

Super porous organic–inorganic poly(*N*-isopropylacrylamide)-based hydrogel with a very fast temperature response

B. Strachotová*, A. Strachota, M. Uchman, M. Šlouf, J. Brus, J. Pleštil, L. Matějka

Department of Polymer Networks and Mechanical Properties, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nam. 2, CZ-162 06 Prague, Czech Republic

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Abstract

Porous organic–inorganic (O–I) hydrogels showing a very fast temperature response, including very fast reswelling were prepared: only 6 s are needed for 72% deswelling (gel collapse) as well as for 72% reswelling. Both deswelling and reswelling are practically complete in 14 s. The gels were prepared from *N*-isopropylacrylamide (NIPA), *N,N'*-methylenebisacrylamide (BAA) and tetramethoxysilane (TMOS) by simultaneous radical polymerization and hydrolytic polycondensation of TMOS. The syntheses were carried out at temperatures below the lower critical solution temperature (LCST) of poly(NIPA) in two steps: during the first stage the temperature was held at $T = +15\text{ }^{\circ}\text{C}$ and during the second the temperature was lowered below the freezing point of the reaction mixture, $T = -18\text{ }^{\circ}\text{C}$. The ice crystals, which grew during the second stage, served as the pore-forming agent. The best samples were obtained if the second stage was started shortly before the gel point of the reaction mixture. The introduction of the inorganic phase (silica) is necessary for the ability of fast reswelling and also results in a strong improvement of the hydrogels' mechanical properties, while the maximum swelling degree remains nearly unaffected.

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1. Introduction

Poly(*N*-isopropylacrylamide) (poly(NIPA)) hydrogels are a subject of lively scientific interest for a long time [1], due to the discontinuous volume transition, which they show under certain conditions. The theoretical study of discontinuous volume transitions in gels was initiated by Dušek and Patterson [2]. Ten years later, Tanaka [3] discovered this phenomenon (induced by solvent changes) experimentally for a partly ionized acrylamide gel in a mixture of acetone and water. Later, such a volume-phase transition of gels was found to be generated not only by changing the composition of the solvent [4] but also by pH change [5] and by temperature change [6]. The thermally induced volume transition of the aqueous poly(NIPA) gels, first described by Hirokawa and Tanaka [7], is a “network analogue” of the LCST effect (Lower

Critical Solution Temperature) in aqueous solutions of linear poly(NIPA), which precipitate at temperatures above LCST ($=32\text{ }^{\circ}\text{C}$). The ability for volume transitions makes the poly(NIPA)-based hydrogels very interesting for various applications like drug delivery systems [8,9], *e.g.* as microspheres [10], as actuators [11], for the immobilization of enzymes [12], as nano-valves [13,14], *etc.* The ability of fast response to environmental stimuli, *i.e.* of fast swelling and deswelling, plays a decisive role in the assessment of the gels' suitability for practical use. However, the swelling and deswelling of conventional homogeneous gels proceeds by solvent diffusion and is a slow process, dependent on the gel size. Only very small samples can reach a swelling equilibrium in a reasonably short time. Moreover, the so-called “skin effect” significantly decelerates the deswelling of larger gel pieces: a surface layer of the sample deswells, becomes less permeable for solvent transport (“skin”), and thus additionally hinders further deswelling.

An interconnecting porous structure is known to be a key solution to avoid the “skin effect” in gels and to promote their

* Corresponding author. Tel.: +420 296 809 285; fax: +420 296 809 410.
E-mail address: beata@imc.cas.cz (B. Strachotová).

fast volume changes in response to environmental stimuli. Channels of open-cell pore structures allow the solvent to be expelled or absorbed by convection, a much faster process, than by diffusion. Many methods have been used to prepare microporous poly(NIPA) hydrogels: they were prepared by addition of various pore-forming agents like inorganic compounds [15,16], organic polymer microspheres [17], incorporation of dendrimers [18], by polymerization of a phase separated system above the LCST of the polymer [19,20], by polymerization in the presence of a sucrose solution which undergoes phase separation in the later reaction stages [21], by introduction of side chains (comb-grafted structures) [22–24], by impregnation of the hydrogel with microgels [25], by a freeze drying and hydration process [26,27], by polymerization in vacuum at room temperature (water vapor bubbles as porogen) [28] or by introduction of solvent crystals as pore templates [29] (synthesis at a low, “freezing” temperature, Zhang and Zhuo), [30,31]. Usually, however, only the deswelling rate was significantly increased, while the gel reswelling still remained relatively slow. Park and Chen [32] prepared relatively fast reswelling hydrogels: their macroporous foam-like products need *ca.* 70 s for nearly complete deswelling as well as for reswelling. Unfortunately, these products show poor mechanical properties, which limit their applicability. In a previous paper, we presented our first results with heterogeneous, silica- and siloxane-modified hybrid organic–inorganic (O–I) poly(NIPA) hydrogels [33], concluding that the incorporation of the inorganic phase improved the rate of deswelling and reswelling of the products.

In this work we describe the preparation of very fast responsive highly porous organic–inorganic hybrid gels based on cross-linked poly(NIPA), which contain rigid, *in situ*-formed silica structures. The silica domains were formed simultaneously during the poly(NIPA) network formation *via* sol–gel process from tetramethoxysilane (TMOS), similarly as described in our previous paper [33]. The hydrogels display not only very rapid deswelling (gel collapse), but – according to the authors’ knowledge – they also show an unusually fast reswelling in contrast to fast responsive poly(NIPA) gels presented until now in the literature. The inorganic domains were found to play a very important role in the gels, as they stabilize the pore structure of the fastest responsive O–I hydrogels besides improving their mechanical properties.

The hydrogels were prepared in a two-step process which was designed as a new development and improvement of a procedure described by Zhang and Zhuo [29]. In the first step the organic and inorganic networks grew in a homogeneous aqueous solution. In the second step the mixture was cooled down below the freezing point of the aqueous reaction mixture. The system separated into a concentrated aqueous solution, in which the growth of both organic and silica networks continued, and into crystals of pure ice, which took the role of pore templates.

Two processes might affect the final poly(NIPA) hydrogel microstructure: water crystallization and the reaction systems’ gelation as a crucial point in the network formation. Therefore, in order to elucidate the microstructure formation of the

porous gels, we prepared two groups of hydrogels differing in the polymerization procedure: (a) samples frozen before the gel point of the reaction mixture and (b) samples frozen after the gelation of the homogeneous mixture. An interesting finding from the scientific point of view was that the samples frozen (pore generation) before their gel point performed dramatically better than those frozen after their gelation. A synthesis similar to the presented two-step procedure was already published by Huglin et al. [30,34], for the preparation of porous poly(NIPA) gels in dimethylsulfoxide and in water, respectively. In contrast to the presented work, in their case, the gelation of all described systems occurred at room temperature, and the solvent was crystallized only in the post-gel stage. Systems frozen before gelation were not studied because of very poor mechanical properties. Our results, especially the role of the timing of gelation and pore generation, also offer some additional interpretation and explanation of hydrogel studies presented recently by Kato et al. [26,27] (see Section 4). The two preparation procedures presented by us highlight the effect of the difference in the polymer matrix, in which the pores are being generated: we studied the gel microstructure and properties for pore generation (by water crystallization) either in pre-gel or in an early post-gel stage of the polymerizing mixture, respectively. The mentioned pore-stabilizing effect of the silica particles in the hydrogels, which enables very fast reswelling, is also an important finding because the fastest responsive hydrogels presented in the literature *e.g.* [26,27,29,30,34] show fast deswelling and slow reswelling. Obviously the porous microstructure in such single-phase gels “glues together” after their shrinking and needs time to be regenerated during reswelling. In contrast to that, the described gels with stabilized pores are ready for fast reswelling while they are in the deswollen state.

2. Experimental part

2.1. Materials

N-Isopropylacrylamide (NIPA), *N,N'*-methylenebis(acrylamide) (BAA), tetramethoxysilane (TMOS), ammonium peroxydisulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were purchased from Aldrich and used without further purification.

2.2. Synthesis of poly(NIPA)-based organic–inorganic hybrid gels

Composite hydrogels “S-PN” were prepared in aqueous solution by network radical copolymerization of NIPA and BAA (crosslinker) in the presence of a simultaneously proceeding hydrolysis condensation of TMOS. The radical polymerization was initiated and accelerated by APS and TEMED (the latter reactant also causes a basic pH for the TMOS reaction). Analogous silica-free poly(NIPA) hydrogels were also synthesized and designated as “PN”. The composition (amounts of reactants and solvent) of the hydrogels prepared is given in Table 1. The following parameters were

Table 1
Composition of organic–inorganic and reference poly(NIPA)-based gels during synthesis

Component	“S-PN” gels	“PN” gels
	Mass (mg)	Mass (mg)
<i>N</i> -Isopropylacrylamide (NIPA)	300	300
Methylene- <i>N,N'</i> -bis(acrylamide) (BAA)	6.3	6.3
Tetramethoxysilane (TMOS)	104	—
Water	2677	2781
<i>N,N,N',N'</i> -Tetramethylethylenediamine (TEMED)	8.9	8.9
Ammonium peroxodisulfate (APS), 1% aqueous solution	542.6	542.6

S-PN – silica-containing gels.

PN – reference poly(NIPA) gels.

kept constant: the concentration of vinyl groups at 0.75 mol/L, the amount of crosslinking structure units in poly(NIPA) chains at 3 mol% and the ratio of the inorganic building blocks to the organic ones at 0.25 ($=n(\text{Si})/n(\text{vinyl groups})$). All the hydrogels' syntheses were carried out in two temperature stages, first at +15 °C and thereafter at –18 °C (“freezing stage”, pore generation). The freezing stage was started either before or after the gelation of the reaction mixture (suffix “-before” or “-after” in the samples' names). The reaction times in both stages for the samples prepared are given in Table 2.

The starting compounds were mixed in glass tubes (*ca.* 10 mm diameter) at the temperature of the first synthesis stage, +15 °C, and purged with nitrogen. Thereafter the reaction was left to proceed at this temperature till the beginning of the second stage, when it was put into a –18 °C cold bath. After the end of the second stage, the frozen samples were taken out of the tubes and put for 4 days into water, at a temperature of 25 °C. The water was changed every day in order to extract unreacted monomers and the samples were swollen to equilibrium. Thereafter they were cut into cylinders with $\varnothing = 1$ cm, $h = 0.6$ cm.

The descriptions of the hydrogels prepared are shown in Table 2.

2.3. ^{29}Si NMR spectroscopy

^{29}Si single pulse MAS NMR spectra were measured with a Bruker (Karlsruhe, Germany, 2003) AVANCE 500 NMR spectrometer at the frequency of 99.32 MHz. The MAS frequency was 7 kHz.

Table 2
Synthesis procedures (temperature steps) and gel fractions of the hydrogels

Sample	Duration of stage 1 (at +15 °C) [min]	Duration of stage 2 (at –18 °C) [h]	w_g	$w(\text{Si})$	w_g of organic phase
PN-before	3 ($=0.5 \times t_{\text{gel}}$)	24	0.72	0	0.72
S-PN-before	3	24	0.87	0.41	0.91
PN-after	7 ($=1.2 \times t_{\text{gel}}$)	24	1.00	0	1.00
S-PN-after	7	24	0.94	0.62	0.96

$w(\text{Si})$ is the “incorporation fraction” of silica in the gel.

Under the preparation conditions of the hydrogels, the hydrolysis of methoxy-silane groups of the tetramethoxysilane monomer ($\text{Si}(\text{OCH}_3)_4$, TMOS) to Si–OH groups was complete, as confirmed by ^{13}C NMR spectroscopy. The condensation conversion of TMOS was defined as $\alpha = (\sum iQ_i)/4$, where Q_i indicates the fraction of Si atoms with i siloxane bonds –O–Si attached to them. The number of hydroxyl groups per Si atom is then $N(\text{OH}) = 4(1 - \alpha)$. If the silica product is defined for practical reasons as $\text{SiO}_2 \cdot n(\text{H}_2\text{O})$, then the number of chemically bound water molecules (in the form of hydroxyl groups Si–OH) per Si atom is $n(\text{H}_2\text{O}) = 2(1 - \alpha)$ (“chemical hydration degree of silica”). The assignment of the NMR bands is as follows: Q_2 from –91 to –93 ppm, Q_3 from –100 to –102 ppm, Q_4 from –111 to –113 ppm.

2.4. Electron microscopy (SEM)

The morphology of the prepared hydrogels was checked with a low-vacuum scanning electron microscope Aquasem (Tescan, Brno, Czech Republic). The pressure in the Aquasem microscope chamber was in the range 500–1100 Pa, which made it possible to observe samples containing frozen water. The samples were prepared by cutting the hydrogel in water with a razor blade: from the middle of the hydrogel a thin cross-section (*ca.* 0.5 mm thick) was cut off, removed from water and instantly frozen in liquid nitrogen. The frozen sample was placed on the cooled sample stage (–20 °C) of the Aquasem microscope, where it was “glued” with a tiny drop of water (the water freezes immediately after touching the cooled sample stage). The samples were observed using two backscattered-electron detectors in combination with an ionization detector.

2.5. Small-angle X-ray scattering (SAXS)

Measurements were performed on an upgraded Kratky camera with a 60 μm entrance slit and a 42 cm sample-to-detector distance. Ni-filtered Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) was recorded with a linear position-sensitive detector. The experimental (smeared) SAXS curves are presented as a function of the magnitude of the scattering vector $q = (4\pi/\lambda)\sin \theta$ (2θ is the scattering angle).

2.6. Gel fraction and related experiments

The gels were extracted in water and then dried 1 day in air and thereafter under vacuum at 100 °C till mass constancy. The gel fraction w_g of samples was determined as $w_g = m_{\text{exd}}/m_0$, where m_{exd} is the mass of the extracted and dried sample and m_0 is the theoretical gel mass; m_0 was calculated from masses of the incorporated components taking into account the degree of chemical hydration of silica $n(\text{H}_2\text{O})$ (describing the amount of Si–OH groups) determined by ^{29}Si NMR.

The gel fraction of the organic phase alone and the “incorporation fraction” of the silica phase ($w(\text{Si})$) in the samples were determined as follows: the mass of dry extracted gel

m_{exd} was determined first, thereafter the silica content as mass of SiO_2 in the sample was determined (see below). The mass of chemically hydrated (as Si-OH) silica $\text{SiO}_2 \cdot n(\text{H}_2\text{O})$ was calculated using the chemical hydration degree $n(\text{H}_2\text{O})$ determined by ^{29}Si NMR. The mass of the organic phase $m(\text{poly}(\text{NIPA}))$ was then calculated as $m(\text{poly}(\text{NIPA})) = m_{\text{exd}} - m_{\text{(hydrated silica)}}$. The gel fraction of the poly(NIPA) network was then calculated from $m(\text{poly}(\text{NIPA}))$ and the masses of the monomers (NIPA, BAA) used in the synthesis. The incorporation fraction of silica in the sample, $w(\text{Si})$, was calculated from the chemical amount of TMOS used and from the amount of SiO_2 found in the sample.

The silica content in the form of anhydrous SiO_2 mass was determined for the prepared hydrogels by ash analysis. Each sample was put into a platinum pot together with the double of its mass of sulfuric acid and this mixture was slowly pyrolyzed in air. The remaining ash was heated to *ca.* 1000 °C for 15 min. The pyrolysis with sulfuric acid was repeated once more with the ash. The dry SiO_2 ash was then weighed, yielding the silica content as mass of SiO_2 .

2.7. Temperature dependence of degree of swelling Q

The swelling degree Q of the gels was defined as the ratio of the mass of the swollen gel (m_s) to the mass of the dry gel (m_d , determined in the same way as for gel fraction): $Q = (m_s/m_d)$. The temperature dependent Q was determined after the sample was immersed in a water bath at a given temperature for 24 h. Q was evaluated in the temperature range $T = 25\text{--}40$ °C with a temperature step of 2 °C. Cylindrical gel specimens with 10 mm diameter and 6 mm thickness were used (size of the gel swollen in equilibrium in water at 25 °C).

2.8. Deswelling (gel collapse) and reswelling 'kinetics'

The gels swollen in equilibrium at 25 °C were immersed in a water bath at 40 °C and the time dependent swelling degree was determined by recording the mass of the samples every 2 min. In some cases the swelling degree was determined in shorter intervals by measuring the changing sample diameter and by subsequent calculation of the swelling degree. In the case of the slow responding samples, the experiment was carried out for several days. After the gels deswelled to equilibrium at 40 °C, they were used for an analogous investigation of reswelling kinetics at 25 °C. Cylindrical gel specimens with 10 mm diameter and 6 mm thickness were used (size of the gel swollen in equilibrium in water at 25 °C).

2.9. Reversible fast thermal response

The hydrogel samples, previously swollen in water till equilibrium at 25 °C, were immersed in 40 °C water for 2 min and their new swelling degree was determined. Subsequently the samples were put into the 25 °C bath again, for the next 2 min. These alternating steps were repeated 8 times. After each swelling or deswelling, respectively, the samples were weighed and their Q was determined. Cylindrical gel

specimens with 10 mm diameter and 6 mm thickness were used (size of the gel swollen in equilibrium in water at 25 °C).

2.10. Shear modulus of swollen gels

Mechanical experiments with swollen gels at room temperature were carried out in uniaxial compression [35]. The samples were compressed to a ratio λ ($\lambda = l/l_0$, where l and l_0 , respectively, are compressed and initial heights of the sample) and the force f was measured after a 30 s relaxation. Usually 10 values of λ and f were determined ($0.8 < \lambda < 1$). The shear modulus G was calculated using the following equation:

$$G = f / [S_0(\lambda - \lambda^{-2})],$$

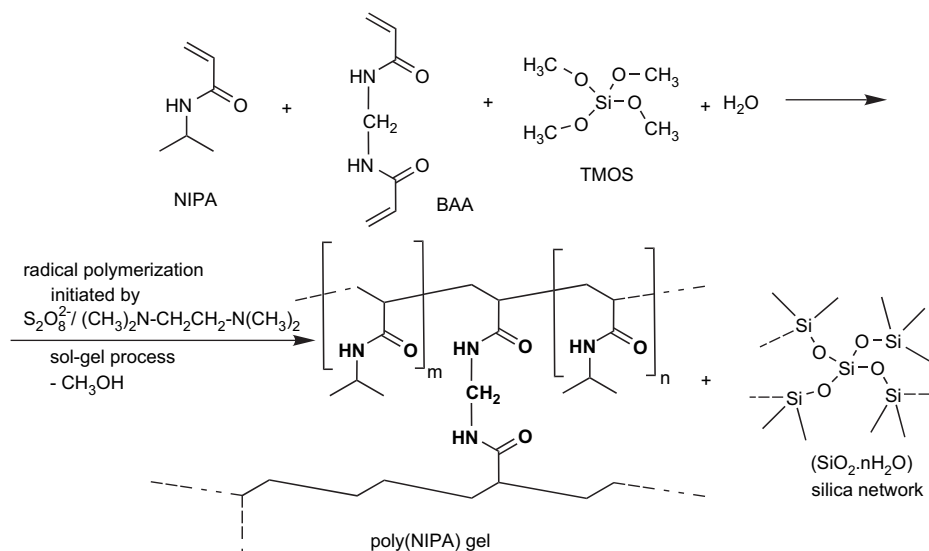
where S_0 is the initial cross-section of the sample before measurement. The shear modulus was measured using cylindrical gel specimens with 10 mm diameter and 6 mm thickness (size of the gel swollen in equilibrium in water at 25 °C).

3. Results

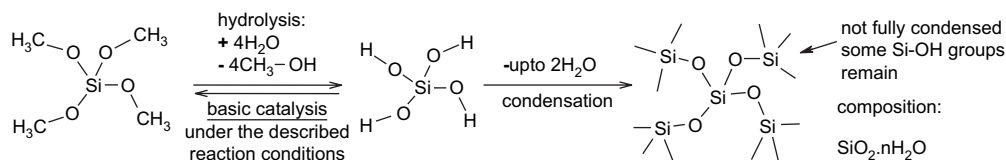
3.1. Gels' preparation

The organic–inorganic hydrogels (S-PN-before and S-PN-after) were prepared by simultaneous crosslinking radical copolymerization of the NIPA/BAA monomers and hydrolytic polycondensation of TMOS (see Scheme 1 and also [33]). The formation of silica domains in the poly(NIPA) network from TMOS and water is a sol–gel process, and is depicted in Scheme 2. Hydrogels without silica structures (PN-before and PN-after) were prepared in order to determine the “silica effect” in the products. As already mentioned, the porous structure was generated in the hydrogels *via* crystallization (“freezing”) of a part of the solvent, either before (PN-before and S-PN-before) or after the gel point (PN-after and S-PN-after) of the reaction mixture. The description of the products is given in Tables 1–3.

The standard procedures of hydrogel synthesis – A and B – used in this work are depicted in Scheme 3. In addition, the scheme describes other related procedures C–F including those not yielding a gel. During the “mixing stage” (Scheme 3), the sol–gel process leading from TMOS to silica already starts. The fast radical copolymerization of NIPA and BAA is initiated 10 min later (“Stage 1” in Scheme 3). The build-up of both organic and silica networks continues during the “freezing stage” (“Stage 2” in Scheme 3), though with a reduced speed. The concentration of reactants in the liquid or gel phase, respectively, increases because a large part of the solvent leaves the reaction mixture in the form of pure solvent crystals. The decrease in reaction temperature counters the concentration effect. In the cases investigated, the effects lead to a significant decrease in the reaction rate. Thawing the solvent crystals during the “workup stage” (see Scheme 3), after warming the reaction mixture to room temperature, results in the formation of pores filled with liquid water in the places previously occupied by the hard and solid solvent



Scheme 1. Formation of poly(NIPA)-based O–I networks with silica structures dispersed in the organic matrix.



Scheme 2. Sol–gel process of tetramethoxysilane in detail.

crystals. These water filled pores are surrounded by the gel phase.

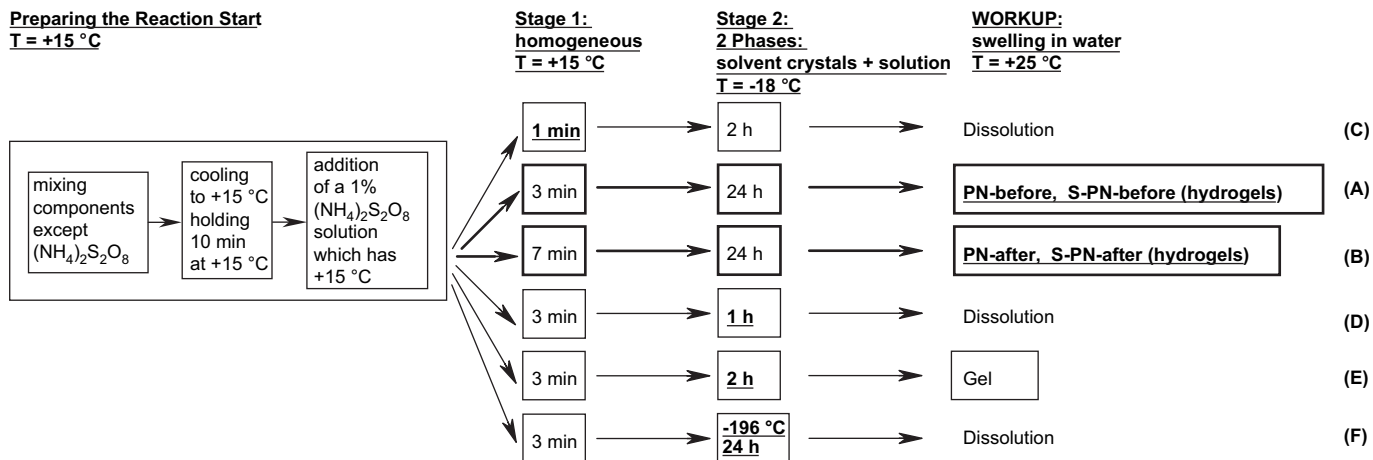
The O–I system gels in 6 min under the experimental conditions applied in “Stage 1” ($T = 15^\circ C$). The slow but real progress of network formation during the “frozen stage” (“Stage 2” in Scheme 3) of the syntheses presented is proven and can be illustrated by comparing the results of the procedures A and E vs. F and D depicted in Scheme 3. (Concerning reactions in “frozen” solutions see also [36].) If a sample is prepared like PN-before or S-PN-before, but “completely frozen” during “Stage 2” ($-196^\circ C$ instead of $-18^\circ C$; see procedure F in Scheme 3), all chemical reactions are standing still during this stage. During the workup, this sample dissolves, because no gelation took place. Also if the second synthesis stage is shortened to 1 h (at $-18^\circ C$) (see procedure D in Scheme 3), no gel is formed because the reaction time in “Stage 2” is not sufficient for gelation. At least 2 h of the reaction at $T = -18^\circ C$ are necessary for the gelation of the

prereacted system, *i.e.* conditions corresponding to the procedure E. Similarly, if the reaction progress in the “Stage 1” is too small, as in the case of procedure C compared to procedure E (see Scheme 3), the reaction time in both synthesis stages is no more sufficient to yield a gel.

The fastest responsive hydrogels were obtained by freezing the reaction mixture shortly before the gel point of the system (at $t = 0.5 \times t_{gel}$, *i.e.* 3 min; at $+15^\circ C$ for the system investigated). These products show a large swelling ratio at room temperature and exhibit very fast deswelling and reswelling (only the silica-containing specimens) kinetics. Only 6 s are needed for 72% deswelling as well as for 72% reswelling. This rapid response was attributed to the well-developed macroporous structure and interconnectivity of the pores (see results below). On the contrary, the hydrogels which were frozen only after gelation exhibit a much lower swelling below LCST and a much smaller thermoresponsivity (this was attributed to their closed-cell pore structure, see results further below).

Table 3
Characteristics of the hydrogels

Sample	Theoretical wt% of SiO_2 in dry gel	Measured wt% of SiO_2 in dry gel	Equilibrium swelling degree (Q) at $25^\circ C$	wt% of SiO_2 in swollen gel at $25^\circ C$	Equilibrium swelling degree (Q) at $40^\circ C$	wt% of SiO_2 in swollen gel at $40^\circ C$
PN-before	0	—	24.2	—	5.9	—
S-PN-before	11.7	5.6	20.6	0.27	7.7	0.73
PN-after	0	—	14.1	—	6.9	—
S-PN-after	11.7	7.9	11.4	0.69	5.8	1.36



Scheme 3. Variations of the synthesis procedure.

3.2. Gel fraction, silica content and condensation degree of silica

The gel fractions (w_g) of the samples, the “incorporation fraction” of silica and the gel fraction of the organic phase (poly(NIPA) crosslinked with BAA) are given in Table 2. It can be seen that all the gel fractions are significantly lower for the samples frozen before the gelation (PN-before, S-PN-before). The difference is especially pronounced for the incorporation fraction of silica in these gels (0.41 vs. 0.62 for S-PN-before and S-PN-after, respectively). The gel fraction of the organic phase follows the above described trend, but is typically high (above 0.90), with the only exception of the sample PN-before (only 0.72). The low fraction of silica in the gels means that a sizeable amount of the silica was not incorporated in the organic matrix and was extracted as colloid during the sample workup. The lower organic gel fractions in the products PN-before and S-PN-before imply a lower NIPA and BAA conversion and hence also a less efficient crosslinking, leading to products with longer elastic chains able to reach higher swelling degrees.

The polycondensation conversion α of the incorporated silica was determined by ^{29}Si NMR (unhydrolyzed $\text{CH}_3\text{—O—Si}$ groups were not found by ^{13}C NMR). In the samples investigated, the degree of silica polycondensation was always very similar and close to 0.90 (S-PN-before: 0.88, S-PN-after: 0.90). This conversion α did not change with longer storage (swollen at 25 °C) as well as under more drastic conditions like 1 day heating at 100 °C in vacuum. This finding is not surprising, as the silica particles were dispersed in an organic matrix and had limited possibility for further condensation and also because probably many of the Si—OH groups inside the particles might be sterically hindered for further condensation. Table 3 compares the theoretical silica content in the hydrogels prepared (calculated from monomers’ amounts) with the values found experimentally in dry gels. The values for gels swollen to equilibrium at 25 °C and at 40 °C are also calculated (often discussed states of the gels). It is noteworthy that the SiO_2 amount in the fast responsive gel S-PN-before

is 5.6 wt% in the dry gel and only 0.27 wt% in the gel swollen to equilibrium at 25 °C. This relatively small amount of silica is responsible for the difference in the behaviour of the gels PN-before and S-PN-before.

3.3. Temperature dependence of the swelling degree

The temperature dependence of the swelling degree Q for the studied hydrogels is shown in Fig. 1. The hydrogels which were frozen before gelation (S-PN-before, PN-before, Fig. 1) exhibit a significantly larger Q at 25 °C than the hydrogels frozen after gelation (S-PN-after, PN-after, Fig. 1). This can be explained by a lower crosslinking density (due to lower conversion) in PN-before and S-PN-before networks. The “before” gels display not only a lower fraction of gel (*cf.* Table 2) but also a significantly lower modulus (see further below): the swelling degree of “before” gels is *ca.* 2 times higher than that of “after” gels, while their modulus is lower by one or two orders of magnitude, for silica-containing and silica-free

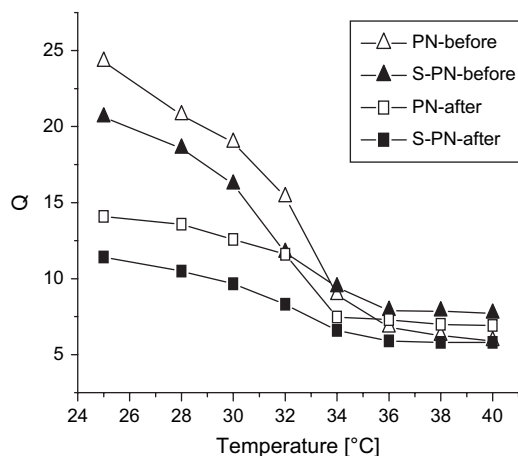


Fig. 1. Temperature dependence of swelling degree (Q) for O-I poly(NIPA)-based gels, which were frozen during their preparation before and after the gel point of the reaction mixture. (The samples were (S-PN) or were not (PN) modified by introduction of silica.)

samples, respectively. Another interesting finding is that the silica-reinforced gels S-PN show below LCST a somewhat lower swelling degree than the silica-free gels PN. This is in agreement with our previous results [33] showing that incorporation of silica domains results in a mild decrease in swelling. The residual swelling degree after deswelling at 40 °C till equilibrium is nearly the same for all the samples prepared ($Q = 6-8$). This residual swelling is probably due to water, which fills the shrunken but still present pores in the gels. This explanation is in agreement with the authors' finding that pore-free bulk gels otherwise similar to the presented ones (with 5 mol% crosslinks from BAA: see [33]) exhibit a much lower residual swelling degree (typically $Q = 2-3$) in equilibrium, than the porous ones (the gels presented or previously prepared heterogeneous gels synthesized above LCST [33]). The residual swelling in simple bulk hydrogels ($Q = 2-3$) can be assigned to their remaining hydrophilicity above LCST. Due to this swelling the shrunken gels are in a rubbery state, while the fully anhydrous poly(NIPA) is glassy ($T_g(\text{poly(NIPA)}) = \text{ca. } 144 \text{ }^\circ\text{C}$) at our experiments' conditions ($T = 25-40 \text{ }^\circ\text{C}$).

3.4. Deswelling (gel collapse) ‘kinetics’

The hydrogels S-PN-before and PN-before show a very fast deswelling at 40 °C (see Fig. 2a) compared to the samples frozen after gelation (Fig. 2b). The silica-containing gel S-PN-before shows the fastest deswelling among the samples prepared, releasing most of the ‘mobile’ water (72%) in 6 s and practically all (96.6%) in 1 min (inlay in Fig. 2a). The ‘final’ swelling degree after 2 min ($Q = 8.3$), 18 min ($Q = 8$) and 1 week ($Q = 7.7$) at 40 °C is practically the same. The silica-free sample PN-before is slower but still relatively fast in deswelling: it releases 69% of ‘mobile’ water in 2 min and 86% in 4 min.

In contrast to the samples S-PN-before and PN-before, the hydrogels S-PN-after and PN-after show an extremely slow deswelling (see Fig. 2b). The fastest progress can be seen in the first 5 h of the deswelling process (release of 11.8% or 11.7% of ‘mobile’ water for S-PN-after and PN-after, respectively). After nearly 1 week (150 h) 52% and 47% of mobile water was released from S-PN-after and PN-after, respectively, and even after 11 days, the water release was not complete (release of 65% and 62% for S-PN-after and PN-after, respectively). In spite of the (imperfect, closed-cell) pore structure, there seems to be a ‘skin effect’, which is less pronounced if the sample is warmed to 40 °C gradually (see Fig. 1: lower Q are reached faster). The slow kinetics suggests a predominantly diffusion-controlled deswelling in PN-after and S-PN-after.

3.5. Reswelling ‘kinetics’

The hydrogels S-PN-before and PN-before display a much faster reswelling (Fig. 3a) in comparison to the samples frozen after gelation (Fig. 3b). Especially, the silica-reinforced gel S-PN-before shows the fastest reswelling kinetics. The sample

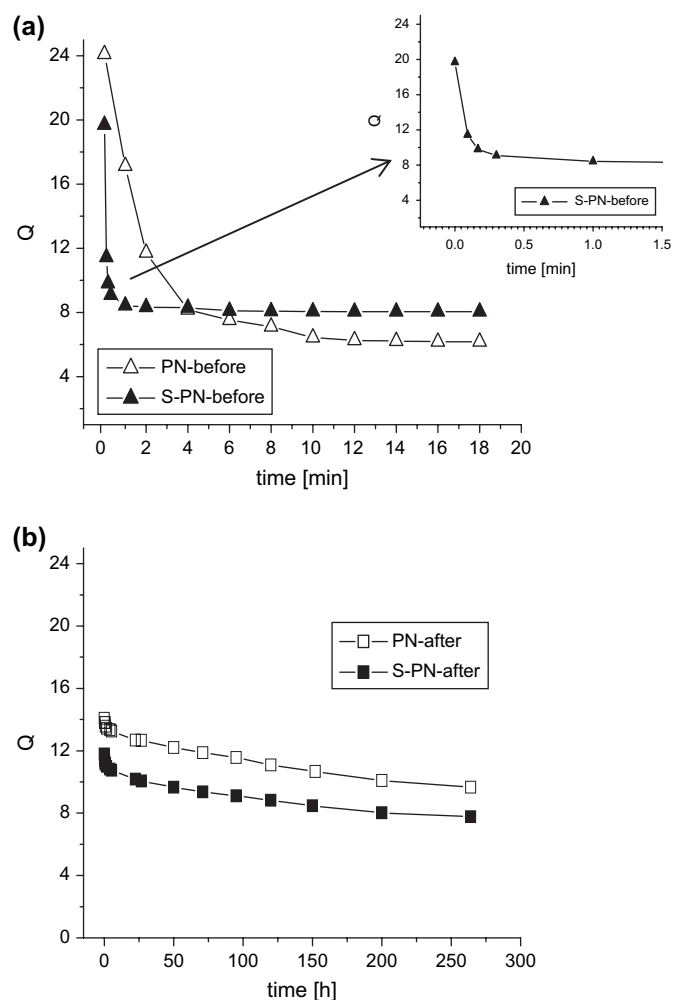


Fig. 2. Deswelling kinetics of O-I poly(NIPA)-based gels, which were frozen during their preparation before (a) (inlay: detail of PN-before) and after (b) the gel point of the reaction mixture. The samples were (S-PN) or were not (PN) modified by introduction of silica. Deswelling temperature = 40 °C.

S-PN-before reswells unusually fast at 25 °C, taking up 72% of mobile water in 6 s and practically all (94%) in 14 s (inlay in Fig. 3a). The silica-free sample PN-before exhibits a considerably slower reswelling: 9% water uptake in 2 min, 31% in 14 min and practically all (94%) in 1.5 h (92 min, not shown in the graph).

The samples S-PN-after and PN-after exhibit a much slower reswelling (see Fig. 3b), the fastest progress being observed in the first 4 h (uptake of 66% or 76% of water for S-PN-after and PN-after, respectively). Interestingly, the reswelling rate of the samples S-PN-after and PN-after is *ca.* 10 times faster than their deswelling rate. This is probably due to the formation of a swollen and more water permeable surface layer, leading to a sort of ‘reversed skin effect’.

The reswelling of the fast responsive sample S-PN-before was also studied for the dried gel as starting state (drying: 1 day in air and thereafter under vacuum at 100 °C till mass constancy). The reswelling of dried S-PN-before (not depicted) was slower than that of deswollen S-PN-before, but still very fast (water uptake: 2 min: 49%, 4 min: 65%, 6 min: 92% of total water uptake).

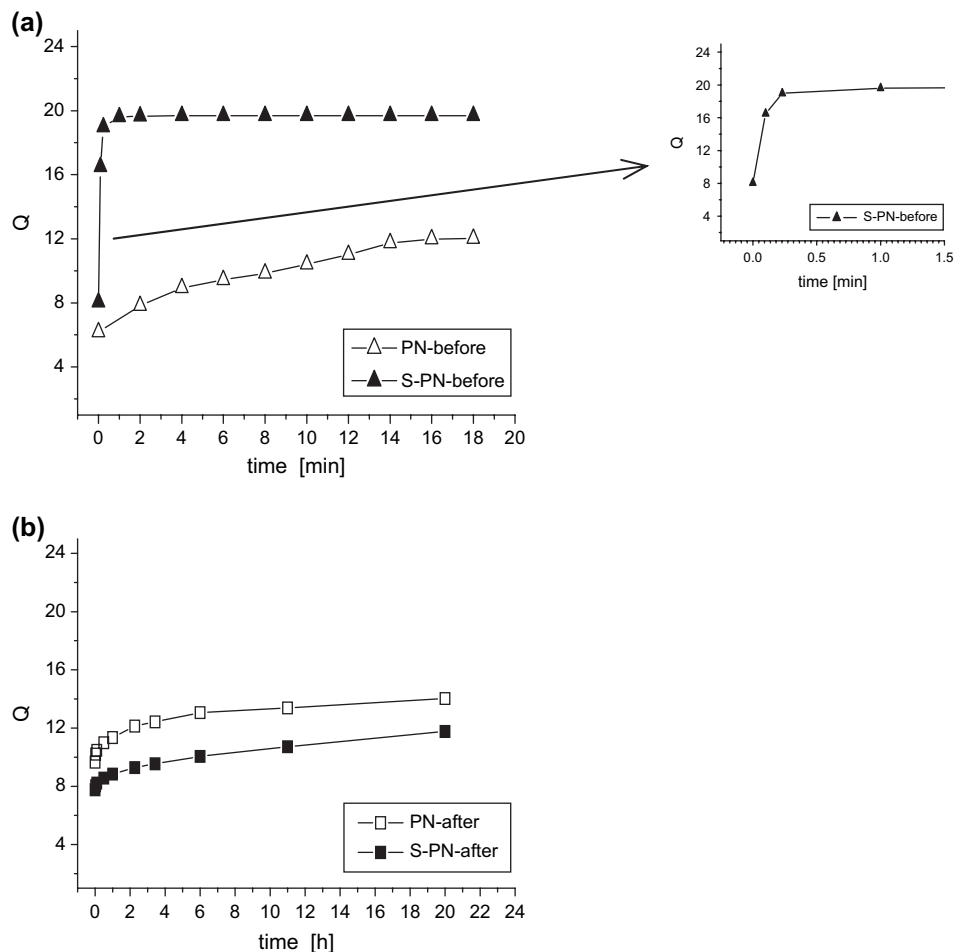


Fig. 3. Reswelling kinetics of O–I poly(NIPA)-based gels, which were frozen during their preparation before (a) (inlay: detail of S-PN-before) and after (b) the gel point of the reaction mixture. The samples were (S-PN) or were not (PN) modified by introduction of silica. Reswelling temperature = 25 °C.

3.6. Reversible thermal response

The reversible volume change of the “fast thermoresponsive” samples (PN-before and S-PN-before) and of the other hydrogels (PN-after and S-PN-after) is shown in Fig. 4. The fastest responsive gel, S-PN-before, shows highly regular oscillations with a high amplitude ($Q_{\max} = 20$, $Q_{\min} = 6.7$) as a response to temperature oscillations. The hydrogel PN-before displays decreasing oscillations due to its slow reswelling.

The samples S-PN-after and PN-after (frozen after their gel point) show only very small but visible oscillations near the maximum swelling degree under the conditions of the experiment (temperature oscillating between 40 °C and 25 °C, being held constant for only 2 min at each value). This finding is a result of low deswelling and swelling rates of these products.

3.7. Gel morphology

The pore structure of the hydrogels prepared and the size of the silica domains in them were studied by means of electron microscopy (SEM) and SAXS. The SEM and SAXS results comparing the gels S-PN-before and S-PN-after are shown in Figs. 5 and 6, respectively.

The comparison of the SEM pictures (Fig. 5) shows the different porous structures of both gels, which were created by freezing the aqueous reaction mixtures during the samples’ preparation (with forming ice crystals serving as pore templates). The sample S-PN-before (Fig. 5a), which was frozen before its gelation, displays large pores (typically *ca.* 25 μm). The pores form an interconnecting “open-cell structure”. This system of channels makes possible a fast convective water transport, inwards as well as outwards, in such gels. The sample S-PN-after in Fig. 5b shows few isolated very large pores (50 μm and more) as well as domains with mainly small pores (2–10 μm , exceptionally up to 20 μm). These pores possess a closed-cell structure, not allowing a fast convective transport of water. There are mainly “bubbles” instead of “channels”.

The SAXS investigations (see Fig. 6) suggest the size of heterogeneities, corresponding to silica domains, to be 120 Å in S-PN-before and a larger size, approximately 150 Å (according to a rough estimate by Guinier analysis) in S-PN-after. The sample S-PN-after, which has a higher silica incorporation fraction, also possesses the larger silica domains. In view of the particle size, the silica phase could be described as “nano-domains” or “nano-gel particles”.

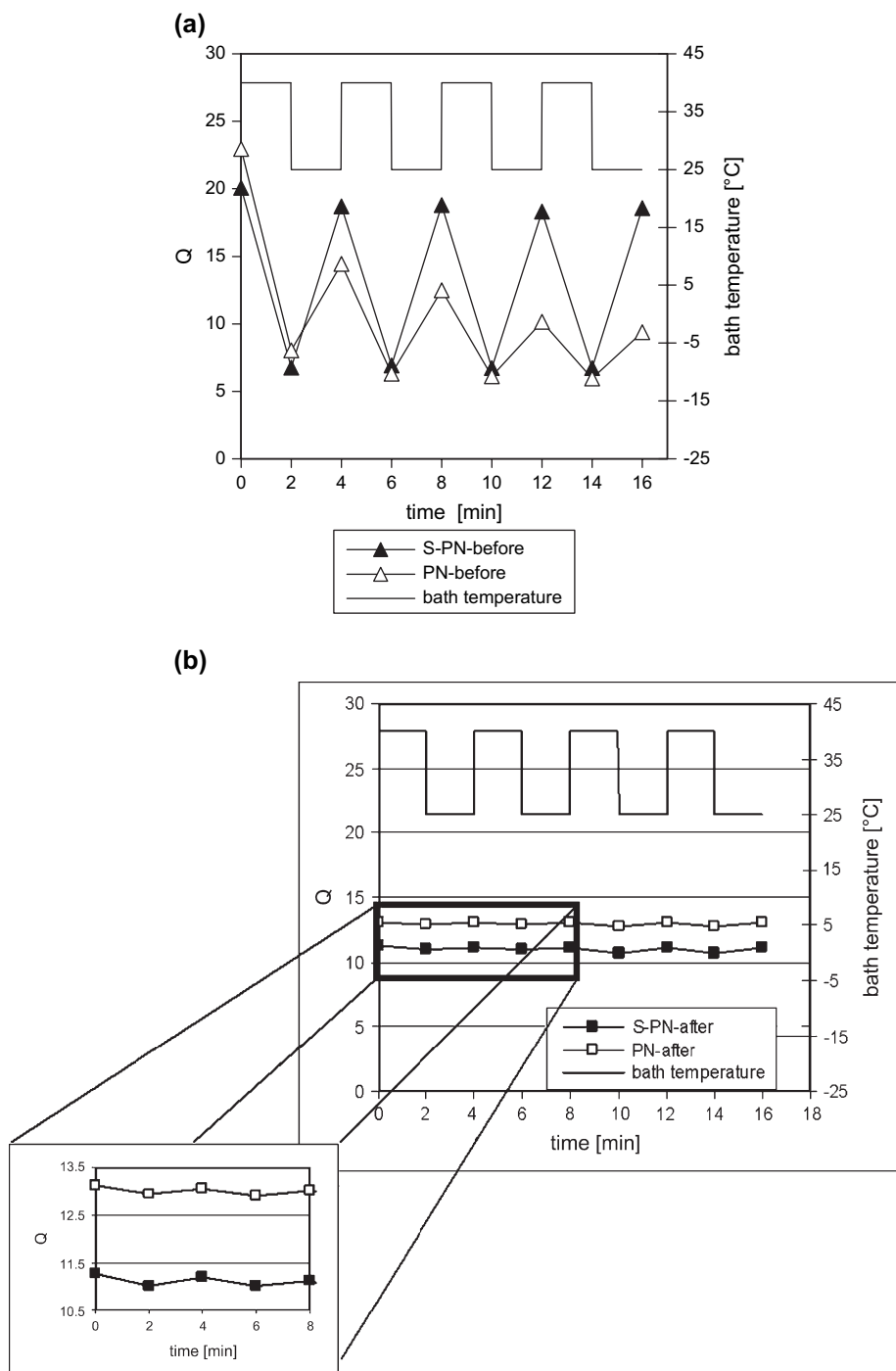


Fig. 4. Oscillation shrinking–swelling kinetics as a thermal response of O–I poly(NIPA)-based gels, which were frozen during their preparation before (a) and after (b) the gel point of the reaction mixture. The samples were (S-PN) or were not (PN) modified by introduction of silica. The temperature of the bath, in which the samples were immersed, is shown at the top of the graphs.

3.8. The mechanical properties

The gels S-PN-before and PN-before show a much higher maximum swelling degree and hence much lower shear moduli (G) at 25 °C than the gels S-PN-after and PN-after (see Fig. 7). The modulus of PN-before is *ca.* 100 times smaller than the modulus of PN-after (200 Pa vs. 20 000 Pa, respectively). The incorporation of silica improves the mechanical properties, especially in the case of the soft gels.

Introducing silica (0.27% SiO₂ in the swollen gel) into the hydrogel PN-before leads to the O–I gel S-PN-before with a 10 times higher modulus at a swelling degree of *ca.* 21 (only slightly smaller swelling than PN-before ($Q = ca.$ 24)). In the cases of the stiffer hydrogels PN-after and S-PN-after, the reinforcing effect of silica is smaller (G increases 1.4 times). This latter effect can be fully explained by a lower swelling degree of S-PN-after (PN-after: $Q = 14$, S-PN-after: $Q = 11$).

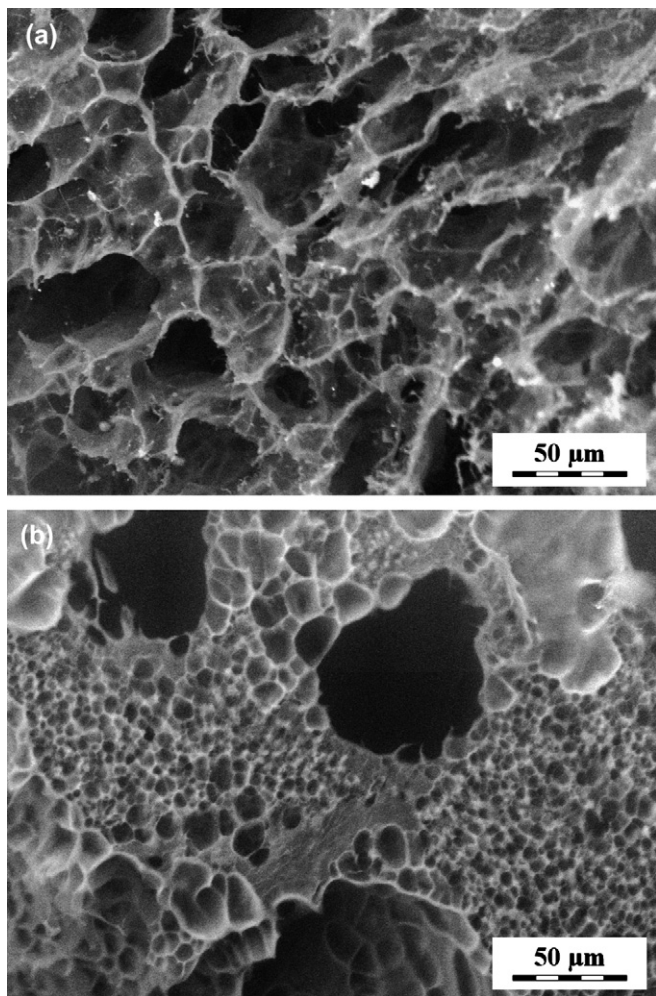


Fig. 5. AquaSEM pictures of the O–I poly(NIPA)-based gels S-PN-before (a) and S-PN-after (b).

4. Discussion

The above presented results have shown the importance of the exact preparation procedure of the hydrogels. Highly thermoresponsive hydrogels require the presence of an inter-connecting and stable internal channel system, which would enable fast convective water transport inwards or outwards. Bulk hydrogels or porous ones, with a closed-cell pore structure, exchange water with their environment only through diffusion, which is a slow process. The presented morphology results (SEM and SAXS) gave an insight into the internal structure of the different hydrogels prepared. Especially the differences in the pore structure were obvious.

The very strong dependence of the thermoresponsivity of the poly(NIPA) gels on the preparation “details” can be explained by considering the pore formation process in a detailed way. The solvent crystals (pore templates) are formed either in a homogeneous solution of NIPA monomer and of branched but soluble poly(NIPA) (pre-gel state) or in a cured – though incompletely – swollen network (early post-gel state), which are strongly different conditions.

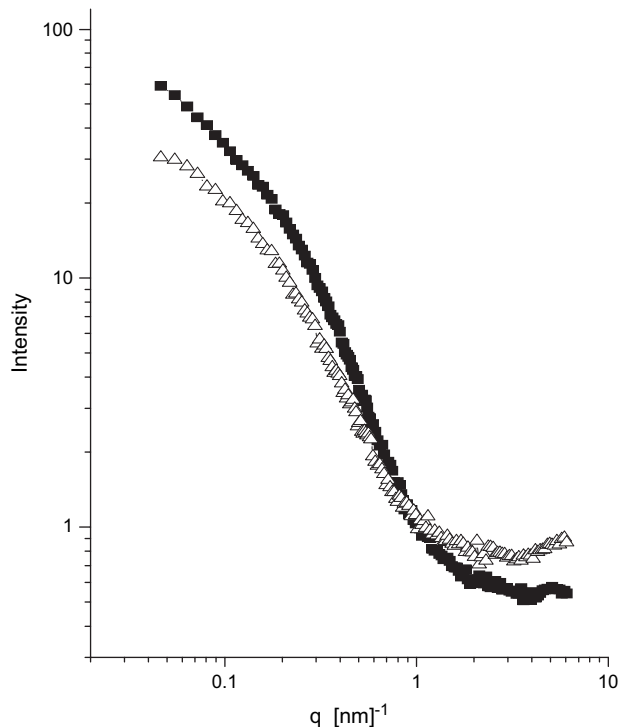


Fig. 6. SAXS profiles of S-PN-after (■) and S-PN-before (△).

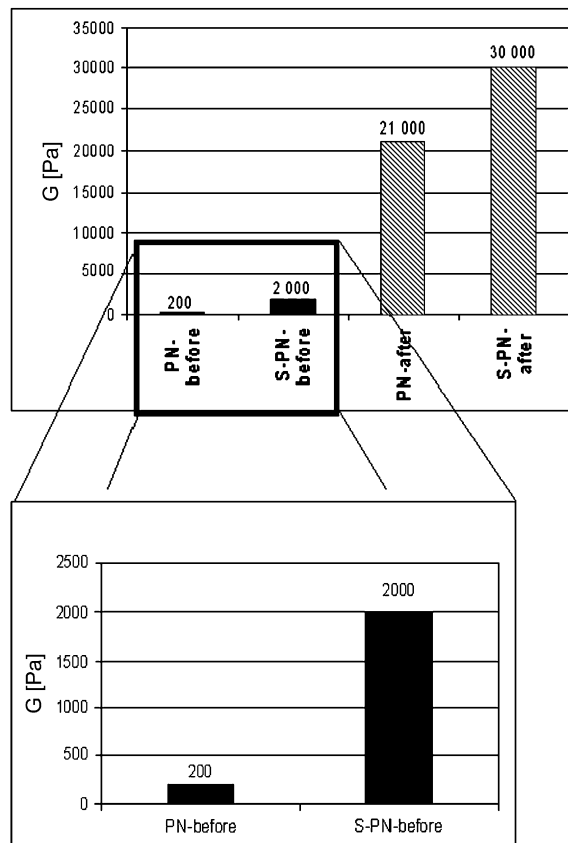


Fig. 7. Shear moduli of the O–I poly(NIPA)-based gels in swollen equilibrium state at 25 °C.

If freezing occurs in the pre-gel state, the crystal growth is not hindered by any network structures, the remaining concentrated reaction mixture is a homogeneous liquid which recedes without significant resistance before the growing crystals, and those can grow freely. The continuous needle-like ice phase interpenetrates the pre-gel system, and is preserved and fixed in the network which is formed in the later stage. After the polymerization at the freezing temperature, the ice crystals thaw at room temperature, leaving interconnecting pores within the elastic poly(NIPA) gel. The channel-like pores make possible fast swelling and deswelling by water convection. The silica particles in the hybrid gels stabilize thoroughly the pore system.

In the case of crystal growth in the early post-gel state (here at $t = 1.2 \times t_{\text{gel}}$), the reaction mixture, from which the ice crystals have to separate, is no more a liquid but a gel matrix. The network structures hinder and thus significantly affect the solvent crystals' growth. The formation of continuous interconnecting ice regions is less probable, and more likely, ice domains dispersed within the organic network are formed. As a result, a predominantly closed-cell pore structure finally appears. Water transport by slow diffusion through the pore walls dominates instead of convection and the deswelling/swelling kinetics is hence slow. One can expect that the final pore size in the gel is proportional to the mesh size of the network, which gradually decreases during polymerization as the crosslinking density of the network increases. In that case the gel porosity could be controlled by mesh size at a moment of the crystal growth, *i.e.* by the time of freezing the reaction mixture during polymerization.

Our gels PN-after and S-PN-after show similar properties like some of the poly(NIPA) hydrogels prepared by Kato and Takahashi [26] by conventional homogeneous radical polymerization of NIPA/BAA in water, followed by freeze drying of the fully cured swollen hydrogels. Similarly like in our PN-after and S-PN-after gels, Kato and Takahashi generated porosity by water freezing in the post-gel state, but at a later moment, after the completion of the curing. Another difference was the sublimation of ice during the freeze drying by Kato and Takahashi, which probably increases the interconnectivity of the reported predominantly closed-cell pore structure by the formation of cracks or holes in the pore walls. Kato and Takahashi prepared their gels at various original swelling degrees Q and found that in gels with $Q < 10$, the pore generation by freeze drying was insufficient and that the swelling/deswelling kinetics of such products was slow, approaching the rates in conventional bulk gels. Obviously, the ice domains in such gels were too small and their walls too thick for breaking or piercing by the sublimating water vapor, thus making impossible the additional increase in interconnectivity. In pores with small Q , a pore structure was not observed by Kato and Takahashi. Our gels PN-after and S-PN-after, which were prepared near $Q = 10$ resemble the “slow-responsive” gels of Kato and Takahashi and still display a marked, predominantly closed-cell pore structure as shown in Fig. 5b. As no freeze drying was carried out on our PN-after and S-PN-after gels, no additional interconnectivity was generated.

This comparison suggests the importance of the water sublimation (besides its crystallization) in the freeze drying process as used by Kato and Takahashi to prepare their fast responsive gels.

5. Conclusions

Organic–inorganic poly(NIPA)-based hydrogels with a very fast response to temperature change were prepared. Especially interesting is their very fast reswelling rate. The rates of deswelling (gel collapse) as well as of reswelling are practically the same: *ca.* 6 s are needed for the completion of both processes.

Crucial for the fast thermoresponsive deswelling/reswelling behaviour of the gels was the internal system of pores and channels. This pore system was generated by crystallization of a large part of solvent (here water), in which the samples were being prepared, a method already reported in the literature. In this work we found that for the final properties of the product, the moment at which the growth of solvent crystals starts is crucial. For the system investigated, it was ideal to start the solvent crystallization before the gelation point of the reaction mixture, namely at $t = 0.5 \times t_{\text{gel}}$, so that the polymer is still liquid and not seriously hindering the crystal growth.

A very important finding is the stabilization of pores and channels by the silica phase. This effect is very pronounced in the case of the fast responsive gels S-PN-before and PN-before, which have an efficient system of channels, enabling a fast intake or expelling of water *via* convection. The silica-containing hydrogel S-PN-before shows a much faster temperature response than the otherwise same, but silica-free sample PN-before (20 times slower deswelling, 60 times slower reswelling). The incorporation of the silica phase into the fast responsive hydrogels prepared also leads to an improvement of their mechanical properties, which is especially strong in the case of the fast responsive (and hence most interesting) materials S-PN-before and PN-before. The maximum swelling degree decreases only slightly due to silica incorporation: S-PN-before: $Q_{\text{max}} = 19$, PN-before: $Q_{\text{max}} = 23$.

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