Novel rapid response clay/poly(N-isopropylacrylamide) nanocomposite hydrogels by post treatment with HCl solution

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Abstract: A series of high clay content Laponite XLS/poly (N-isopropylacrylamide) (PNIPAAm) nanocomposite hydrogels (S-N gels) have been successfully prepared by in-situ ultraviolet (UV) initiated polymerization. The effects of post treatment with HCl solution on swelling/deswelling behaviour of the S-N gels have been investigated in detail. The results indicate that the Laponite XLS/PNIPAAm nanocomposite hydrogels with HCl solution post treatment (S-N-H gels) exhibit great swelling ratio and rapid deswelling response rate; much higher and faster than other reported clay/PNIPAAm nanocomposite hydrogels.

Introduction

In the last two decades, Poly (N-isopropylacrylamide) (PNIPAAm) hydrogels have attracted much attention as the advanced soft materials because of thermo-sensitivity, resulting from phase transition at their lower critical solution temperature (LCST≈32 °C) [1]. Due to the coexistence of hydrophilic (amide) and hydrophobic (N-isopropyl) groups, PNIPAAm chains are hydrated, expanded, flexible random-coil conformations below the LCST; dehydrated and collapse to globular conformations above the LCST [2].

Clay/PNIPAAm nanocomposite hydrogels (S-N gels) retaining amounts of water (e.g., 90 wt. %) consist of a unique inorganic/polymer (clay/PNIPAAm) three-dimensional network [3–4]. As reported previously, we have successfully prepared high clay content nanocomposite hydrogels by using Laponite XLS, one kind of clay modified by tetrasodium pyrophosphate (Na$_2$P$_2$O$_7$) (i.e. ionic dispersant), which can be easily dispersed in water to form a low viscous aqueous dispersion at high clay content (above 10 wt%). The S-N gels have shown excellent mechanical properties (tensile strength, 1MPa; elongation at break, 1430%) [5], compared to the conventional chemically cross-linked hydrogels (OR gels). It is found that with increasing clay content, mechanical properties of the S-N gels increased, but the swelling/deswelling rate and ratio of those are gradually decreased. This demerit makes it inadequate for applications such as drug delivery systems [6], separation devices [7], micro-scale actuators [8] and recyclable absorbents [9], etc.

In respect of the above considerations, a new temperature-sensitive clay/PNIPAAm hydrogels with rapid responsive rate would be preferable. Because the network structure of S-N gels is noncovalent, essentially different from the covalent network
structure of OR gels, the structure and properties of S-N gels should be affected by a post treatment, such as a solvent, heat, or light, etc. Generally, several methods have been used to improve the response dynamics, such as freeze-drying for forming porous structure, and preparation with phenol aqueous solution [10-11]. In this paper, we successfully prepared a series of S-N gels by in-situ ultraviolet (UV) initiated polymerization, and a kind of rapid responsive nanocomposite hydrogels (S-N-H gel) were obtained by post treatment with HCl solution. The swelling/deswelling behavior of S-N-H gels has been systematically investigated by modulating post treatment time and the concentration of HCl solution. Furthermore, it was surprisingly found that the swelling ratio of the S-N gel was enhanced via HCl solution post treatment, for example, from 6.91g/g for S-N gel to 22.99 g/g for S-N-H1T2 gel. And the deswelling rate of these were also greatly increased by the post treatment, i.e. shrank and lost over 72% water within 3 minutes, much faster than that reported for clay/PNIPAAm nanocomposite hydrogels.

Results and Discussion

The FTIR spectroscopy analysis of S-N and S-N-H gels

The FTIR spectra of S-N and S-N-H gels are displayed in Figure 1. As shown in Figure 1, a broad band in the range of 3100–3700 cm\(^{-1}\) belongs to N–H stretching vibration, the peaks at 1650 cm\(^{-1}\) and 1550 cm\(^{-1}\) can be ascribed to the typical amide I and II bands of NIPAAm, while the peak at 1007cm\(^{-1}\) corresponds to Si-O stretching vibration of clay. Therefore, the curves of S-N and S-N-H gels had almost the same characteristic groups, indicating that the chemical components of S-N gel did not change through HCl solution post treatment.

![Fig. 1. FTIR spectra of S-N and S-N-HmTn gels (a) S-N gel; (b) S-N-H0.1T4 gel; (c) S-N-H0.1T8 gel.](image)

The Elements Analysis of S-N and S-N-H gels

In hydrogel network, neighboring clay platelets act as a super-multifunctional cross-linking agent, linked by large numbers of long, flexible polymer chains. Herein, the interaction between PNIPAAm chains and clay platelets, which is not covalent bonding, is a mixture of ionic interaction and hydrogen bonding interaction [12]. Table 1 indicated that the contents of metal ions (e.g. Mg\(^{2+}\), Na\(^{+}\), Li\(^{+}\)) on the surface of clay platelets were gradually decreased in the process of HCl solution post treatment.
There were probably ionic exchanges among H\(^+\) in HCl and metal ions in clay, resulting in the reduction of the effective cross-linking density between PNIPAAm chains and clay platelets and the damage of physical interaction in S-N gel partly.

**Tab.1.** All the feed compositions of S-N and S-N-H gels.

<table>
<thead>
<tr>
<th>Element</th>
<th>S-N (mg/g)</th>
<th>S-N-H0.1T2 (mg/g)</th>
<th>S-N-H0.1T8 (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(^{2+})</td>
<td>74.50</td>
<td>41.09</td>
<td>18.48</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>11.64</td>
<td>2.71</td>
<td>0.86</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>1.36</td>
<td>0.72</td>
<td>0.37</td>
</tr>
</tbody>
</table>

* Most Na\(^+\) comes from Na\(_2\)P\(_2\)O\(_7\), which is the ionic dispersant for clay.

**Transmittance of S-N and S-N-H gels**

The transmittance of S-N and S-N-H gels was measured by UV-vis spectrometry. As shown in Figure 2, the transmittance of those samples was affected by HCl solution post treatment; decreased with increasing the concentration of HCl solution, for example, from 68.35% for S-N gel to 0% for S-N-H0.5T2 gel. It might be due to the existence of ionic exchanges between H\(^+\) in HCl and metal ions in clay during the post treatment, leading to the aggregation of some clay platelets, then the formation of random hydrogel network from uniform one in previous.

![Fig. 2.](image)

**Fig. 2.** (a) Transmittance of S-N and S-N-H gels post treated by different concentration of HCl solution; (b) Photo of S-N and S-N-H gels (a S-N gel, b S-N-H0.1T2 gel, c S-N-H0.2T2 gel, d S-N-H0.5T2 gel).

**XRD Analysis of Dried S-N and S-N-H gels**

To reveal the level of dispersion of clay platelets in nanocomposite gels, XRD measurements were undertaken on dried S-N gel and S-N-H gels post treated by different concentration of HCl solution. Figure 3 shows XRD patterns of dried S-N and S-N-H gels and, for comparison, of clay. All samples were powders. Clay shows a strong diffraction peak at around 2\(\theta\)=7.1° (d=1.25nm), corresponding to the spacing between clay sheets. For S-N gel, dried sample also showed a clear diffraction peak.
at around 2θ=3.4° (d=2.59nm). Since the spacing was much larger than that of clay itself (diameter=30 nm, thickness=1 nm), the diffraction peak observed for dried S-N gel was attributed to a clay-polymer-clay intercalated structure. Furthermore, the intensity of the diffraction peak became weak promptly with the increase of the concentration of HCl solution, which meant the regular stacking of clay/polymer intercalation were disappearing and a significant amount of polymer chains disrupted formation of the layered structure.

![X-ray diffraction profiles with Cu Kα X-rays for milled dried materials of clay, S-N and S-N-H gels.](image)

**Fig. 3.** X-ray diffraction profiles with Cu Kα X-rays for milled dried materials of clay, S-N and S-N-H gels.

**Swelling behavior of S-N and S-N-H gels**

Figure 4(a) shows the effects of HCl solution (0.1 mol/L) post treatment time on swelling behavior of S-N and S-N-H gels in deionized water at 25 °C (below its LCST). The swelling kinetics of non-ionic hydrogel such as PNIPAAm mainly depends upon two factors: (1) the polymer/water mixing and (2) network elasticity [13]. Hydrogels in the dehydrated state are glassy. In the presence of water, hydrogels absorb a significant amount of water to form elastic gels. To S-N gel, in the initial stage, it rapidly absorbed water, and then its absorbing rate leveled off. After 5982 min, the swelling ratio reached its equilibrium value. From the curves in Figure 4(a), it could be seen that the equilibrium swelling rate of all S-N-HmTn gels was slower than that of S-N gel. And it was decreased with increasing HCl solution post treatment time. Figure 4(b) displays the effects of the concentration of HCl solution on swelling behaviors of S-N gels. It was found that the swelling rate was decreased with increase in the concentration of HCl solution, whose result was almost same to that shown in Figure 4(a). However, both the improvements of post treatment time and the concentration of HCl solution had the positive effects on equilibrium swelling ratio. From Table 2, we could see that the equilibrium swelling ratio of S-N gel was greatly enhanced after the post treatment (e.g., from 6.91 g/g for S-N gel to 22.99 g/g for S-N-H1T2 gel). The oxygen atoms of the clay surface can form hydrogen bonds with the amide proton of NIPAAm, and the metal ions on the surface of clay platelets may form a complex with the carboxyl oxygen of NIPAAm. The clay platelets in a 100 nm cube ($10^6 \text{nm}^3$) act as multifunctional cross-linking agents with an average effective functionality around 50 [14]. Therefore, it is reasonable for a single PNIPAAm chain...
to interact with different clay platelets and one clay platelet to interact with several repeat units of the same PNIPAAm chain [15]. Since the polymer/water mixing parameter is generally independent of cross-linking, network elasticity, which is affected by the cross-linking density of hydrogels, is the major factor that controls the equilibrium swelling behavior. It indicated that some repeat PNIPAAm units interacting with clay platelets detached from the surface of clay platelets during the ionic exchanges, leading to the decrease in cross-linking density of S-N gel which in turn brought the increase in swelling ratio of hydrogels.

![Fig. 4. (a) Effect of HCl solution post treatment time on swelling behavior of S-N and S-N-H gels (b) Effect of the concentration of HCl solution on swelling behavior of S-N and S-N-H gels.](image)

The hydrogel swelling mechanism drawn from three processes [16] are (1) penetration of water into the hydrogel; (2) the relaxation of PNIPPAm chains; and (3) extension of the whole polymer chains in the hydrogel network. According to the Higuchi's square root of time model, if process (1) dominated the swelling kinetics, the water absorbed has a linear relationship to square root of time, which was in accordance with the plot of S-N gel in Figure 5; if process (2) dominated, the plot of the water absorbed versus square root of time was in S-shape, which was in accordance with those of S-N-H gels in Figure 5. It could be seen that the curves of S-N-H gels were all in S-shape, quite different from that of S-N gel, which were characterized by a low initial stage, followed by two accelerated stages prior to the approach to equilibrium.

**Tab. 2.** The equilibrium swelling ratios of S-N and S-N-H gels.

<table>
<thead>
<tr>
<th>Gel samples</th>
<th>S-N</th>
<th>S-N-H0.05T2</th>
<th>S-N-H0.1T1</th>
<th>S-N-H0.1T2</th>
<th>S-N-H1T2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium SR (g/g)</td>
<td>6.91</td>
<td>14.00</td>
<td>14.22</td>
<td>16.72</td>
<td>22.99</td>
</tr>
</tbody>
</table>

The dynamic swelling properties of polymer hydrogels include the water absorption rate, the rate of approach to equilibrium swelling and the transport mechanism controlling water absorption. The transport mechanism, which indicates the relative importance of diffusion and relaxation, is determined by the following equation \(M_t / M_\infty \leq 0.6\) [17].

\[ F = M_t / M_\infty = kt^n \]
where $M_t$ and $M_\infty$ denote the amounts of the water absorbed into the hydrogel at time $t$ and infinite time (at equilibrium), respectively; $k$ is a constant related to the structure of the network and exponent $n$ is the swelling kinetic parameter, indicating the transport mechanism: Fickian diffusion or Case I transport ($n \leq 0.5$), relaxation controlled or Case II transport ($n \geq 1$), non-Fickian diffusion or anomalous transport ($0.5 < n < 1$).

![Graph of swelling kinetic as a function of square root of time.](image)

**Fig. 5.** Plot of swelling kinetic as a function of square root of time.

To evaluate the type of diffusion for S-N and S-N-H gels, graphs were plotted $\ln F$ versus $\ln t$ in Figure 6, and the slope was the value of $n$. From Figure 6 and Table 3, it could be observed that the curve for S-N gel yielded straight line and $n$ took value of 0.69, indicating the diffusion was anomalous or complex behavior, of non-Fickian nature, in which the rate of diffusion of the water and that of relaxation were of the same magnitude. Water diffused through the polymer network at a constant velocity, and the rate of macromolecular relaxation of PNIPAAm chains was almost of the same magnitude or, possibly, the rate of diffusion of the water ($V_D$) was relatively slower than that of relaxation of the polymer chains ($V_R$). However, the graphs of S-N-H gels were quite different from that of S-N gel.

![Graph of $\ln F$ percent swelling ratio of S-N and S-N-H gels as a function of $\ln t$.](image)

**Fig. 6.** Plot of $\ln F$ percent swelling ratio of S-N and S-N-H gels as a function of $\ln t$. 
Tab. 3. Kinetic parameters of S-N and S-N-H gels.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>k (×10^3)</td>
<td>n</td>
<td>r^2</td>
</tr>
<tr>
<td>S-N</td>
<td>13.18</td>
<td>0.69</td>
<td>0.99</td>
</tr>
<tr>
<td>S-N-H0.05T2</td>
<td>1.46</td>
<td>0.68</td>
<td>0.99</td>
</tr>
<tr>
<td>S-N-H0.1T2</td>
<td>1.68</td>
<td>0.63</td>
<td>0.97</td>
</tr>
<tr>
<td>S-N-H1T2</td>
<td>1.56</td>
<td>0.60</td>
<td>0.98</td>
</tr>
</tbody>
</table>

* k means kinetic constant, n means swelling exponent, r^2 means correlation coefficient.
* - means untested.

According to the different value of n, we discussed the diffusion mechanism into three periods (Period I, II, III), in order to analyze the dynamic swelling properties of S-N-H gels in detail. In Period I, a linear dependence could be observed, and n of all the S-N-H gels took values in between 0.68 and 0.60, indicating the diffusions of those were of non-Fickian nature, which were same to that of S-N gel. Then, the values of n took between 0.43 and 0.28 in Period II, indicating the diffusions were of Fickian nature, under the water diffusion control, in which V_D was much less as compared with V_R. Last, n took values in between 0.97 and 1.50 in Period III, thereby suggesting the swelling behavior was relaxation controlled, in which V_R was slower as compared with V_D. Moreover, both the values of n in Period I and II gradually decreased with increasing the concentration of HCl solution, tending to that stress relaxation process was faster than the rate of diffusion. By contrast, Period III in which V_D was higher than those in Period I and II the value of n was not decreased. The kinetics tended to become relaxation controlled. During the post treatment, ionic exchanges were happening among H^+ in HCl and metal ions in clay, leading to aggregation of some clay platelets and detachment of PNIPAAm chains in the hydrogel network. The aggregation of clay platelets would produce a kinetic constraint on the swelling behavior in the initial stage. Thus, the sudden acceleration of swelling rate and ratio in the next stage was related to the disappearance of the aggregation of clay platelets, the reduction of cross-linking density between PNIPAAm chains and clay platelets, and the improvement of PNIPAAm chains mobility after post treatment. Integrated with the results of transmittance and element analysis of S-N and S-N-H gels, this situation including both aggregation and detachment of S-N gel was enhanced with increasing post treatment time and the concentration of HCl solution.

Deswelling behavior of S-N and S-N-H gels

Figure 7(a) shows the effects of the concentration of HCl solution on deswelling behavior of S-N and S-N-HmT2 gels in deionized water at 50 °C (above its LCST). Deswelling rate of all S-N-HmT2 gels increased with increasing the concentration of HCl solution. As for S-N-H1T2 gel, immersed in the highest concentration HCl solution had the fastest deswelling rate, which shrank and lost over 72% water within 3 minutes. In contrast, about 35% water was released from S-N gel within the same time frame. The physical network structure and the thermodynamic nature of the components played a key role in the swelling/deswelling behavior [18-19]. At temperature above LCST, the intrinsic affinity of PNIPAAm chains was enhanced due to thermal dissociation of hydrating water molecules from themselves. Hydrophobic interactions between isopropyl groups increased and the hydrogels appeared to be
hydrophobic and the PNIPAAm chains started to aggregate and phase separation took place. Also, it was well known that high clay content would decelerate deswelling rates [9], due to the hydrophilicization influence of clay platelets on the coil-globule conformation change of PNIPAAm chains [20-21]. Because the FTIR results showed that the chemical components of S-N gel did not change through the post treatment, the improvement of deswelling rate of S-N-H gels should result from the change in the physical structure of the hydrogel network [12].

![Graph](image1)

**Fig. 7.** (a) Effects of different concentration of HCl solution on deswelling behavior of S-N and S-N-H gels (b) Effects of different HCl solution post treatment time on deswelling behavior of S-N and S-N-H gels.

Figure 7(b) shows the effects of HCl solution (0.1mol/L) post treatment time on deswelling behavior of S-N gel and S-N-H0.1Tn gels in deionized water at 50 °C. It was clearly that the deswelling rate of all the S-N-H0.1Tn gels was much faster than that of S-N gels. As for S-N-H0.1T8 gel, it shrank and lost over 67% water within 2 minutes in 50 °C water. It indicated that deswelling rate of S-N-H gels thereby increased with the post treatment time in 0.1mol/L HCl solution. Thus, the HCl solution post treatment could weaken the cross-linking density between PNIPAAm chains and clay platelets and enhanced the mobility of PNIPAAm chains, resulting in the improvement of deswelling rate of S-N gel. Moreover, the deswelling behavior of all these S-N-H gels in Figure 7(b) exhibited almost the same trend of increasing response rate as above mentioned in Figure 7(a), in response to the concentration and post treatment time in HCl solution.

**LCST behavior of S-N and S-N-H gels**

LCST is the typical feature of temperature sensitive PNIPAAm hydrogels and it means the critical temperature where hydrophobic interactions of isopropyl groups of PNIPAAm outweigh the hydrophilic nature of the amide groups on the pendant groups [22]. The LCST thermograms obtained by DSC measurements for S-N and S-N-H gels are shown in Figure 8, which can evaluate the chain flexibility of PNIPAAm. The phase transition was unobservable in S-N gel with high clay content (more than 5wt%), due to the limitation of the coil-globule conformation change of PNIPAAm chains throughout the temperature range examined [9]. From Figure 8, we could see that the peak of phase transition became clearer with increasing HCl solution post treatment time. Thus, the HCl solution post treatment, accompanied...
with the ionic exchanges in the hydrogels network, resulting in the detachment of PNIPPAm chains and the improvement of mobility, had a significant influence on the LCST behavior. The results were in sound agreement with the deswelling/swelling behavior as mentioned above.

![Fig. 8.](image)

Conclusions

A series of rapid response nanocomposite hydrogels (S-N-H gels) were obtained after S-N gels post treatment by HCl solution. It was discovered for the first time that the properties of S-N gels could be modulated by HCl solution post treatment; the swelling ratio was apparently improved through the post treatment [e.g. from 6.91g/g for S-N gel to 22.99 g/g for S-N-H1T2 gel]. And the deswelling rate was also greatly increased, much faster than any other reported S-N gel, such as the water retention reduced from 65% for S-N gel to 28% for S-N-H gels within 3 minutes. These results were attributed to the ionic exchanges among H⁺ in HCl and metal ions in clay, leading to the changes of physical structure in hydrogel network. Compared with S-N gels, S-N-H gels show higher swelling ratio, faster deswelling rate and slower swelling rate, respectively. It resulted from the aggregation of some clay platelets and the detachment of PNIPPAm chains from clay platelets during the process of HCl solution post treatment, which could weaken the cross-linking density between PNIPPAm chains and clay platelets, and enhance the mobility of the PNIPPAm chains. We believe that the finding of the effects of HCl solution post treatment on the properties of S-N gels would help us to further investigate the structure of S-N gels and present a new approach to controlling the properties and structure of S-N gels. Furthermore, the S-N-H gels with high swelling ratio and fast deswelling rate is very useful for meeting their various applications in the future, such as drug fast delivery system and microcomponents, etc.

Experimental

Materials

N-Isopropylacrylamide (NIPAAm) (99%, Acros Co., Belgium), Laponite XLS (Clay-S) (Rockwood Co., U.S., 92.32wt% Mg_{5.34}Li_{0.66}Si_{8}O_{20}(OH)_{4}Na_{0.66}, 7.68wt%Na_{4}P_{2}O_{7}),
α-ketoglutaric acid (Shanghai Chemical Reagent Co., Analytic Reagent), HCl (PingHu chemical Reagent Co., Analytic Reagent) were all reagents were used as received and all solutions used were prepared in deionized water.

**Synthesis of S-N gels**

Uniform aqueous solution containing monomer (NIPAAm, 1.5 g), cross-linking agent (Clay, 1.5 g), and UV initiator (α-ketoglutaric acid, 2wt%, based on NIPAAm) was prepared first at room temperature. Then, the solution was introduced into a sealed container (interior size: length × width × thickness = 65 mm×15 mm×2 mm) and kept below 25 °C for 1 h for UV initiated polymerization. For measurements of swelling/deswelling behavior, hydrogels were used as-prepared in order to retain the equal water/monomer/clay/UV initiator ratio (10/1/1/0.02, w/w/w/w) for all gel samples.

**HCl solution post treatment of S-N gels**

After the polymerization, the samples (length× width × thickness = 20 mm×15 mm×2 mm) were immersed in HCl solution (0.05-1 mol/L) for several hours (1-8 h). Then, they were further washed by excessive deionized water at 25 °C for 72 h. During the washing process, the water was replaced every several hours with fresh water in order to leach out redundant HCl solution and other chemical residues. The feed compositions are listed in Table 4.

In this paper, hydrogels are expressed as S-N-H\textsubscript{m}T\textsubscript{n} gels, where S, N, H\textsubscript{m} and T\textsubscript{n} stand for Laponite XLS (Clay-S), NIPAAm, the concentration of HCl solution, post treatment time, respectively. For example, S-N-H0.1T4 stands for the S-N gel post treated by 0.1mol/L HCl solution for 4 hours.

**Tab. 4. All the feed compositions of S-N and S-N-H gels.**

<table>
<thead>
<tr>
<th></th>
<th>S-N-H0.1T\textsubscript{n} gel</th>
<th>S-N-HmT\textsubscript{n} gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>HCL (mol/L)</td>
<td>Time (h)</td>
</tr>
<tr>
<td>S-N</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S-N-H0.1T1</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>S-N-H0.1T2</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>S-N-H0.1T4</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>S-N-H0.1T8</td>
<td>0.1</td>
<td>8</td>
</tr>
</tbody>
</table>

**Fourier Transform Infrared (FTIR) Spectroscopy**

The infrared spectra of the samples taken as KBr pellets were measured with a Nicolet Nexus-670 FTIR spectrophotometer.

**Elements Analysis (EA)**

The element contents of dried S-N and S-N-H gels were analyzed by inductive coupled plasma atomic emission spectrometry (ICP-AES, Leeman Labs New Hampshire, USA).

**Measurements of X-ray Diffraction**

X-ray diffraction (XRD) measurement was carried out using dried S-N and S-N-H gels.
Samples were dried under atmospheric conditions (20 °C) for 12 h and then at 60 °C under vacuum for 4 h. XRD profiles of milled dried samples and clay were measured using an X-ray diffractometer (D/MAX-2550PC, RIGAKU, Japan) with Cu Kα radiation, 1.5°<2θ<10°.

**Measurement of Transmittance**

The transmittances of S-N and S-N-H gels were measured with a TU-1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd.), at 600 nm.

**Measurement of swelling behavior**

Swelling behavior of hydrogels was measured gravimetrically at 25 °C (below its LCST) after wiping off the excess surface water with moistened filter paper. Furthermore, the samples (length × width × thickness = 20 mm×15 mm×2 mm) for swelling kinetic study were dried from prior swollen ones. Swelling ratio (SR) is defined as follows:

$$SR = \frac{W_t}{W_d},$$

where $W_t$ is the weight of the swollen gel at the particular time, $W_d$ is the weight of the dry gel.

**Measurement of deswelling behavior**

The deswelling behavior of hydrogels was measured gravimetrically at 50 °C (above its LCST) after wiping off the excess surface water with moistened filter paper. All gel samples were cut in the same size (length × width × thickness = 20 mm×15 mm×2 mm). Before this measurement, the samples reached equilibrium in deionized water at 25 °C. Water retention (WR) is defined as follows:

$$WR = 100 \times \frac{(W_t - W_d)}{W_s},$$

where $W_s$ is the weight of equilibrium swollen gel and others are the same as defined above.

**Measurement of LCST behavior**

The LCST behavior of S-N-H gels was determined using DSC (TA 2910 Modulated DSC, TA instruments, USA). The samples were placed in a hermetic sample pan and then sealed. The thermal analyses were performed at a heating rate of 1 °C/min under a dry nitrogen atmosphere (flow rate of 40 ml/min).

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