# Semi-Interpenetrating Networks Based on Poly(*N*-isopropyl acrylamide) and Poly(*N*-vinylpyrrolidone)

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**ABSTRACT:** Three series of novel semi-interpenetrating polymer networks, based on crosslinked poly(*N*-isopropylacrylamide), PNIPA, and different amounts of the linear poly(*N*-vinylpyrrolidone), PVP, were synthesized to improve the mechanical properties and thermal response of PNIPA gels. The effect of the incorporation of the linear PVP into the temperature responsive networks on the temperature-induced transition, swelling/deswelling behavior, and mechanical properties was studied. Polymer networks with four different crosslinking densities were prepared with varying molar ratios (25/1 to 100/1) of the monomer (*N*-isopropylacrylamide) to the crosslinker (*N*,*N*′-methylenebisacrylamide). The hydrogels were characterized by determination of the equilibrium degree of swelling, the dynamic shear modulus and the effective crosslinking density, as well as tensile strength and elongation at break. Furthermore, the deswelling kinetics of the hydrogels was studied by measuring their water retention capacity. The inclusion of the linear hydrophilic PVP in the PNIPA networks increased the equilibrium degree of swelling. The tensile strength of the semi-interpenetrating networks (SIPNs) reinforced with linear PVP was higher than that of the PNIPA networks. The elongation at break of these SIPNs varied between 22% and 55%, which are 22 – 41% larger than those for pure PNIPA networks. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1593–1603, 2009

**Key words:** thermosensitive hydrogels; semi-interpenetrating networks (semi-IPN); swelling/deswelling kinetics; mechanical properties

## INTRODUCTION

A polymer hydrogel consists of an elastic crosslinked polymer network capable of absorbing and retaining large amounts of water in the interstitial space of the network.[1,2] Because of their high water contents and soft consistency, hydrogels more than any other class of synthetic biomaterials resemble natural living tissue.[3] For this reason, polymer hydrogels were projected for a large number of various applications in medicine as well as in pharmacy. Stimuli-sensitive hydrogels offer great possibilities for different uses since the physicochemical and mechanical properties can be controlled by the change of some external parameters, such as pH, temperature, ionic strength, and electric field. Some of the important applications of hydrogels are as biomedical materials for soft contact lenses, artificial skin, and muscles, immobilization of bioactive substances such as enzymes and drugs, immobilization of microorganisms, wound and burn dressing, in separation processes, sensors, actuators.[4]

Polymers that respond to external chemical and physical stimuli have recently attracted a lot of scientific attention and interest in their technical applications. Hydrogels based on crosslinked poly(*N*-isopropylacrylamide), PNIPA, are known to exhibit a volume transition at about 34°C.[5] This is slightly higher than the lower critical solution temperature (LCST ≈ 32°C) of the linear polymer in aqueous solution. Linear PNIPA polymers exhibit a sharp conformation transition in water by releasing structured water molecules around the polymer chains. In PNIPA hydrogels, the volume transition is induced by the cooperative dehydration of the hydrophobic isopropyl groups in the main chain, coupled with the entropic force of the chains, which shrinks the gel. The volume transition of PNIPA depends on the ratio of the hydrophilicity of the amide groups and the hydrophobicity of the isopropyl groups, which changes with temperature.

The main disadvantages of PNIPA hydrogels are a slow response to temperature changes and their relatively low mechanical strength, which limit their utility in many fields. Fast responses are required for some specific applications, such as chemical sensors and artificial organs. For example, polymer gels used

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for artificial muscles have to exhibit moduli comparable with those found in living systems (0.2–1 MPa) for power generation and fast response rate (<10 ms). These target values of modulus and response rate could be achieved by molecular design and synthesis of polymer gels with improved mechanical properties and faster swelling–shrinking deformation. Many investigators have made significant efforts to develop thermally sensitive PNIPA hydrogels with fast shrink/swell behavior. Kaneko et al.[6] suggested an acceleration of the thermoresponsive gel swelling–deswelling changes through a modification of the molecular structure by incorporation of poly(ethylene oxide) graft chains into the PNIPA network. Hydrophilic PEO graft chains with freely mobile ends form channels for water molecules within the skin layer, which permits water release and increases the response rate compared to conventional PNIPA gels. Çaykara et al.[7] studied the effect of poly(ethylene glycol) as a pore-forming agent on the synthesis of PNIPA macroporous hydrogels and the swelling–deswelling kinetics. Incorporation of a linear polymer into the PNIPA hydrogel networks can also greatly increase the response rate. Many other methods for enhancing the temperature sensitivity of hydrogels are well known in the literature, such as cold-treatment of the gel network, synthesis of the gels in aqueous glucose solution,[8] polymerization/crosslinking in mixed solvents, and the phase separation technique carried out at a temperature above the LCST.[9] Geever et al.[10] reported on the physically crosslinked complexes of poly(*N*-vinylpyrrolidone), PVP, and PNIPA random copolymer, prepared by photopolymerization, as matrices for controlled drug-delivery systems. Unfortunately, some modifications also have unfavorable effects, such as loss of mechanical strength.

Hydrogels based on PNIPA are too weak and fragile to withstand the high levels of stress and strain required for various applications. Many approaches have been considered to solve the problem of the poor mechanical properties of the gels, such as changing the type and concentration of the crosslinking agent, using special comonomers or altering their compositions[11] and optimizing the polymerization conditions (temperature, reaction time, type, and amount of the solvent). Of these attempts, better mechanical properties could be achieved by increasing the crosslinking density,[12] using hydrophobic co-monomer,[13] or by synthesis of full or semi-interpenetrating networks (SIPNs),[14–18] as well as using inorganic clay instead of an organic crosslinker to prepare nanocomposite hydrogels.[19,20]

Responsive hydrogels may have useful applications in mechanical devices but their relatively low strength, because of the reduced concentration of network chains in the swollen state, lack of intermolecular bonding, and short relaxation times during crack propagation, considerably affect their utility. An ideal PNIPA hydrogel would have the high strength and toughness, high swelling ratio and fast deswelling rate, achieved simultaneously. A high molecular weight linear component in SIPN introduces entanglements and reinforces the networks and may also affect the solvent polymer interactions and change the responsiveness of a gel. The addition of linear chains was found to reduce the fragility of the swollen gels.[18] Two factors were found to contribute to the gel strength: the concentration of chains per unit volume, which is related to the degree of swelling, and the entanglement effect, which is supposed to retard crack propagation. The chemical structure of the linear polymer chains plays an important role in modifying the swelling behavior and mechanical properties of hydrogels. Hydrogels reinforced with a linear hydrophilic polymer absorb a large amount of water and, therefore, have a high degree of swelling, while a hydrophobic copolymer decreases the degree of swelling and simultaneously improves the mechanical properties. In our previous article, it was shown that semi-interpenetrating PNIPA networks reinforced with cationic and nonionic polyacrylamide exhibited better mechanical properties because of lower swelling and thus, higher concentration of chains per unit volume.[18]

Most data on the strength of gels found in literature were obtained in the compression mode and at a fixed degree of swelling, usually lower than the equilibrium degree of swelling. If a gel would serve as a device, which releases water upon shrinkage and picks up water during expansion reversibly, then it has to be permanently immersed in water. This also means that it would reach a maximum swelling in equilibrium. Comparison of gels in the equilibrium state at different degrees of swelling is important for understanding operation of the devices based on these gels.

The objective of this study was to optimize the structure and properties of thermoresponsive hydrogels by using SIPNs and increase the tensile strength and modulus as well as improve the swelling/shrinking thermal response. Four series of SIPN gels with different crosslinking densities were prepared with *N*-isopropylacrylamide (NIPA)/*N*,*N*′-methylenebisacrylamide (MBA) ratios 25 : 1; 50 : 1; 75 : 1 and 100 : 1. Each series of SIPNs were prepared in 1, 2 and 3 wt % solution of PVP and the references were pure PNIPA gels, making 16 samples in total. PVP was used because of high hydrophilic character, high molecular weight, and some useful properties. It is known that linear PVP besides having good physiological inertia and biocompatibility with the human body has the ability to bind reversibly to various molecules, such as dyes, metals, and some polymers by forming association complexes.[21] Zhuang et al.[22] reported that

PNIPA/PVP interpenetrating networks were promising materials for enhancing the solubilization of drugs and the development of a long-term controlled release system. The hydrogels were synthesized by free radical polymerization in aqueous media as described in literature.[23,24] The SIPNs and PNIPA hydrogels were characterized by determining the equilibrium degree of swelling at 25°C, the dynamic shear modulus and the effective crosslinking density, as well as tensile strength and elongation at break at maximum swelling. Furthermore, scanning electron microscopy (SEM) was used to investigate the morphology of the PNIPA and SIPNs hydrogels. Kinetics of swelling was used to estimate the responsiveness of the gels.

## EXPERIMENTAL

### Materials

NIPA was obtained from Acros Organics (New Jersey, USA), and purified by recrystallization from benzene/*n*-hexane (35/75). PVP, $M_w = 1.3\times10^6$ g/mol, MBA as the crosslinker, ammonium persulfate as the redox initiator, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) as the accelerator were purchased from Fluka, Sigma-Aldrich (Germany), and used as received.

### Synthesis

SIPN hydrogels based on crosslinked PNIPA and various amounts of the linear PVP, were synthesized using the following procedure. PVP solutions (from 1 to 3 wt %) were prepared by mixing the appropriate amount of polymer and water at 80°C and stirred until the polymer was completely dissolved. Two grams of NIPA (0.0177 mol) and the required amount of MBA were added to 20 mL of PVP solution. The reaction mixture was bubbled with the nitrogen for 30 min at ≈ 4°C. After the addition of 0.2 mL of ammonium persulfate (freshly prepared 10 wt % aqueous solution) and 4.8 μL of TEMED, the polymerization was carried out at ≈ 4°C for 24 h in a glass molds (12.5 cm × 12.5 cm plates) separated by a 2-mm thick rubber gasket. The amount of MBA was varied to obtain polymer networks with four different crosslinking densities (molar ratio of NIPA to MBA from 25/1 to 100/1).

### Sample designations

In this article, the samples are designated as SIPNs or PNIPA, for semi-IPNs and pure PNIPA hydrogels, respectively, with different molar ratio NIPA to MBA from 25/1 to 100/1. Designations 1–3 wt % refer to the concentration of linear PVP polymer in aqueous solution during synthesis. At the same time, the concentration of NIPA gel was kept constant at 10%. Thus, the relative amount of PVP in SIPN gels in water were 10 parts of NIPA and 1, 2, or 3 parts of PVP or the concentration of linear chains relative to the network chains varied from about 9 wt % (1%) to about 23 wt % (3%). The sample composition and designations are summarized in Table I.

### Characterization

Disk-shaped specimens of 1 cm diameter were incubated in distilled water and swollen to equilibrium for at least 4 days. The degrees of swelling, *Q*, in the temperature range from 22 to 45°C were measured gravimetrically after removal of the excess surface water with filter paper. The average value of five

**TABLE I**
**Some Structural and Physical Characteristics of the PNIPA and SIPN Hydrogels in their Equilibrium Swollen State**

| Sample | | Equilibrium degree of swelling, $Q_e$ | SIPN in the swollen state (%) | PNIPA in the swollen state (%) | φ | $k \times 10^3$ ($min^{-1}$) | LCST |
|---|---|---|---|---|---|---|---|
| PNIPA / MBA | PVP (wt %) | | | | | | |
| 25/1 | 0 | 7.2 | 13.54 | 13.54 | 0.131 | 10.99 | 34.0 |
| 50/1 | 0 | 9.5 | 10.33 | 10.33 | 0.100 | 13.81 | 32.7 |
| 75/1 | 0 | 11.4 | 8.59 | 8.59 | 0.083 | 10.9 | 31.4 |
| 100/1 | 0 | 12.2 | 8.05 | 8.05 | 0.078 | 10.16 | 33.9 |
| 25/1 | 1 | 6.7 | 14.89 | 13.54 | 0.131 | 3.57 | 32.4 |
| 50/1 | 1 | 9.4 | 10.62 | 9.66 | 0.094 | 3.88 | 32.2 |
| 75/1 | 1 | 13.6 | 7.36 | 6.67 | 0.064 | 3.80 | 32.4 |
| 100/1 | 1 | 14.9 | 6.70 | 6.09 | 0.059 | 3.97 | 32.7 |
| 25/1 | 2 | 9.6 | 10.49 | 8.72 | 0.085 | 3.71 | 32.4 |
| 50/1 | 2 | 12.2 | 8.17 | 6.82 | 0.066 | 4.21 | 31.0 |
| 75/1 | 2 | 15.2 | 6.61 | 5.51 | 0.053 | 4.18 | 29.8 |
| 100/1 | 2 | 16.8 | 6.01 | 5.02 | 0.048 | 3.69 | 32.0 |
| 25/1 | 3 | 10.2 | 9.86 | 7.52 | 0.073 | 5.05 | 32.1 |
| 50/1 | 3 | 12.7 | 7.82 | 6.01 | 0.058 | 4.26 | 31.0 |
| 75/1 | 3 | 14.3 | 6.99 | 5.38 | 0.052 | 3.84 | 30.7 |
| 100/1 | 3 | 14.9 | 6.70 | 5.14 | 0.050 | 3.91 | 31.7 |

measurements was taken for each sample. The degree of swelling, $Q$, was calculated as:

$$Q = m_t/m_d \quad (1)$$

where $m_t$ is the weight of the polymer specimen swollen at time $t$, and $m_d$ is the weight of the dry hydrogel.

Measurements of the kinetics of deswelling were performed gravimetrically at 40°C with hydrogels previously swollen to equilibrium in distilled water at 25°C. The weight changes of the hydrogels were recorded during the course of the deswelling process at different times. Water retention (WR) can be defined as:

$$\mathrm{WR}\,[\%] = 100 \cdot W_t/W_e = 100\,(m_t - m_d)/(m_e - m_d) \quad (2)$$

where $W_t$ and $W_e$ are the weight of water at time $t$ and in the equilibrium swollen state, respectively.

The viscoelastic properties of the hydrogels were studied using a Rheometrics, model "RMS 605" mechanical spectrometer operating in the shear mode. The diameter of the plates was 25 mm and the gap between the two parallel plates was around 3 mm. The storage modulus, $G'$, the loss modulus, $G''$, and the loss tangent, tan δ were analyzed as a function of frequency (varied from 0.1 to 100 rad/s) and the amount of PVP, at a shear strain of 10%.

To measure tensile properties, the hydrogels were cut in their equilibrium swollen state into 70 mm × 5 mm strips. A 10 N load cell was used with the strain rate set at 10 mm/min. The swollen hydrogel samples were fixed on the paper frame and mounted in the jaws of the tensile tester, with gauge length of 50 mm. The initial dimensions and length of the hydrogel were measured to obtain cross-section area and the percent of strain. The tensile strength, elongation at break, and elastic modulus of the synthesized hydrogels, were measured on at least five specimens.

The morphology of hydrogel samples was examined with a scanning electron microscope (SEM, JEOL JSM-5800). To conserve the structure of the hydrogel without collapse, each sample was rapidly frozen and subsequently freeze-dried for 24 h under vacuum at −40°C. The freeze-dried pieces were plunged into liquid nitrogen and carefully cut with a scalpel to observe the interior morphology of the gels. Finally, the samples were rotationally coated with a thin layer of Pd-Pt alloy and the microstructure was imaged in the SEM at an acceleration voltage of 20 kV.

## RESULTS AND DISCUSSION

### Structure of PNIPA and the SIPNs

Three series of polymer SIPNs and one series of PNIPA networks with four different crosslinking densities were synthesized by varying the NIPA to MBA molar ratio from 25/1 to 100/1. In the equilibrium swollen state, the content of crosslinked PNIPA in hydrogels varied in the range from 5.0 to 13.5 wt %, whereas the concentration of semi-interpenetrating polymer network in water including linear PVP was in the range from 6.0 to 14.9, depending on the degree of crosslinking. (Table I).

### Morphology of PNIPA and SIPNs

The interior matrix structure of solid samples of the PNIPA and SIPNs with linear PVP chains was analyzed by SEM. Representative SEM microphotographs of the hydrogels, presented as a function of the crosslinking density and the amount of linear PVP incorporated in the hydrogels, are shown in Figure 1(a,b). The samples retained the porous structure that they had in the swollen state because of the employed freeze drying method. It can be seen from the micrographs that SIPNs and PNIPA hydrogels had a similar morphology characterized by a broad polydispersity of three-dimensional pores and very thin pore walls. The pore sizes of the prepared SIPNs and PNIPA hydrogels were in the range from 40 to 90 μm and irregular, as evidenced by the large standard deviation, in the range from 13 to 30 μm.

The SEM microphotographs revealed a tendency for the pore size of the SIPN networks to decrease with increasing amount of added linear PVP in almost all cases, but unambiguous conclusion could not be given, because of the large irregularity and polydispersity of the pore sizes. The pore sizes in the PNIPA hydrogel (NIPA/MBA 75/1) were found to be irregular with an average value 62 ± 17 μm in diameter, whereas the SIPN hydrogel with 3 wt % PVP (NIPA/MBA 75/1) had the smallest pore sizes of about 47 ± 13 μm in diameter. It is well established that the main factor controlling the rate of water diffusion during deswelling is the structure of the matrix, i.e., the number and size of the channels into which water diffuses.

Increasing the content of crosslinker also led to a reduction in the average pore size of the hydrogel networks. The structure of the hydrogel with the highest degree of crosslinking (NIPA/MBA, 25/1) was completely irregular, consisting of areas with very large channels and other areas with a very large number of small pores. These networks exhibited a very fast response to the temperature change, manifested as the volume shrinkage during the deswelling process. For the other PNIPA hydrogels, decreasing the crosslinking density caused an increase in the pore size in the range from 64 to 80 μm; whereas for the SIPNs with 3 wt %, the increase was in the range from 40 to 60 μm. Despite larger channels, the rates of deswelling of these hydrogels were lower, possibly because of lower entropic forces at lower concentration of chains in the gels (higher swelling).

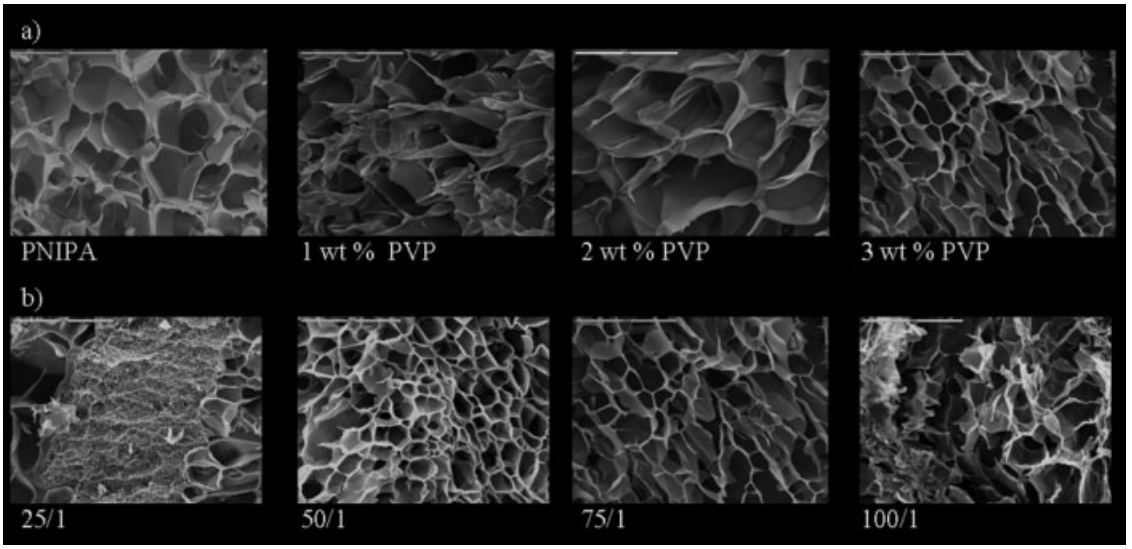


**Figure 1** SEM images of hydrogels with (a) 0, 1, 2, and 3 wt % PVP, with a NIPA/MBA molar ratio of 75/1 and (b) with 3 wt % PVP and different NIPA/MBA molar ratios (bar = 200 μm).

### Degree of swelling of PNIPA and the SIPNs

The equilibrium degree of swelling of PNIPA and the SIPN hydrogels as a function of the crosslinking density and weight content of linear hydrophilic PVP in water at 25°C, is shown in Figure 2. Each point represents the average from five measurements.

The SIPN hydrogels had higher swelling ratios than the PNIPA hydrogels at temperatures below the LCST. As the NIPA/MBA molar ratio increased from 25/1 to 100/1, the degree of swelling of the PNIPA hydrogels increased from 7 to 12.

The degree of swelling of the SIPNs series increased 20 to 42% with increasing content of linear hydrophilic PVP in the hydrogels from 0 to 3 wt %. In the presence of 3 wt % PVP, a small decline of the degree of swelling in the samples with 75/1 and 100/1 the NIPA/MBA molar ratio is observed, which could be the consequence of a higher crosslinking density of the gel, due to the reinforcement caused by entanglements, and the different structure of the matrix, i.e., the number and size of the pores. These results showed that the effect of the chemical composition and structure of SIPNs on the swelling of the hydrogels was complex. In addition to the morphology of a hydrogel and the contribution of reinforcement, the swelling behavior also depends on the effective interaction parameter, $\chi_{ef}$, which includes solvent/network, solvent/linear chain, and linear chain/network interaction parameters.[25]

### Thermoresponse of PNIPA and SIPNs

The equilibrium degree of swelling of PNIPA and SIPNs with PVP were determined at different temperatures, in the range from 25°C and 40°C. The thermoresponse of the PNIPA and SIPN hydrogels is illustrated with SIPNs with the highest crosslinking density and different concentration of PVP, Figure 3(a), and SIPNs gels of different crosslinking density, Figure 3(b). It can be seen that the equilibrium degree of swelling increased with increasing concentration of PVP but the volume phase transition was less sharp, i.e., the weight loss was more gradual. The more gradual temperature-induced volume transition in the presence of the hydrophilic PVP can be assigned to better solvation of the polymer network chains due to the stronger interaction between the PVP chains and water molecules. It appears that PVP was holding water during the transition. The LCSTs were estimated from the inflection points on the equilibrium swelling degree vs. temperature curves and the values are presented

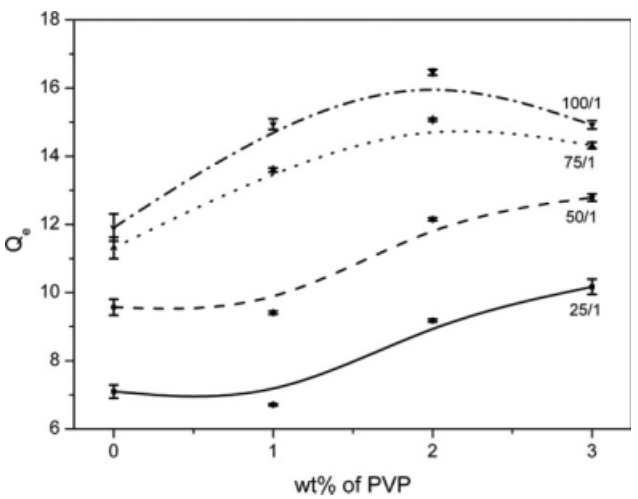


**Figure 2** Equilibrium degree of swelling of the PNIPA and SIPN hydrogels as a function of PVP concentration at different NIPA/MBA molar ratios.

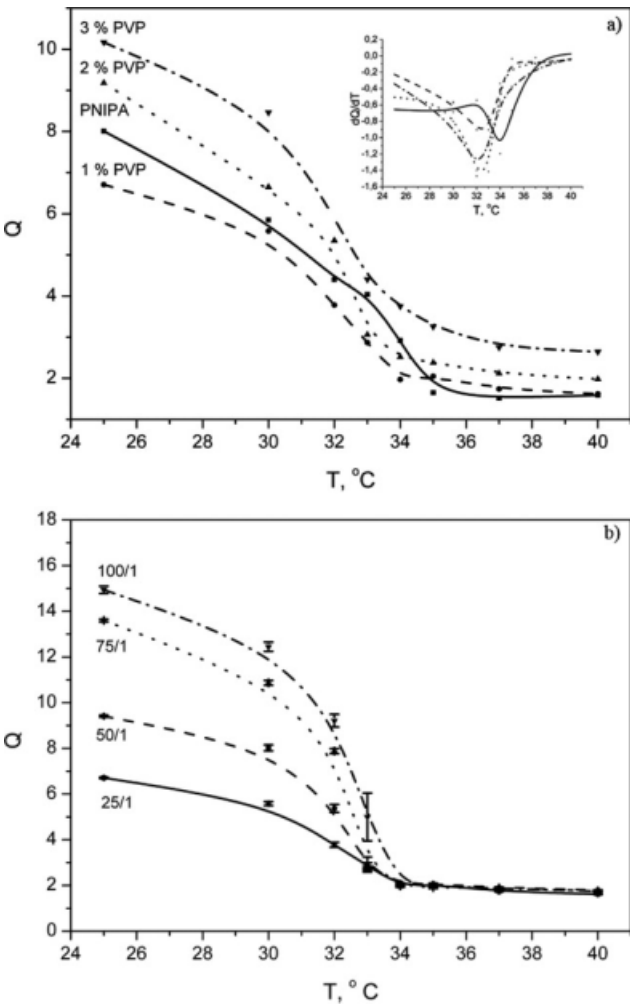


**Figure 3** Equilibrium degree of swelling as a function of temperature for (a) samples at different PVP concentrations and molar ratio NIPA/MBA 25/1 (insertion: derivative of $Q$ vs. temperature) and (b) SIPN with 1 wt % of PVP and different crosslinking densities.

in Table I. The temperature-dependent volume phase transition for the PNIPA hydrogels was in the range from 31.5 to 34°C, which is very close to the value reported earlier.[26] In addition, it is known that the LCST of PNIPA-type gels can be adjusted to near human body temperature by copolymerization or utilization of additives, which makes them suitable for *in vivo* applications. The results showed that the presence of linear hydrophilic PVP in the SIPNs slightly decreases the value of the LCST. They were in agreement with the results of Shin et al.[27], who reported that the LCST of SIPNs decreased with the incorporation of a hydrophilic polymer, because of intermolecular interaction, such as hydrogen bonding. The hydrogen bonding protected PNIPA from exposure to water and this resulted in a significant hydrophobic contribution to the LCST. As the temperature was raised above the LCST (Fig. 3), the degree of swelling decreased sharply, indicating the occurrence of phase separation and volume change. At temperatures above the LCST, the degree of swelling of the SIPNs and PNIPA hydrogels was almost constant (at about 2–3) because the hydrophobicity became dominant.

The effect of the crosslinking density of the polymer network on the LCST was not so evident, due to the superposition of the effects of incorporation of the hydrophilic PVP and the increase of the crosslinking density. It was assumed that in the presence of linear PVP in the reaction mixture, phase separation of the formed interpenetrating networks occurred during the crosslinking reaction, leading to a heterogeneous structure, which plays major role in the thermal sensitive response of hydrogels.

From the obtained results, it was concluded that only the degree of swelling could be controlled by incorporation of the linear hydrophilic PVP in PNIPA hydrogels, while at the same time, there was only a small change in the LCST. This is an advantage for SIPNs with PVP and makes them candidates for many different applications.

## Dynamics of water sorption

Measurements of water uptake of PNIPA and SIPNs were carried out on punched hydrogel samples after they had been dried in a vacuum oven at 60°C to constant weight, to determine the swelling rate constants at 25°C.

The water uptake data were analyzed using a first order kinetic equation[28]:

$$\ln[W_e/(W_e - W_t)] = kt \tag{3}$$

where $W_e$ is the water uptake at equilibrium, $W_t$ is the water uptake at time $t$ and $k$ is the rate constant.

To put into prospective the results of this calculation let us first explain the definition of water uptake. If we define the rate of water absorption as $dQ/dt$, i.e., the amount of water absorbed per unit time, then the fastest water uptake is in samples with lower crosslinking density in all series. However, in eq. (3), this rate is divided by the final water uptake producing a relative water uptake, reducing more the values for samples with higher degree of swelling. In this case, the dependence on crosslinking density may change as shown in Table I. The values of the swelling rate constant, $k$, of PNIPA and the SIPNs in water given in Table I show an increase in the swelling rate with increasing content of crosslinker in all four series PNIPA and SIPNs hydrogels, which is consistent with previous studies on PNIPA hydrogels.[29]

The rate of water uptake was the highest for the PNIPA hydrogels without linear polymer. However, addition of 1% PVP reduces significantly the water uptake, and then increases with increasing PVP

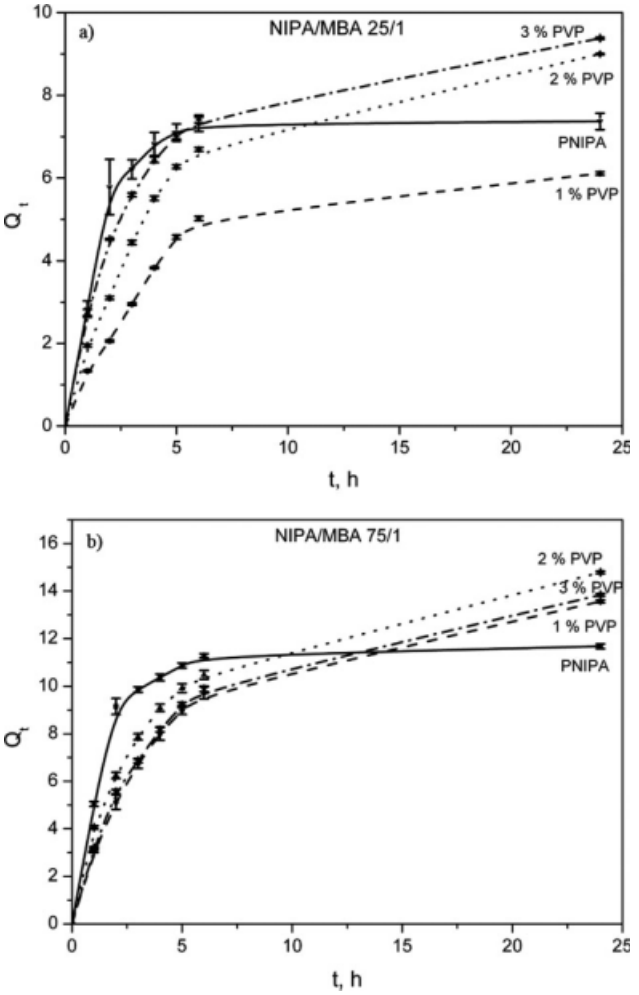


**Figure 4** Swelling kinetics of hydrogels with different PVP concentrations at a molar ratio NIPA/MBA 25/1 (a), and 75/1 (b).

content as shown in Figure 4. Such behavior may be linked to the macroporosity of the samples, which is affected in a different way by drying of gels with different PVP contents prior the test.

### Deswelling experiments

The deswelling tests were performed on samples that had been previously equilibrated at ambient temperature and then quickly transferred into distilled water at a temperature of 40°C. Surprisingly, although the rate of swelling of PNIPA gels was the highest, their rate of deswelling was the lowest. This was explained by the formation of a dense surface skin layer, which acted as a diffusion barrier, whereas PVP kept the channels more open. The PNIPA hydrogels showed volume shrinkage in the range from 10 to 20% within 5 min. According to the experimental data, inclusion of the linear PVP in the hydrogel network enhanced the thermal response of the hydrogels (Fig. 5). Considerably improved deswelling kinetics and volume shrinkage of SIPN hydrogels was achieved by the addition of 2 and 3 wt % PVP. The samples of hydrogels with higher crosslinking densities (NIPA/MBA 25/1 and 50/1) shrunk rapidly and lost more than 70% water within 1 min and deswelling equilibrium was achieved within the next few minutes. The other samples required a few hours to reach the equilibrium state.

It is well known that the processes of swelling and deswelling or gel collapsing are diffusion controlled. Their kinetics strongly depends on the size of the gels as well as on the heterogeneity or the matrix structure of the samples. It was reported that the swelling and collapsing rate could be improved by introducing a surfactant into PNIPA hydrogels.[30]

To monitor the thermal response of the SIPNs and PNIPA hydrogels, the deswelling process in water at a temperature of 40°C of these gels under load, seen as linear shrinkage of gel stripes, was recorded with a camera. The photographs of two SIPNs with molar ratios NIPA/MBA of 25/1 and 75/1 reinforced with

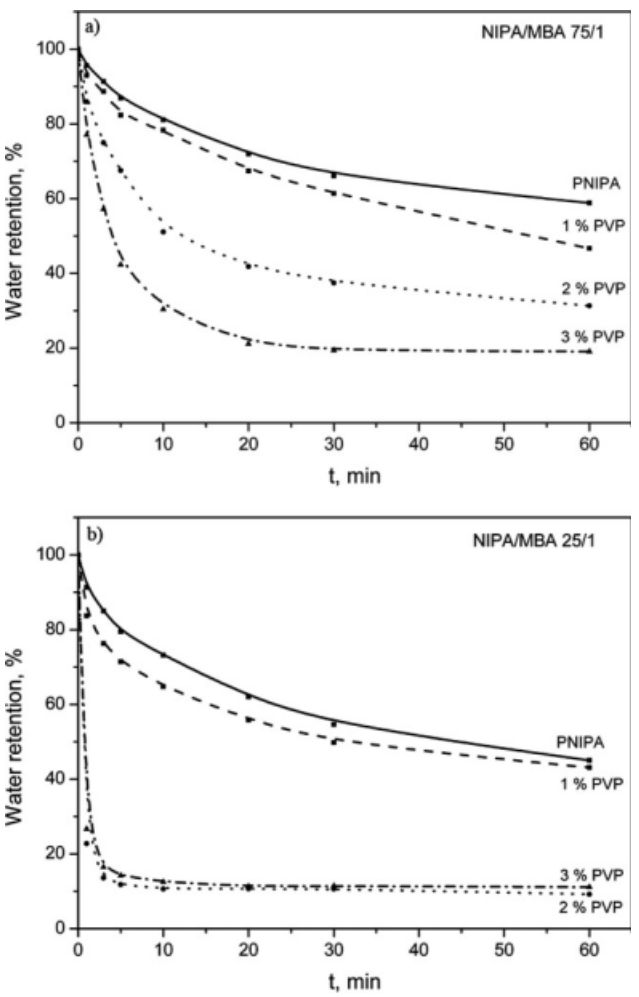


**Figure 5** Deswelling kinetics of PNIPA and SIPN hydrogels in water at 40°C as a function of crosslinking density and the content of linear PVP at NIPA/MBA ratio 75/1 (a) and 25/1 (b).

3% PVP are given in Figure 6. These tests also confirmed that gels with high crosslinking density contracted rapidly, within 1 min, whereas the other hydrogels required 30 min to 1 h to reach their equilibrium state.

### Mechanical properties of PNIPA and SIPNs

Dynamic mechanical properties of the PNIPA and SIPN series of hydrogels in the swollen state were investigated by measuring the shear storage ($G'$) and loss modulus ($G''$) at room temperature (Table II). For all SIPN hydrogels, the equilibrium shear storage $G'$ values varied in the range from 3.0 to 20.5 kPa. The equilibrium shear storage modulus $G'$ values of the hydrogels were greater than the $G''$ values, indicating that the synthesized interpenetrating hydrogels were soft viscoelastic solids. The plateau values of the loss modus, $G''$, are about 1 – 4% of $G'$. Significantly larger $G'$ than $G''$ values are indicative of a well-developed crosslinked structure of hydrogels.[31] In all the series, storage $G'$ modulus of the SIPNs and PNIPA decreased with decreasing crosslinking density. The values of $G'$, the reduced storage modulus, $G'_{red}$, the apparent crosslinking density and the efficiency of crosslinking are presented in Table II.

Modulus of gels decreases with the degree of swelling and for comparison it should be reduced to the dry state. The shear modulus in a swollen state $G_{swollen}$ is related to the shear modulus in the dry state, $G_{red}$, and volume fraction of polymer, φ, or degree of swelling ($Q$=1/φ), by[32,33]:

$$G_{swollen} = G_{red}\,\varphi^{1/3} = G_{red}Q^{-1/3} \qquad (4)$$

Equation (4) is based purely on geometrical considerations that at lower concentrations the number of strands per unit volume decreases. However, the competing effect of higher stretching of strands at lower concentrations changes the relationship, and the scaling exponent may vary with polymer-solvent interaction. For swelling in athermal solvent $G$ was found to be scaling with $Q^{-1.75}$ but other exponents may be applicable for different solvent qualities.[34] Instead of equilibrium shear modulus, we used storage shear modulus $G'$ as a first approximation.

The dependence of $G'$ on the volume fraction of PNIPA showed different slopes, in double-logarithmic $G'$-φ plots. The exponent obtained for PNIPA and the three series of SIPNs was in the range of –2.46 to –0.29 (PNIPA, –2.46; SIPN-1, –1.94; SIPN-2, –1.24; SIPN-3, –0.29) for a relatively narrow range of equilibrium degrees of swelling $Q$ (6.7–16.8). For all the

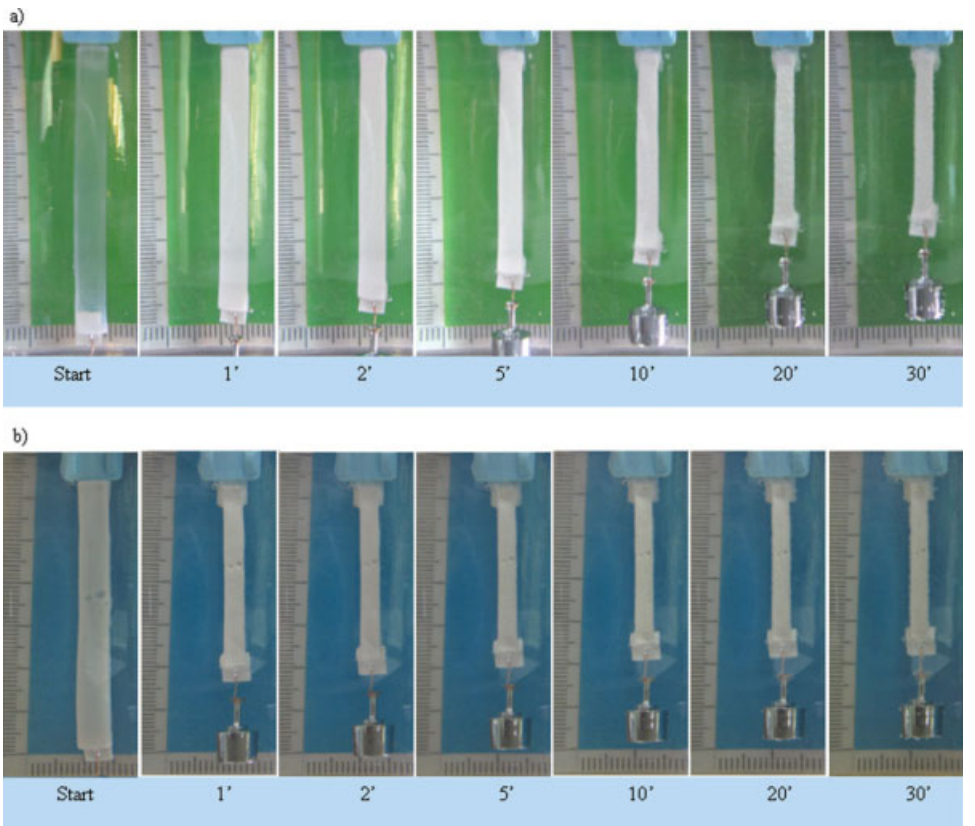


**Figure 6** Photographs of the contraction of SIPNs strips with 3 wt % PVP in water, at 40°C under a load of 2 g. Upper row- NIPA/MBA molar ratio 75/1; lower row: and NIPA/MBA = 25/1. Numbers designate time in minutes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**TABLE II**
**Effect of the Structure of the Hydrogels on the crosslinking Density and crosslinking Efficiency**

| Sample | | | | | | $n_c \times 10^4$ (mol/cm$^3$) | | Efficiency of |
|---|---|---|---|---|---|---|---|---|
| PNIPA /MBA | PVP (wt %) | $G'$ (kPa)[a] | φ (PNIPA) | $G'_{red}$ (kPa) | $M_c \times 10^{-3}$ (g/mol) | Exp. | Calcd. | crosslinking |
| 25/1 | 0 | 17.1 | 0.131 | 216.0 | 5.91 | 1.74 | 6.9 | 0.25 |
| 50/1 | 0 | 9.5 | 0.100 | 169.0 | 7.55 | 1.36 | 3.5 | 0.39 |
| 75/1 | 0 | 6.5 | 0.083 | 146.1 | 8.73 | 1.18 | 2.4 | 0.49 |
| 100/1 | 0 | 4.3 | 0.078 | 105.0 | 12.15 | 0.85 | 1.8 | 0.47 |
| 25/1 | 1 | 20.5 | 0.131 | 260.1 | 4.91 | 2.10 | | 0.30 |
| 50/1 | 1 | 11.6 | 0.094 | 222.9 | 5.72 | 1.80 | | 0.51 |
| 75/1 | 1 | 4.6 | 0.064 | 142.9 | 8.93 | 1.15 | | 0.48 |
| 100/1 | 1 | 3.7 | 0.059 | 127.4 | 10.01 | 1.03 | | 0.57 |
| 25/1 | 2 | 11.2 | 0.085 | 244.0 | 5.23 | 1.97 | | 0.29 |
| 50/1 | 2 | 8.5 | 0.066 | 254.1 | 5.02 | 2.05 | | 0.58 |
| 75/1 | 2 | 5.3 | 0.053 | 208.4 | 6.12 | 1.68 | | 0.70 |
| 100/1 | 2 | 4.6 | 0.048 | 204.7 | 6.23 | 1.65 | | 0.92 |
| 25/1 | 3 | 3.7 | 0.073 | 97.5 | 13.09 | 0.79 | | 0.11 |
| 50/1 | 3 | 4.0 | 0.058 | 140.5 | 9.08 | 1.13 | | 0.32 |
| 75/1 | 3 | 3.4 | 0.052 | 136.9 | 9.34 | 1.10 | | 0.46 |
| 100/1 | 3 | 3.0 | 0.050 | 126.9 | 10.06 | 1.02 | | 0.57 |

[a] Swollen to equilibrium at 25°C

samples of the prepared hydrogels with various crosslinking densities and degrees of swelling, the dependence of $G'$ on the volume fraction of PNIPA in the swollen state could be presented as a single curve with an exponent –1.25, i.e. $G'_{red} = G'_{swollen}/\ \varphi^{1.25} = G'_{swollen}\ /(1/Q)^{1.25}$. Hence, this value of the exponent was used in eq. (4) for the $G'_{red}$ calculations.

In our previous article on PNIPA hydrogels reinforced with nonionic as well as with ionic polyacrylamide, an exponent for the $E'_{red}$ calculation was –1.19.

The extent of reinforcement obtained by the incorporation of linear PVP into PNIPA networks is depicted in Figure 7. Addition of PVP does not affect $G'$ for 75/1 and 100/1 significantly but causes the reduction of $G'$ for gels with 25/1 and 50/1 crosslinking ratios at 2 and 3% of PVP. However when the results are presented as $G'_{red}$ vs. PVP concentration, then increasing modulus is observed in all samples with 1 and 2% PVP but not at 3%.

### Network parameters of the hydrogels in their equilibrium swollen state

The apparent effective crosslinking density, $n_c$, and the molecular weight between crosslinks, $M_c$, of the PNIPA and SIPNs hydrogels were calculated from $G'_{red}$ at 25°C. The frequency independent modulus G′ (plateau modulus) in the swollen state corresponds to the equilibrium shear modulus $G_e$ in the theory of rubber elasticity. If they form a homogeneous network of Gaussian chains, then[35]:

$$G_{red} = F\, n_c R\, T\ = F\, \rho\, R\, T\, /M_c \qquad (5)$$

where ρ is the polymer density (1.03 g/cm$^3$), $R$ is the universal gas constant and $T$ is the absolute temperature. The front factor $F$ is equal to $1 - 2/f$ for a phantom network, where $f$ is the functionality ($f = 4$ for MBA). The front factor is 0.5 for a phantom network and this model represents a swollen hydrogel better than the affine model. The values of $M_c$ calculated using a phantom network model for PNIPA were 1.1 to 3.9 times higher than the values based on stoichiometry.

The crosslinking efficiency of hydrogels ranged from 0.11 to 0.92, calculated as the ratio of the experimentally determined value $n_c$ to the theoretical crosslinking density (assuming that each MBA molecule formed one crosslink). Hydrogels prepared in solution contain a large number of elastically ineffective chains because of side reactions, which occurred in the dilute solution polymerization. It has been suggested that crosslinker monomers are less efficient in the formation of network junctions, due to cyclization and multiple crosslinking reactions, as

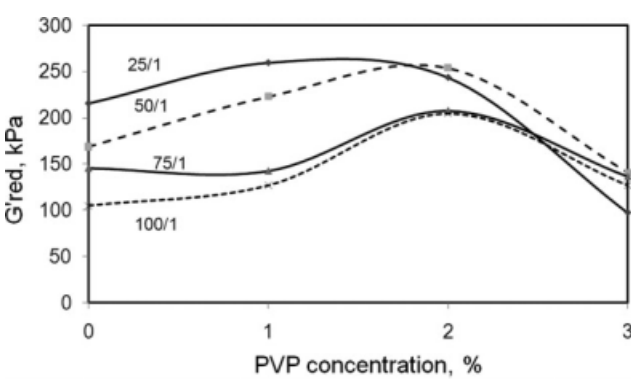


**Figure 7** G′red of PNIPA and SIPNs as a function of PVP content at different crosslinking densities.

the concentration of the crosslinker increases.[21,36] In the cyclization reaction, a cycle is formed when a macroradical attacks the pendant vinyl groups in the same kinetic chain; whereas in multiple crosslinking, the macroradical attacks pendant double bonds on other chains, which leads to the formation of highly crosslinked regions in the final network and therefore greater inhomogeneity. It could be concluded that there was an increase in crosslinking efficiency with increasing monomer/crosslinker ratio (NIPA/ MBA). As was already reported, at low crosslinker content, the concentration of pendant vinyl group surrounding the growing macroradical is relatively low and, therefore, there is a small possibility of the occurrence of multiple crosslinking reactions, while at higher crosslinker concentrations, the possibility of multiple crosslinking reaction is enhanced, due to the higher pendant group concentration and higher MBA reactivity.[37]

### Mechanical strength of PNIPA and SIPNs

PNIPA hydrogels exhibit very low mechanical properties and are easily ruptured by the applications of external stresses. Therefore, they have to be reinforced for applications where they are stretched or bent. The mechanical properties of hydrogels are usually examined in uniaxial compression tests. There are only a few studies on the mechanical properties of PNIPA hydrogels in the tension mode, which would be quite instructive for their application for artificial devices.[18,38] The fracture mechanics of swollen gels was studied by a number of authors[39–41] but, to the best of our knowledge, there is no theory relating the tensile strength of gels, particularly interpenetrating networks, to the degree of swelling.

A basic tensile test method was used to evaluate elongation at break and tensile strength, as well as the Young's modulus, $E$, of the SIPNs. The tensile strengths of the SIPNs reinforced with hydrophilic PVP at the equilibrium swollen state were improved in gels with higher crosslinking density but were virtually unchanged in gels with 75/1 and 100/1 NIPA/ MBA ratios [Fig. 8(a)]. The tensile strength of the hydrogels depend on the crosslinking density taking into account both chemical and physical crosslinking (contribution of PVP entanglements), content of polymer chains as well as on the morphology of the samples. The results showed that in SIPNs hydrogels at 75/1 and 100/1 NIPA/ MBA ratios, the contribution of entanglements was small due to their high degree of swelling (high degree of swelling favor disentanglement). The results of the break stress reduced to the dry state, $\sigma_o$, calculated from the relationship $\sigma = \sigma_o (1/Q)^{2/3}$ [Fig. (8b)], showed also that the PVP reinforced the PNIPA networks more in networks with 25/1 and 50/1 NIPA/ MBA ratios. The exponent 2/3 simply reflects the change of area and with increasing volume since stress is calculated per unit area. The highest tensile strength achieved was with 2 wt % of PVP (55 kPa). The elongation at break of SIPNs with 25/1 and 50/1 NIPA/ MBA ratios linearly increased with increasing PVP concentration, but gels with a low degree of crosslinking showed fairly large scattering of results and significant improvement with 1 wt % of PVP (Fig. 9). It should be emphasized that these results were obtained at equilibrium i.e., maximum swollen gels, with very low concentration of network chains per unit volume. Addition of PVP made new SIPN hydrogels less fragile and allowed easier testing in the tensile mode (samples of NIPA gels break easily in the jaws of a tensile tester).

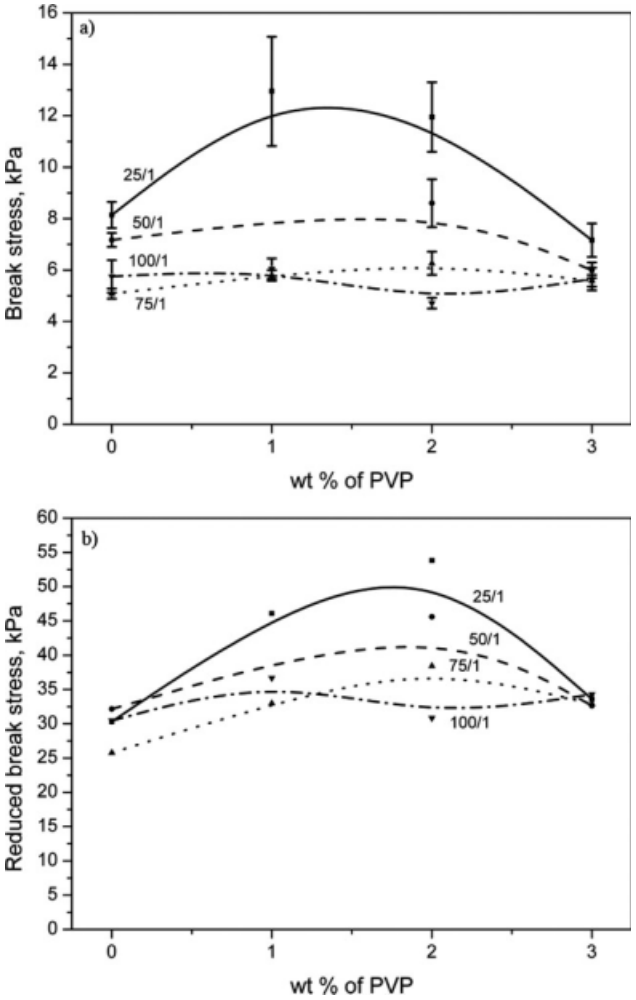


**Figure 8** Break stress (a) and reduced break stress (b) of hydrogels as a function of PVP content at different crosslinking densities.

Tensile measurements in the present study showed that the optimum was achieved with the presence of 1 and 2 wt % of hydrophilic PVP polymer in the hydrogel, while further increase in the PVP content

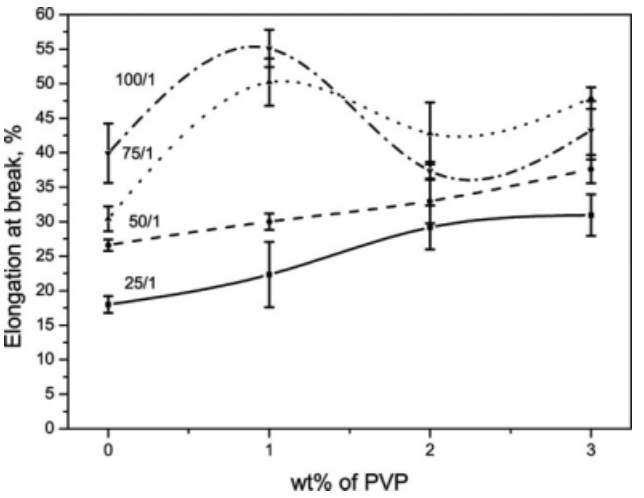


**Figure 9** Elongation at break of hydrogels as a function of PVP content and crosslinking density.

decreased the ultimate properties due to the higher degree of swelling.

## CONCLUSIONS

Three series of novel responsive gels based on PNIPA SIPNs and linear PVP were prepared with the intention of improving thermal response and mechanical properties. The results have shown that improvement in tensile strength and elongation at break of highly swollen gels was obtained by including PVP, particularly in highly crosslinked systems. Also the degree of swelling was increased but the transition from the swollen to the collapsed state was less sharp in the presence of PVP. The degree of swelling below LCST considerably increased with the addition of PVP particularly in lightly crosslinked gels (75/1 and 100/1 NIPA/MBA). The SIPNs hydrogels with higher crosslinking densities (NIPA/MBA 25/1 and 50/1) exhibited rapid shrinking during temperature-induced transition and lost more than 70% water within 1 min, whereas the PNIPA hydrogels showed a shrinkage in the range from 10 to 20% within 5 min. These results were strongly affected by macroscopic porosity as was illustrated by SEM. The addition of 2 wt % linear hydrophilic PVP into the PNIPA hydrogels provided for improvements in thermal response and mechanical properties of the traditional PNIPA hydrogels and may have great potential application in both the fields of biomedical and biotechnology.

## References

1. Osada, Y.; Gong, J. P.; Tanaka, Y. J Macromol Sci: Polym Rev 2004, 44, 87.
2. Zhang, J.-T.; Cheng, S.-X.; Zhuo, R.-X. Colloid Polym Sci 2003, 281, 580.
3. Peppas, N. A.; Bures, P.; Leobandung, W.; Ichikawa, H. Eur J Pharm Biopharm 2000, 50, 27.
4. Zhang, X.-Z.; Zhuo, R.-X. Eur Polym J 2000, 36, 2301.
5. Tanaka, T. Sci Am 1981, 244, 124.
6. Kaneko, Y.; Nakamura, S.; Sakai, K.; Aoyagi, T.; Kikuchi, A.; Sakurai, Y.; Okano, T. Macromolecules 1998, 31, 6099.
7. Çaykara, T.; Kiper, S.; Demirel, G.; Demirci, S.; Çakany, C. Polym Int 2007, 56, 275.
8. Zhang, J.-T.; Cheng, S. X.; Zhuo, R. X. J Polym Sci Part A: Polym Chem 2003, 41, 2390.
9. Zhang, J.-T.; Huang, S.-W.; Zhuo, R. X. Macromol Biosci 2004, 4, 575.
10. Geever, L. M.; Devine, D. M.; Nugent, M. J. D.; Kennedy, J. E.; Lyons, J. G.; Higginbotham, C. L. Eur Polym J 2006, 42, 69.
11. Quintana, J. R.; Valderruten, N. E.; Katime, I. J Appl Polym Sci 2002, 85, 2540.
12. Zhang, X. Z.; Wu, D.-Q.; Chu, C. C. J Polym Sci Part B: Polym Phys 2003, 41, 582.
13. Xue, W.; Champ, S.; Huglin, M. B. Polymer 2001, 42,
14. Zhang, X. Z.; Chu, C. C. J Appl Polym Sci 2003, 89, 1935.
15. Zhang, X. Z.; Wu, D.-Q.; Chu, C. C. Biomaterials 2004, 25, 3793.
16. Stile, R. A.; Chung, E.; Burghardt, W. R.; Healy, K. E. J Biomater Sci: Polym Ed 2004, 15, 865.
17. Muniz, E. C.; Geuskens, G. Macromolecules 2001, 34, 4480.
18. Djonlagić, J.; Petrović, Z. S. J Polym Sci Part B: Polym Phys 2004, 42, 3987.
19. Ma, J.; Xu, Y.; Zhang, Q.; Zha, L.; Liang, B. Colloid Polym Sci 2007, 285, 479.
20. Haraguchi, K.; Song, L. Macromolecules 2007, 40, 5526.
21. Jin, S.; Liu, M.; Zhang, F.; Chen, S.; Niu, A. Polymer 2006, 47, 1526.
22. Zhuang, Y.; Yang, H.; Wang, G.; Zhu, Z.; Song, W.; Zhao, H. J Appl Polym Sci 2003, 88, 724.
23. Gehrke, S. H.Responsive Gels: Volume Transition; Springer-Verlag: New York, 1993.
24. Rathjen, C. M.; Park, C. H.; Goodrich, P. R.; Walgenbach, D. D. Polym Gels Networks 1995, 3, 101.
25. Petrović, Z. S.; MacKnight, W. J.; Koningsveld, R.; Dušek, K. Macromolecules 1987, 20, 1088.
26. Gehrke, S. H.; Palasis, M.; Akhtar, M. K. Polym Int 1992, 29, 29.
27. Shin, B. C.; Jhon, M. S.; Lee, H. B.; Yuk, S. H. Eur Polym J 1998, 34, 171.
28. Zhao, S. P.; Ma, D.; Zhang, L. M. Macromol Biosci 2006, 6, 445.
29. Coughlan, D. C.; Corrigan, O. I. J Pharm Sci 2008, 97, 318.
30. Chen, X.; Tsujii, K. Macromolecules 2006, 39, 8550.
31. Calvet, D.; Wong, J. Y.; Giasson, S. Macromolecules 2004, 37, 7762.
32. Treloar, L. R. G. The Physics of Rubber Elasticity, 3rd ed.; Clarendon Press: Oxford, 2005; p 70.
33. Jonson, B.; Niedermaier, D. J.; Crone, W. C.; Moorthy, J.; Beebe, D. J.Mechanical properties of a pH sensitive hydrogel. 2002 SEM Annual Conference Proceedings; Milwaukee, WI.
34. Rubinstein, M.; Colby, R.Polymer Physics, Oxford University Press: Oxford, 2006; p 276.
35. Ferry, J. D.Viscoelastic Properties of Polymers, 3rd ed.; Wiley: New York, 1980; p 234.
36. Gundogan, N.; Melekaslan, D.; Okay, O. Macromolecules 2002, 35, 5616.
37. Kizilay, M. Y.; Okay, O. Polymer 2003, 44, 5239.
38. Tagikawa, T.; Yamawaka, T.; Takahashi, K.; Masuda, T. Polym Gels Networks 1997, 5, 584.
39. Chun, H.; Gent, A. N. J Polym Sci Part B: Polym Phys 1996, 34, 2223.
40. Gent, A. N.; Tobias, R. H. J Polym Sci: Polym Phys Ed 1982, 20, 2051.
41. Ahagon, A.; Gent, A. N. J Polym Sci: Polym Phys Ed 1975, 13, 1903.