

One-Shot Synthesis of a Poly(*N*-isopropylacrylamide)/Silica Hybrid GelP. Banet,^{*,†} P. Griesmar,[‡] S. Serfaty,[‡] F. Vidal,[§] V. Jaouen,[†] and J.-Y. Le Huerou[‡]

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Class I hybrid poly(*N*-isopropylacrylamide)/silica hydrogels, PNIPAM/SiO₂, were prepared by a new one shot synthesis. In this approach, the free-radical polymerization of vinyl groups of *N*-isopropylacrylamide (NIPAM) and the hydrolysis-condensation of alkoxy groups of tetramethoxysilane (TMOS) are performed concomitantly using sodium persulfate and 3-(dimethylamino)-propionitrile, a well-known couple to initiate the organic polymerization. The cross-linker is *N,N*-methylenebisacrylamide. The kinetic study of mechanical properties from the sol-to-gel state for different ratios of TMOS/NIPAM was investigated by rheological ultrasonic measurements. The thermoresponse of hybrid materials was investigated by differential scanning calorimetry and the measurements showed that hybrid gels present a lower critical solution temperature, which is similar with one of single organic hydrogel.

Introduction

For a biomedical application, an interesting challenge is the change of the swelling behavior of the organic gel by an external stimulus such as pH, solvent composition, or temperature. The poly(*N*-isopropylacrylamide) (PNIPAM) network is a well-known thermosensitive hydrogel that can be used for innovative applications.¹ In water, under its lower critical solution temperature (LCST, 32 °C), the polymer is in a coil state. The polymer chains collapse in water above the LCST near to the body temperature of human beings. During this phase transition an abrupt shrinkage of PNIPAM volume occurs.² PNIPAM hydrogel is used for drug delivery^{3,4} but its poor mechanical properties, however, limit the application domain. Organic–inorganic hybrid materials combine the mechanical strength characteristic of the inorganic part and the required properties of the organic network.^{5,6} Therefore, they are used more and more for their large range of adjustable properties (electrical, magnetic, optical, or biocompatibility).^{7,8}

Hybrid polymer–silica gels elaborated at room temperature by the sol–gel process^{9,10} present many advantages. Indeed, silica gels are often used as an inorganic network for their thermal and mechanical stability and their biocompatibility. Up to now, hybrid PNIPAM–silica gels have been prepared by various step by step processes. Zhang et al. reported the preparation of thermoresponsive silica nanoparticle/PNIPAM hybrid particles by aqueous surface-initiated atom transfer radical polymerization (ATRP) at room temperature.¹¹ Park et al. also prepared thermosensitive PNIPAM-grafted mesoporous silica particles by radical copolymerization of prefunctionalized mesoporous silica by 3-(trimethoxysilyl) propylmethacrylate and NIPAM (*N*-isopropylacrylamide).¹² PNIPAM cross-linked by polyhedral oligomeric silsesquioxane was synthesized by Mu and co-workers.¹³ PNIPAM, preformed by RAFT (reversible addition–fragmentation chain transfer) polymerization, was

chemically attached at the surface of mesoporous silica nanoparticles by You et al.¹⁴

In our work, a one-shot one-pot synthesis of PNIPAM/SiO₂ class I hybrid is described (i.e., the organic and inorganic networks are prepared simultaneously). This molecular architecture can be described also as an interpenetrating polymer network (IPN). Indeed IPNs are defined as a combination of two or more polymer networks synthesized in juxtaposition. The presence of entangled cross-links increases the miscibility of the polymers compared to usual blends and leads to a material with better mechanical properties and a possibly improved combination of the properties of its components, although this last point cannot be considered as being always true.¹⁵ In the first part of this paper the investigation of the optimal reactants and conditions of compatibility between organic and inorganic polymerization is presented. To optimize the process, a monitoring of mesoscopic viscoelastic properties is performed using an ultrasonic technique developed in our laboratory.^{16,17} The kinetic formation of the hybrid gel is presented for different TMOS/NIPAM (tetramethoxysilane) ratios. The different characteristics of synthesized gels are discussed.

Experimental Section: Materials and Methods

Reactants. *N*-Isopropylacrylamide 97% (NIPAM), tetramethoxysilane 98% (TMOS), and 3-(dimethylamino)-propionitrile 98% (DAPN) have been purchased from Aldrich, and *N,N'*-methylenebisacrylamide 99% (BA) has been purchased from Sigma-Aldrich. All the products were used without any further purification.

Synthesis. Poly(*N*-isopropylacrylamide) Gels (PN). PNIPAM gel is prepared at room temperature by the free radical polymerization of *N*-isopropylacrylamide using sodium persulfate (SPS) and dimethylaminopropionitrile as initiators and BA as cross-linker. A typical run is as follows: 565.8 mg of NIPAM (5 mmol) and 23.1 mg of BA (0.15 mmol) are dissolved in 9.49 mL of water. After 10 min of stirring, 255 μ L of a 7 wt % SPS solution (0.075 mmol) is added. After 10 more minutes, 254 μ L of a 10 v % DAPN solution (0.225 mmol) is added to initiate NIPAM polymerization (the initial NIPAM concentra-

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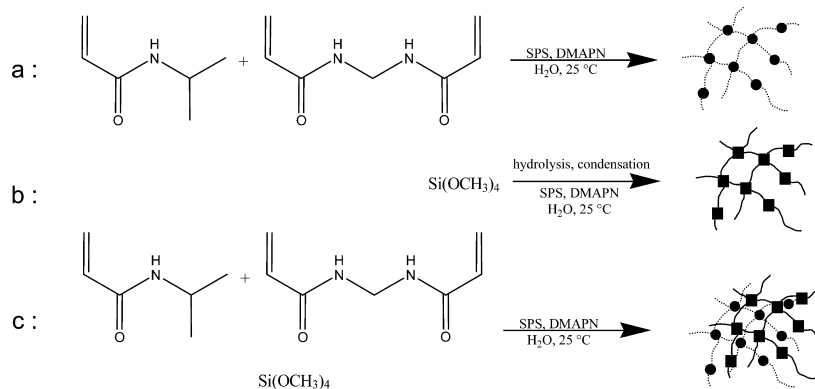


Figure 1. Formation of different networks: (a) single organic network (PN), (b) single inorganic network (S), (c) class I hybrid material (H_r ; no covalent bond exists between the two networks).

tion is equal to 0.5 M). The mixture is stirred for 1 min to obtain a homogeneous solution.

SiO_2 Gels (S). A total of 8.75 mL of water is added to 0.761 g of TMOS (5 mmol). The mixture is stirred for 10 min to allow solubilization of the silica precursor. Then 255 μL of a 7 wt % SPS solution is added. After 10 min, 254 μL of DMAPN (0.225 mmol) solution is added. The initial TMOS concentration is equal to 0.5 M.

Class I PNIPAM/ SiO_2 Hybrid (H_r). Different class I hybrids were prepared from sol, where $[\text{NIPAM}] = 0.5 \text{ M}$ and with various molar ratios $r = [\text{TMOS}]/[\text{NIPAM}]$. For each preparation, r has been adjusted to study the effect of the inorganic/organic networks ratio. A total of 565.8 mg NIPAM (5 mmol) and 23.1 mg BA (0.15 mmol) are dissolved in 8.75 mL of water. Then an amount of $0.761 \times r \text{ g}$ TMOS ($5 \times r \text{ mmol}$) is added. The solution is stirred for 10 min to obtain a homogeneous solution. Finally, 255 μL of SPS solution (0.075 mmol) and 254 μL of DMAPN solution (0.225 mmol) are added. In the following text, H_r stands for a class I hybrid material obtained with a molar ratio $r = [\text{TMOS}]/[\text{NIPAM}]$.

Figure 1 shows the different processes for the formation of different networks of each investigated gel.

Methods of Characterization. Several techniques are used in this paper to monitor the evolution of the new hybrid material properties.

(1) The stress strain constitutive relations suggest the experimental determination of complex shear moduli through observing the differential relationship between stress and strain in a specimen undergoing simple harmonic deformation.¹⁸ During the formation of the hybrid gel, the characteristic size of the three-dimensional gel network strongly evolves (typically from 10 to 1000 nm). Taking into account that the typical shear wave velocity in silica gels is around $10 \text{ m} \cdot \text{s}^{-1}$, the frequency range of the harmonic shear waves chosen between 1 and 60 MHz allows an investigation in the suitable scale.^{16,19} The rheological evolution of sol–gel materials is monitored using ultrasonic shear waves at high frequency. This investigation, performed at 6 MHz, uses a resonator with high sensitivity. To extract the complex viscoelastic parameters (the storage, G' , and the loss, G'' , shear moduli) of the material in contact with the sensor, a new model has been developed in our laboratory.²⁰ This model takes into account the mechanical and electrical interactions due to the mesoscopic evolution of complex materials during their formation.^{18,21} A characteristic time (t_{vs} : viscous elastic time) of gelation can be singularly determined. t_{vs} is an interesting criteria because it characterizes the kinetic reactions before the gelation time.¹⁶ This time corresponds to the moment when the material is no more a Newtonian liquid.

(2) To control the thermoreversibility properties and the organic–inorganic ratio of materials at gel state, two thermal analyses are performed. The first one measures the LCST by differential scanning calorimetry (DSC). Measurements were performed on a TA DSC Q100 apparatus in the range from 25 to 40 °C, with a heat rate of 1 °C/min under argon. The second measures the mass organic-to-inorganic ratio using thermal gravimetric analyses (TA TGA Q50). Samples are heated from 20 to 700 °C at the rate of 5 °C/min under air.

To estimate the amount of unreacted starting material in the final material and, thus, the efficiency of cross-linking reactions, a known weight of product was extracted in a Soxhlet with methanol for 2 days. After extraction, the sample was dried in a vacuum oven for 8 h at 50 °C. The extractable content (EC) is given as weight percentage

$$\text{EC}(\%) = \frac{(W_0 - W_e)}{W_0} \times 100 \quad (1)$$

where W_0 and W_e are the sample weights before and after extraction, respectively.

Results and Discussion

Hybrid PNIPAM/ SiO_2 One-Step Synthesis Description.

Both syntheses of PNIPAM hydrogels and silica gels have commonly been described. On one hand, the PNIPAM hydrogels are usually prepared by the free-radical copolymerization of NIPAM and BA using thermal decomposition of persulfate at a temperature around 70 °C to initiate the polymerization.^{22,23} When persulfate and DMAPN are used as the redox initiator system, the polymerization can be realized at room temperature.²⁴ On the other hand, silica gels are obtained by the sol–gel process. Starting from an alkoxide dissolved in a water–alcohol mixture, a catalyst (acid or base) is added to accelerate the gelation.²⁵ Materials combining organic and inorganic networks have been already synthesized by multistep synthesis.²⁶

To synthesize PNIPAM–silica hybrids in a one-pot, one-shot process, it is necessary to have compatible free-radical polymerization and hydrolysis–condensation conditions. However, to obtain silica monolithic gels, alcohol is used as the common solvent between alkoxide and water and unfortunately even if PNIPAM is soluble in the two single solvents (alcohol and water) the “co-nonsolvency” phenomenon due to water–alcohol mixture involves a nonsolubility of PNIPAM.^{27–29} To avoid this phenomenon, the alkoxide is added to the water without alcohol. A homogeneous phase is obtained when the first hydrolyzed

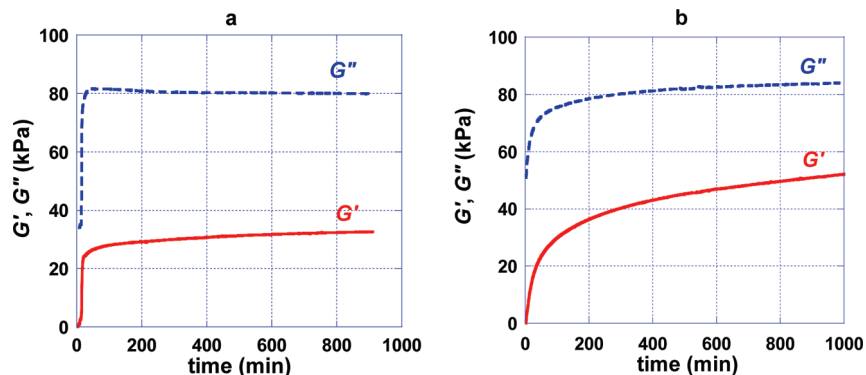


Figure 2. Temporal evolution of the elastic (G') and viscous (G'') moduli of different networks: (a) single organic network (PN), (b) single inorganic network (S; $T = 25\text{ }^{\circ}\text{C}$).

species are formed (this process takes few minutes). As DMAPN, the redox initiator of the organic polymerization at room temperature, is also a nucleophilic activator, it can be used also to catalyze the formation of the inorganic network. Furthermore, the SPS, required in the free-radical polymerization of NIPAM, will modify the ionic strength and accelerate the gelation process.³⁰ To obtain simultaneously a growth of both organic and inorganic networks, the elaboration modes have been adjusted to get similar gelation time. The different protocols are chosen to obtain a gelation time around 20 min. This characteristic time can be easily changed by adjusting the different parameters (precursor concentration for example). The addition of both SPS and DMAPN results in a faster TMOS gelation process than using single water or only SPS or DMAPN (10–15 min instead of several hours). For these reasons this way is chosen to achieve simultaneously organic and inorganic gelation.

The hybrid material can be then optimized by monitoring the rheological properties evolution and by adjusting the TMOS/NIPAM molar concentration ratio. The results are compared with single inorganic and organic gels.

Viscoelastic Properties Investigation of Materials. The viscoelastic evolution of single organic PNIPAM gels (PN), single silica gels (S), and organic–inorganic hybrids gels (H_r) are monitored with the high frequency rheometer made in our laboratory.

Typical Viscoelastic Evolution of Organic and Inorganic Gels. On one hand, poly(*N*-isopropylacrylamide) hydrogels (PN) were prepared using $[\text{NIPAM}] = 0.5\text{ M}$ and in molar ratio: 3% of BA, 1.5% of SPS, and 4.5% of DMAPN. On the other hand, inorganic silica gels (S) were prepared by a hydrolysis–condensation process from an aqueous solution of TMOS, 0.5 M, with addition of SPS and DMAPN in the amount used in NIPAM polymerization. Both syntheses and monitoring of the evolution of the mechanical properties are performed at $25\text{ }^{\circ}\text{C}$.

Figure 2a and b present G' and G'' for PN and S, respectively.

In both cases the viscoelastic characteristics strongly increase to reach finally a plateau. At the beginning, the shear elastic modulus values (G') can be considered equal to zero. This value means that, in the first steps of formation, the two materials can be considered as Newtonian liquids. Note that for the inorganic synthesis (Figure 2b) this hypothesis remains valid though the solubilization step of the silica precursor in single water (10 min of stirring) in which the measurements cannot be performed.

After a few minutes, the polymerization/cross-linking reaction changes the mesoscopic and the macroscopic characteristics. G' becomes significantly different to zero according to the

emergence of the elastic properties of the network. The viscosity also increases with a similar evolution of G'' .

Near the PNIPAM percolation threshold (at gelation time t_g about 17 min), G' and G'' sharply increase. From that point, the material becomes a gel at the macroscopic scale. Comparing the figures 2a and 2b, it is interesting to note that in the plateau (in the gel phase) the G' and G'' values of the organic and inorganic network are quite similar. Therefore, the macroscopic viscoelastic properties are assumed comparable.

Typical Viscoelastic Evolution of Hybrid Gels. To achieve an optimal “one-pot one-shot” synthesis, different molar ratios r of inorganic/organic precursors have been prepared. The temporal evolution of G' and G'' of the different hybrid networks H_r are studied for $0.1 \leq r \leq 0.90$ at $T = 25\text{ }^{\circ}\text{C}$ and is presented in Figure 3a,b. As described in the Synthesis section, the NIPAM concentration is fixed to 0.5 M.

Given the shape of the curves (Figures 2 and 3), the kinetic evolution of G' and G'' of hybrid materials clearly shows the influence of the organic polymerization. Similar large increases at $t_g = 17\text{ min}$ (outlining the liquid and gel phases) can be observed. At the gel phase, the slight evolution of the viscoelastic properties is due to the continuous and slim evolution of the inorganic polymerization. From the sol phase to the gel phase the values of G' and G'' are increased at least by 10.

Furthermore, a new trend is observed in the kinetic profile. Both G' and G'' exhibit a maximum during the gel formation. This maximum occurs around 30 min. This time is very close to the moment when the viscous modulus reaches a plateau for the single organic gel (Figure 2a). We believe that consecutive to the growth of the inorganic network, the cross-linked PNIPAM is formed in a reduced volume, and these new conditions imply mechanical constraint of the organic network that relaxes slowly to reach an equilibrium state.

Moreover, in Figure 3a,b we can observe that the mechanical properties of the hybrid materials depend on r . When r increases from 0.1 to 0.8, G' and G'' also increase, whereas for a higher ratio a slow decrease is observed. Hence, there is an optimal value of r for which moduli of the hybrid are the highest. To determine the accurate value of this ratio, the evolution of G' and G'' at the plateau (i.e., when no more major structural evolution of the material is expected/observed) was plotted against r (Figure 4).

This figure shows that for a narrow range of r ($0.70 < r < 0.80$) both G' and G'' reach maximum values. This result confirms that the two network growths cannot be considered independently and that strong interactions exist between the PNIPAM and the SiO_2 networks.

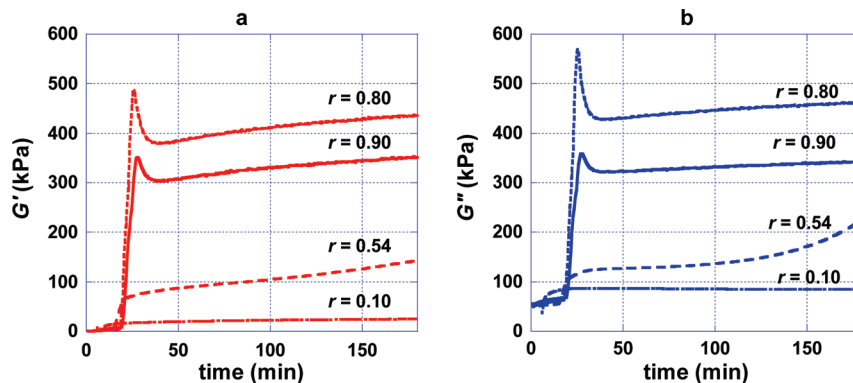


Figure 3. Temporal evolution of the elastic G' modulus (a) and viscous G'' modulus (b) of different hybrid networks H_r ; $0.10 \leq r \leq 0.90$ at $T = 25^\circ\text{C}$, with $r = [\text{TMOS}]/[\text{NIPAM}]$.

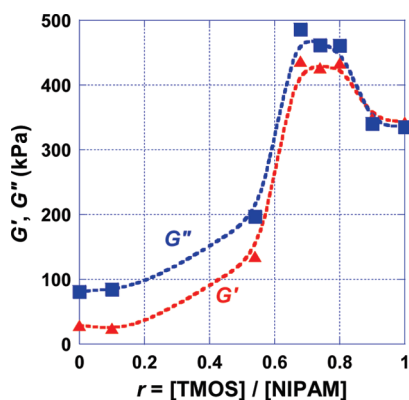


Figure 4. Evolution of the elastic G' and viscous G'' moduli at 150 min for different hybrid networks H_r ; $0.0 \leq r = [\text{TMOS}]/[\text{NIPAM}] \leq 1.0$ at $T = 25^\circ\text{C}$.

Note that when r increases only the amount of TMOS introduced in the medium increases and the NIPAM concentration is the same for all experiments. Consequently, on one hand the total amount of initial precursor in the middle increases. And the viscoelastic parameters should regularly increase with r . On the other hand, the amount of released methanol (during hydrolysis and condensation reactions) increases with r and the “co-nonsolvency” effect is more and more pronounced. Consequently, the interactions between the two networks are less important leading a decrease of the viscoelastic parameters.

Composition of the $H_{0.8}$ Materials and Thermosensitivity Investigations. For the synthesis ratio for which the values of G' and G'' are the greatest ($H_{0.8}$) the composition and the thermosensitivity have been investigated. The organic/inorganic composition of the hybrid gels was determined by thermogravimetric analysis and the thermosensitivity has been studied by DSC. First of all, the material has been Soxhlet extracted and the extractable content reaches 13 wt %, indicating that both networks are reasonably well cross-linked under those experimental conditions.

TGA measurement performed on wet gel is presented on Figure 5. A first weight loss is observed between 20 and 120 $^\circ\text{C}$ and it is followed by a plateau until 220 $^\circ\text{C}$. Then, a second weight loss occurred between 220 and 650 $^\circ\text{C}$ and a new plateau is reached from 650 to 700 $^\circ\text{C}$. The first loss corresponds to the evaporation of the liquid phase (water and alcohol) and the second is due to the calcination of the organic part of the hybrid material. Assuming that SiO_2 is obtained at 700 $^\circ\text{C}$, the amount of PNIPAM gel present into the hybrid material can be calculated from the second weight loss. Results are presented in Table 1.

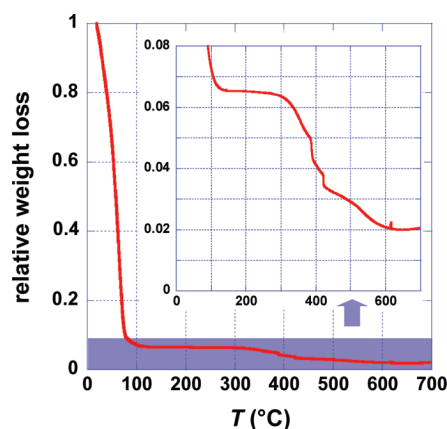


Figure 5. TGA measurement of a wet gel ($H_{0.8}$) under air (inset: zoom of the darkened area).

TABLE 1: Organic Weight Ratio (Measured (meas) and Calculated (cal)) and Critical Temperature, T_c , of Different Gels (for Single Organic and Hybrid Material: $H_{0.8}$)

sample	org (wt %; meas)	org (wt %; cal)	T_c ($^\circ\text{C}$)
PN	100	100	31.5
$H_{0.8}$	70	72	31.8

$H_{0.8}$ is effectively a hybrid material as it exhibits both organic and inorganic parts. Moreover, the mass ratio found is in agreement with the theoretical ratio calculated from the molar composition of the two precursors. It is noteworthy that after the thermal treatment there remains one block of silica in the nacelle (i.e., there is no silica powder). This seems to indicate that at least the silica network is continuous in space.

The thermosensitivity of single PNIPAM and hybrid material $H_{0.8}$ is studied by DSC measurements. Figure 6 shows the heat flow versus the temperature for three temperature sweeps between 25 and 40 $^\circ\text{C}$.

During the first heat rate an endothermic peak is observed for PN and $H_{0.8}$. This phenomenon is characteristic of the coil to globule transition of PNIPAM (LCST corresponds to the peak extremum). For the period of the temperature decrease, the smaller exothermic peak observed at a temperature lower than LCST corresponds to the globule to coil transition. For further heat rates and runs, the same peaks are also observed. Here, only three sweeps are presented in the figures. The results prove that the thermosensitivity and thermoreversibility of the PNIPAM network are preserved in the hybrid materials. Transition temperatures of materials are listed in Table 1. A slight LCST shift between PN and hybrid material can be noticed. This result

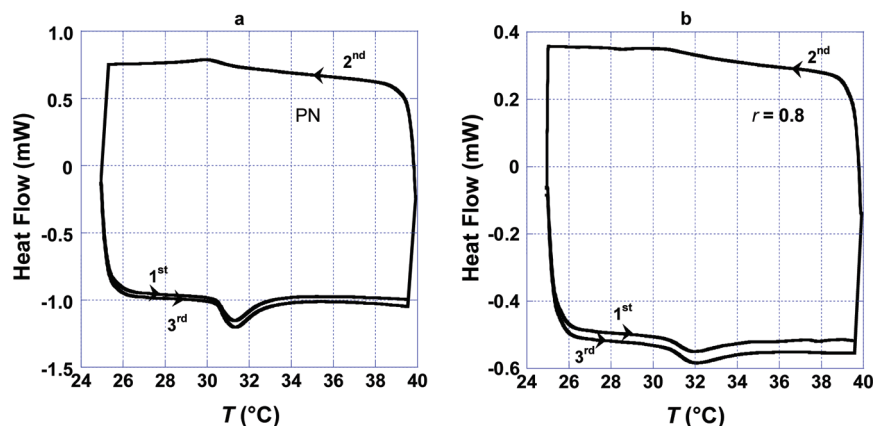


Figure 6. DSC measurements of PN (a) and hybrid materials $r = 0.8$ (b) between $T = 25$ and 40 °C.

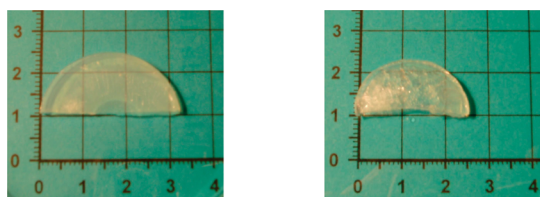


Figure 7. Photography of hybrid material ($r = 0.8$) (a) under LCST (25 °C) and (b) above LCST (40 °C).

is in agreement with previous results concerning PNIPAM grafted from the surface of solid substrates³¹ and cross-linked hydrogels.³²

To point out the volume contraction, the hybrid material immersed in water were placed alternatively in two thermostatted baths at 25 and 40 °C (i.e., under and upper the LCST). Figure 7 presents the camera pictures of $H_{0.8}$ at the two temperatures when the equilibrium state is reached. At 25 °C the hybrid gel is in a swollen state and is translucent (Figure 7a). At 40 °C as the PNIPAM gel is shrunk, a volume contraction occurs and the gel is slightly white. When the temperature is cooled to 25 °C, the gel gets back in its initial swollen state.

The macroscopic shrinkage of hybrid gel shows that the PNIPAM phase is a continuum. As the silica network is also a continuum it can be assumed that the hybrid materials display an Interpenetrating Polymer Network architecture.

Conclusions

A new synthetic method of hybrid poly(*N*-isopropylacrylamide)/silica hydrogels was presented in this paper. It is the first report to our knowledge of a one-step synthesis. Usually, silica and poly(*N*-isopropylacrylamide) networks are prepared sequentially. Moreover, both kinetic reactions are controlled and in the same duration range. As a consequence, the obtained hybrid is an IPN.

The kinetic studies of the mechanical properties evolution during the sol-to-gel transition reveal that with this protocol mechanical properties of hybrid materials are improved. This increase depends on the ratio of TMOS versus NIPAM, and an optimal ratio has been pointed out ($r = 0.8$).

For future biomedical applications, it is noteworthy that the hybrid gels keep thermosensitivity and thermoreversibility of the poly(*N*-isopropylacrylamide) part. The LCST is close to 32 °C. A fair volume contraction was observed during the phase transition. Hence, these hybrids gels could be used to control the release of molecule introduced into their pores by temperature increase.

An objective to improve these hybrid materials is the control of the LCST and particularly its increase to a value near of 37

°C. A covalent link between the silica network and the poly(*N*-isopropylacrylamide) network should ensure this increase. That is why we are currently working on the synthesis of new precursors able to condensate with TMOS and to polymerize with NIPAM to obtain class II hybrids.

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