance. The equilibrium weight swelling ratio q_w was calculated as:

$$q_w = swollen\ mass / dry\ mass \qquad (1)$$

The volume swelling ratio of PNIPA networks was measured using an image analyzing system consisting of a stereo microscope (Olympus Stereomicroscope SZ), a video camera (TK 1381 EG) and Pentium 2 PC with a data analyzing software (BS-200 BAB). First, the diameters of dry networks were measured. Then, the networks were immersed in vials filled with distilled water of 20 ± 0.1 ^{0}C. The change in the diameter of the gel samples was followed in situ under microscope. The images were captured at various swelling times and the diameters of the cylindrical specimens were measured using BS-200 BAB data analyzing software. The equilibrium volume swelling ratio of the gels q_v was calculated as

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

where D and D_{dry} are the diameters of the equilibrium swollen and dry gels, respectively.

Uniaxial compression measurements were performed on PNIPA gels after preparation state. All the mechanical measurements were conducted in a thermostated room of 21 ±*0.1*^{0}C. The stress-strain isotherms were measured by using an apparatus described

before [9]. The elastic modulus G was determined from the slope of linear dependence [10]:

$$f = G\left(\alpha - \alpha^{-2}\right) \qquad (3)$$

where f is the stress, and α is the corresponding compression ratio (deformed length/initial length).

The pore sizes, the pore size distribution and the total porosity of PNIPA networks were determined by mercury porosimetry (Micromeritics AutoPore 9220). Specific surface areas of the networks were determined by adsorption of oxygen according to the BET method. Scanning electron microscopy studies were carried out at a magnification of 5000 times (Jeol JXA-840A).

Table 1. Properties of PNIPA networks prepared at 30 wt % BAAm concentration. T_{prep} = gel preparation temperature. c % = initial monomer (NIPA + BAAm) concentration in gram/100 mL. q_w and q_v = equilibrium weight and volume swelling ratios in water at 20^{0}C, respectively. P = total porosity measured by mercury porosimetry. P_s = swollen state porosity calculated using eq. (4). S_{BET} = specific surface area. G = elastic modulus of PNIPA hydrogels after their preparation measured at 21^{0}C. The standard deviations are given in the parenthesis.

T_{prep} (^{0}C)	c %	q_w	q_v	P	P_s	S_{BET} (m^2/g)	G (kPa)
12	20	4.1 (0.2)	4.7 (0.1)	0.10	0	< 0.5	260 (2)
22.5	20	5.0 (0.2)	2.2 (0.1)	0.60	0.58	51 (2)	44 (4)
26	20	-	-	0.36	-	-	66 (5)
30	20	5.0 (0.1)	2.4 (0.1)	0.36	0.54	25 (2)	73 (5)
40	20	4.8 (0.1)	2.2 (0.1)	0.42	0.56	25 (2)	19 (2)
50	20	5.2 (0.1)	2.2 (0.1)	0.44	0.60	21 (2)	28 (5)
22.5	5	14 (1)	7.9 (0.6)	*)	0.47	*)	0.48 (0.04)
22.5	10	9.4 (0.3)	4.9 (0.2)	0.50	0.51	-	5.8 (0.5)
22.5	20	5.0 (0.2)	2.2 (0.2)	0.60	0.58	51 (2)	44 (4)

*) Samples were too weak for the measurements

Results and discussion

Two sets of PNIPA networks were prepared each with a crosslinker (BAAm) content of 30 wt %. In the first set (set A), the initial monomer concentration c was fixed at 20 w/v %, while the gel preparation temperature T_{prep} was varied between 12 and 50^{0}C. In the second set (set B), T_{prep} was fixed at 22.5^{0}C while the initial monomer concentration c was varied between 5 and 20 w/v %. The characteristics of the network samples are compiled in Table 1.

Figures 1A and 1B show the weight swelling ratios q_w (swollen mass / dry mass of the network) of the networks from the sets A and B, respectively plotted as a function of the swelling time. The swelling measurements were carried out at 20± 0.1^{0}C in water. The network formed at T_{prep} = 12^{0}C swells in water very slow. As seen from the inset in Figure 1A, this network attains its equilibrium state in water after about 400 min. However, for the networks prepared at higher temperatures (T_{prep} = 22.5 – 50^{0}C), the swelling process is very rapid; they reach the equilibrium state in water after about 2 min, i.e., they swell about 200 times faster than the network formed at 12^{0}C. Thus, the results indicate that there is a critical gel preparation temperature,

above which the rate of swelling dramatically increases. Figure 1B shows that the initial monomer concentration c also influences the swelling rate of the networks significantly. The network formed at c = 5 w/v % needs about 40 days to reach the equilibrium in water, while those formed at c = 10 or 20 w/v % attain their equilibrium state within one minute. PNIPA networks at c > 20 w/v % cannot be prepared since monomer mixtures were not soluble in water. Moreover, the inset in Figure 1B indicates that the swelling of the network formed at c = 5 w/v % occurs in two stages; a relatively rapid initial swelling period followed by a slow swelling period from 300 min up to about 40 days.

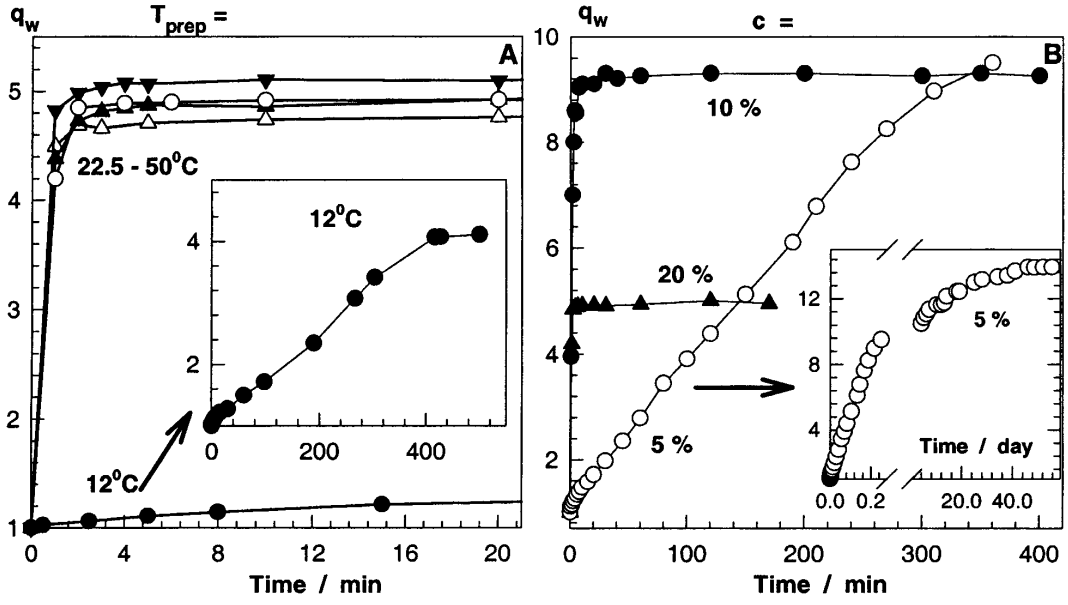

Figure 1. Weight swelling ratio q_w of PNIPA networks in water at 20°C shown as a function of the swelling time. (A): c = 20 w/v %, T_{prep} = 12 (◠), 22.5 (◪), 30 (π), 40 (ρ), and 50°C (θ). (B): T_{prep} = 22.5°C. The initial monomer concentrations c are indicated in the figure.

The low swelling rate of the networks indicates that the absorption of water by the network takes place by a diffusive process, which is very slow due to the high crosslinker content used in the gel preparation (30 wt %). On the other hand, high swelling rates indicate existence of interconnected pore structure in the network samples. In this case, absorption of water by the network polymer occurs through the pores by convection, which is much faster that the diffusion process. Thus, from the swelling curves shown in Figures 1A and 1B, one may expect that the networks formed at $T_{prep} \geq 22.5^0$C and $c \geq 10$ w/v % should have a porous structure in dry state.

In Figures 2A and 2B, the integral size distributions of the pores in PNIPA networks from sets A and B, respectively, are given. The total porosities P and the specific surface areas S_{BET} of the networks are collected in Table 1. All the measurements were conducted at room temperature (24 ± 1^0C). Note that the total porosity P is defined as the total volume of pores in one mL of the network sample. Figure 2A shows that, in accord with the results of the swelling rates, the porosity of the network formed at T_{prep} = 12°C is low and it increases with increasing gel preparation temperature. Interestingly, the network formed at 22.5°C exhibits the highest porosity

and the highest specific surface area. Increasing porosity in PNIPA networks with rising T_{prep} is expected due to the simultaneous increase of the degree of phase separation during the gel formation process [8]. Unexpected is, however, the maximum porosity observed at T_{prep} = 22.5^{0}C. This result can be explained with the loose structure of the networks formed at higher temperatures. Indeed, we always observed that the PNIPA hydrogels formed at T_{prep} > 22.5^{0}C are weak, while those formed below this temperature are relatively hard. The pores in such weak matrices may collapse upon drying of the hydrogels from their swollen states. Note that the collapse of the pores during drying has been reported before in loosely crosslinked styrene – divinylbenzene copolymer networks [8,11,12]. Figure 2B shows the effect of the initial monomer concentration c on the porosity of the networks. Porosity measurements cannot be carried out on network samples prepared at c = 5 w/v % due to the weak network structure. As seen in Table 1 and Figure 2B, as the initial monomer concentration c is increased from 10 to 20 w/v %, the porosity slightly increases.

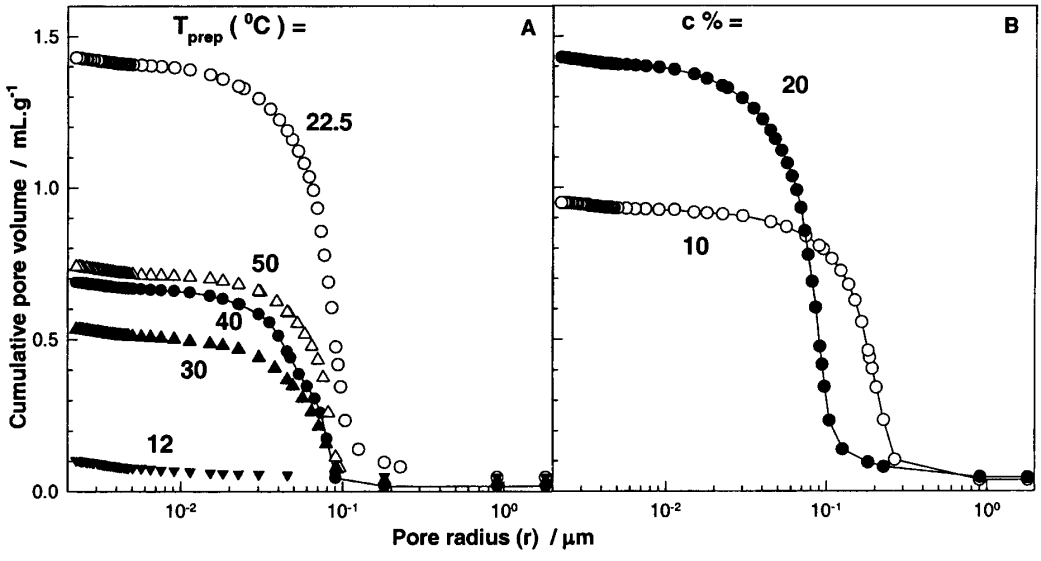

Figure 2. Integral size distributions of the pores in PNIPA networks. (A): c = 20 w/v %. (B): T_{prep} = 22.5^{0}C. Synthesis variables are indicated in the Figures.

The experimental data given in Figures 2A and 2B show that porous PNIPA networks start to form at temperatures much below the LCST of PNIPA. This finding can be explained with the exothermic reaction profiles of the crosslinking copolymerization of NIPA and BAAm monomers. Recently, we monitored phase separation in PNIPA hydrogels by using photon transmission and temperature measurements [13]. We observed that the temperature of the reaction system increases sharply with time, attains a maximum value, which is about 7^{0}C higher than the initial temperature, and then decreases continuously at longer reaction times due to dissipation of reaction heat to the surroundings [13]. Thus, the gel preparation temperature T_{prep} reported in the present work does not correspond to the actual polymerization temperature. The formation of porous networks at T_{prep} = 22.5^{0}C indicates that the temperature of this reaction system approaches to the LCST of PNIPA during the gel formation process, so that the system phase separates and results in the formation of porous structures.
Figure 2 also shows the existence of pores of about 0.1 µm in radius in the network

samples. In Figure 3, scanning electron micrograph (SEM) of the network sample formed at T_{prep} = 22.5^{0}C is given. From the SEM picture, one can identify spherical domains called microspheres of about 0.1 – 0.5 μm in diameter. The microspheres are connected to aggregates of 1-2 μm in diameter. The aggregates are further agglomerated into big clusters. From Figures 2 and 3, one may conclude that the distance between the microspheres is mainly responsible for the porosity of PNIPA networks.

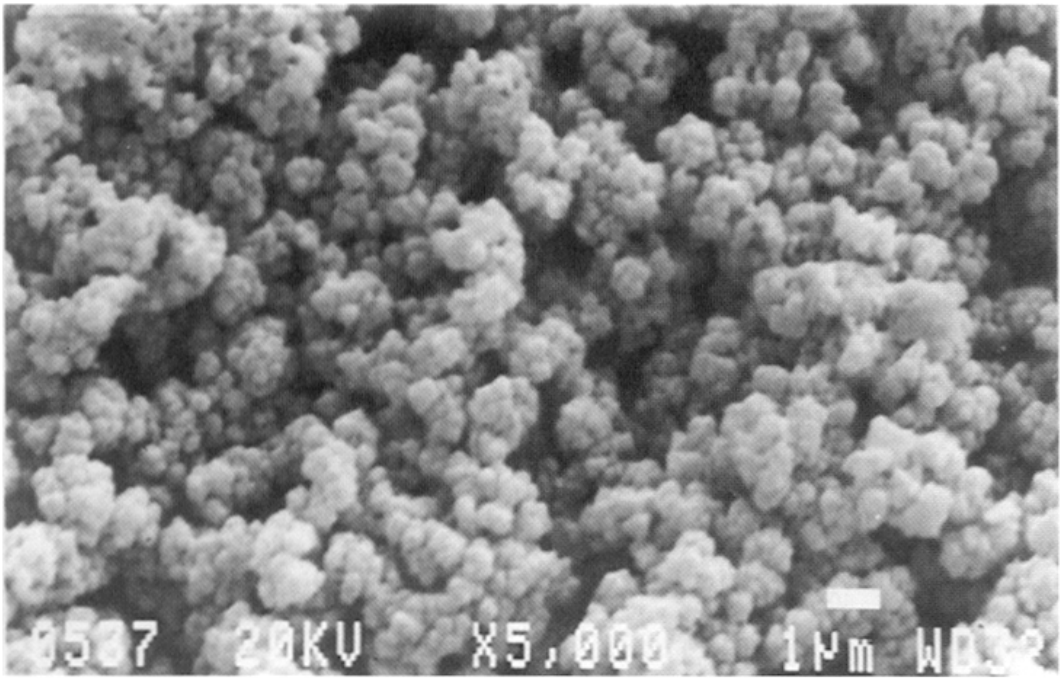

Figure 3. SEM image of PNIPA network at 5000x (1μm bar in the lower right corner). c = 20 w/v %, T_{prep} = 22.5^{0}C.

The results of the elastic moduli measurements carried out at 21^{0}C are also collected in Table 1. It is seen that the modulus G of the hydrogel formed at T_{prep} = 12^{0}C is 260 kPa, which is much higher than the moduli of the hydrogels formed at higher temperatures. Further, G decreases rapidly between T_{prep} = 12^{0}C and 22.5^{0}C, indicating that the network structure changes drastically in this range of temperature. A network consisting of large polymer domains becomes a macroporous network consisting of agglomerates of microspheres (Figure 3). As a result, bending-type deformations become also operative with increasing T_{prep} due to the buckling of the pore walls or, of chains connecting the microspheres. This leads to a rapid decrease in G with increasing T_{prep} from 12 to 22.5^{0}C. As seen in Table 1, G also decreases rapidly with decreasing initial monomer concentration c due to the simultaneous decrease of the network chain concentration in the hydrogel samples.

In Figure 4, the equilibrium weight (q_w) and the volume swelling ratios (q_v) of the networks, measured using separate techniques, are shown as a function of the gel preparation temperature T_{prep} (filled symbols) and monomer concentration c (open symbols). The experimental q_w and q_v data are shown in the Figure by circles and triangles, respectively. The equilibrium weight swelling ratio q_w of the networks formed at c = 20 w/v % equals to 5.0± 0.2, and independent on the gel preparation

temperature T_{prep}. Moreover, except the network formed at 12^0C, the equilibrium volume swelling ratio q_v of these samples is also constant and equals to 2.2 ± 0.1. The sample formed at 12^0C swells however much more by volume than other samples and, its volume swelling ratio is close to the weight swelling ratio. Furthermore, as the initial monomer concentration decreases, both the volume and the weight swelling ratios decrease continuously.

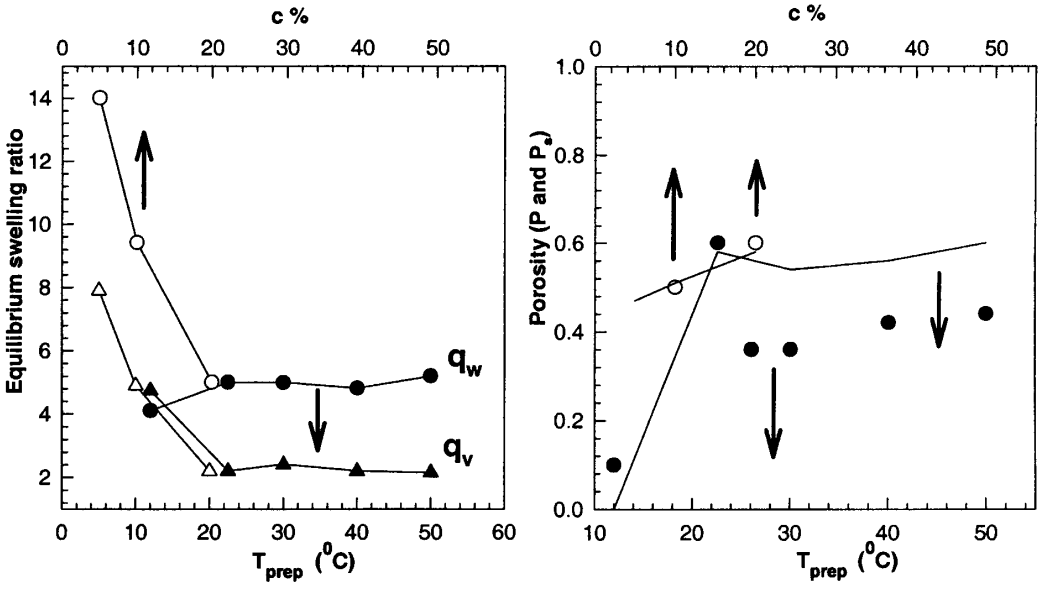

Figure 4 (left): Equilibrium weight (q_w) and volume swelling ratios (q_v) of the networks shown as function of the gel preparation temperature T_{prep} (filled symbols) and the initial monomer concentration c (open symbols). Circles and triangles represent the q_w and q_v values, respectively. **Figure 5 (right):** Total porosities of the networks P shown as function of the gel preparation temperature T_{prep} (filled symbols) and the initial monomer concentration c (open symbols). The lines were calculated using eq. (4) and they represent the swollen state porosities P_s.

The relative values of the weight and the volume swelling ratios of the networks provide information about the internal structure of the porous networks in the swollen state [8,14]. 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 [8]:

$$P_s = 1 - q_v\left[1 + d_2\left(q_w - 1\right)/ d_1\right]^{-1} \quad (4)$$

where d_1 and d_2 are the densities of solvent and polymer, respectively. Assuming that d_1 = 1 g/mL and d_2 = 1.06 g/mL [15], we calculated swollen state porosities P_s of the networks by use of eq. (4). The calculation results are given in Figure 5 as solid curves plotted as functions of the gel preparation temperature and monomer concentration. For comparison, dry state porosities P are also given as symbols. For the networks prepared at $T_{prep} \leq 22.5^0$C and $c \geq 10$ w/v %, the swollen state porosity P_s is close to the dry state porosity P. This indicates that the pores in these networks are stable and they do not collapse during the drying process. However, swollen state porosities of the networks formed at higher temperatures or at lower monomer concentrations are considerable higher than those measured in their dry states. This finding demonstrates the collapse of the pores in these samples.

In conclusion, we described the synthesis conditions of fast response macroporous PNIPA networks. We have shown that PNIPA networks with a stable porous structure can be prepared at T_{prep} = 22.5^{0}C and at an initial monomer concentration c > 5 w/v %. The experimental data show the collapse of the porous structure in PNIPA networks formed at higher temperatures.

It is worth noting that a reproducible synthesis of PNIPA gels is difficult to achieve [9,16]. This is due to the LCST of PNIPA chains, which is close to the usual polymerization temperatures, as well as due to the exothermic reaction profile of NIPA – BAAm copolymerization. It was shown that, depending on the heat characteristics of the synthesis molds, PNIPA gels prepared from the same monomer solution exhibit conflicting physical properties [17]. Therefore, the experimental procedure described here is reproducible only, if the size and the geometry of the synthesis reactor (glass tubes of 5 mm internal diameter and about 10 cm long, immersed in a thermostated water bath) are fixed.

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