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Solvents Triggered Coil-to-Globule-to-Coil Transition of Dual Nanocomposite Hydrogels with Inorganic Hybrid Crosslinking

This paper presents the study on the reentrant solvation of dual nanocomposite hydrogel poly-N-isopropylacrylamide/Laponite/SiO_2 (PNIPAM/Laponite/SiO_2) upon shrinkage/reswelling process. Depending on the unique hierarchical microstructure of inorganic hybrid crosslinking of Laponite and $SiO_{2,}$ as well as the preferential interaction of polar solvents with PNIPAM chains, the hydrogel exhibited rapid coil-to-globule-to-coil transition in water-polar solvent mixtures. The solvation behavior could be controlled through varying types of organic solvents. Shrinkage in water-polar solvent mixtures occurred as a consequence of strong interaction between polar solvents and PNIPAM chains, whereas reswelling resulted from the direct interaction of the solvent molecules with the intermolecular water in the hydrogel. The attractive competing effects on forming hydrogel-water and hydrogel-polar solvent hydrogen bonds were considered to be indispensable to the solvation. The rapid response rate was attributed to the synergistic effect of the unique heterogeneous microstructure with inorganic hybrid crosslinking and preferential interaction of polar solvents with polymer chains. The mechanism proposed in this paper provides a new reference on design of smart soft matter systems. Moreover, several solvation effects described in this paper can be incorporated in theory of cononsolvent-induced conformational transitions in the nanocomposite hydrogels with inorganic hybrid crosslinking.

Keywords: inorganic hybrid crosslinking, dual nanocomposite hydrogel, coil-to-globule-to-coil transition, poly-N-isopropylacrylamide, polar solvent.

Introduction

Smart hydrogels have attracted increasing attention since they can exhibit dramatic change of volume or other properties in responding to external stimuli, such as temperature [1–3], pH [4–8], humidity [9–12], special ions or molecules [13–16], ionic strength or electric field [17, 18]. They are often involved in liquid environments, i.e., salt solutions, organic solvents, or both of them when applied in the field of cell culture, drug delivery, plant cultivation, soft actuator, etc. Therefore, it is crucial to have a better understanding of the swelling behavior of gels in different medium. The swelling of chemically crosslinked hydrogels are mainly focused in different salt solutions [19–22], polymer aqueous solutions [21, 23], or aqueous solutions of organic solvents [24–29]. It was found that the composition of solution has a great impact on the swelling behavior of the hydrogel. Cononsolvency is one of the most intriguing phenomena in physical chemistry of polymers, where a polymer perfectly soluble in two different solvents becomes insoluble in mixtures of both. The typical example is poly-N-isopropylacrylamide (PNIPAM) in water-methanol mixtures [30–32]. At a fixed temperature, PNIPAM can be easily dissolved in both pure water and pure methanol to form an optically transparent solution. However, mixing the two solvents in certain proportions led to the precipitation of polymer phases. Many efforts have been made to control the cononsolvency of PNIPAM hydrogels by shifting the content of alcohols. So far, most of those trials focus on the cononsolvency of organically crosslinked PNIPAM hydrogels. However, such hydrogels usually have a limited application owing to poor mechanical properties [33].

Haraguchi et al. reported a physically crosslinked PNIPAM/Laponite nanocomposite hydrogel which has remarkable mechanical properties (i.e., elongation at break: about 1000 %, tensile strength: 1.00 MPa) [33–35]. The nanoscaled Laponite platelets are uniformly dispersed in the gel and a large number of polymer chains are attached to their surfaces forming physical crosslinking points [36]. As a result, the thermosensitivities and swelling/deswelling of the nanocomposite hydrogel was subject to steric hindrance by clay platelets and the coil-to-globule transition was prohibited at high Laponite content (greater than 10×10^{-2} mol/L). This may be due to the restriction of the thermal molecular movement of PNIPAM chains attached to the hydrophilic clay nanosheets [34, 35]. In our previous work, a dual nanocomposite hydrogel (PNIPAM/Laponite/SiO_2) with inorganic hybrid crosslinking network was successfully fabricated through simultaneous sol-gel technique and free radical polymerization. The gel exhibited high stiffness and toughness (i.e., elongation at break: 1845%, fracture strength: 271.41 kPa; compression stress: 7.06 MPa; fracture energy: 1185.53 $J\cdot m^{-2}$) [37]. It is a promising candidate for various disciplines such as biomedicine, tissue engineering, soft actuators, etc.

We found that the hydrogel showed an interesting and rapid coil-to-globule-to-coil transition in polar solvents at ambient temperature. The hydrogel could become opaque (collapsed) quickly at first within short intervals when soaked in polar solvents (such as ethanol and dimethyl formamide), and then turned to transparent (reswelled) gradually in hundreds of minutes. The phenomenon inspired us to explore the solvation behaviors and possible mechanism. Herein, different polarity and contents of solvents were used to investigate the competitive interactions (hydrogen bond) between polymer-water and polymer-organic solvents. The dependence of the response rate of the hydrogel on the gel microstructure and interaction of polymer-solvents was discussed. The reentrant solvation mechanism was proposed.

Experimental

Materials

Tetraethyl orthosilicate (TEOS) was purchased from Sigma-Aldrich Co.; *N*-isopropylacrylamide (NIPAM) was bought from J&K Scientific; *N,N,N',N'*-tetramethylethylenediamine (TEMED) was provided by Aldrich Chemical Co.; potassium peroxydisulfate (KPS) was purchased from Beijing Beihua Fine Chemicals Co. and Laponite XLG [$Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$] was provided by Rockwood Co.; *N,N'*-methylene-bis-acrylamide was obtained from China Medicine Group Shanghai Chemical Reagent Corporation; ethanol and acetone were supplied by Tianjin Yongsheng Fine Chemicals Co.; tetrasodium pyrophosphate ($Na_4P_2O_7$) was bought by Shanghai Kechang Fine Chemicals Company; dimethyl formamide (DMF) was purchased from Tianjin Yongda Chemical Reagents Co. Ltd.; dimethyl sulfoxide and cyclohexane were provided by Tianjin Zhiyuan Chemical Reagent Co. Ltd.; benzyl alcohol was bought from Tianjin Guangfu Institute of Fine Chemicals. All reagents were used as received without any further purification. Deionized water was used in all experiments.

Hydrogel synthesis

The PNIPAM/Laponite/SiO_2 dual nanocomposite hydrogel was prepared by simultaneous *in-situ* free radical polymerization and sol-gel technique. Typically, a transparent aqueous dispersion consisting of water (10.0 g), Laponite (0.5 g), $Na_4P_2O_7$ (0.0384 g), NIPAM (1.0 g) and TEOS (1.0 g) was prepared under stirring at room temperature for 48 h until a transparent and stable dispersion was obtained. Then, initiator KPS (2 wt%, 1.0 mL) and catalyst TEMED (50.0 μL) were added into the above dispersion with stirring, respectively. Afterwards, the pre-polymerization dispersion was transferred to a sealed glass tube and the polymerization was carried out at room temperature for 72 h to obtain the PNIPAM/Laponite/SiO_2 dual nanocomposite hydrogel.

As a control, PNIPAM/Laponite nanocomposite hydrogel was fabricated in a similar manner except for the free of TEOS, and the organically crosslinked PNIPAM hydrogel was synthesized by the same procedure described above except for using organic crosslinker *N,N'*-methylene-bis-acrylamide instead of Laponite and TEOS, respectively.

Characterization

Fourier transform infrared (FTIR) measurements were recorded on a Fourier transform infrared spectrometer (VERTEXFTIR, Bruker). All spectra in the range of 400–4000 cm^{-1} with 2 cm^{-1} spectral resolution were obtained. Scanning electron microscope (SEM) images were obtained on a scanning electron microscope (TM3030, Hitachi) at an accelerating voltage of 20 kV. The SEM samples were prepared by immersing the gel into ethanol (or DMF), water and ethanol (or DMF) in turn to reach phase equilibrium. The samples obtained through the every procedure above were freeze drying (FD-1C-50, Beijing Boyikang) for 48 h. Afterwards, the dry hydrogels were coated with gold prior to SEM analysis. The heat effect associated to the coil-to-globule-to-coil transition of the dual nanocomposite hydrogels in water/organic solvent mixtures were measured using a differential scanning micro-calorimeter (DSC, Q2000, TA) by modulation mode. The difference in the heat capacity of gels containing different volume fraction of water and organic solvents and the heat capacity of the gels were measured upon heating at a rate of 2^{o}C/min.

Results and Discussion

Solvents triggered coil-to-globule-to-coil transition

The PNIPAM/Laponite/SiO_2 dual nanocomposite hydrogel exhibited an interesting solvation behavior when soaked in ethanol: it became opaque (collapsed) quickly at first within 0.25 min, and then turned to transparent (reswelled) gradually after 245 min. During this process, the gel underwent an uneven solvation, and the periphery became transparent more quickly than the center (Fig. 1*a*). We further immersed the gel into the mixtures with different volume fraction of ethanol and water, and found that the reentrant coil-to-globule-to-coil transition was dependent of volume fraction of ethanol. When the ethanol volume fraction was low (below 20%), the gel remained transparent and the collapse-reswelling transition did not occur. It was probably because that low content of ethanol was hardly disturbed the interaction between PNIPAM chains and water. The solvation occurred gradually with the increase of ethanol content. When the volume fraction of ethanol was 30%–60% ($n_{ethanol}$:n_{water} from 0.13 to 0.47 accordingly), the gel turned to translucent within 0.25 min, and then became opaque (collapsed) gradually. There was no further change observed even after 3 days. These results were in good agreement with those reported by Hirotsu et al. and Wu et al. They found that the organically crosslinked PNIPAM gel and linear PNIPAM became opaque when $n_{ethanol}$:n_{water} from 0.17 to 0.50 [38, 39]. This suggested that the coil-to-globule transition was independent of the type of crosslinking. However, further to increase the volume fraction of ethanol (above 80%), the gel could experience the reentrant coil-to-globule-to-coil transition (i.e., the transparent gel quickly became opaque after contacting with ethanol solution, and then became transparent again) in a relatively short period because of the dissolution of the aggregated PNIPAM chain segments (Fig. 1*a*). Those phenomena made it possible to realize controllable solvation of the dual nanocomposite hydrogels upon the composition of organic solvents and soak time. Besides, the unusual phase behavior was independent of the shape of the gel (Fig. 1*b*). These results provided the possibility of programmable control of solvation of the gel by changing the solvent composition.

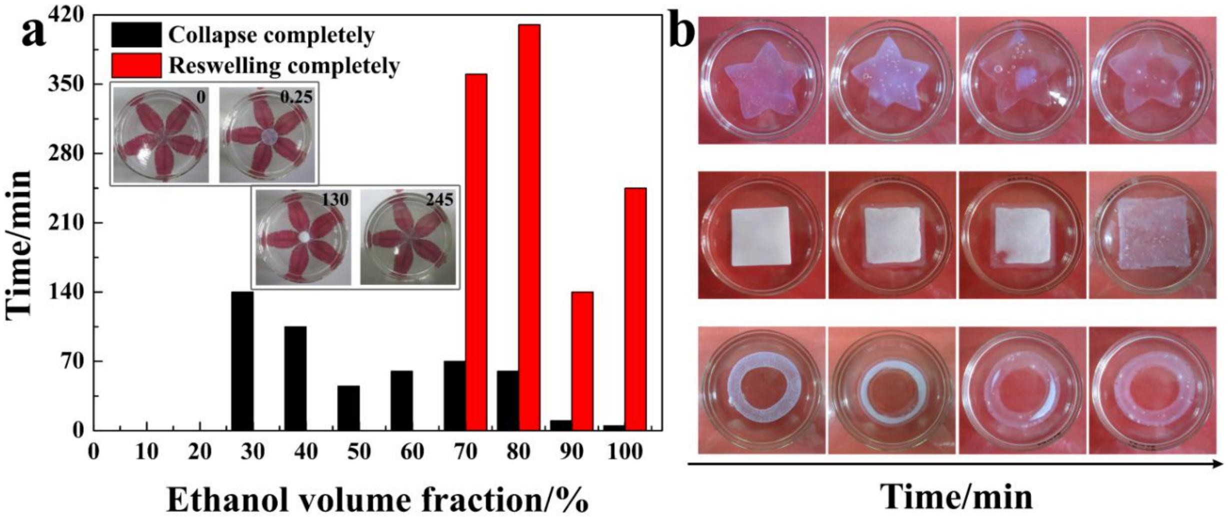

Figure 1. *a* — The influence of ethanol volume fraction on the reentrant coil-to-globule-to-coil transition of the dual nanocomposite gels (the inset: optical photographs of the reentrant solvation of the gels in 70% ethanol volume fraction observed at room temperature); *b* — The dual nanocomposite gels with various shapes (pentagram, square, and annulus) were immersed in ethanol

Both shrinkage and reswelling procedures of the dual nanocomposite hydrogel were reversible. When the gel reached phase equilibrium in ethanol first, and then immersed it in water, the transparent gel could become opaque quickly and eventually turned transparent. If the same gel block was re-submersed in ethanol again, it still showed a significant contraction-expansion transition in hundreds of minutes. As the gel finished solvation in ethanol, it exhibited a heterogeneous structure and the pores size of the gel network became more irregular (Fig. 2*b*) in contrast with the gel which reached swelling equilibrium in water (Fig. 2*a*). When the gel reached phase equilibrium in water again, the pore size of the gel network was recovered in some degree and became more uniform (Fig. 2*c*). Although the gel achieved phase separation in ethanol completely, the pores of the gel presented a serious irregular shrinkage due to further destruction of the gel network (Fig. 2*d*). The microstructure of the hydrogel is a critical factor in the response rate of the solvation process. The response rate of the hydrogel is inversely proportional to the size of the gel. However, in our work, the bulk dual nanocomposite gel could quickly collapse (opaque) in ethanol within 0.25 min and then reswell (transparent) again since the synergistic effect of the unique heterogeneous microstructure of dual nanocomposite and preferential interaction of ethanol with PNIPAM chains (Fig. 2*e*). The hydrophobic interaction led to rapid dehydration and solvation of the gel, while the dual nanocomposite configuration could provide an interconnected water release channel throughout the hydrogel and the free water could diffuse out quickly. Combined with the above results, it could be seen that the change of gel microstructure caused by solvent is closely related to its reentrant coil-to-globule-to-coil transition.

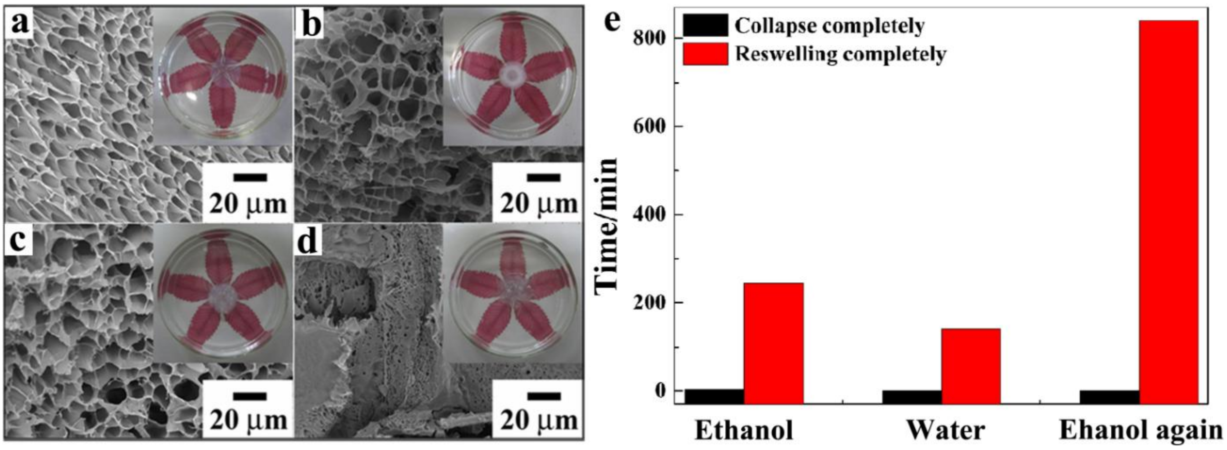

Figure 2. SEM micrographs of the dual nanocomposite hydrogels treated through following processing: *a* — the gel reached swollen equilibrium in water; *b* — the gel reached phase equilibrium in ethanol beforehand; *c* —and then in water; *d* — finally in ethanol again(the orange circles represent the gel collapsed completely, the pink circles represent the gel reswelled completely, respectively); *e* — The influence of alternate treated process on the reentrant coil-to-globule-to-coil transition of the dual nanocomposite hydrogels

Different solvents were used to account for the influence of polarity on the reentrant coil-to-globule-to-coil transition. It was found that these complex solvations were closely driven by the preferential binding of polar or non-polar solvents with PNIPAM chains in the hydrogel matrix (Fig. 3*a*). The gel experienced an obvious reentrant collapse-reswelling transition in polar solvents (such as dimethyl sulfoxide, DMF, ethanol, and acetone). However, the gel had no significant change when was immersed into non-polar solvent (such as cyclohexane). It is speculated that the favorable interaction with water and polar solvents lead to the different solvation behavior. Initially, the gel was surrounded by cages of water molecules due to the stable hydrogen bonds formed between polymer chains and water molecules. As a result, the gel was transparent. When non-polar solvents were added, the solvent could not destroy the structure of water due to the poor solute-solvent interactions. At this time, the gel could still remain transparent. However, when polar solvents were added with favorable interaction with the water surrounded the gel, the competition between PNIPAM molecular chain shrinkage and interchain aggregation decreased the stability of the hydrogen-bonded water structure, ultimately leading to phase separation (the coil-to-globule transition) of the dual nanocomposite hydrogel. As a result, the gel became opaque. This is consistent with the report of Grosberg and Yang [40, 41]. With the proceeding of process, all the water molecules around the gel were combined with the polar solvent, resulting in the interaction between the polar solvent and PNIPAM chains stronger than that between the polymer and water. Finally, the gel became transparent again (the transition of globule-to-coil).

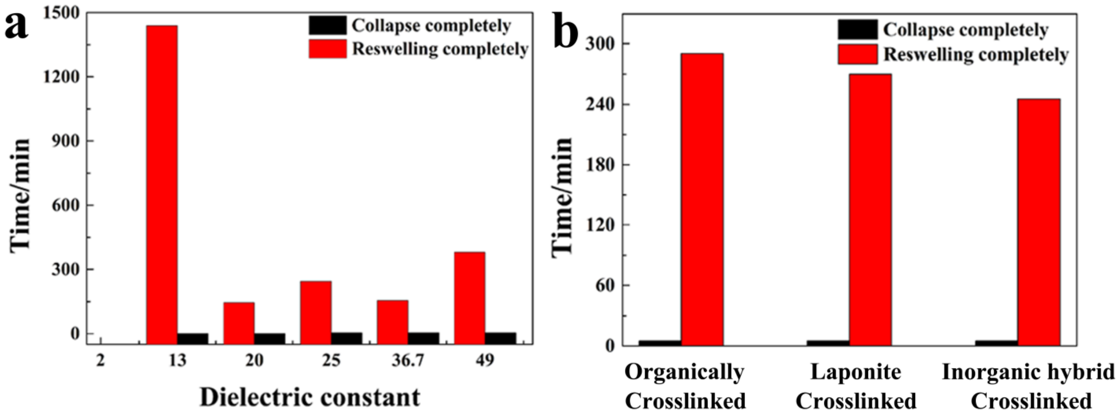

Figure 3. The influence of solvents polarity (*a*) and crosslinked network (*b*) on the reentrant coil-to-globule-to-coil transition of the dual nanocomposite hydrogels, respectively

To figure out the impact of crosslinked network on the solvation, gels with different crosslinking networks (organically crosslinking, Laponite crosslinking, and hybrid inorganically crosslinking) were soaked in ethanol. The results showed that this uneven solvation behavior still existed despite the different types of crosslinking. In comparison, the gel with hybrid inorganically crosslinking network reached phase equilibrium in a relatively short time (Fig. 3*b*). Those were mainly attributed to the dual nanocomposite network structure in which clay platelets and SiO_2 particles, uniformly dispersed on nanoscale, act as multifunctional cross-linking units whereby a large number of polymer chains are attached to the surface of clay platelets and SiO_2 particles forming hybrid cross-linking points. The unique heterogeneous dual nanocomposite network structure could facilitate the diffusion of solvent in the gel network. It indicated that the solvation behavior was related to the strong interactions between the hydrogel backbone polymer and the polar solvents, while the response rate was mainly attributed to the unique nanocomposite network structure.

The pretreatment process would influence the solvation of the gel. When the gel reached swelling equilibrium in water at first, and then immersed into DMF solutions with different volume fractions, all gels experienced the same reentrant collapse-reswelling behavior: from transparent to opaque, and eventually become transparent again. However, if the gel reached phase equilibrium in DMF solutions with different volume fractions beforehand and then immersed into water, a different solvation phenomenon was observed instead. At low volume fractions of DMF (below 40%), the gel could maintain transparent all the time. As the DMF volume fraction increased (from 50% to 70%), the gel underwent an opaque-to-transparent transition. Further enhancing the volume fraction of DMF (from 80% to 100%), the transparent gel became opaque at first and then turned to transparent again in a few minutes (Table 1). When immersed into DMF first, the strong interaction between the water surrounded the gel and DMF molecules could disturb the hydrogen bonding between gel and water, which led to a decrease in the transparency of the gel after the phase equilibrium was reached. Afterwards, the competing interaction between DMF and water occurred, and finally the gel became transparent again in water in all circumstances due to formation of durable cages of water molecules surrounding the gel.

Table 1

The phenomena of the dual nanocomposite hydrogels reached phase equilibrium in the DMF-water mixture with different DMF volume fractions first, and then soaked it in water

DMF volume fraction	Phenomenon
	Reached phase equilibrium in DMF-water beforehand → Then immersed in water → Reached phase equilibrium in water finally
1	2
0 %	Transparent 

Continuation of Table 1

1	2
10 %	Transparent 
20 %	Transparent 
30 %	Transparent 
40 %	Transparent 
50 %	Opaque → Transparent 
60 %	Opaque → Transparent 
70 %	Opaque → Transparent 
80 %	Transparent → Opaque → Transparent 
90 %	Transparent → Opaque → Transparent 
100 %	Transparent → Opaque → Transparent 

Solvation mechanism

The effects of solvents on the solvation of the dual nanocomposite hydrogels were further investigated using DSC analysis. To avoid the evaporation of ethanol due to its low boiling point (78.0^{o}C), DMF (152.8^{o}C) was employed as the model solvent for exploration on solute-solvent interaction. The solvation temperature of the gel was 36.0^{o}C in water, accompanying sharp change in polymer conformation from a balance between hydrogen bonding of water on the chain (hydration) and hydrophobic aggregation of isopropyl groups, and presented an obvious endothermic peak in DSC curves [42]. The hydrogels demonstrated a significant shift in the transition temperature as the volume fraction of DMF varied (Fig. 4*a*). This observation was consistent with the initial experiments by Winnik et al., in which the effect of methanol as a cosolvent for linear PNIPAM in dilute aqueous solutions was investigated [31]. With the increasing of DMF volume fractions, the interaction between the gel and water was broken, and the interactions between the gel and polar solvents were dominated. As a consequence, the endothermic peak around 36.0°C became unapparent and then disappeared gradually. Instead, some new endothermic peaks at higher solvation temperature were observed at low DMF volume fraction, suggesting a strong interaction formed between DMF and water. In the end, only a solvation temperature of 51.2°C was found owing to the interaction between the gel and DMF. It is conjectured that there existed a competitive effect between the gel and water, as well as the gel and DMF. With the augment of DMF, the interaction between gel and water was substituted by DMF and gel. It was clearly observed that the solvation temperature was 51.2 °C when the gel was immersed in pure DMF, while it exhibited two distinct solvation temperatures (36.0 °C and 49.5 °C) when immersed in water afterwards. Finally, the solvation temperature changed to 50.5°C when soaked in pure DMF again (Fig. 4*b*). SEM images showed that when the hydrogel was soaked in DMF first, the pores became irregular and collapsed to a certain extent (Fig. 4*c*) in contrast with the gel which reached swelling equilibrium in water (Fig. 2*a*). After the gel attained phase equilibrium in water again, the gel network was recovered in some degree (Fig. 4*d*). However, when the gel achieved phase separation in DMF completely once again, the pores of the gel were severely damaged again due to further destruction of the gel network (Fig. 4*e*). The SEM morphology of the gel in different solvents showed that the collapse and reswelling transformation was reversible, which also confirmed the strong interaction between the polar solvent DMF and the hydrogel.

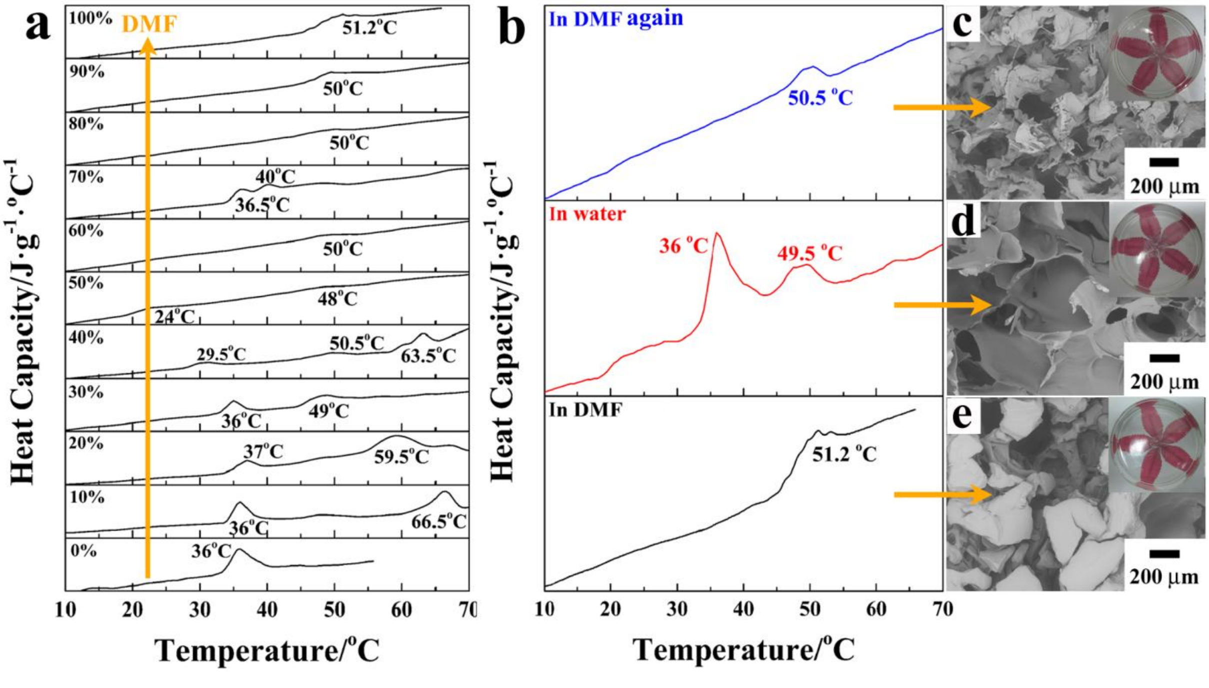

Figure 4. Temperature dependence of the heat capacity of PNIPAM/Laponite/SiO_2 dual nanocomposite hydrogels: *a* — in DMF-water mixtures with various volume fractions of DMF; *b* — treated through the following processing: the gel reached phase equilibrium in DMF beforehand, and then in water, finally in DMF again (left were the SEM images of the gels in above process)

To verify the conjecture above, the solvent dependence of the absorption bands of the dual nanocomposite hydrogel in varied volume fraction of DMF-water mixtures (0%–100%) was explored by FTIR. The absorption bands at about 1652 cm^{-1} and 1500 cm^{-1} could be attributed to the vibration of C=O hydrogen bonded with N–H from DMF (1600–1700 cm^{-1}) and C–N bond from DMF bonded with water and the gel (1500–1600 cm^{-1}), respectively [43–46]. The bands at 1652 cm^{-1} shifted to higher wavenumbers while the intensity of the bands increased significantly with the increase of DMF volume fraction (Fig. 5*a*). Similarly, the bands at 1500 cm^{-1} also shifted to higher wavenumber, while the intensity of the band rose but in a lower degree compared with the one at 1652 cm^{-1}. This evidence confirmed that with the increase of DMF volume fraction, the C=O groups of the hydrogel dehydrated gradually and previous hydrogen bonds (C=O···H–O) was replaced by new hydrogen bonds (C=O···N–H). Thus, a blue shift and intensity increase were observed. Besides, it was further confirmed that intermolecular hydrogen bonds acted a key role in solvation behaviors owing to a blue shift of the adsorption peaks. A similar trend was found for the peaks at 1500–1600 cm^{-1} since it was contributed to breakage of C–N···H–O–H and formation of C–N···H–N. As Tanaka reported, the sharp reentrant coil-to-globule-to-coil transition of PNIPAM chain in a mixture of water and methanol was caused by competitive hydrogen bonds between water and methanol molecules onto the polymer chain [47]. In Figure 5b, after the same block of dual nanocomposite hydrogel was treated by DMF, water and DMF alternatively, there was a noticeable change concerning the bands of C=O hydrogen bonded with N–H (1600–1700 cm^{-1}) and C–N···H–O–H, as well as C–N···N–H (1500–1600 cm^{-1}) together with an intensity increase at about 1652 cm^{-1} and 1500 cm^{-1} when reached phase equilibrium in the presence of DMF. The destruction of C=O···H–O–H hydrogen bonds between the gel and intermolecular water took place on a very short time scale, faster than the formation of C=O···H–N, C–N···H–O–H, and C–N···H–N hydrogen bonds [48, 49]. Also, it is clearly observed that the gel has recovered in some degree, which was in consistent with SEM (Fig. 2*a*–*d*) and DSC analysis (Fig. 4*b*) of the gel. In conclusion, the competitive hydrogen bonding occurred between DMF and the gel was the main reason for the special solvation of the gel.

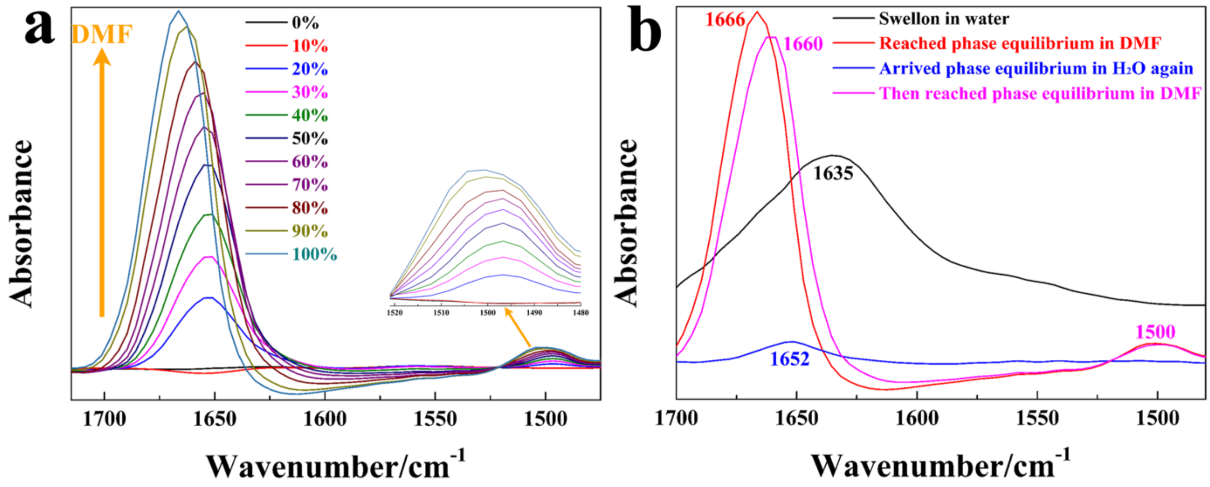

Figure 5. FTIR spectra of PNIPAM/Laponite/SiO_2 dual nanocomposite hydrogels recorded between 1750–1400 cm^{-1}: *a* — as a function of DMF volume fraction; *b* — treated through the following processing: made the gel reach phase equilibrium in DMF beforehand, and then let the same block of gel reach phased equilibrium in water, finally made this gel reach phase equilibrium in DMF again

The solvation mechanism of the dual nanocomposite hydrogel in polar solvents was proposed as follows with DMF as an example: at a lower content of polar solvent, the interaction between PNIPAM chain and water is stronger than that between polar solvent and water. In this case, water clathrate cavities for DMF molecules may be formed (Figure 6*a*). Therefore, the gel maintains transparent and the collapse-swelling transition does not occur due to unbroken interaction between PNIPAM chains and water. With the increasing of polar solvent content, the interaction between gel and water is broken, and the interaction between gel and polar solvent is dominant. As a result, the gel undergoes a coil-to-globule transition (opaque) within a few minutes. It is because no sufficient water molecules to provide clathrate cavities for all the DMF molecules, and DMF breaks the partial hydrogen bonds of C=O···H–O–H and C–N···H–O–H while forms new hydrogen bonds of C=O···N–H and C–N···H–N (Scheme 1b). On this basis, by further increasing the contents of polar solvents, the gel can experience a coil-to-globule-to-coil transition in a relatively short period. In contrast, in non-polar solvents, they can coexist peacefully with the intermolecular water owing to the unfavorable interactions with non-polar solvents and the water surrounded the gel (Figure 6*c*).

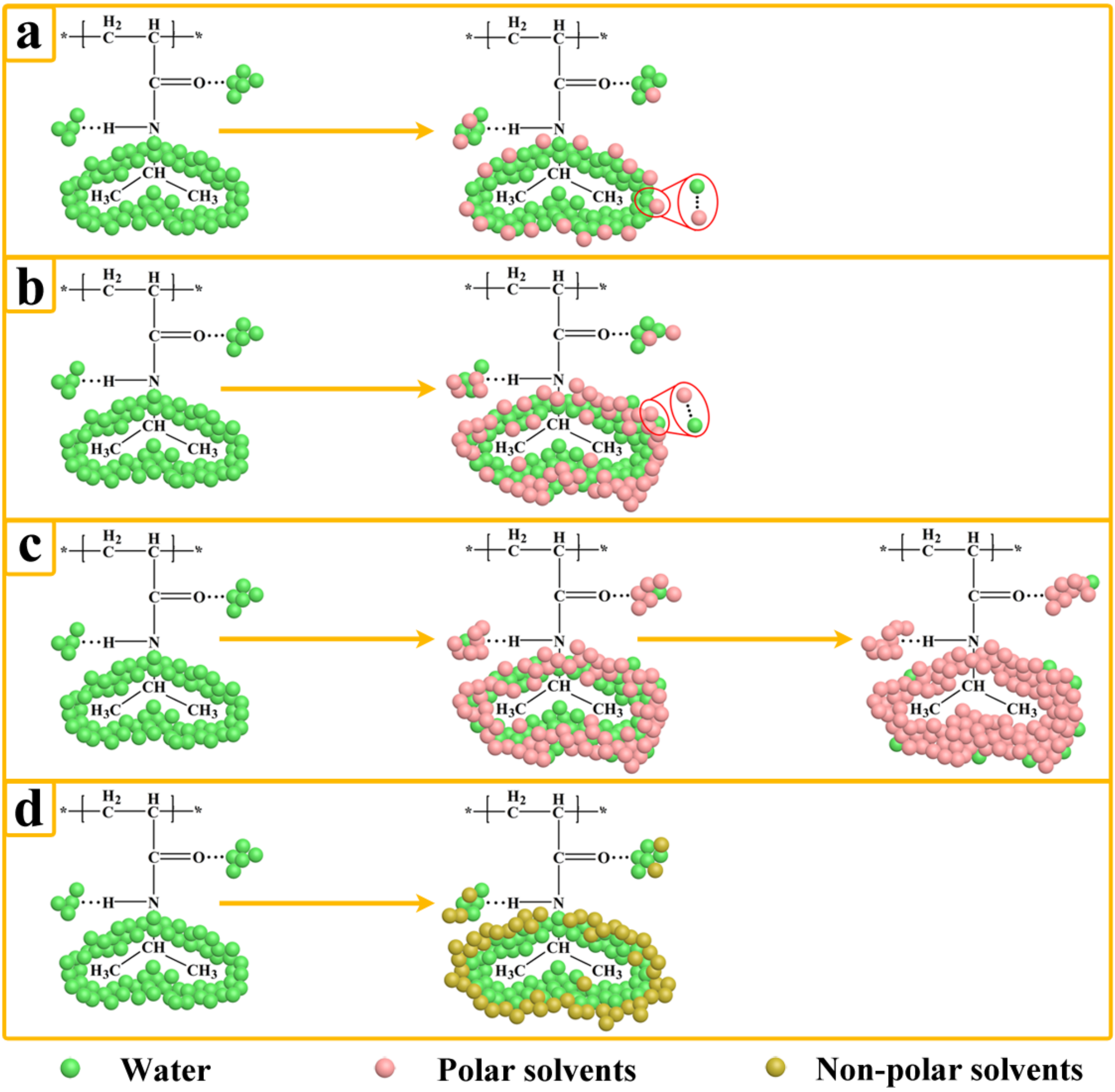

Figure 6. The reentrant solvation mechanism of PNIPAM/Laponite/SiO_2 dual nanocomposite hydrogel soaked in different solvents: *a*, *b* and *c* — in polar solvents (take DMF as an example: *a* — the volume fraction of DMF was below 50 %; *b* — the volume fraction of DMF was between 50 % and 70 %; *c* — the volume fraction of DMF was above 70 %); *d* — pure non-polar solvents

Conclusions

In conclusion, rapid collapse and reswelling behaviors were observed in dual nanocomposite hydrogels PNIPAM/Laponite/SiO_2. The solvation of the hydrogels could be easily controlled by adjusting the type and concentration of solvents and soaking time. The reentrant coil-to-globule-to-coil transition was attributed to competitive interactions between the hydrogel backbone polymer and the solvents: the breakdown or formation of hydrogen bonds between the polymer chains and water/polar solvents. With the increasing of polar solvents, the intramolecular hydrogen bonds between the C=O or C–N groups of PNIPAM and water molecules were damaged and new intra- and inter-chain bonds were formed between PNIPAM and polar solvents. Besides, the rapid response rate was attributed to the synergistic effect of the unique heterogeneous microstructure and preferential interaction of polar solvents with the polymer chains. The dual nanocomposite hydrogel exhibited fast and reversible solvent-responsive collapse-reswelling characteristics, as well as improved mechanical properties. It will be highly attractive and promising in many applications for on-off switches, artificial organs and actuators in liquid environments.

Acknowledgments

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Хуан Ду, Шимей Сюй

Бейорганикалық гибридті айқаспалы қос нанокомпозитті гидрогельдердің еріткішпен индукцияланған «клубок–глобула–клубок» ауысуы

Жұмыста қос нанокомпозитті поли-N-изопропилакриламид/лапонит/SiO_2 (PNIPAM/лапонит/ /SiO_2) гидрогелінің шөгу/қайта ісіну кезіндегі кері сольвациясы зерттелген. Лапонит пен SiO_2 бейорганикалық гибридті қиылысуының бірегей иерархиялық микроқұрылымына, сондай-ақ полярлы еріткіштердің PNIPAM тізбегімен преференциялық әрекеттесуіне байланысты гидрогель су-полярлы еріткіш қоспаларында жылдам «клубок-глобула-клубок» ауысуын көрсетті. Шешім әрекетін органикалық еріткіштердің әртүрлі түрлерімен басқаруға болады. Су-полярлы еріткіш қоспаларындағы шөгу полярлы еріткіштердің PNIPAM тізбегімен күшті әрекеттесуі нәтижесінде, ал қайта ісіну еріткіш молекулаларының гидрогельдегі молекулааралық сумен тікелей әрекеттесуі нәтижесінде пайда болды. Сольватация үшін алынған гидрогель-су және гидрогель-полярлы еріткіш сутегі байланыстарында бәсекелес тартылу эффектілері қажет деп саналды. Жоғары жауап беру жылдамдығы бейорганикалық гибридті айқаспалы байланыстары бар бірегей гетерогенді микроқұрылымның синергиялық әсерімен және полярлы еріткіштердің полимерлі тізбектермен преференциялық әрекеттесуімен түсіндіріледі. Мақалада ұсынылған механизм интеллектуалды жұмсақ заттар жүйелерін жобалауға жаңа сілтеме береді. Сонымен қатар, мақалада сипатталған кейбір сольвационды әсерлерді бейорганикалық гибридті айқаспалы байланысы бар нанокомпозиттік гидрогельдердегі еріткішпен индукцияланған конформациялық ауысулар теориясына қосуға болады.

Кілт сөздер: бейорганикалық гибридті кросс-байланыс, қос нанокомпозитті гидрогель, «клубок-глобула-клубок» ауысуы, поли-N-изопропилакриламид, полярлы еріткіш.

Хуан Ду, Шимей Сюй

Индуцируемый расворителями переход «клубок–глобула–клубок» двойных нанокомпозитных гидрогелей с неорганической гибридной сшивкой

В статье исследована возвратная сольватация двойного нанокомпозитного гидрогеля поли-N-изопропилакриламид/лапонит/SiO_2 (PNIPAM/лапонит/SiO_2) в процессе усадки/повторного набухания. В зависимости от уникальной иерархической микроструктуры неорганического гибридного сшивания лапонита и SiO_2, а также предпочтительного взаимодействия полярных растворителей с цепями PNIPAM гидрогель демонстрировал быстрый переход «клубок–глобула–клубок» в смесях вода–полярный растворитель. Поведением сольватации можно управлять с помощью различных типов органических растворителей. Усадка в смесях вода–полярные растворители происходила в результате сильного взаимодействия полярных растворителей с цепями PNIPAM, тогда как повторное набухание возникало в результате прямого взаимодействия молекул растворителя с межмолекулярной водой в гидрогеле. Для сольватации считалось необходимым наличие конкурирующих эффектов притяжения в образующихся водородных связях гидрогель–вода и гидрогель–полярный растворитель. Высокая скорость отклика объясняется синергетическим эффектом уникальной гетерогенной микроструктуры с неорганическими гибридными сшивками и преимущественным взаимодействием полярных растворителей с полимерными цепями. Предложенный авторами статьи механизм дает новую ссылку на проектирование интеллектуальных систем мягкой материи. Кроме того, описанные в статье некоторые эффекты сольватации могут быть включены в теорию индуцированных сорастворителем конформационных переходов в нанокомпозитных гидрогелях с неорганической гибридной сшивкой.

Ключевые слова: неорганическая гибридная сшивка, двойной нанокомпозитный гидрогель, переход «клубок–глобула–клубок», поли-N-изопропилакриламид, полярный растворитель.

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