

Thermosensitive PNIPA-Based Organic–Inorganic Hydrogels

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ABSTRACT: Thermosensitive organic–inorganic (O–I) hydrogels have been synthesized by modification of poly-*(N*-isopropylacrylamide) (PNIPA) gels with silica from tetramethoxysilane (TMOS) or with [3-(methacryloyloxy)propyl]trimethoxysilane (MPTMOS). Inorganic silica and silsesquioxane domains were formed *in situ* by sol-gel process within the organic matrix. Two methods of PNIPA-based gel synthesis have been employed—polymerization under homogeneous and heterogeneous conditions. The hybrid hydrogels swollen in water exhibited swelling transition around 32 °C. Introduction of the inorganic phase into the PNIPA gels resulted in faster deswelling kinetics and better mechanical properties of the gels prepared under homogeneous conditions. Further acceleration of deswelling and swelling kinetics was achieved by applying heterogeneous conditions of synthesis above the lower critical solution temperature. [doi:10.1295/polymj.PJ2005112]

KEY WORDS Hydrogel / *N*-Isopropylacrylamide / Siloxane / Organic–Inorganic Network /

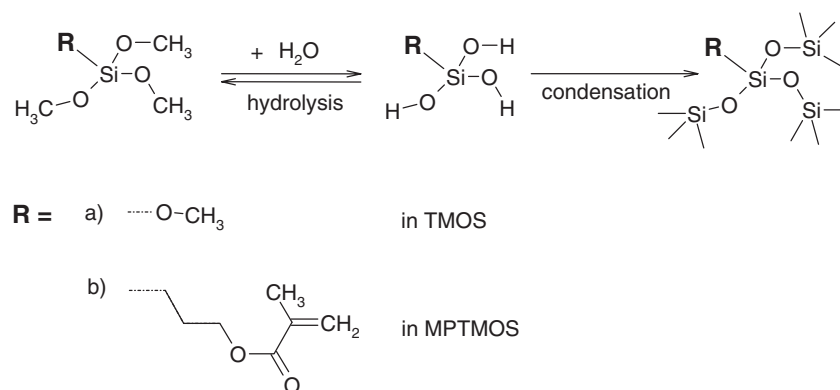
Hydrogels based on *N*-isopropylacrylamide (NIPA) have been the subject of investigation for many years.^{1–3} The main interest in these materials is due to their sensitivity to different environmental stimuli, like temperature^{3–5} or pH changes.⁶ It is well known that at increasing temperature, crosslinked PNIPA gels exhibit discontinuous volume transition similar to coil-globule transition of peptides. The critical temperature for this process is *ca.* 32 °C. Below this temperature a gel immersed in water is in the swollen state, keeping water inside thanks to strong hydrophilic interactions between water molecules and amide groups of the PNIPA network. Above this temperature phase separation takes place, hydrophobic interactions become predominant and water is expelled from the gel. The volume transition temperature can be shifted by copolymerization of NIPA with a monomer containing charged domains within its structure (acrylic acid, methacrylic acid, etc.). These features make PNIPA-based systems very attractive subject for investigation, with many potential applications, like in drug delivery systems,^{7,8} actuators,⁹ immobilization of enzymes,¹⁰ etc. In many applications thermosensitive aqueous microgels or core-shell structures are used.^{11,12}

Apart from undoubtful advantages of these materials, there are some problems that need to be overcome. Among them are: poor mechanical properties and slow swelling-deswelling kinetics. Much attention has been devoted to improvement of these gel characteristics. During deswelling of homogeneously synthesized PNIPA gels, a dense skin is formed on the gel surface. This is caused by the fact that the deswelling

begins first on the surface of the gel. This skin hinders water transport from interior and can significantly decrease the rate of water expelling. The phenomenon of phase separation under formation of gels with percolating pore structure, making possible a faster water diffusion, has been studied for a long time. Various techniques have been employed to eliminate this inconvenience, such as synthesis under heterogeneous conditions,¹³ synthesis of comb-grafted structures,¹⁴ utilization of the freeze-drying techniques,¹⁵ addition of inorganic compounds^{16–21} and synthesis of PNIPA/PNIPA interpenetrating networks.²² The two last techniques proved to be useful, also in improvement of mechanical properties. Although, big progress has been made in these fields, especially in terms of acceleration of the deswelling process, there are still problems in speeding up the reswelling of such systems.

The aim of this work was to synthesize heterogeneous organic–inorganic (O–I) PNIPA-based gels showing an accelerated swelling/deswelling process and better mechanical properties. We have prepared PNIPA gels modified with silica domains dispersed in the organic matrix or with silsesquioxane (SSQO) structures covalently bonded to the PNIPA network. We investigated the effect of the inorganic phase on the thermosensitive behaviour of the gel and its mechanical properties. The inorganic domains were formed *in situ* in the organic matrix by sol-gel process involving hydrolytic polycondensation of alkoxy-silane monomers-tetramethoxysilane (TMOS) and [3-(methacryloyloxy)propyl]trimethoxysilane (MPTMOS) (Scheme 1).

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Scheme 1. Sol-gel process of tetramethoxysilane (TMOS).

Syntheses of the O–I hydrogels were performed by polymerization under homogeneous or heterogeneous conditions. Homogeneous synthesis took place in methanol or in water at a temperature below the lower critical solution temperature (LCST). Heterogeneous synthesis conditions were achieved by carrying out the reaction in water at a temperature above LCST. This procedure led to microphase separation of PNIPA during polymerization, resulting in a highly porous product structure and favoring an acceleration of the swelling/deswelling processes.¹³

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPA), *N,N'*-methylenebisacrylamide (BAA), azobisisobutyronitrile (AIBN), ammonium peroxydisulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) from Aldrich were used for gel synthesis. Inorganic modifiers such as tetramethoxysilane (TMOS) and [3-(methacryloyloxy)propyl]trimethoxysilane (MPTMOS) as well as methanol and hydrochloric acid (aqueous, 35%) were also used as supplied by Aldrich.

Preparation of O–I Hydrogels

Organic–inorganic gels were prepared by simultaneous polymerization of NIPA and hydrolytic polycondensation of alkoxy silanes, TMOS and MPTMOS. The sol-gel process was catalyzed with TEMED or HCl. Crosslinking of the systems was performed either with the organic crosslinker *N,N'*-methylenebisacrylamide (BAA) or through the formed SSQO structures (from MPTMOS) serving as multifunctional network junctions. Two types of the O–I networks were synthesized as described in Schemes 2 and 3.

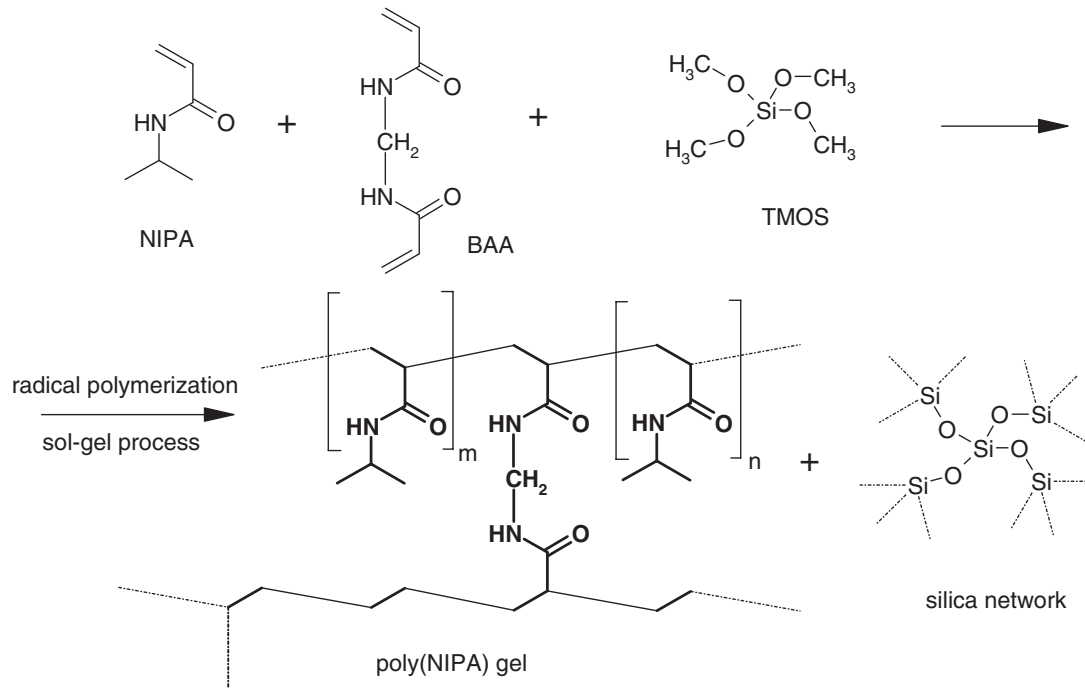
A. The network of PNIPA crosslinked with BAA containing dispersed silica domains (Scheme 2). The silica structures were built by the sol-gel process from tetramethoxysilane (TMOS).

B. The networks with SSQO domains covalently attached to the organic matrix (Scheme 3). The system was prepared by copolymerization of NIPA with MPTMOS and crosslinked by sol-gel polymerization of MPTMOS. The formed SSQO structures serve as junction domains of the network.

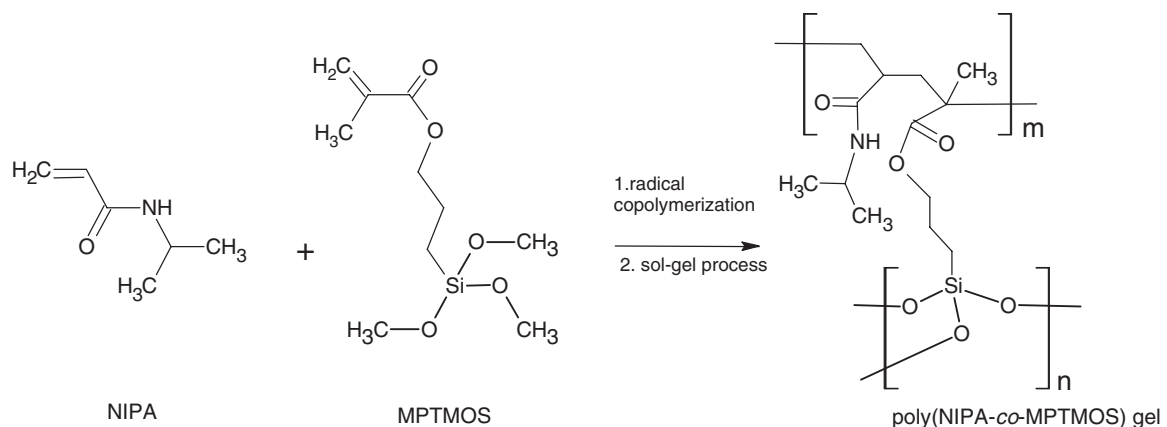
The polymerization took place under (a) homogeneous or (b) heterogeneous conditions. The synthesis was carried out in cylindrical tubes with 10 mm diameter in nitrogen atmosphere for 24 h. The reaction conditions and the hydrogels compositions are given in Table I and II. The solvent amounts needed for the syntheses were calculated so, that the concentration of double bonds had to be 1 mol/kg for the syntheses in water and 1.3 mol/kg for syntheses in methanol, resulting in a constant molar concentration ($c = 1$ mol/L) of double bonds in all syntheses.

(a) Under homogeneous conditions, the hydrogels were prepared in methanol or in water at a temperature below LCST. In methanol, the reaction was carried out at 60 °C using AIBN as an initiator. First, the monomers (NIPA, BAA or MPTMOS and eventually TMOS, see Table I) and the initiator (AIBN) were dissolved in methanol. Thereafter, water ($n(\text{H}_2\text{O})/n(\text{SiOR}) = 5$) and HCl ($n(\text{HCl})/n(\text{SiOR}) = 0.1$) were added to start and catalyze the hydrolysis and condensation of TMOS or MPTMOS. In water, the syntheses of the gels were carried out at 5 °C (a temperature well below LCST) in order to exclude the phase separation, using the initiating system–APS/TEMED. The monomers were dissolved in cold water (5 °C) (10–14 wt % solution), thereafter, TEMED and finally the initiator APS, were added. The silica free gels were fully transparent and the products modified with silica exhibited increasing opacity with increasing silica content.

(b) The gels prepared under heterogeneous conditions were synthesized in water at a temperature above LCST, using the initiating system–APS/TEMED. After mixing the reactants at room temperature (25 °C),



Scheme 2. Formation of PNIPA-based O–I networks with silica structures dispersed in the organic matrix.



Scheme 3. Formation of PNIPA-based O–I networks with SSQO domains covalently attached to the organic matrix.

the reaction vessel was transferred into a 40 °C water bath (a temperature above LCST), which resulted in microphase separation of forming PNIPA and the synthesis continued in a heterogeneous mixture. Thereafter, the sol phase was extracted by immersing the gels alternately in hot (40 °C) and cold (25 °C) water to induce shrinking and swelling of gels. Heterogeneously synthesized hydrogels were white and opaque even in the case of the silica free systems.

As a reference, the silica free polymer network consisting of PNIPA crosslinked with BAA (5% mol of double bonds from BAA) was prepared under homogeneous and heterogeneous conditions in water and methanol.

After preparation, the gels were kept in water for several days in order to extract the sol fraction and eventually methanol, when used as a solvent. Also

progress of the sol-gel process of TMOS or MPTMOS to equilibrium was allowed. Finally, the gels were cut to 5 mm thick (for shear moduli: 10 mm thick) pieces and stored in water at room temperature.

As an example, the preparation of “0.1 Sil_{hom}-H₂O” is described in detail:

In a tube, 400 mg NIPA (3.535 mmol), 14.3 mg BAA (0.093 mmol), 56 mg TMOS (0.372 mmol) and 12 mg TEMED (0.104 mmol) were dissolved in 2.49 mL of water and 738 mg of a 1% aqueous solution of APS (0.0324 mmol) were added. The reaction mixture was stirred at room temperature and purged with nitrogen. Thereafter, the reaction was left to proceed for 24 h at 25 °C. Subsequently, the sample was taken out of the tube and put for 5 d into water, at a temperature of 25 °C. The water was changed every day in order to extract unreacted monomers and to swell the sample

Table I. Composition and conditions of synthesis of O–I gels prepared under homogeneous conditions in water and methanol as solvents

Sample name	mol% of BAA double bonds	n(Si) / n(double bonds)	mol% of MPTMOS double bonds	Solvent	Initiator, Catalyst	Reaction temperature [°C]	Concentration mol(C=C) / l	Gelation time
0 Sil_hom_H ₂ O	5	-	-	water	n(APS) / n(C=C) 0.0087 n(TEMED) / n(C=C) 0.028	5	1	1 min
0 Sil_hom_MeOH	5	-	-	MeOH	n(AIBN) / n(C=C) 0.01	60	1	~ 4 h
0.1 Sil_hom_H ₂ O	5	0.1	-	water	n(APS) / n(C=C) 0.0087 n(TEMED) / n(C=C) 0.028	5	1	1 min
0.3 Sil_hom_H ₂ O	5	0.3						
0.5 Sil_hom_H ₂ O	5	0.5						
0.1 Sil_hom_MeOH	5	0.1	-	MeOH	n(AIBN) / n(C=C) 0.01 n(H ₂ O) / n(SiOR) 5 n(HCl) / n(SiOR) 0.1	60	1	~ 4 h
0.3 Sil_hom_MeOH	5	0.3						
0.5 Sil_hom_MeOH	5	0.5						
Mpt 5_hom_H ₂ O	-	-	5	water	n(APS) / n(C=C) 0.0087 n(TEMED) / n(C=C) 0.028	5	1	1 min
Mpt 10_hom_H ₂ O			10					
Mpt 15_hom_H ₂ O			15					
Mpt 5_hom_MeOH	-	-	5	MeOH	n(AIBN) / n(C=C) 0.01 n(H ₂ O) / n(SiOR) 5 n(HCl) / n(SiOR) 0.1	60	1	~ 4 h
Mpt 10_hom_MeOH			10					
Mpt 15_hom_MeOH			15					

to equilibrium. The sample was finally cut into cylinders with thickness of 5 or 10 mm. These gel pieces were stored under water at room temperature.

Swelling Behaviour of Gels

All the samples used for the swelling/deswelling experiments were standard sized cylindrical pieces displaying 5 mm thickness and 10 mm in diameter if swollen in equilibrium at 25 °C.

Swelling Degree

The swelling degree Q ($= W_S/W_d$) of gels was measured gravimetrically, at temperatures ranging from 25 to 40 °C. W_S and W_d are the weights of the swollen and dry sample. The gels were immersed in water for 24 h. Swelling ratio S_r was defined as $S_r = W_S/W_{40}$, where W_{40} is the weight of the deswollen sample equilibrated at 40 °C.

Deswelling and Reswelling Kinetics

The thermosensitive PNIPA-based gels deswell in water at temperatures above LCST. The rate of deswelling of the gels was measured by recording the weight of the sample every 2 min, after the swollen gel was immersed in 40 °C water. After 30 min, the shrunken gel was transferred to a bath at room temperature and the reswelling kinetics was obtained by similar measurements. The water retention or water uptake was plotted as the relative weight (RW) versus time. Relative weight was defined as $RW = W_t/W_{s0}$, where W_t is the weight of the sample at a given time and W_{s0} is the initial weight of the swollen sample.

Mechanical Properties-Shear Modulus

Mechanical experiments with swollen gels at room temperature were carried out in uniaxial compression.²³ The samples were compressed to a ratio λ

Table II. Composition and conditions of synthesis of O–I gels prepared in water under heterogeneous conditions

Sample name	mol% of BAA double bonds	n(Si) / n(double bonds)	mol% of MPTMOS double bonds	Solvent	Initiator/ catalyst	Reaction temperature [°C]	Concentration mol (C=C) / 1	Gelation time
0 Sil_het	5	-	-	water	n(APS) / n(C=C) 0.0087 n(TEMED) / n(C=C) 0.028	40	1	1 min
0.1 Sil_het	5	0.1	-	water	n(APS) / n(C=C) 0.0087 n(TEMED) / n(C=C) 0.028	40	1	1 min
0.3 Sil_het	5	0.3	-					
0.5 Sil_het	5	0.5	-					
Mpt 5_het	-	-	5	water	n(APS) / n(C=C) 0.0087 n(TEMED) / n(C=C) 0.028	40	1	1 min
Mpt 8_het	-	-	8					
Mpt 10_het	-	-	10					
Mpt 15_het	-	-	15					

($\lambda = l/l_0$, where l and l_0 , respectively, are compressed and initial heights of the sample) and 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 eq (1)

$$G = f/[S_0(\lambda^2 - \lambda^{-1})], \quad (1)$$

where S_0 is the initial cross-section of the sample before measurement. The samples measured were cylinders displaying 10 mm in height (l_0) and 10 mm in diameter if swollen to equilibrium at 25 °C.

Gel Fraction

The gel was extracted in water and then dried under vacuum at 100 °C. The gel fraction w_g was determined as $w_g = m_{\text{exd}}/m_0$, where m_{exd} is the mass of the extracted dry 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 hydrolysis and condensation of TMOS and MPTMOS, as determined by NMR.

NMR Spectroscopy:

^{29}Si and ^1H single pulse MAS NMR spectra were measured with a Bruker (Karlsruhe, Germany) DSX 200 NMR spectrometer at frequencies of 39.75 and 200.14 Hz for ^{29}Si and ^1H , respectively. Cross-polarization techniques were used to acquire most of the ^{29}Si MAS NMR spectra. The MAS frequency was 4 kHz.

Conversion during sol-gel polymerization of TMOS and MPTMOS was defined as $\alpha = (\sum iQ_i)/4$ for TMOS, and $\alpha = (\sum iT_i)/3$ for MPTMOS, where Q_i and T_i indicate the fraction of the units with i siloxane bonds $-\text{O}-\text{Si}-$ attached to the central silicon. The assignment of the NMR bands is as follows (see Figure 7): Q_2 from -91 to -93 ppm, Q_3 from -100 to -102 ppm, Q_4 from -111 to -113 ppm. T_0 from -41 to -43 ppm, T_1 from -49 to -50 ppm, T_2 from -58 to -59 ppm and T_3 from -65 to -67 ppm.

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 $\text{CuK}\alpha$ 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).

Scanning Electron Microscopy and X-ray Microanalysis

Both scanning electron microscopy (SEM) and X-ray microanalysis (EDS) were carried out with microscope Quanta 200 FEG (FEI, Czech Republic), which was equipped with cooling stage (FEI, Czech Republic) and energy-dispersive microanalysis (EDAX Genesis, USA).

Low Vacuum Scanning Electron Microscopy (LV-

SEM). The specimens (approx. $2 \times 2 \times 2$ mm) for microscopy observation were cut with a sharp blade from the samples submerged in water. Then the specimens were taken with tweezers and flash-frozen in the liquid nitrogen. The frozen specimens were fastened to a microscopic cooling stage, whose temperature was kept at -10°C , by means of small drop of water: if the water drop is put at the cooled stage, it freezes within 2 seconds, during which it is possible to fix the frozen specimen by means of freshly formed ice. In the next step, the upper layer of the ice-fixed specimen was cut off with a sharp blade that was cooled for a few seconds in the liquid nitrogen. At the end, the chamber with the ice-fixed specimen, still kept at -10°C , was closed and the sample was observed in LowVac mode, using chamber pressure 140 Pa and high voltage 30 kV.

High Vacuum Scanning electron microscopy (HV-SEM) and energy dispersive analysis of X-rays (EDS). The samples in water were transferred to diethylether, which was left to evaporate completely. The dried samples were broken at laboratory temperature and fixed on microscopic support with adhesive carbon tape. The specimens were sputtered with 4 nm platinum layer (vacuum sputter coater SCD 050, Balzers) and observed in high vacuum ($>10^{-3}$ Pa) at accelerating voltage 10 kV. Secondary micrographs, backscattered micrographs and EDS spectra were all collected from several locations on each studied sample. The experimental conditions for HV-SEM and EDS were identical except for the electron beam spot size, which had to be slightly adjusted to get optimal EDS signal.

RESULTS AND DISCUSSION

The O–I hydrogels with various amounts of the inorganic phase formed *in situ* were investigated. (A) The PNIPA-BAA gel was modified by addition of 9–33 mol % of TMOS to form silica domains dispersed in the polymer network. (B) The copolymer PNIPA-MPTMOS contained 5–15 mol % of MPTMOS monomer as a precursor of SSQO structures and network crosslinks domains. The former system PNIPA-BAA-TMOS was crosslinked by the radical polymerization with BAA, while the latter by the hydrolytic condensation of MPTMOS.

Conversion and Gel Fraction

The sol-gel analysis reveals a higher crosslinking efficiency of BAA. The gel fraction is higher in PNIPA-BAA-TMOS, $w_g = 0.94\text{--}0.96$, compared to PNIPA-MPTMOS network, $w_g = 0.81\text{--}0.94$. In the latter case w_g decreases with decreasing content of the MPTMOS crosslinker. The high gel fraction in

PNIPA-BAA-TMOS hybrid proves likely a presence of an interpenetrating O–I network. The gel fraction is significantly lower in the networks prepared heterogeneously. $w_g = 0.72\text{--}0.76$ in the case of the silica modified samples, and $0.58\text{--}0.64$ in the case of MPTMOS modified samples. For the swelling experiments only the extracted gels were used in order to prevent a sol extraction during the measurements, which would affect the results. The conversion of alkoxysilane groups in the gels is not complete, reaching the value $0.80\text{--}0.85$ for TMOS and ~ 0.70 in the case of MPTMOS. These values, however, do not change during the swelling experiments and the samples are stable.

The homogeneously prepared hydrogels were obtained as transparent, opalescing, eventually turbid materials. The heterogeneous gels were always white and opaque.

Thermally Induced Swelling Transition in PNIPA-based O–I Gels

A. PNIPA-BAA-TMOS Network Containing Dispersed Silica Domains The O–I gels exhibit a thermosensitive behaviour and volume changes typical of PNIPA gels swollen in water. Figure 1 shows the temperature dependence of the volume of the swollen hydrogels modified with silica (from TMOS) characterized by degree of swelling Q . The samples with varying silica amounts were prepared under homogeneous conditions in water, in methanol (very similar behaviour, Figure 1a) and under heterogeneous conditions (Figure 1b). A steep decrease in swelling, and thus in the volume of the hydrogels is observed around 32°C . The swelling degree below this temperature decreases with increasing silica (from TMOS) content. All the PNIPA-BAA gels were prepared with 5 mol % of the BAA crosslinker. This crosslinker amount was selected as an optimum amount, ensuring a sufficient crosslink density for the formation of a mechanically stable organic (PNIPA-BAA) network and still a sufficiently high swelling, which is necessary for a big and steep swelling transition.

The samples prepared in water under heterogeneous conditions exhibit a high swelling below LCST, but in contrast to the “homogeneous” samples, they show also a quite large equilibrium swelling at temperatures above LCST. This is likely an effect of the “residual water” filling the macropores in these hydrogels.

B. PNIPA-MPTMOS Network with Covalently Attached SSQO Domains

Incorporation of MPTMOS into the system was performed in order to check the effect of the chemical bonding of the inorganic phase to an organic matrix on the properties of the gel. Figure 2 illustrates the

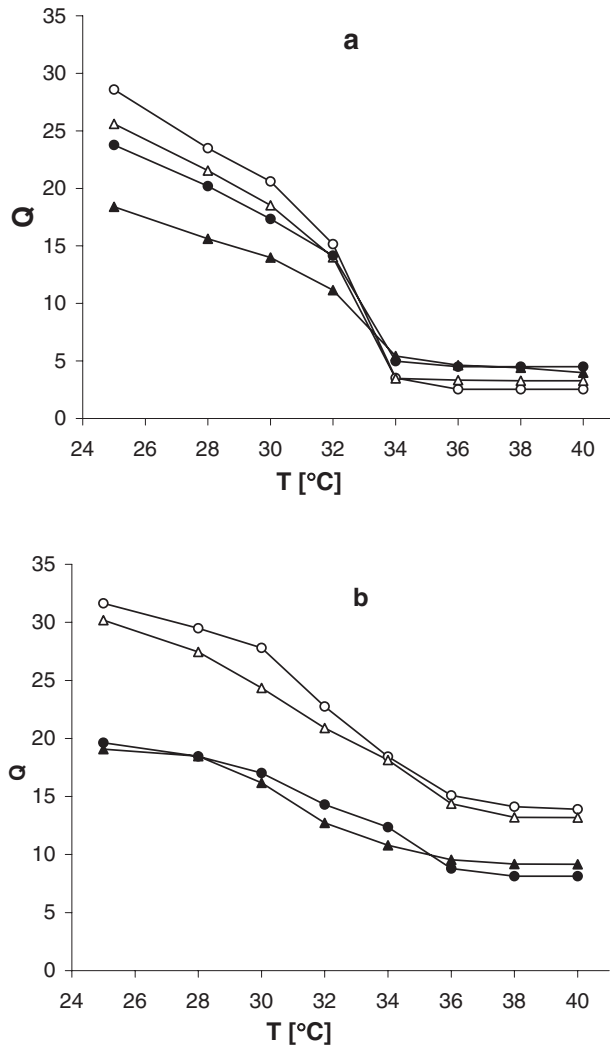


Figure 1. Swelling degree (Q) of gels modified with silica (from TMOS) as a function of temperature. (a) Polymerization in methanol: Samples: (○) 0 SiLhom_MeOH, (△) 0.1 SiLhom_MeOH, (●) 0.3 SiLhom_MeOH, (▲) 0.5 SiLhom_MeOH, (b) Polymerization in water under heterogeneous conditions: Samples: (○) 0 SiLhet, (△) 0.1 SiLhet, (●) 0.3 SiLhet, (▲) 0.5 SiLhet.

temperature induced swelling transition of the PNIPA-MPTMOS gels.

PNIPA-MPTMOS gels prepared in water, similarly to gels modified with TMOS, display a decrease of the swelling with increasing amount of inorganic structures. The curve profiles of the systems prepared in water (Figure 2a) are very similar to those of TMOS-modified gels, with a steep decrease in swelling around 32 °C.

However, the profiles change significantly, when methanol is used as a solvent during polymerization. The value of LCST shifts to lower temperatures with increasing MPTMOS content. Moreover, the swelling rapidly decreases with amount of MPTMOS (Figure 2b) and is very low for the system modified with 15 mol % MPTMOS as a result of a high crosslinking density, which has a strong influence on mechanical

properties.

Heterogeneously prepared PNIPA-MPTMOS gels show a similar behaviour like the silica modified “heterogeneous” PNIPA gels, but the MPTMOS gels show a 2 times smaller swelling (Figure 2c).

Deswelling of Gels

PNIPA gels deswell when the temperature is raised above 32 °C forming a dense deswollen layer on the surface, thus slowing down further deswelling of the bulk gel (skin-effect). Introduction of inorganic heterogeneities results in formation of a porous structure, which makes possible a faster deswelling of the O–I gel during the swelling transition. Figure 3 compares the deswelling kinetics of the non-modified PNIPA-BAA gels (5 mol % BAA double bonds), and the gels modified with 33 mol % TMOS or 5 mol % MPTMOS. The gels were prepared under homogeneous conditions in water or methanol, and under heterogeneous conditions. The hydrogels containing silica or SSQO structures exhibit a faster temperature response when immersed in a 40 °C bath mainly in the first stage of deswelling than the unmodified PNIPA-BAA gel. The gels prepared homogeneously in water show a faster deswelling than those prepared in methanol.

Further acceleration of the deswelling kinetics was achieved by synthesis of PNIPA gels in water under heterogeneous conditions, at a temperature above LCST of PNIPA. In contrast to the transparent or slightly turbid “classic” systems, the gels prepared under heterogeneous conditions are fully opaque and white. As it can be seen from Figure 3c, the heterogeneous preparation dramatically increases the rate of deswelling. The water is almost completely expelled from the interior of the gels in 2 min. In the case of these phase-separated systems, the rate of deswelling is nearly independent of the gel composition. This indicates that the heterogeneous structure formed by microphase separation of PNIPA above LCST plays the key role in the gel swelling and deswelling behavior.

Reswelling of the Gels

The systems prepared under homogeneous conditions exhibit a slow rate of reswelling in comparison with the rate of deswelling independently of the presence of inorganic structures. Reswelling is slowing down with time in all cases and a swelling equilibrium can eventually be reached only after a long time as illustrated in Figure 4a (“water” and “methanol” gels are very similar).

An improvement of reswelling kinetics was obtained with the heterogeneously synthesized gels. Figure 4b shows the reswelling kinetics of a series of the heterogeneous hydrogels both unmodified and modified with TMOS and MPTMOS. The reswelling

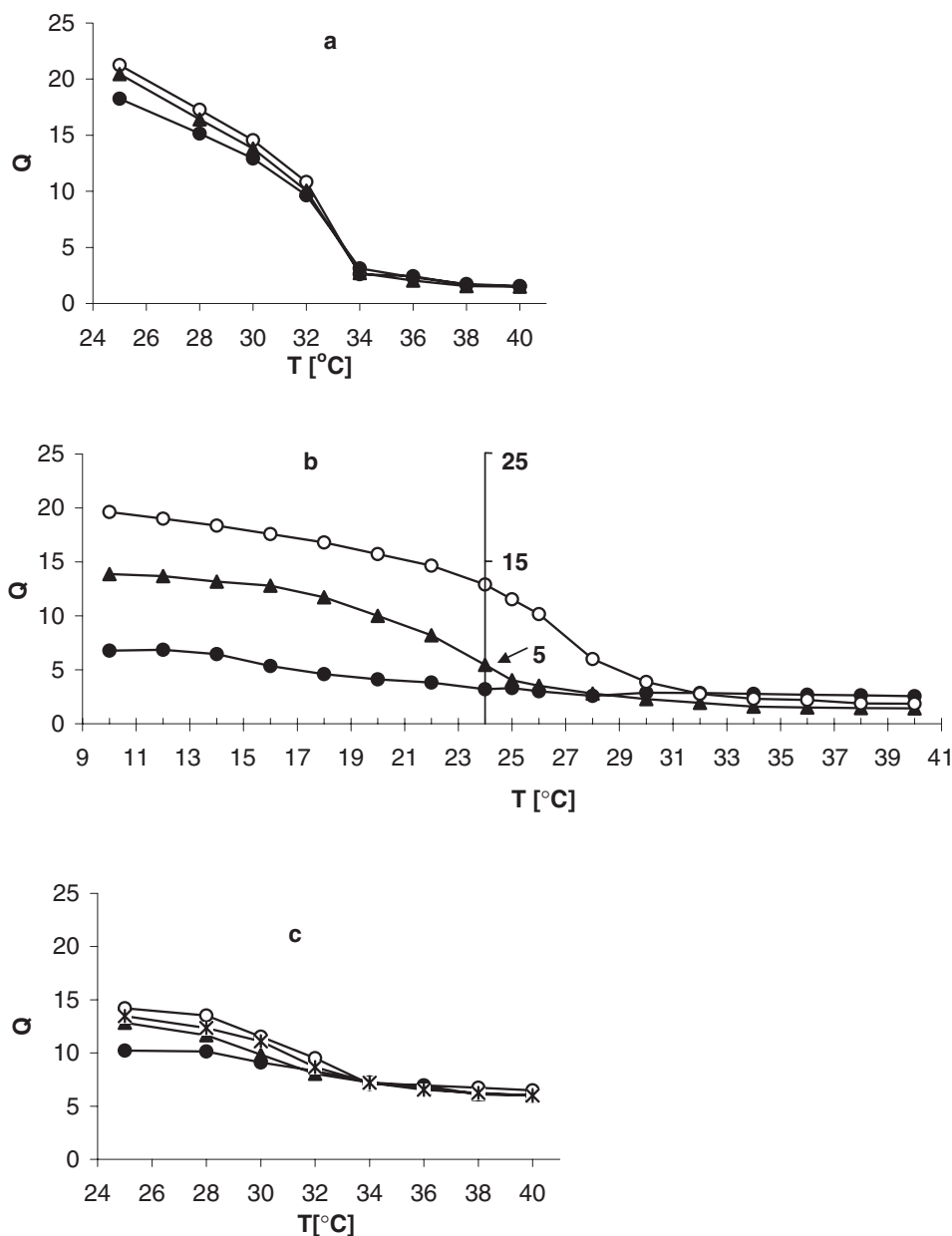


Figure 2. Swelling degree (Q) as function of temperature for PNIPA gels modified with MPTMOS prepared in (a) water: Samples: (○) Mpt 5_hom.H₂O, (▲) Mpt 10_hom.H₂O, (●) Mpt 15_hom.H₂O, (b) methanol: Samples (○) Mpt 5_hom.MeOH, (▲) Mpt 10_hom.MeOH, (●) Mpt 15_hom.MeOH, (c) water under heterogeneous conditions: Samples: (○) Mpt 5_het, (*) Mpt 8_het, (▲) Mpt 10_het, (●) Mpt 15_het.

rate is rather low for the unmodified sample and for the MPTMOS containing system. However, the gels with 23 and 33 mol% of TMOS “0.3 SiL_het” and “0.5 SiL_het” reswell rapidly and almost reach the initial state in 4 min.

Reversible Temperature Response

The very fast swelling/deswelling response on changing the temperature is an important feature of the gels modified with a high amount of TMOS, prepared under heterogeneous conditions. In all other cases it was impossible to achieve fast oscillations because of the limited reswelling rate. An approximately equal rate of reswelling in comparison with the rate of

deswelling is the necessary condition for a fast periodic reversible response. Figure 5 shows thermal responses of the homogeneously and heterogeneously prepared gels modified with silica (from TMOS). The responses were measured by immersing the sample several times alternately in 40 and 25 $^{\circ}\text{C}$ water for 2 min each time. The gels synthesized under heterogeneous conditions and modified by 23 or 33 mol% of TMOS change their volume almost reversibly by 40 or 50%, respectively. On the contrary, slow reswelling prevents reaching the equilibrium value within a short time for the gels prepared under homogeneous conditions.

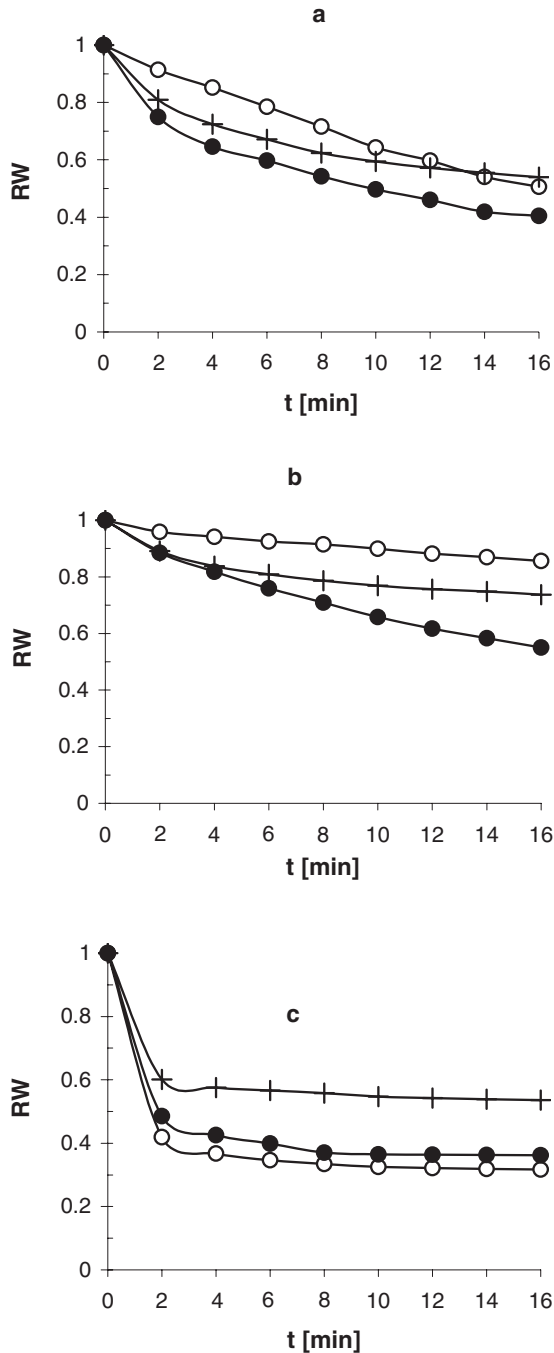


Figure 3. Deswelling kinetics of PNIPA-based O–I gels prepared in (a) water (○) 0 SiI_hom_H₂O, (+) 0.5 SiI_hom_H₂O, (●) Mpt 5_hom_H₂O, (b) methanol (○) 0 SiI_hom_MeOH, (+) 0.5 SiI_hom_MeOH, (●) Mpt 5_hom_MeOH, (c) water under heterogeneous conditions, (○) 0 SiI_het, (+) 0.5 SiI_het, (●) Mpt 5_het. Deswelling temperature $T = 40^\circ\text{C}$, RW is the relative weight of the swollen gel.

Mechanical Properties of the PNIPA-based O–I Gels.

Mechanical properties of gels depend on the network crosslinking density ν and the swelling degree of a gel Q , characterized by volume fraction of the polymer in the swollen gel ν_2 , which is inversely proportional to Q . The eq 2 for the equilibrium shear modulus of a gel holds:

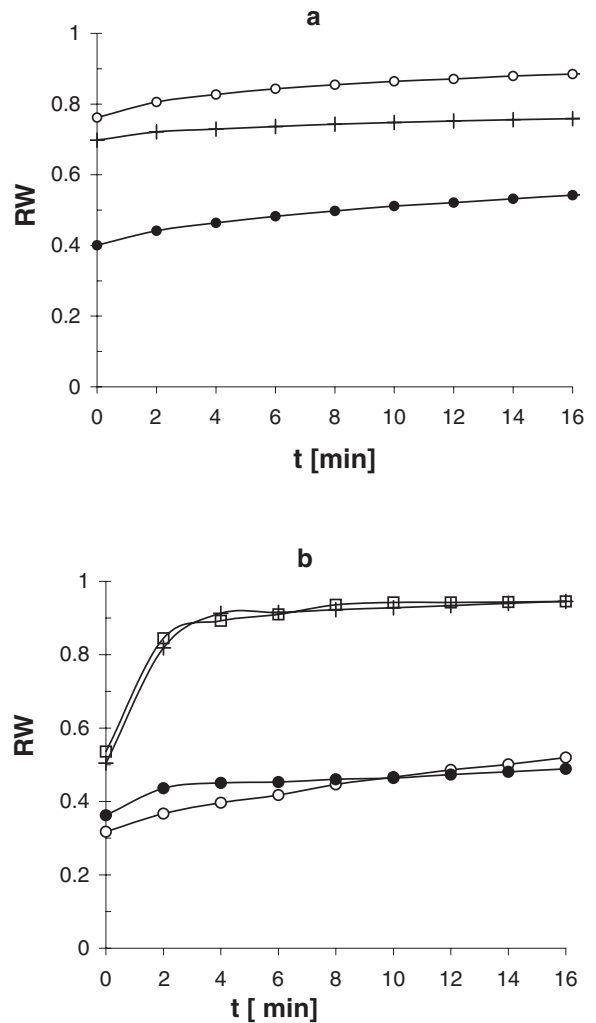


Figure 4. Reswelling kinetics of PNIPA-based O–I gels prepared in (a) methanol: Samples (○) 0 SiI_hom_MeOH, (+) 0.5 SiI_hom_MeOH, (●) Mpt 5_hom_MeOH, (b) water under heterogeneous conditions (○) 0 SiI_het, (+) 0.5 SiI_het, (□) 0.3 SiI_het, (●) Mpt 5_het. RW is the relative weight of the swollen gel.

$$G = \nu ART\nu_2^{1/3}, \quad (2)$$

where A is a front factor defined in the network model.²⁴ In the PNIPA gels the crosslinking density is crucial for mechanical properties because it also controls the degree of the gel swelling. The PNIPA gels of a low crosslinking density show a high swelling and rather low moduli of elasticity. The gel reinforcement is very important. The use of a higher amount of crosslinker improves mechanical properties of the gels; however, the increase in crosslinking density results in smaller swelling and eventually in suppression of the thermal swelling transition effect of PNIPA polymer networks.

Another solution is to reinforce PNIPA gels with an inorganic filler by blending or by chemical bonding. The influence of an inorganic phase on mechanical properties was characterized by the shear modulus of the series of gels modified with various amounts

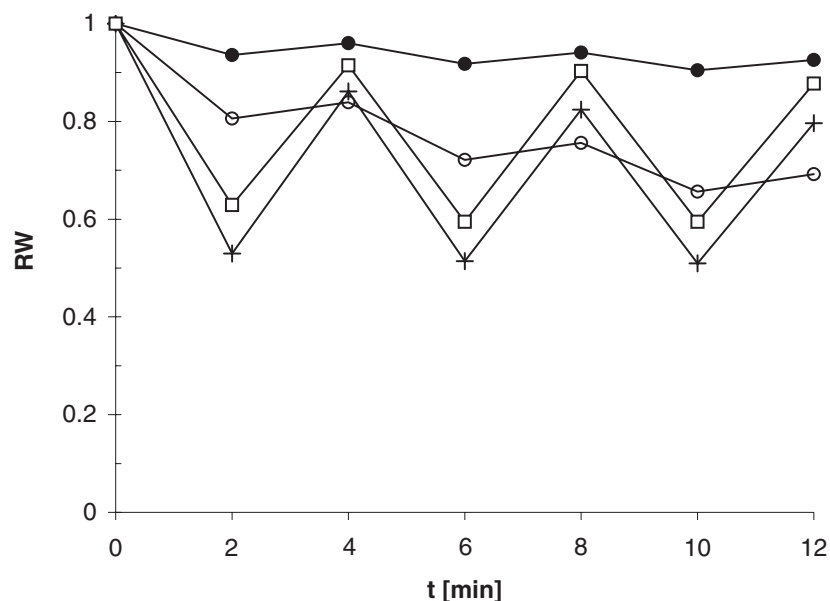


Figure 5. Thermal response of the “homogeneous” and “heterogeneous” PNIPa gels modified with different amounts of silica (from TMOS). RW is the relative weight of the swollen gel: Homogeneously prepared: (●) 0.3 Sil_{hom}-H₂O, (○) 0.5 Sil_{hom}-H₂O, heterogeneously prepared: (□) 0.3 Sil_{het}, (+) 0.5 Sil_{het}.

of TMOS and MPTMOS. Figure 6 shows that reinforcement of the PNIPa gel by inorganic structures is quite efficient. The modulus increases with increasing content of the inorganic filler and depends also on polymerization conditions.

In the series of homogeneous TMOS-modified gels in Figure 6b, the modulus of the gel containing 33 mol % of TMOS increases almost by an order of magnitude for the networks prepared in methanol solution. On the contrary, the gel containing the same amount of TMOS prepared in water under homogeneous conditions (Figure 6a) shows only a 3 times higher modulus compared with the unmodified PNIPa gel. In the homogeneous MPTMOS-modified systems, the modulus increases with increasing MPTMOS content for the gels prepared in methanol (Figure 6b). The modulus of the gel with 10 mol % of MPTMOS is higher than that of the PNIPa gel crosslinked with 5 mol % of BAA by an order of magnitude. However, PNIPa-MPTMOS gels prepared in water, at a temperature below LCST ($T = 5^\circ\text{C}$), show very poor mechanical properties and, surprisingly, their shear modulus is independent of the content of SSQO structures (Figure 6a).

The difference in mechanical properties of PNIPa-MPTMOS gels prepared in water and methanol is associated with a different swelling behavior. The gels prepared homogeneously in water are highly swollen with $Q = 18\text{--}22$ for 5–15 mol % MPTMOS at 25°C . In contrast, the gels polymerized in methanol exhibit a low swelling: $Q = 3\text{--}11$ for 5–15 mol % MPTMOS (*cf.* Figure 2). As a result, the “water” gels show low and “methanol” gels high moduli.

Shear moduli of the gels prepared under heterogeneous conditions are shown in Figure 6c. The PNIPa-BAA-TMOS gels exhibit moduli practically independent of the silica content, while the PNIPa-MPTMOS gels show an increase of modulus at high MPTMOS contents.

Structure of the O-I Hydrogels

In order to elucidate the strong differences between the homogeneous PNIPa-MPTMOS gels prepared in water and methanol, their structure was investigated by means of NMR, SAXS and electron microscopy. These gels are crosslinked by the sol-gel polymerization of the trimethoxysilyl dangling groups resulting in SSQO junctions between PNIPa chains (see Schemes 1 and 3). The conversion α characterizes the extent of the polycondensation to form Si–O–Si bonds. The ^{29}Si NMR results prove that in both homogeneous polymerization procedures, in methanol and water, there is no difference in conversion ($\alpha \sim 0.70$). However, a detailed NMR analysis reveals in the “water” gel a slightly higher amount of T_3 units, corresponding to silicon with three reacted functionalities –Si–O–; $T_3 = 0.27$ (polymerization in water), $T_3 = 0.19$ (polymerization in methanol). Formation of larger compact SSQO structures in the gel polymerized in water is a possible interpretation of the NMR data. The resulting material is more heterogeneous containing more compact SSQO-rich domains. Due to this fact the organic phase is more easily accessible to water. In contrast, the “methanol gels” are probably more homogeneous, with interpenetrating siloxane structures containing mainly T_2 units, which form

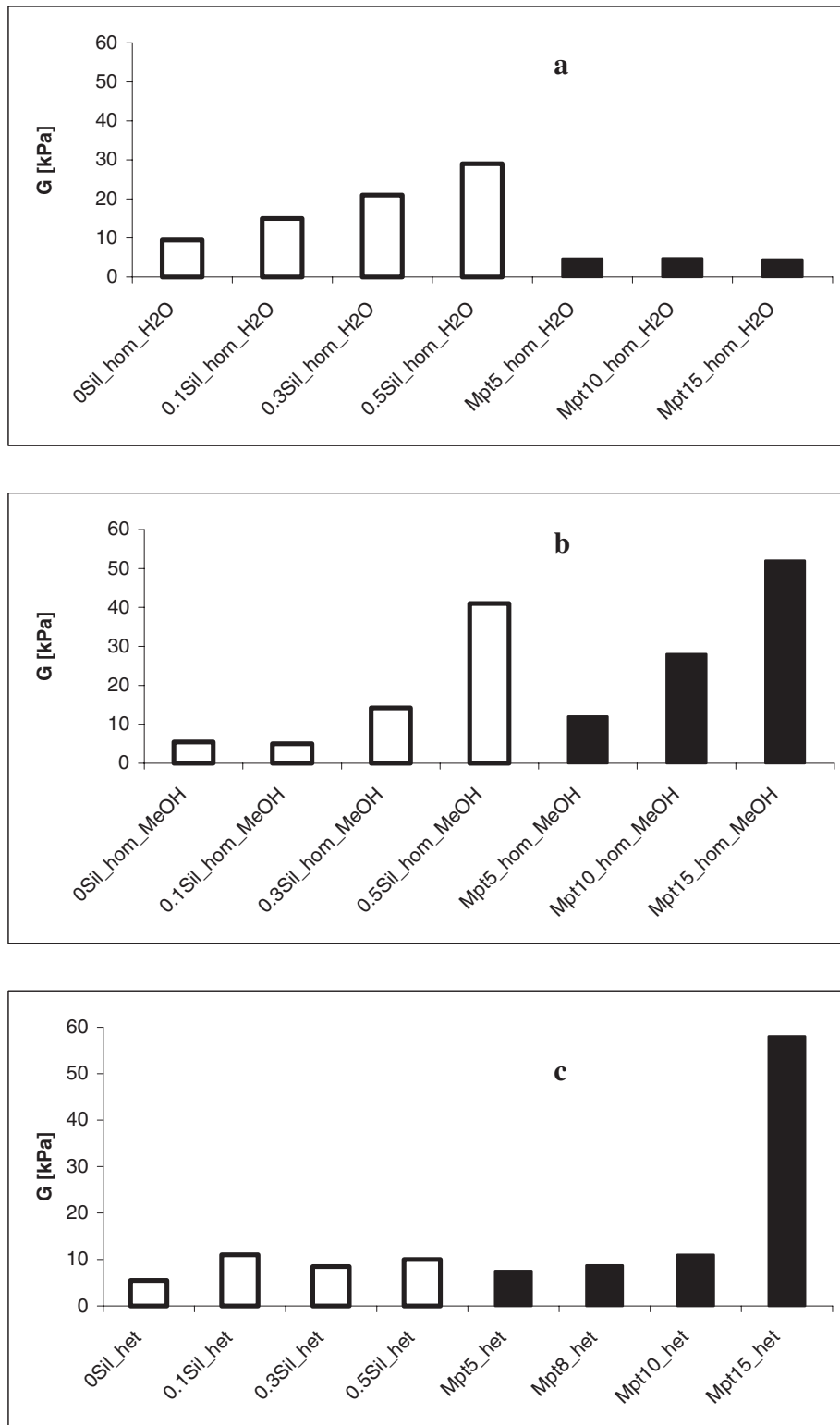


Figure 6. Shear modulus of selected PNIPA based O–I gels as a function of the content of silica (from TMOS, white columns) or MPTMOS (black columns), respectively: the gels were prepared (a) homogeneously in water, (b) homogeneously in methanol, (c) heterogeneously in water.

siloxane chains restricting swelling of the polymer system.

Figures 7c and 7d show the ^1H MAS NMR spectra of “water” and “methanol” gels, respectively, modified with 15 mol % MPTMOS (“Mpt 15_hom_H₂O”

and “Mpt 15_hom_MeOH”). In the case of the gel prepared in water, “Mpt 15_hom_H₂O” (Figure 7c), the intense signal at *ca.* 4.5 ppm can be assigned to the swelling water (the swelling degree of this gel is high: $Q = ca.$ 18). In the case of the gel polymerized in

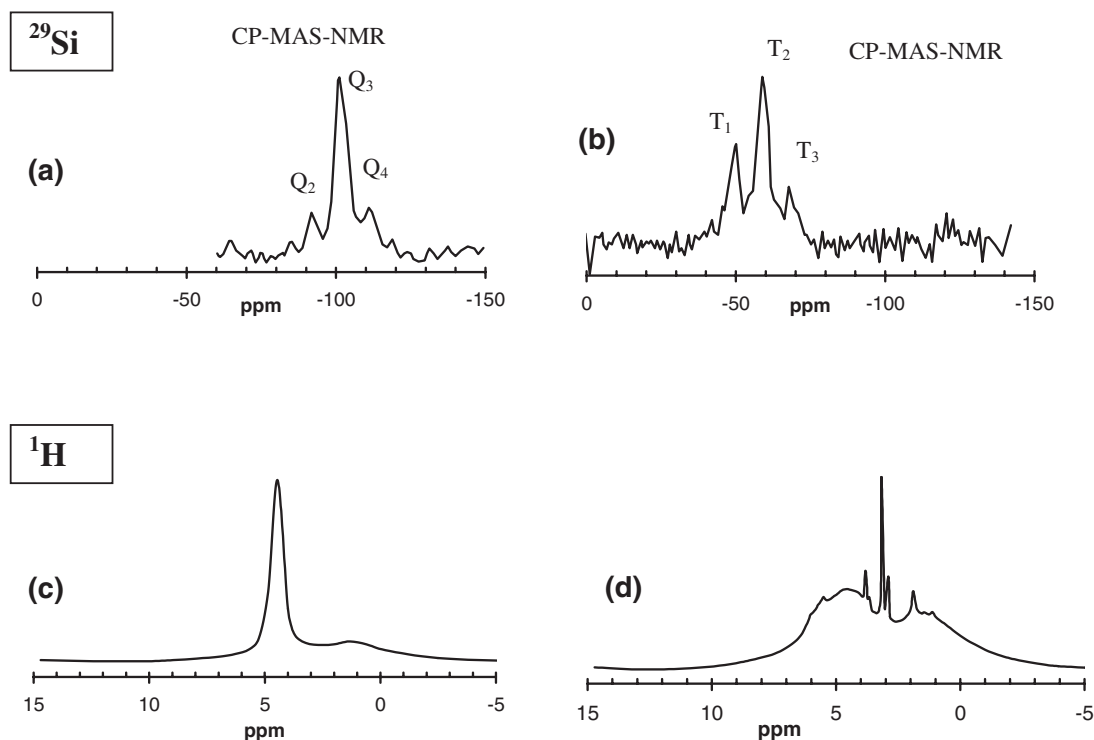


Figure 7. NMR spectra of selected hydrogels: (a) ^{29}Si -CP-MAS-NMR of “0.3 SiL_hom_H₂O”, (b) ^{29}Si -CP-MAS-NMR of “Mpt 15_hom_MeOH”, (c) ^1H -MAS of “Mpt 15_hom_H₂O”, (d) ^1H -MAS of “Mpt 15_hom_MeOH”.

methanol, “Mpt 15_hom_MeOH”, (Figure 7d) there is no such an intense water peak and the spectrum is more structured. This corresponds to the low swelling degree of the “methanol” gels ($Q = ca. 3$). Consequently, the results of ^1H MAS NMR spectra indicate the presence of strongly hydrogen-bonded water molecules in “water” gels at equilibrium conditions. The molecules can be attributed to the internal water tightly bound in the bulk of polymer.

Figure 8 shows SAXS intensity profiles of the dry and swollen gels PNIPA-MPTMOS (15 mol %) prepared in water and methanol. In the dry state, the gels polymerized in water exhibit much higher scattered intensity I at low q values than the gels prepared in methanol. In the swollen state, the intensity is lower in the case of “water” gels and, on the contrary, it increases in the “methanol” systems. At high angles, $q = 5\text{--}6\text{ nm}^{-1}$, the maximum appears in the scattered profiles, with exclusion of the swollen gel prepared in water. This maximum corresponds to the intramolecular interference within silsesquioxane structures in the PNIPA matrix.

The results could be explained by concentration and component contrast effects. Figure 2 shows that the gel containing 15% MPTMOS prepared in water swells *ca.* 5–6 times more than the “methanol” gel. The highly swollen “water” gel is strongly diluted, which results in a substantial decrease in concentration of SSQO domains and disappearance of the corresponding maximum at $q = 5\text{ nm}^{-1}$. The concen-

tration of SSQO structures in other systems is sufficient to be seen in SAXS profiles. Therefore, the maximum is observed in dry samples and in the swollen “methanol” gel, showing a very low swelling. Due to this low degree of swelling, there is only a small decrease in the scattering maximum after swelling the “methanol” gel, in contrast to the “water” gel. Dilution of the system by swelling is also a reason for the decrease in intensity at low angles in the case of the “water” gel. Moreover, swelling of the organic matrix of a heterogeneous system, containing SSQO domains results in an increase in the electron contrast between the organic and inorganic phases, assuming that SSQO structures do not swell. Hence, the scattered intensity grows when the SSQO concentration is constant. In the swollen “methanol” gel, the effect of the electron contrast prevails over the concentration effect because of a very low degree of swelling and a small dilution.

The scattered intensity I at low q values varies linearly in a log-log plot, implying the existence of large structures which are out of resolution range of our SAXS apparatus measurement; $>100\text{ nm}$. The characteristic exponent x of the SAXS profiles measured with an infinitely long primary beam ($I \sim q^{-x}$) is related to the mass fractal dimension: $D = x + 1$. The determined dimensions indicate a more compact structure and a stronger phase separation in the dry gel prepared in water ($D = 3.9$) compared with the “methanol” dry gel, $D = 3.2$. This is consistent with

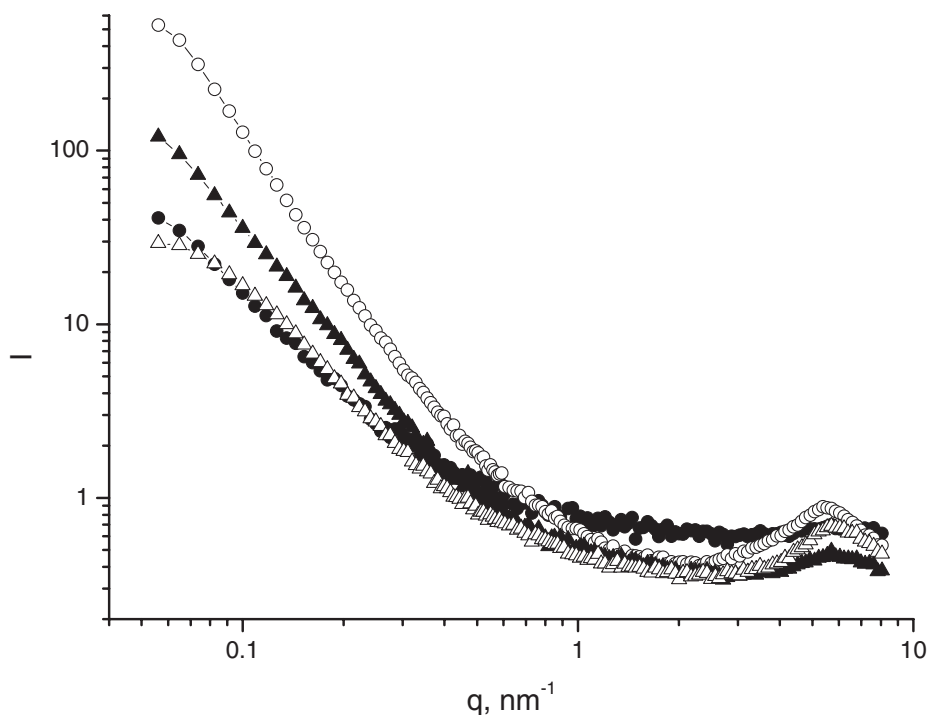


Figure 8. SAXS profiles of dry and swollen gels modified with MPTMOS: (○) Mpt 15_hom_H₂O, dry, (●) Mpt 15_hom_H₂O, swollen, (△) Mpt 15_hom_MeOH, dry, (▲) Mpt 15_hom_MeOH, swollen.

the NMR analysis.

The NIPA-MPTMOS (15 mol %) “water” and “methanol” hydrogels prepared under homogeneous conditions were also studied and compared using electron microscopy in order to prove large structures (>100 nm) found by SAXS. The sample “Mpt 15_hom_H₂O” shows a porous structure with inorganic particles of the size 0.5–5 μm, that manifest themselves in the form of white faceted objects in LV-SEM (Figure 9a). In HV-SEM, the porous structure is completely lost due to the preparation procedure, but the small inorganic particles are still clearly visible (Figure 9c). EDS analysis of the selected big particle (see white cross in Figure 9c) proves that the particle contains Si and O (*cf.* Figures 9e and 9f). The sample “Mpt 15_hom_MeOH” exhibits a more homogeneous structure in both LV-SEM and HV-SEM, with no inorganic particles, which indicates much better dispersion of inorganic structures (Figure 9b). Small pores in the structure are observable at a higher magnification in HV-SEM (Figure 9d). Matrix in both “Mpt 15_hom_H₂O” and “Mpt 15_hom_MeOH” contains just a small amount of Si as illustrated in Figure 9f. Certain amount of Si was found in all studied locations, which suggests that at least part of SSQO is finely dispersed in the matrix.

We assume the following explanation of the formed structure, mechanical and swelling properties of the PNIPA-MPTMOS (15 mol %) gels. It is well known that radical polymerization of vinyl-divinyl monomers

leads to strong cyclization and formation of a heterogeneous polymer involving intramolecularly crosslinked compact microgel particles.²⁵ In the system of the vinyl monomers NIPA-MPTMOS, the latter substitutes a divinyl monomer as methoxysilane groups serve as crosslinking functionalities. The crucial point is a very high rate of the radical NIPA polymerization and gelation under homogeneous conditions in the “water” gel using TEMED in the initiating system, compared to a slow polymerization in methanol (*cf.* Table I). In water, a high molecular weight copolymer with pendant methoxysilane groups is quickly formed. Crosslinking of methoxysilane groups by sol-gel process is a slower reaction. In the dilute system of such a high functional polymer, however, the cyclization by the intramolecular reaction of these groups is strongly favored. Large intramolecularly crosslinked compact domains are formed, which is consistent with SAXS results and the high fraction of *T*₃ units determined by NMR. Therefore, the intermolecular crosslinking reaction of the methoxysilane groups is limited only to surface of these domains. As a result, the final crosslinking density of the network as well as the elastic modulus are low (*cf.* Figure 6) and swelling is high (*cf.* Figure 2). There is no increase in modulus with growing content of MPTMOS, however swelling decreases because of increasing incompatibility in water. On the contrary, the radical polymerization in methanol is slow, its rate being comparable with hydrolytic condensation of the

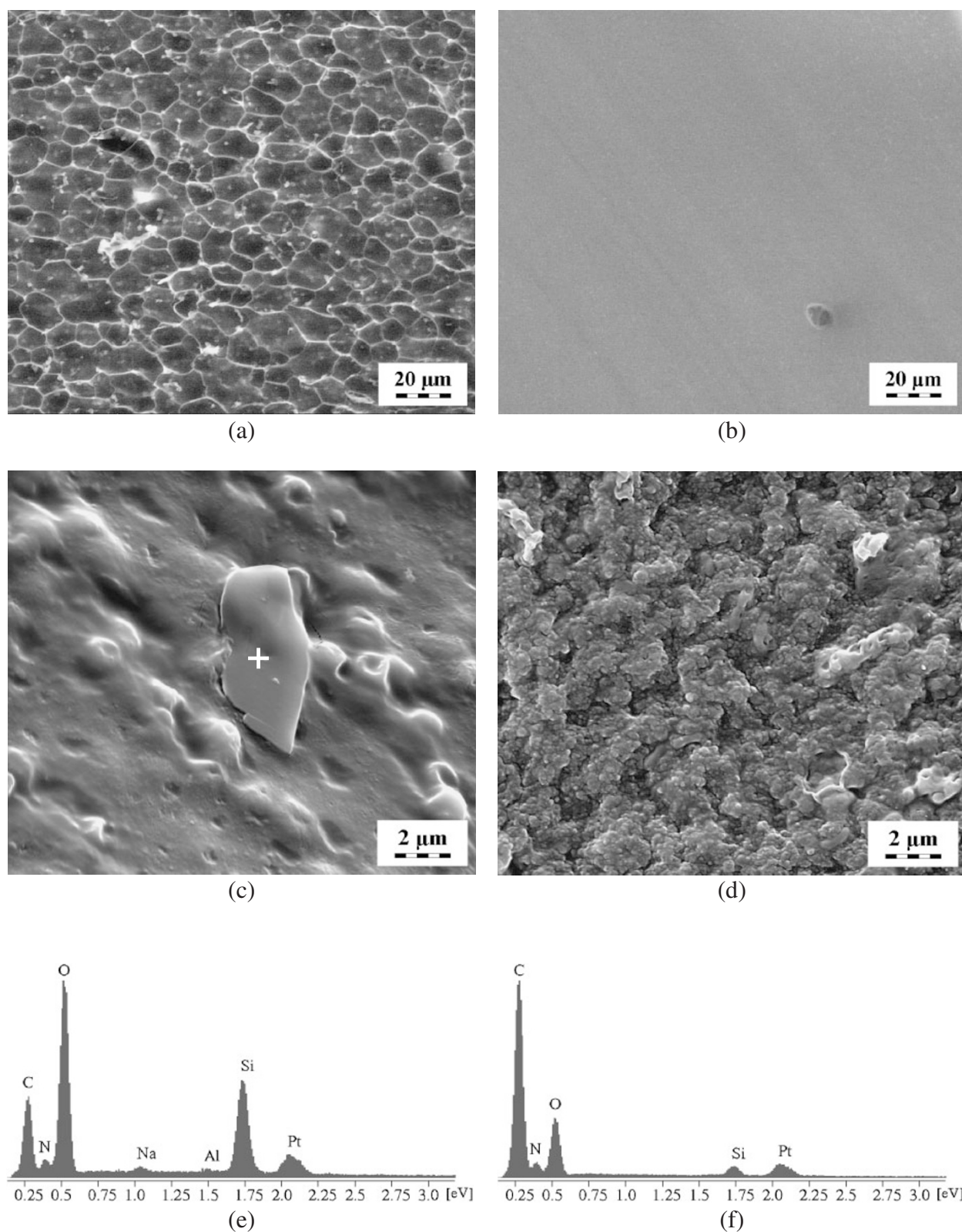


Figure 9. Microscopic structure and composition of “Mpt 15_hom_H₂O” and “Mpt 15_hom_MeOH”. (a,b) LV-SEM at lower magnification, (c,d) HV-SEM at higher magnification and (e,f) characteristic EDS spectra. Spectrum (e) corresponds to bigger particles in “Mpt 15_hom_H₂O”, such as this shown in the centre of HV-SEM micrograph (c); spectrum (f) corresponds to matrix in both “Mpt 15_hom_H₂O” and “Mpt 15_hom_MeOH”.

methoxysilane groups. Hence, low-molecular weight, low-functional polymers are involved in the reaction of the methoxysilane groups. In this case the cycliza-

tion is less extensive and the intermolecular crosslinking prevails. The system is more homogeneous as determined by SAXS and electron microscopy. The

crosslinking density and modulus are higher and strongly dependent on the content of MPTMOS crosslinker (see Figure 6).

No such an effect was observed for the network NIPA-BAA-TMOS. In this case, formation of the silica domains is independent of radical polymerization of NIPA-BAA and does not affect the crosslinking density. Silica structures are not covalently bound to the network. The increase in modulus both in “water” and “methanol” gels is given by the reinforcing effect of the hard silica domains dispersed in the organic matrix.

CONCLUSIONS

PNIPA-based gels modified by incorporation of silica (from TMOS) and of MPTMOS were synthesized under homogeneous or heterogeneous conditions. The O–I gels show thermosensitive behaviour characterized by a temperature dependent swelling transition typical of PNIPA-based gels around $T = 32\text{ }^{\circ}\text{C}$.

The homogeneously prepared O–I gels exhibit acceleration of swelling-deswelling kinetics in comparison with non-modified PNIPA gels. The deswelling of the MPTMOS modified hydrogels is faster than in the case of TMOS modified samples. At the same time, introduction of silica or SSQO structures improves mechanical properties. Polymerization procedure was shown to affect significantly the structure and mechanical properties of the O–I gels with covalently bound SSQO domains.

The gels prepared under heterogeneous conditions, show generally a faster deswelling rate in comparison to homogeneously prepared gels. Additionally, the TMOS-modified gels show a very fast reswelling rate providing the reversible volume change within 2 minutes. The disadvantages of heterogeneously prepared systems are their poor mechanical properties. Introduction of MPTMOS solved this problem only partly because the swelling effect disappeared in this case and the composition must be optimized. Addition of TMOS preserved the swelling effect but did not improve mechanical properties. Using both modifiers simultaneously or addition of other alkoxy silane monomers is a possibility currently investigated in order to obtain a fast responsive hydrogel with good mechanical properties.

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REFERENCES

1. M. Heskins and J. E. Guillet, *J. Macromol. Sci., Chem.*, **A2**, 1441 (1968).
2. M. Shibayama and K. Nagai, *Macromolecules*, **32**, 7461 (1999).
3. Y. Hirokawa and T. Tanaka, *J. Chem. Phys.*, **81**, 6379 (1984).
4. E. Matuo and T. Tanaka, *J. Chem. Phys.*, **89**, 1695 (1988).
5. Y. Bae, T. Okano, and S. W. Kim, *J. Polym. Sci., Part B: Polym. Phys.*, **28**, 923 (1990).
6. D. Dhara and P. R. Chatterji, *Polymer*, **41**, 6133 (2000).
7. B. M. Novak, *Adv. Mater.*, **5**, 422 (1993).
8. U. Schubert, N. Hüsing, and A. Lorenz, *Chem. Mater.*, **7**, 2010 (1995).
9. Y. Osada, H. Okuzaki, and H. Hori, *Nature*, **355**, 242 (1992).
10. S. Takeuchi and I. Omodaka, *Makromol. Chem.*, **194**, 1991 (1993).
11. R. Pelton, *Adv. Colloid Interface Sci.*, **85**, 1 (2000).
12. C. D. Jones, *Macromolecules*, **33**, 8301 (2000).
13. B. G. Kabra and S. H. Gehrke, *Polym. Commun.*, **32**, 322 (1991).
14. R. Yoshida, K. Uchida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai, and T. Okano, *Nature*, **374**, 240 (1995).
15. N. Kato, Y. Sakai, and S. Shibata, *Macromolecules*, **36**, 961 (2003).
16. W. F. Lee and W. Y. Yuan, *J. Appl. Polym. Sci.*, **84**, 2523 (2002).
17. T. Serizawa, K. Wakita, and M. Akashi, *Macromolecules*, **35**, 10 (2002).
18. K. Haraguchi, T. Takehisa, and S. Fan, *Macromolecules*, **35**, 10162 (2002).
19. Y. Imai, N. Yoshida, K. Naka, and Y. Chujo, *Polym. J.*, **31**, 258 (1999).
20. S. Kurihara, A. Minagoshi, and T. Nonaka, *J. Appl. Polym. Sci.*, **62**, 153 (1996).
21. X. Z. Zhang and R. X. Zhuo, *Langmuir*, **17**, 12 (2001).
22. J. T. Zhang, S. W. Huang, S. X. Cheng, and R. X. Zhuo, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 1249 (2004).
23. M. Ilavský, *Adv. Polym. Sci.*, **109**, 173 (1993).
24. B. Erman and P. J. Flory, *J. Phys. Chem.*, **68**, 5363 (1978).
25. K. Dušek, “Advances in Polymerization” R. N. Haward, Ed., Applied Science, Barking 1982.