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The effect of preparation temperature on the swelling behavior of poly (*N*-isopropylacrylamide) gels

Çigdem Sayil[1], Oguz Okay[1, 2*]

[1] TUBITAK Marmara Research Center, Department of Chemistry,
P.O. Box 21, 41470 Gebze, Kocaeli, Turkey
[2] Istanbul Technical University, Department of Chemistry, Maslak, 80626 Istanbul, Turkey

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Summary

The role of the preparation temperature of poly(N-isopropylacrylamide) (PNIPA) gels on their swelling behavior in water and in aqueous solutions of sodium dodecylbenzenesulfonate was investigated. PNIPA gels were prepared by free-radical crosslinking copolymerization of N-isopropylacrylamide and N,N'-methylene(bis) acrylamide in water at fixed monomer and crosslinker concentrations. The equilibrium swelling ratio of the gels increases first slightly up to about 20°C then rapidly with increasing gel preparation temperature. Magnitude of the collapse transition in water at 34°C becomes larger as the gel preparation temperature increases. Calculations indicate a decrease in the effective crosslink density of PNIPA gels with increasing preparation temperature. The gels prepared at temperatures higher then 20°C were heterogeneous consisting of highly crosslinked regions interconnected by the PNIPA chains.

Introduction

Poly(N-isopropylacrylamide) (PNIPA) gel is a typical temperature sensitive gel exhibiting volume phase transition at approximately 34°C (1). 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 (2-5).

PNIPA hydrogels have been prepared by free-radical crosslinking copolymerization of N-isopropylacrylamide (NIPA) monomer with N,N'-methylene(bis)acrylamide (BAAm) as a crosslinker in aqueous solutions. The usual synthesis parameters affecting the swelling properties of hydrogels are known to be the monomer and the crosslinker concentrations in the initial reaction mixture. However, since water is a good solvent for PNIPA at low temperatures but a poor one at high temperatures, the preparation temperature appears to be as an additional synthesis parameter for the PNIPA gels affecting their properties. Indeed, previous works have shown that both physical and chemical characteristics of PNIPA hydrogels strongly depend upon their preparation temperature (6-9). It is worth nothing, however, that the reported dependencies of the swelling behavior of PNIPA gels on their preparation temperature are conflicting (7, 8). Moreover, it was also shown that a reproducible synthesis of PNIPA gels is diffucult to achieve (10).

* Corresponding author

In the present study, a series of PNIPA gels in the form of rods were prepared at various temperatures. The swelling capacities of the hydrogels in water at various temperatures as well as in aqueous solutions of sodium dodecylbenzenesulfonate (SDBS) were determined. Using the theory of swelling equilibrium, the crosslink densities of PNIPA gels were also calculated As will be shown below, the preparation temperature of PNIPA gels is an important parameter to regulate their effective crosslink densities. Increasing gel preparation temperature decreases the effective crosslink density of PNIPA gels, which is reflected by their increased swelling degrees in water as well as in SDBS solutions.

Experimental

The monomer NIPA (Aldrich), the crosslinker BAAm (Fluka), the initiator ammonium persulfate (APS, Fluka), and the accelerator N,N,N',N'-tetramethylethylenediamine (TEMED, Aldrich) were used as received. Sodium dodecylbenzenesulfonate (SDBS) was prepared by mixing equimolar amounts of dodecylbenzene sulfonic acid (Henkel) and NaOH (Merck) in aqueous solutions. PNIPA gels were prepared by free-radical crosslinking copolymerization of NIPA and BAAm in aqueous solutions. The polymerization reactions were initiated using 3.5 mM APS and 0.24 v/v % TEMED. NIPA, BAAm and APS were first dissolved in distilled water and then, the solution was purged with nitrogen gas for 10 min. After addition of TEMED, the solution was transferred to small tubes of 4 mm in diameter. After one day of polymerization time, the gels were cut into specimens of approximately 10 mm in length and immersed in a large excess of water to wash out any unreacted monomers and the initiator.

Two different sets of PNIPA gels were prepared in which all the synthesis parameters were fixed but only the gel preparation temperature was varied. In the first set of gels, called Gels A, the initial monomer concentration C_0 and the crosslinker ratio X (mole ratio of the crosslinker BAAm to the monomer NIPA) were 8 w/v% and 1/85, respectively. In the second set of gels, called Gels B, both C_0 and X were increased to 20 w/v% and 1/25, and they were kept constant at these values.

For the swelling measurements, the PNIPA gel samples were immersed in vials filled with distilled water or with aqueous SDBS solutions. Aqueous SDBS solutions were prepared by the dilution of a 61.35 mM SDBS stock solution with various volumes of water. The volume of the SDBS solutions in the vial was much larger than the gel volume so that the concentration of the solution was practically unchanged. The vials were set in a temperature-controlled bath of ± 0.1 °C. In order to reach the equilibrium degree of swelling, the gels were immersed in solutions at least for one week. The diameter of the gel samples was measured by a calibrated digital compass. The equilibrium swelling ratio of the gels related to the network formation state V/V_0, where V and V_0 are the volumes of the gel after equilibrium swelling and after preparation, respectively, was calculated as

$$V/V_0 = (D/D_0)^3 \qquad (1)$$

where D and D_0 are the diameter of the gels after equilibrium swelling and after preparation, respectively.

Results and discussion

Fig. 1A shows the equilibrium volume swelling ratios V/V_0 of Gels A (filled symbols) and Gels B (open symbols) measured in water at 22 °C plotted as a function of their preparation temperature T_{prep}. Transparent gels were obtained at T_{prep} < 20°C whereas slightly opaque or opaque gels were formed at higher temperatures. Gels A prepared at temperatures higher than 32°C were with poor mechanical performance and cannot be handled after their formation. In order to increase their mechanical performance, both the initial monomer concentration C_0 and the crosslinker ratio X were increased to 20 w/v % and 1/25, respectively. Using this way, we were able to synthesize gels (Gels B) at temperatures up to 50°C. Visual observation revealed appearance of turbidity during the gel formation process at or above 20°C, indicating the occurrence a phase separation during the gel formation process and formation of domains of sizes of the order of the visible light. For example, micrographs shown in Fig. 2 were taken from Gels B prepared at 9.5 and 50°C. Low temperature gel was glassy in appearance and brittle whereas high temperature gel was opaque and weak, indicating a change in the network structure of PNIPA gels depending on the preparation temperature.

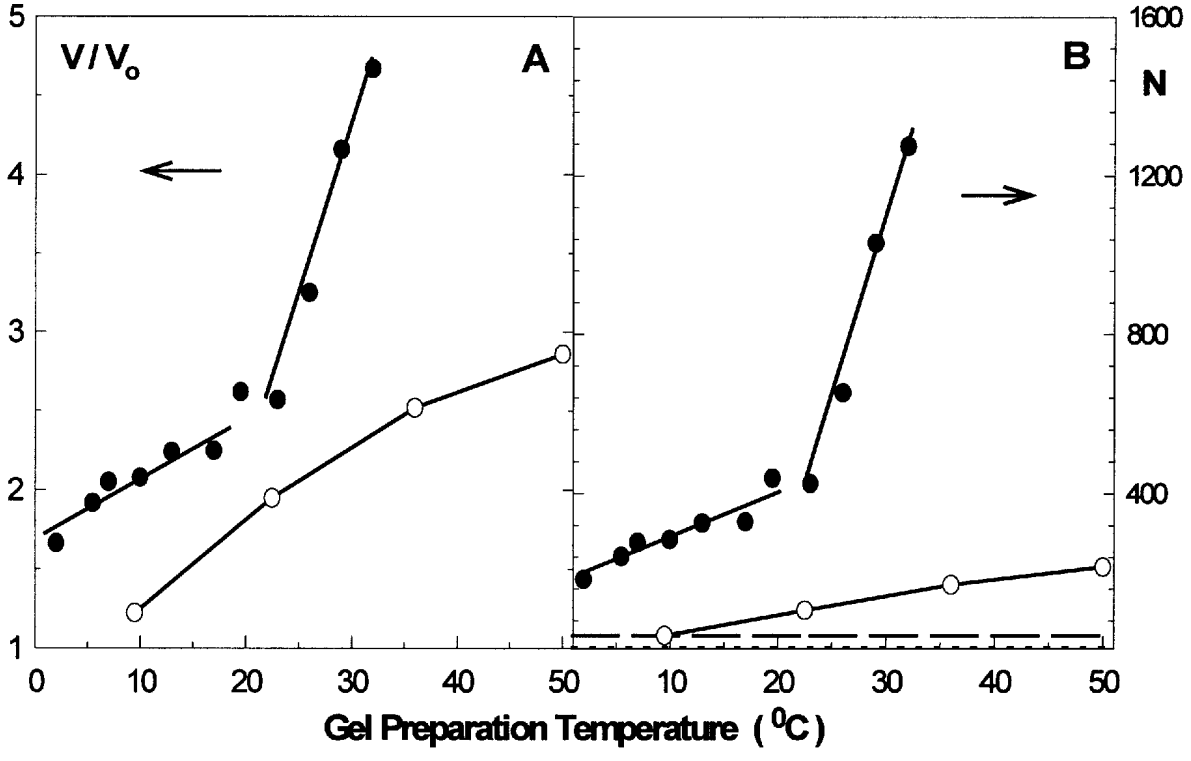
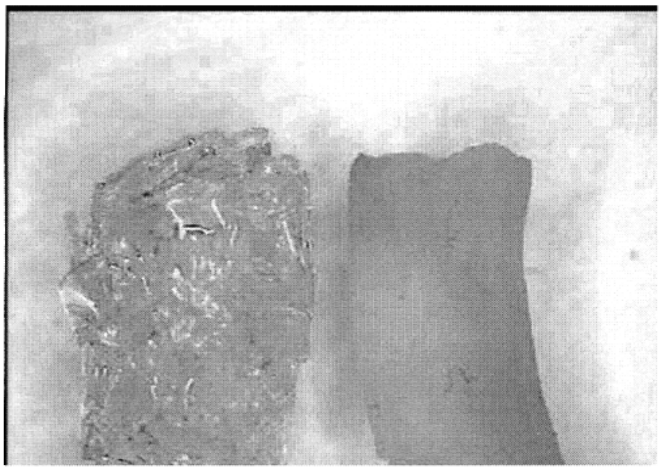


Fig. 1 Variations of the volume swelling ratio V / V_0 (A) and the number of units between two successive crosslinks N (B) of PNIPA gels with the gel preparation temperature. Gels A: C_0 = 8 w/v %, X = 85^{-1} (●); Gels B: C_0 = 20 w/v %, X = 25^{-1} (○) The solid curves show the trend of data. The dashed and dotted lines in Fig. 1B illustrate the stoichiometric value of N expected from the crosslinker ratio used in the synthesis of Gels A and B, respectively.



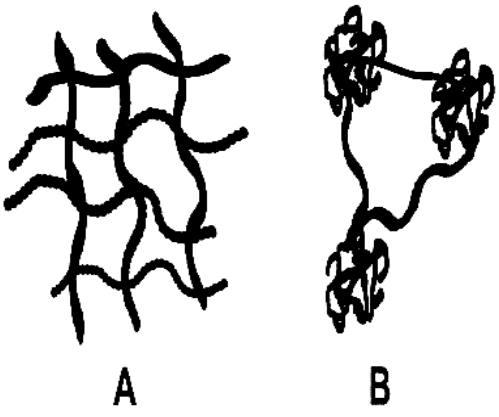


Fig. 2 (left). Micrographs of PNIPA gels (Gels B) formed at 9.5 (left) and 50°C (right). C_0 = 20 w/v%. X = 25^{-1}.
Fig. 3 (right). Schematic representation of the network structures of PNIPA gels formed at low (A) and high temperatures (B).

Fig. 1A shows that the swelling ratio V/V_0 of PNIPA gels is an increasing function of their preparation temperature T_{prep}. These results are consistent with those of our previous study (8), but contradict to those of Rathjen et al. (7). For transparent gels, the increase of V/V_0 with T_{prep} is slight, whereas for opaque gels (Gels A) V/V_0 steeply increases with T_{prep} from 2.5 to 4.5. For Gels B, an increase in the volume swelling ratio with increasing preparation temperature from 9.5 to 50°C was also observed.

According to the theory of equilibrium swelling, the swelling ratio of the gels is related to their effective crosslink density through the equation (11):

$$\ln(1-v_2) + v_2 + \chi v_2^{\,2} + N^{-1}\left(v_2^{1/3} v_2^{0\,2/3} - v_2/2\right) = 0 \qquad (2)$$

where v_2 and v_2^0 are the volume fractions of polymer network in the equilibrium swollen gel and after the gel preparation, respectively, χ is the polymer - network interaction parameter and N is the number of segments between two successive crosslinks. In order to account for the volume phase transition in gels, the χ parameter is assumed to be concentration dependent and has the following form (12):

$$\chi = \chi_1 + \chi_2 v_2 \qquad (3a)$$

where

$$\chi_1 = (\Delta H - T\Delta S)/kT \qquad (3b)$$

k is the Boltzman constant, T is the temperature, and χ_2 is a constant. For the calculation of the crosslink density of PNIPA gels using eq. (2), we used the following values for PNIPA-water system evaluated by Hirotsu (13): χ_2 = 0.518, ΔH =

-12.46×10^{-21} J, and $\Delta S = -4.717 \times 10^{-23}$ J/K. Moreover, polymer volume fractions after equilibrium swelling and after gel preparation, v_2 and v_2^0 respectively, relate to the volume swelling ratio and the synthesis parameters by the following equations:

$$v_2 = v_2^0 (V/V_0)^{-1} \quad \text{(4a)}$$

$$v_2^0 = C_0/(100\rho) \quad \text{(4b)}$$

where ρ is the polymer density taken as 1.35 g/cm^3. Substitution of the experimental V/V_0 values into eqs. (2) and (3) leads to the crosslink density N^{-1} of PNIPA gels. Fig. 1B shows how the N values vary with the preparation temperature of Gels A (solid symbols) and B (open symbols). The dashed and dotted lines in the figure represent the stoichiometric value of N (N_{chem}) calculated from the crosslinker ratios used in the preparation of Gels A and B, respectively. Since both C_0 and X are constant in each series of gels, one may expect *N* values which are independent on the gel preparation temperature T_{prep}. However, as seen in Fig. 1B, N is an increasing function of T_{prep}. For Gels A, N increases with increasing T_{prep} first slightly from 200 to 400, but then rapidly increases up to 1300 at still higher temperatures. For Gels B, N increases continuously with increasing T_{prep} from 9.5 to 50°C. Comparison the experimental and stoichiometric N values indicates the existence of a large number of ineffective crosslinks in PNIPA gels; this number increases rapidly with increasing T_{prep} for T_{prep} > 20°C. These findings can be explained with a change of the network structure of PNIPA gels at about 20°C, as schematically illustrated in Fig. 3. At low temperatures, since the polymerization solvent water is a good solvent for the growing chains, the free-radical crosslinking copolymerization of NIPA and BAAm proceeds in a homogeneous manner and results in the formation of a network of primary chains (structure A in Fig. 3). For these homogeneous gels, the difference between N and N_{chem} originates from cyclization and multiple crosslinking reactions leading to the formation of wasted BAAm links (14-17). However, at temperatures higher than 20°C, phase separation during crosslinking leads to the formation of polymer-rich domains which are highly crosslinked. Aggregation of these domains through linear or branched PNIPA chains to a macroscopic network is responsible for the macrogelation. Thus, at temperatures higher than 20°C, a macroscopic network of interconnected clusters forms (structure B in Fig. 3) In such networks, the highly crosslinked regions act as single crosslinks during the gel swelling and thus, necessarily decrease the effective crosslink density N^{-1} of the hydrogels. It should be noted that the use of eq. (2) to calculate N^{-1} of such heterogeneous networks is only approximate. However, increasing degree of swelling with increasing T_{prep} shows, at least qualitatively, that the crosslinking efficiency is a decreasing function of T_{prep}. Note that, although the volume phase transition in PNIPA gels occurs at 34°C, phase separation during crosslinking takes place below this temperature. This may be related, as pointed out before (6), to the rise in temperature of the polymerization system due to the gel effect.

In the following, the swelling behavior of PNIPA gels was investigated in water at various swelling temperatures as well as in aqueous solutions of SDBS. Since Gels A swell much more than the Gels B, we conducted these experiments only with Gels A. In Fig. 4, the equilibrium volume swelling ratios V/V_0 of PNIPA gels formed at

various T_{prep} are plotted as a function of the swelling temperature, which was varied between 17 and 43°C. As expected, at low temperatures, the gels are swollen, at high temperatures the gels are collapsed. The gels undergo deswelling transition between 33 and 34°C. Furthermore, as T_{prep} increases, the net volume change of PNIPA gels at the transition increases and the volume phase transition becomes more discontinuous. Also, the temperature at which the gel starts collapsing shifts toward higher temperatures with decreasing T_{prep}.

Using eqs. (2) - (3) together with the N values shown in Fig. 1B, we calculated temperature dependent swelling behavior of PNIPA gels formed at various temperatures T_{prep}. The calculation results are collected in Fig. 5. In accord with the experimental data, the theory predicts that the magnitude of the collapse transition becomes larger as the gel preparation temperature increases. This behavior arises due to the decrease in the crosslink density (N^{-1}) of the gels with increasing gel preparation temperature T_{prep}. By varying the crosslinker (BAAm) content in the feed, Oh et al. and Inomata et al reported similar swelling curves for PNIPA gels (18,19). The present results clearly show that T_{prep} is an effective independent variable in the synthesis of PNIPA gels. Increasing T_{prep} decreases the crosslink density of the gels, which is reflected by their increased swelling capacities.

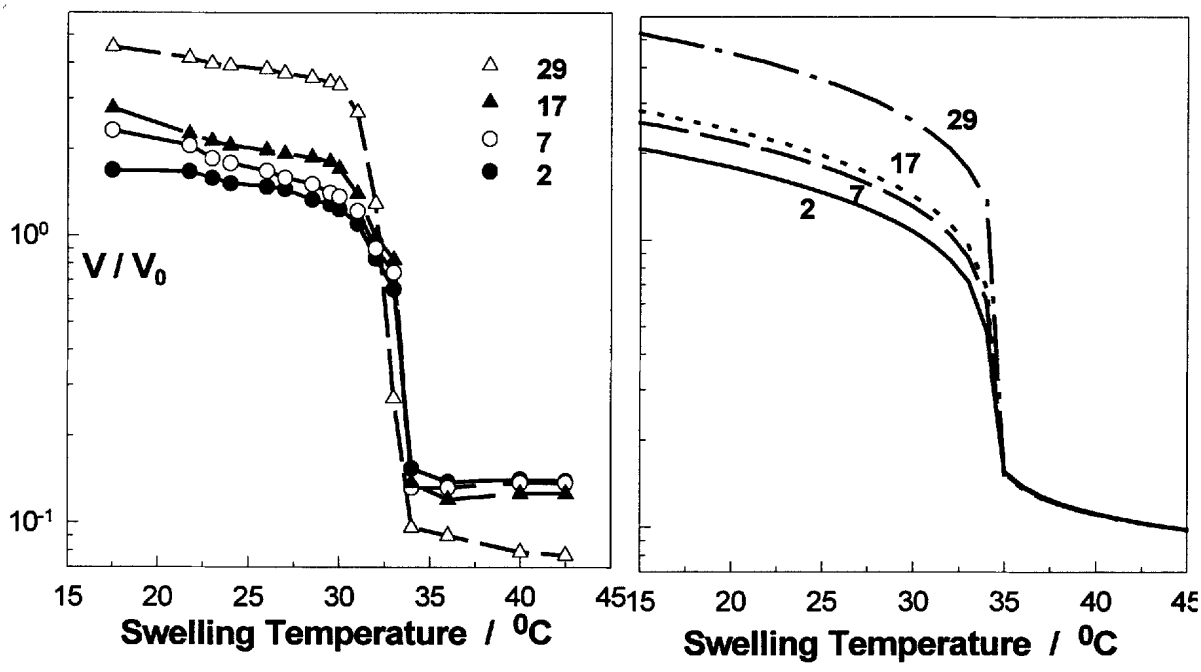


Fig. 4 (left). Equilibrium volume swelling ratio V/V_0 of PNIPA gels prepared at various temperatures shown as a function of the swelling temperatures. C_0 = 8 w/v % and $X = 85^{-1}$. The gel preparation temperatures (in ^{0}C) are indicated in the figure.

Fig. 5 (right). Calculated dependence of V/V_0 on the swelling temperature for gels prepared at various temperatures. Calculations were using eqs. (1) and (2), and using N values shown in Fig. 1B. The gel preparation temperatures (in ^{0}C) are indicated in the figure.

PNIPA gels formed at various temperatures were subjected to swelling experiments in aqueous solutions of SDBS of various concentrations. Fig. 6 shows the swelling ratio of the gels plotted as a function of SDBS concentration in the external solution.

The volume of the gels does not change at SDBS concentrations 0.31 mM or below. This concentration is much lower than the critical micelle concentration (CMC) of SDBS (1.2 mM at room temperature) and corresponds to its critical aggregate concentration (CAC). With increasing SDBS concentration above this value, the gel volume increases and attains a limiting value at about 3 mM. In Fig. 7, the variation of the gel volume in 3.07 mM SDBS solution is shown as a function of the gel preparation temperature. It is seen that, the higher the gel preparation temperature T_{prep}, the higher the swelling ratio of the gels. The swelling curve in SDBS solution is similar to that in water (Fig. 1A). According to Figs. 6 and 7, highly swollen non-ionic PNIPA gels can be obtained by increasing their preparation temperature and by adding SDBS in the external solution.

Increasing volume of the gels with increasing SDBS concentration is expected and originates from the hydrophobic interactions between the isopropyl group of the network chains and the alkyl tail of SBBS molecules in the external solution (20-22). Below CAC, single SDBS molecules cannot enter the gel phase due to the significant loss of their conformational entropy accompanying this process (23). Above CAC, SDBS molecules forming micelles in solution are in much lower conformational entropy state so that they can enter the gel phase without a significant loss of their entropy (23). Absorption of SDBS by the gel results in the formation of mixed aggregates between SDBS and PNIPA and the non-ionic PNIPA gel is converted into an ionic gel. Increasing gel volume with increasing SDBS concentration is a consequence of the increasing osmotic pressure of the counterions (Na^+), which penetrate the gel with SDBS molecules. Figs. 6 and 7 show that the additional swelling of PNIPA gels observed in the presence of SDBS increases as the preparation temperature of the gels increases.

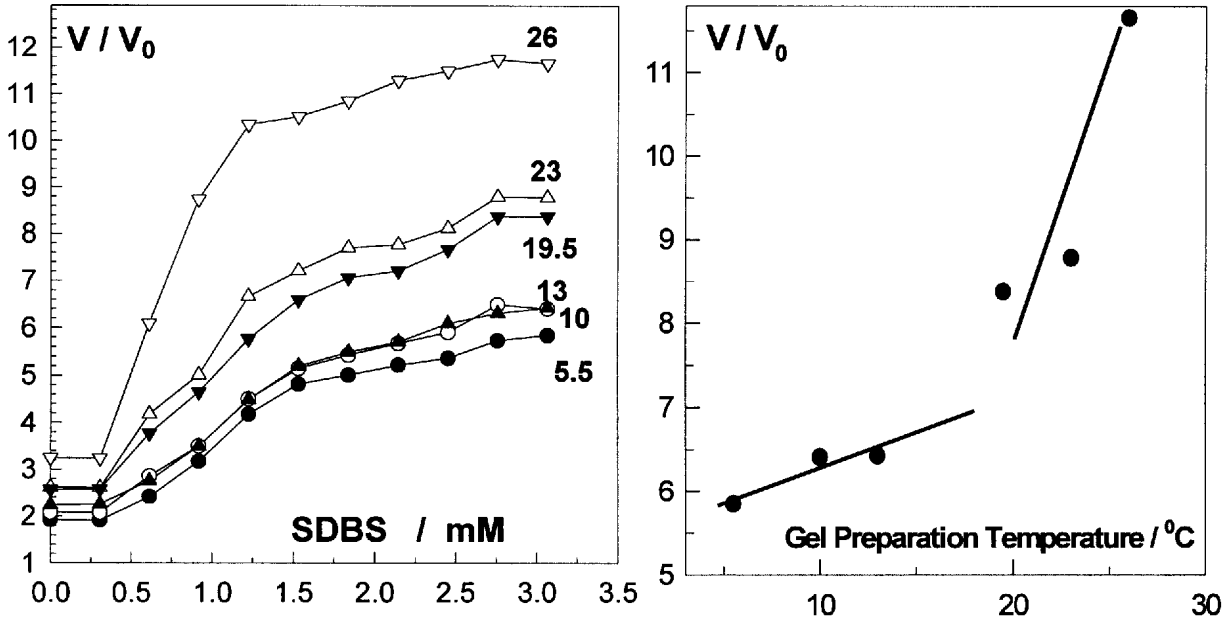


Fig. 6 (left). The volume swelling ratio of PNIPA gels formed at various temperatures shown as a function of the SDBS concentration in the external solution. Swelling temperature = 22°C. The gel preparation temperatures (in °C) are indicated in the figure.

Fig. 7 (right). The volume swelling ratio of PNIPA gels in 3.07 mM SDBS solution shown as a function of the gel preparation temperature. Swelling temperature = 22°C.

In concluding, the preparation temperature dependence of the swelling behavior of PNIPA gels was investigated. It was shown that the gel preparation temperature T_{prep} is an effective independent variable for adjusting the final properties of PNIPA gels. The effective crosslink density of PNIPA gels is inversely proportional to their preparation temperature. The swelling degree of PNIPA gels in water or in SDBS solutions increases and the extent of the deswelling transition at 34°C becomes more discontinuous with increasing gel preparation temperature.

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