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ORIGINAL CONTRIBUTION

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Dynamics studies on thermoresponsive poly(*N*-isopropylacrylamide) hydrogel in tetrahydrofuran/water mixtures

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Abstract The properties of thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel in tetrahydrofuran/H_2O mixtures were studied. Scanning electron microscopic (SEM) images demonstrate that the hydrogel changes from homogeneous to heterogeneous microstructure upon the addition of tetrahydrofuran to water. This heterogeneous PNIPAAm hydrogel in the mixture solvent exhibits a very slow response rate at temperatures above its lower critical solution temperature. The decreased response rate is attributed to the formation of special ternary complexes including the polymer and the two solvents in the tetrahydrofuran/H_2O mixture. Factors controlling the thermoresponse rate are discussed further and several suggestions are provided for designing and developing fast-response PNIPAAm hydrogels in the future.

Keywords Poly(*N*-isopropylacrylamide) · Hydrogel · Heterogeneous · Thermoresponse · Tetrahydrofuran/water mixture

Introduction

Hydrogels showing changes in their structure and physical properties in response to external stimuli, such as temperature and pH, are defined as intelligent hydrogels; such hydrogels are important materials of both fundamental and application interests. Among intelligent hydrogels, poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel is the most studied temperature-sensitive hydrogel, having a critical temperature or lower critical solution temperature (LCST) around 33 °C [1, 2]. During the past decade, considerable efforts have been devoted to understand the phase separation of PNIPAAm that occurs when it is brought to temperatures above its LCST. Owing to this unique property, PNIPAAm hydrogels have been widely used in biomedical fields, including protein–ligand recognition [3], immobilization of enzymes [4] and drug controlled release [5]. However, in some cases, such as on–off switches [6], artificial organs [7] and actuators [8], the practical effects by using conventional PNIPAAm hydrogels are not as good as expected owing to response rate limits. As a result, improving the thermoresponse rate is critically important and several techniques have been proposed to prepare fast-response PNIPAAm hydrogels.

Preparing a PNIPAAm hydrogel with a heterogeneous structure is an effective strategy in accelerating its response rate. One of the original studies was carried out by Kabra et al. [9], where the hydrogel was polymerized at 37.9 °C (above the LCST). At this temperature the polymerizing PNIPAAm chains phase-separated from the monomer solution and the final PNIPAAm hydrogel was heterogeneous in microstructure. This hydrogel exhibits an extremely fast response rate compared with that of the conventional homogeneous PNIPAAm hydrogel. Subsequently, Wu et al. [10] developed a method where fast-response hydrogels were synthesized at 50 °C and the reactor was evacuated near the end of the polymerization. Although they attributed the fast response rate to the macroporous structure produced, they agreed that the three-dimensional hydrogel was formed in a two-phase system (the aggregated polymer chains and the solution of monomer). Yan et al. [11] also prepared a fast-response PNIPAAm hydrogel with a similar method at two continuous polymerization temperatures: 4 °C (below the LCST) and 50 °C (above the LCST). Overall, increasing the polymerization temperature above the LCST was a good method to prepare a heterogeneous hydrogel with fast response rate.

In our previous work [12, 13], siloxane-incorporated PNIPAAm hydrogels with fast responses to temperature changes were created by using 3-methacryloxypropyltrimethoxy silane and ethylenetriethoxy silane as the cross-linking agents. The fast response rate of this hydrogel was attributed to the heterogeneous microstructure based on the hydrophobic cross-linker. Very recently, we used a mixed solvent as the polymerization solvent to prepare a heterogeneous PNIPAAm hydrogel [14, 15]. It was proposed that during the polymerization/cross-linking reaction in a mixed solvent, the monomer and the cross-linker polymerized to give growing polymer chains which phase-separated or collapsed in such mixed solvents. This also leads to the formation of a heterogeneous hydrogel. All these reported techniques are different from each other, but the theory behind is similar since all growing PNIPAAm chains are in a collapsed stage and the resultanting hydrogel networks are formed under certain phase-separated environment.

To date, even though much effort has been spent on strategies to improve the response rate, there is still a lack of clear and extensive explanations for these processes. Although a few primarily explanations have been proposed, the detailed reason why the heterogeneous structure leads to a fast response is still not clear. For instance, Okajima et al. [16] attributed the fast response of their heterogeneous PNIPAAm hydrogel to the nonequilibrated shrinking force at different collapsed regions. They suggested that owing to the heterogeneous microstructure, many shrunken regions appeared to collapse differently during the shrinking process. As time goes by, the freed water in the water-rich regions may transfer into the surrounding dilute regions. Therefore, the water-rich regions connect with each other and form interconnected water-release channels throughout the hydrogel. Finally, the freed water is evacuated quickly and timely from the collapsing network, which results in the fast response rate of the heterogeneous hydrogel.

According to this mechanism, we inferred that a heterogeneous PNIPAAm hydrogel should exhibit a fast response. Furthermore, we deduced that when the swollen hydrogel underwent shrinking in a mixed solvent, such as tetrahydrofuran (THF)/H_2O, instead of pure water, the hydrogel should exhibit a fast deswelling rate at a temperature above LCST, if a heterogeneous structure would be formed in the mixture. Thus, the question is wheather the heterogeneous structure will always guarantee a fast response of PNIPAAm hydrogels, regardless of how the heterogeneous structure is formed, during the polymerization or after the polymerization. In reality, it is very difficult, or nearly impossible, to identify a single factor leading to fast response because all factors act cooperatively to improve the response rate. However, a better understanding is necessary for theoretical or application purposes, and especially for designing and developing fast-response hydrogels in the future.

In this study, the PNIPAAm hydrogel was prepared conventionally, but it was then transferred into the mixed solvent of THF/H_2O. The properties, including the interior morphology, the temperature dependence of the swelling ratios and the response kinetics of the hydrogel in the mixture, were examined and characterized. A further discussion of the factors leading to the fast response rate of the PNIPAAm hydrogel is made.

Experimental

Materials

NIPAAm (Aldrich Chemical, St. Louis, MO, USA) was further purified from benzene/*n*-hexane by recrystallization. *N*,*N*′-Methylenebisacrylamide (MBAAm), ammonium persulfate (APS), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) and THF were purchased from Sigma Chemical (St. Louis, MO, USA) and were used as supplied.

Synthesis of the hydrogel

The hydrogel monomer (100 mg NIPAAm) and MBAAm (cross-linking agent, 3.0 wt% based on NIPAAm) dissolved in distilled water. The free-radical polymerization of the hydrogel was carried out in a glass vessel at room temperature (20 °C) for 3 h, using APS and TEMED as a redox initiator (5.0 wt% based on NIPAAm). After the polymerization, the hydrogels synthesized were immersed in distilled water at room temperature for at least 48 h and the water was refreshed every few hours in order to allow unreacted chemicals to leach out. Finally, the purified PNIPAAm hydrogel was immersed in the mixed solvent, THF/H_2O of different volume ratios (0:1, 1:3, 1:1 and 3:1); the hydrogel in each mixture was designated as $\mathrm{Gel}_{0:1}$, $\mathrm{Gel}_{1:3}$, $\mathrm{Gel}_{1:1}$ and $\mathrm{Gel}_{3:1}$,respectively.

Interior morphology of hydrogels

Each hydrogel sample was first equilibrated in the mixed solvent at room temperature. The equilibrated hydrogel samples were quickly frozen in liquid nitrogen and further freeze-dried in a Virtis freeze drier (Gardiner, NY, USA) under vacuum at −42 °C for at least 3 days until all the solid solvents had sublimed. The freeze-dried hydrogel was then fractured carefully, so that the interior morphology of the hydrogel could be studied by using a scanning electron microscope (SEM, Hitachi S4500, Mountain View, CA, USA). Before SEM observation, specimens of the hydrogel were fixed on aluminum stubs and coated with gold for 40 s.

Equilibrium swelling ratio of hydrogels

For the equilibrium swelling ratio (ESR) study, each PNIPAAm hydrogel sample was immersed in THF/H_2O of a particular volume ratio at a temperature ranging from 5 to 50 °C. The gravimetric method was employed to study the ESR of the hydrogel at each temperature. Briefly, after immersion in the mixture at a predetermined temperature for at least 48 h, the hydrogels were removed from the mixture, blotted with wet filter paper to remove excess solvent on the hydrogel surface, and weighted till a constant weight. After weight measurement at one temperature, the hydrogels were reequilibrated at another predetermined temperature for subsequent ESR measurement. The average value of two measurements was taken for each sample and the ESR was calculated as follows:

$$\mathrm{ESR} = W_\mathrm{s}/W_\mathrm{d} \ , \qquad (1)$$

where W_s is the weight of solvent in the swollen hydrogel at each temperature and W_d is the dry weight of hydrogel.

Temperature response kinetics of hydrogels

The deswelling kinetics of the PNIPAAm hydrogels was measured at 37 °C gravimetrically. The hydrogel samples were first immersed in a mixed solvent at 5 °C to reach equilibrium. Then the equilibrated samples were transferred quickly into a warm mixed solvent of the same composition as the 5 °C one at 37 °C. For example, when $\mathrm{Gel}_{1:1}$ equilibrated at 5 °C was transferred into a mixed solvent at 37 °C to undergo shrinking, the only difference was the temperature: the mixed solvent had the same composition of THF/H_2O (1:1 in volume). The weight changes of the hydrogels were recorded at regular time intervals during the course of shrinking. Solvent retention is defined as follows:

$$\text{Solvent retention} = 100 \times (W_\mathrm{t} - W_\mathrm{d})/W_\mathrm{s} \ , \qquad (2)$$

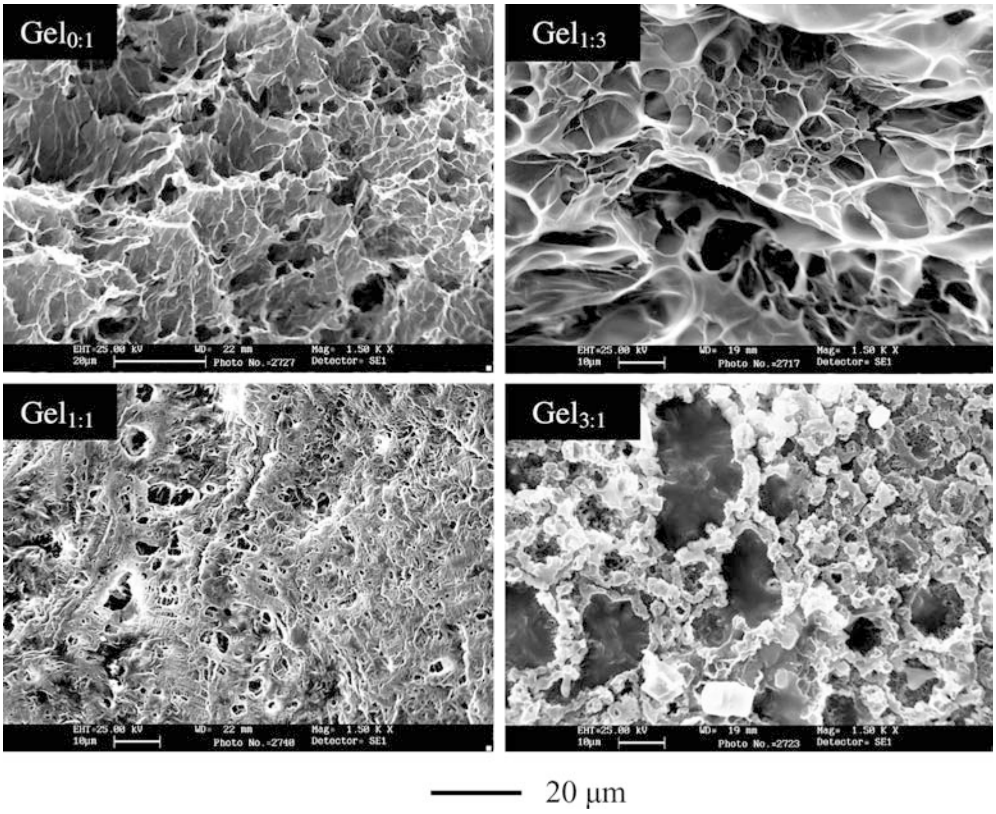
where W_t is the total weight of hydrogel at time t.

Results

Interior morphology

Figure 1 reveals the interior morphology of the freeze-dried hydrogels in THF/H_2O mixtures and exhibits significantly different morphology with the addition of THF. Clearly, the hydrogel in pure water ($\mathrm{Gel}_{0:1}$) represents a homogeneous microstructure, while the other hydrogels ($\mathrm{Gel}_{1:3}$ $\mathrm{Gel}_{1:1}$ and $\mathrm{Gel}_{3:1}$), which were immersed in the THF/H_2O mixtures, exhibit a heterogeneous structure with the matrix heterogeneously distributed throughout the network. As shown in Fig. 1, the average pore size and pore volume of $\mathrm{Gel}_{1:1}$ are the smallest among the three heterogeneous hydrogels. With the increase of the THF ratio in the solvent mixture,

Fig. 1 Scanning electron microscope micrographs of poly(*N*-isopropylacrylamide) (*PNIPAAm*) hydrogels immersed in tetrahydofuran (*THF*)/H_2O mixtures with different volume ratios



$\text{Gel}_{3:1}$ represents a typical heterogeneous network and the matrix exhibits a collapsed phase, although the pore volume is much larger when compared to that of $\text{Gel}_{1:1}$.

Whether in water or in THF, PNIPAAm chains dissolve well and the hydrogel exhibits a swollen state at room temperature. However, the solubility of the PNIPAAm chains is dramatically reduced in the mixture of water and THF with certain THF concentrations. PNIPAAm exhibits a special cononsolvency in mixed solvents [17, 18, 19, 20]; this cononsolvency phenomenon of PNIPAAm is examined in the Discussion section. Owing to this special cononsolvency phenomenon, PNIPAAm hydrogels exhibit a reentrant phase transition [21, 22] when the ratio of these two solvents is monotonically varied. This anomalous aggregation has been observed in a similar mixture like water/acetone [23]. The PNIPAAm hydrogel changes its microstructure to heterogeneous from its conventional homogeneous one in water owing to the cononsolvency phenomenon and reentrant phase transition when THF is added to the aqueous solution to form a THF/H_2O mixture.

Swelling ratio at room temperature

The ESRs of the PNIPAAm hydrogels as a function of the volume fraction of THF in the mixture at room temperature are shown in Figure 2 . It was found that with an increase in THF, there is an initial depression in the ESR value. When the volume fraction of THF is raised to 50%, the ESR reaches the lowest value (around 5, $\text{Gel}_{1:1}$). This is easily understood considering its smallest pore volume, i.e. the available space for solvent, from the SEM morphology observation. With a further incorporation of THF, the ESR increases sharply (around 33, $\text{Gel}_{3:1}$). That is to say, with the initial incorporation of THF into H_2O, the PNIPAAm hydrogel undergoes a volume collapse and remains collapsed as THF concentration increased up to approximately 50%; the hydrogel reswells as THF concentration became greater than 50% in the mixture.

Temperature dependence of swelling ratio

The ESRs of the PNIPAAm hydrogels as a function of temperature were examined to determine the temperature dependence in solvent mixture during the swelling and collapse processes. As shown in Fig. 3, the swelling–temperature data show that all the samples are thermoresponsive, i.e. the swelling ratio of the hydrogel decreases as the temperature increases, although the degree of phase separation is significantly different among the PNIPAAm hydrogels tested. The phase separation of the hydrogels stops at different swelling levels and those hydrogels in mixed solvents do not exhibit complete collapse of structure as the hydrogel in pure water. Here, the deswelling curves in Fig. 3 show that the LCSTs of the hydrogels in the mixture are obviously derived from the water component in the mixed solvent. The accurate LCSTs of PNIPAAm in THF/H_2O mixtures have been determined [17, 18, 19]. The changing LCST upon addition of THF in the water-rich range has been interpreted [17, 20].

Temperature response kinetics

The temperature response kinetics of the PNIPAAm hydrogels in THF/H_2O mixtures upon quick transfer from 5 to 37 °C is shown in Fig. 4. The PNIPAAm hydrogel is a cold-swollen and heat-shrunk material, and will collapse and lose water in response to a sudden increase in temperature. As an intelligent material, the response kinetics are very important in fundamental and application research. The shrinking rates of $\text{Gel}_{1:3}$ and $\text{Gel}_{1:1}$ were very slow, even much slower than that of the conventional hydrogel ($\text{Gel}_{0:1}$). After 215 min at 37 °C,

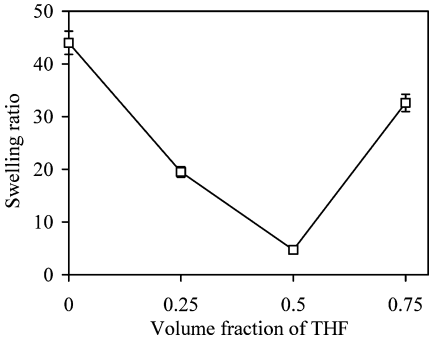


Fig. 2 Equilibrium swelling ratios of PNIPAAm hydrogels as a function of the volume fraction of THF in the mixture at room temperature (20 °C)

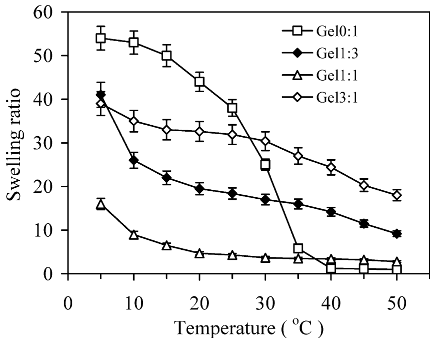


Fig. 3 Temperature dependence of the equilibrium swelling ratios of PNIPAAm hydrogels in THF/H_2O mixtures with different volume ratios

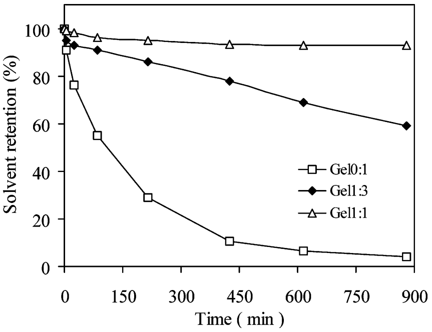


Fig. 4 Thermoresponse kinetics of PNIPAAm hydrogels in THF/H_2O mixtures with different volume ratios at 37 °C

$Gel_{0:1}$ shrank and lost over 70% solvent. In contrast, only about 14 and 5% solvents were evacuated from $Gel_{1:3}$ and $Gel_{1:1}$, respectively within the same time frame. Even after 615 min, only about 30 and 7% solvents were evacuated from $Gel_{1:3}$ and $Gel_{1:1}$,respectively.

After transferring to 37 °C from 5 °C, $Gel_{0:1}$ became translucent and many bubbles appeared thereafter during the first 120 min shrinking. But $Gel_{1:1}$ had only several opaque regions in the inner matrix and virtually no bubbles appeared throughout the shrinking process. $Gel_{1:3}$ became opaque quickly, no bubbles appeared throughout the shrinking process and its skin layer remained smooth.

Discussion

It is known that, owing to the hydrogen bonds between the amide groups and water as well as the hydration shells around the hydrophobic isopropyl groups, PNIPAAm is very soluble in water at temperatures below LCST. When temperature is increased above LCST, these hydrogen bonds are destroyed and the hydration shell ruptures, which exposes the isopropyl groups and, thus, the hydrophobic interactions among the hydrophobic groups become dominant. Subsequently, the polymer chains contract and aggregate abruptly through hydrophobic interactions and entrapped water molecules are freed. The PNIPAAm hydrogel collapses in volume suddenly and a good amount of water is released through the open channels within the network.

From the SEM observations (Fig. 1) of the interior morphology of the hydrogel in the THF/H_2O mixture, it is clear that the hydrogel system became heterogeneous and that the matrix was distributed heterogeneously . As mentioned in the Introduction, the heterogeneous PNIPAAm hydrogel has a good possibility to exhibit a fast response rate when the temperature is above LCST. The microstructure, i.e. morphology of the hydrogel, is a critical factor controlling the response rate during the deswelling process at a temperature above LCST. The heterogeneous microstructure may provide an interconnected water release channel [16] throughout the hydrogel and the freed water may diffuse out quickly and timely. Furthermore, the heterogeneous microstructure may prevent the formation of the thick, dense skin layer [24], which is believed to be less permeable to water during the deswelling process. As the homogeneous PNIPAAm hydrogel is immersed in the hot water, the hydrogel may start the phase transition and shrink in the utmost surface region, resulting in a thick and dense skin layer at the start of the shrinking process. The resultant dense skin layer would act as a barrier for further water permeation and would prevent freed water from diffusing out of the hydrogel matrix quickly. As a result, some parts of the surface would blow up owing to accumulating water underneath the surface layer and, thus, bubbles would appear.

In our experiments, during the shrinking process, nearly no bubbles appeared on the skin layer for both $Gel_{1:3}$ and $Gel_{1:1}$, which further confirmed their heterogeneous microstructure and that their release channels for water are fairly good in the network during this process. However, both $Gel_{1:3}$ and $Gel_{1:1}$ exhibit extremely slow thermoresponse rates (Fig. 4). This means the heterogeneous microstructure of the PNIPAAm hydrogel does not always guarantee a fast response rate. The weak temperature sensitivity of $Gel_{1:1}$ is not a surprise, if its smallest average pore size and decreased interconnectivity, as shown in the SEM micrograph (Fig. 1), are taken into account. The average pore size of the hydrogel network may have an impact on the response dynamics and the macroporous morphology [25] of the hydrogel prefers to exhibit a fast response rate because the freed water can be move quickly through large pores. However, in the case of $Gel_{1:3}$, the fast response rate as we once expected did not appear and it also exhibits a very slow thermoresponse rate, even much slower than that of $Gel_{0:1}$.

A basic requirement for an intelligent hydrogel to react to the external environmental changes is the desire to respond. For PNIPAAm hydrogel, upon heating, the PNIPAAm chains collapse and phase separation at or above LCST takes place. Thus, if the PNIPAAm hydrogel possessed a special microstructure, expressed as the heterogeneity, favorable for collapsing, such as a collapsed conformation with a shortened distance among the hydrophobic groups of PNIPAAm, then at a temperature above the LCST, isopropyl groups of PNIPAAm may interact with each other quickly, conveniently and strongly. The strong hydrophobic interactions would lead to the formation of strong shrinking-forces for the following phase separation. In fact, whether at a high polymerization temperature [9, 10, 11], with the use of hydrophobic cross-linkers [12, 13] or with the use of a mixed polymerization solvent [14, 15], all the PNIPAAm chains are phase-separated from their solvent near LCST, and the final hydrogel has a special conformation as well as compact spaces among the hydrophobic groups. Since the hydrogel is able to retain the memory of its formation history and molecular conformation [26, 27, 28], all the special characteristics of the hydrogel are kept after its formation and a particular hydrogel always wants to collapse quickly once the temperature changes to above its LCST. But, the heterogeneous PNIPAAm structure formed in the THF/H_2O mixture in our study is totally different because it was generated after polymerization, instead of during polymerization. Thus, as temperature reaches above LCST, PNIPAAm does not have the special desire to collapsing, and the shrinking force is similar to or weaker than that of a homogeneous hydrogel.

The previous discussion only interpreted the reason why the heterogeneous $Gel_{1:3}$ did not respond fast, while $Gel_{1:3}$ exhibited a much slower temperature-sensitive feature, when compared with the conventional homogeneous $Gel_{0:1}$ (Fig. 4). The reduced response rate of $Gel_{1:3}$ is believed to be attributed to the cononsolvency phenomenon in the mixed solvent. At a temperature below LCST, as some water was substituted with THF in a THF/H_2O mixture, a special complex structure forms between the PNIPAAm polymer and the two solvents. In the THF/H_2O mixture, several different interactions should exist, including the interactions between water and PNIPAAm, between THF and PNIPAAm and between water and THF. However, the cononsolvency of PNIPAAm in the mixed solvent did not result from the polymer-induced perturbations of the water/solvent interactions, but rather from the changes in local contact between the polymer and the solvents [17]. Winnik and coworkers [29, 30] proposed that the cononsolvency mechanism involved a ternary complex between the polymer chain and the two solvents. The addition of another solvent may lead to perturbation of the structure of polymer–water. This is in contrast to most theoretical assumptions based on the Flory–Huggins theory, which suggests the interactions between the components are considered equally [31, 32, 33]. Recently, Young et al. [34, 35] also proved that the binary interaction parameters cannot provide an adequate interpretation of the conosolvency behavior and a ternary interaction parameter should be considered.

As discussed previously, even with a heterogeneous microstructure, it is impossible for the PNIPAAm hydrogel to exhibit strong and fast temperature-sensitive characteristics in the mixed solvent because of the existence of the special ternary complex in the mixture. Actually, Winnik et al. [18] have confirmed that the PNIPAAm chains remain hydrated, although they undergo phase separation in the mixture. One or several water layers remain bound to the collapsed polymer chain. As a result, the hydrophobic groups, i.e. isopropyl groups, may not contact each other closer enough to initiate strong hydrophobic interactions which is required for more complete deswelling process as found in pure water. Consequently, the response rate of the hydrogel in a mixed solvent medium will be retarded and the amount of water excluded during the phase separation is also greatly reduced.

Therefore, we suggest that several factors given below are important for the PNIPAAm hydrogel to achieve a fast response rate at a temperature above LCST. First, the hydrogel should have a strong desire to respond, expressed through a special microstructure, such as a heterogeneous structure with a collapsed conformation and shortened distance among the hydrophobic groups of PNIPAAm, which is favorable for a rapid and complete collapsing upon heating. The second important factor is the special interactions among the polymer and solvents or ternary complexes. This interaction should be avoided in aqueous solution; otherwise, the polymer chains will remain hydrated even during the phase-separation process and the water layers will stay bound to the collapsed polymer chain. The third factor is to have good release channels throughout the network before shrinking or generated during shrinking for quick and timely diffusion of freed water. Of course, the response dynamics of the PNIPAAm hydrogel is complicated and some other factors may also play a role, but any of the three factors described above would be favorable for a fast response rate. Therefore, we suggest that the fast response rate would be reached, if the modified PNIPAAm hydrogel could meet all these three conditions.

Conclusions

It was found that PNIPAAm hydrogel has a heterogeneous microstructure in THF/H_2O mixtures, but it is different from the heterogeneous one generated during the polymerization. This heterogeneous PNIPAAm hydrogel in the mixture exhibits a very slow thermoresponse rate at temperatures above the LCST, which reveals that heterogeneous microstructure does not always guarantee a fast response rate. The slow response rate is attributed to the formation of ternary complexes between the polymer and the two solvents in the THF/H_2O mixture. Three factors are important for the response rate of thermoresponsive hydrogels during the shrinking process: strong shrinking force or desire to respond, no ternary complexes and good release channels.

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