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Synthesis of the Functional Hydrogels: Poly (N-isopropylacrylamide) Threaded onto the PEG Backbones Via RAFT

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Functional poly(N-isopropylacrylamide) (PNIPAM) hydrogels were prepared by reversible addition fragmentation chain transfer (RAFT) polymerization of NIPAM in the presence of four-arm poly(ethylene glycol) (4A-PEG) as backbone and 4-cyanopentanoic acid dithiobenzoate functional α-cyclodextrin threaded onto the PEG as chain transfer reagent (CTA).The structure of the hydrogels was characterized in detail with FTIR techniques. The analytical results demonstrated that α-cyclodextrin remains in as-obtained hydrogels. The swelling behavior was investigated and the functional hydrogels (functional gels) showed accelerated shrinking kinetics and higher swelling ratio comparing with conventional hydrogel (CG). It could be attributed to the presence of dangling chains. The hydrogel exhibited rapid swelling and deswelling kinetics. In principle, the hydrogel might find a number of applications including an on-off system and drug delivery systems.

Keywords: N-isopropylacrylamide, reversible addition fragmentation chain transfer (RAFT), hydrogel, self-assembly

1 Introduction

Recent advances in supramolecular chemistry are primarily associated with achievements in the study on self-assembly processes according to the guest-host type. Macrocyclic compounds are most often used as host molecules, among which cyclodextrins (CDs) have enjoyed the widest application (1). CDs are a series of cyclic oligosaccharides consisting of six to eight glucose units, named α-, β-, and γ-CD, respectively, which possess internal hydrophobic cavities capable of accommodating various organic and polymeric compounds. Since the first report released in 1990 by Harada and his colleagues that α-CD can form inclusion complexes (ICs) with poly(ethylene glycol) (PEG) (2), a wide variety of polymeric inclusion complexes based on CDs have been prepared and characterized (3–8). Among the ICs reported, stimuli-responsive polyrotaxanes are of special interest. Many research groups have studied rotaxane-derived molecular shuttle in response to external stimuli, e.g., light, pH, and polarity of the environment (9–14).

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Stimuli-responsive polymers have been extensively investigated and used as smart biomaterials and drug-delivery systems (15). The phase transition of polymers is induced by a continuous change in various conditions such as temperature (16), electric field (17), or solvent composition (18).

Poly(N-isopropylacrylamide) (PNIPAM) gel is a widely studied, typical thermosensitive hydrogel, which displays phase transition as the temperature is increased above its lower critical solution temperature (LCST). However, it takes more than several hours to days for completion of volume shrinking, which is the main drawback for their practical usage, such as on-off valves and artificial muscles, and was an important topic to be solved. For this purpose, some successful strategies have been worked out. Comb-type grafted chains have been introduced to PNIPAM backbones and crosslinked for rapid deswelling (19). Okano's group (20) proposed a method for preparing comb-type PNIPAM hydrogels, which could collapse from a fully swollen state in less than 20 min. They also reported a comb-type grafted hydrogel composed of poly(ethylene oxide) (PEO) graft chains in the crosslinked PNIPAM network (21). Lee et al. reported alginate/PNIPAM comb-type grafted hydrogels, which were able to response rapidly to both temperature and PH changes (22). We have synthesized PNIPAM-g-PNIPAM comb-type hydrogels by a living radical polymerization technique (23). Such

hydrogels all exhibited a drastic acceleration of shrinking rate. As expected, micrometer-sized gel particles exhibited a more rapid response rate because of their small size and large surface area (24). Some rapid responding bulk hydrogel systems with microstructure have been reported. The formation of a porous structure has been shown to effectively enhance the deswelling rate of PNIPAM gels. Examples include the incorporation of surfactants (25), hydrogel preparation above its lower critical solution temperature (LCST) (26), by using a freeze drying technique (27), the incorporation of silica microparticles, removed by subsequent acid treatment of the silica (28), and by other means (29). In all cases, the deswelling rate of PNIPAM hydrogels has been enhanced by the formation of porous structures. In recent years, some other strategies were reported to improve the response rate. Cai et al. have made a fast responding bulk hydrogel by crosslinking poly(NIPAM-co-acrylic acid) microgels in a PNIPAM polymer network (30). Zhuo et al. reported fast-responsive bulky PNIPAM hydrogels by incorporating PNIPAM particles into PNIPAM networks to form composite hydrogels, which may be ascribed to the generation of pores that allow water molecules to be quickly squeezed out of the bulky PNIPAM gels (31). Zhuo et al. synthesized PNIPAM with water/acetone as a mixed solvent during the hydrogel crosslinking reaction to obtain a faster deswelling rate (32). Carrying out the polymerization/ crosslinking of NIPAM in solid phase states also resulted in rapidly responsive PNIPAM hydrogels (33). Zhuo et al. also reported that the response rate of the PNIPAM hydrogel could be improved via incorporating siloxane linkage and so on (34).

As mentioned above, the synthesis of fast temperature-responsive hydrogels by a new method has become an intriguing research area, motivated by both their theory and practical applications. In this study, new functional poly(N-isopropylacrylamide) (PNIPAM) hydrogels were prepared by reversible addition fragmentation chain transfer (RAFT) polymerization of N-isopropylacrylamide (NIPAM) in the presence of four-arm poly(ethylene glycol) (4A-PEG) as backbone and 4-cyanopentanoic acid dithiobenzoate functional α-cyclodextrin threaded onto the PEG as chain transfer reagent (CTA). To our knowledge, there is very little reported about the preparation of chemical supramolecular structured hydrogels by RAFT polymerization.

2 Experimental

2.1 Materials

2-Mercaptopropionic acid (99%), carbon disulfide (99%), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, 98%), and benzyl bromide (98%) were purchased from Aldrich and used without further purification. N,N-Dimethylacetamide (99%) was stirred over calcium hydride for 2 days, distilled under reduced pressure, and stored under nitrogen. α-Cyclodextrin (hydrate; Aldrich) was dried over P_2O_5 at 80°C under reduced pressure. Four-arm poly(ethylene glycol) (4A-PEG; number-average molecular weight =32,000; 10,020), N,N′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), N-vinylpyrrolidone, N,N-methylenebisacylamide (BIS) and azo-bis-isobutryonitrile (AIBN) were supplied by the Liming Chemical Engineering Research Institute (China). Acrylic acid (AA) was purified to remove inhibitor by vacuum distillation, and stored at 4°C. Synthesis of 4-cyanopentanoic acid dithiobenzoate (RAFT Acid) was prepared according to Ref. 35.

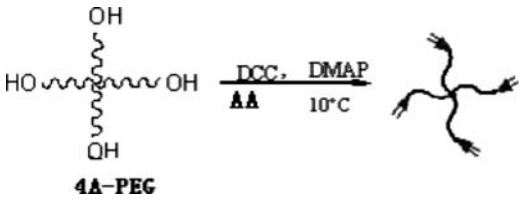

Fig. 1. Preparation of photocurable macromer.

2.2 Preparation of Photocurable Macromer

To synthesize photocurable macromer, a mixture of 4A-PEG (Mn = 10,020/32,000, $2*10^{-3}$ mol), acrylic acid (AA) ($1*10^{-2}$ mol), DCC ($2*10^{-2}$ mol), DMAP ($2*10^{-4}$ mol) and DMF (25 ml) were put into a glass tube, degassed and sealed under nitrogen. The mixture was stirred continuously at 10°C one day. The reaction solution was filtered and then the final solution was precipitated in 200 ml diethyl ether, filtered, and dried *in vacuo* at room temperature to constant weight; yield 80%. The route of the preparation is illustrated in Figure 1.

2.3 Preparation of RAFT Acid-α-CDs

To synthesize RAFT acid-α-CDs, a mixture of α-CDs ($2*10^{-3}$ mol), RAFT acid ($2*10^{-2}$ mol), DCC ($4*10^{-2}$ mol), DMAP ($4*10^{-4}$ mol), DMF (25 ml) were put into a glass tube, degassed and sealed under nitrogen. The mixture was stirred continuously at 10°C one day. The reaction solution was filtered and then the final solution was precipitated in 200 ml diethyl ether, filtered, and dried *in vacuo* at room temperature to constant weight; yield 70%.

2.4 Preparation of Supramolecular Structured Hydrogel by Photopolymerized

A photocurable macromer was dissolved in phosphate buffered saline (PBS, pH 7.4) at room temperature. A saturated aqueous solution of RAFT acid-α-CDs was added according to a predetermined feed molar ratio of CD to the macromer. The solution became turbid, and continued to stir for 2 h. DMSO was added until the reaction

mixture turned transparent. To 1 ml of the resulting clear solution was added 3 ml of photoinitiator solution (100 mg of DMPA dissolved in 1 ml of N-vinylpyrrolidone). About 1 ml of the solution was poured onto a 2.5 cm * 7 cm glass coverslip and exposed to 365 nm LWUV lamp to lead the solution to quickly polymerize within several seconds. The fabricated hydrogel was transparent and colorless when swollen in DMSO. To remove unthreaded α-CDs presumably entrapped in the hydrogel matrix and unreacted macromers, the gels were completely immersed in DMSO at room temperature for 7 days. The solvent was changed every day. After drying under vacuum for 24 h, the gels were again swollen in water at 20°C for two weeks so as to further remove entrapped α-CDs, unreacted macromers, and DMSO in the hydrogel network. Water was also changed every day during the process. Finally, the hydrogels were freeze-dried to constant weight.

Table 1. Feed composition for preparation of the functional hydrogels by chain extension of supramolecular structured hydrogel via RAFT polymerization

Sample	*4A-PEG (g)*	*NIPAM (g)*	*α−CDs (g)*	*RAFT acid (g)*	*Wt of gel (g)*
The sample series 1					
run-1	2.0885	8.4015	0.5005	1.5001	9.8126
run-2	2.0887	10.2009	0.5009	1.5000	12.0081
run-3	2.0883	12.2013	0.5003	1.5004	13.7984
run-4	2.0889	15.2007	0.5002	1.5009	16.8055
run-5	2.0884	18.2012	0.5007	1.5007	19.5921
The sample series 2					
run-1	2.0885	12.2013	0.5005	1.5001	13.8573
run-2	2.0887	12.2007	0.4006	1.2007	13.2181
run-3	2.0883	12.2005	0.3505	1.1025	12.8984
run-4	2.0889	12.2006	0.3009	0.9013	12.6955
run-5	2.0884	12.2002	0.2508	0.7503	12.3756

2.5 Preparation of the Functional Hydrogels by Chain Extension of Supramolecular Structured Hydrogel via RAFT

The above-mentioned hydrogel obtained by photopolymerized was used as functional hydrogel to mediate the polymerization of NIPAM to prepare grafted hydrogel. The dried above-mentioned supramolecular structured hydrogel was immersed in 1, 4-dioxane. After the NIPAM and AIBN were added, the mixture was immersed overnight. The polymerization was left for 60 h, following the procedure above. Results of the polymerization are summarized in Table 1. The supramolecular self-assembly and gelation processes are illustrated in Figure 2. For comparison, CG was synthesized with NIPAM (0.4 g), N, N-methylenebisacylamide (BIS, 13 mg) and AIBN (15 mg) at 70°C. The chemical formula of CG is illustrated in Figure 3.

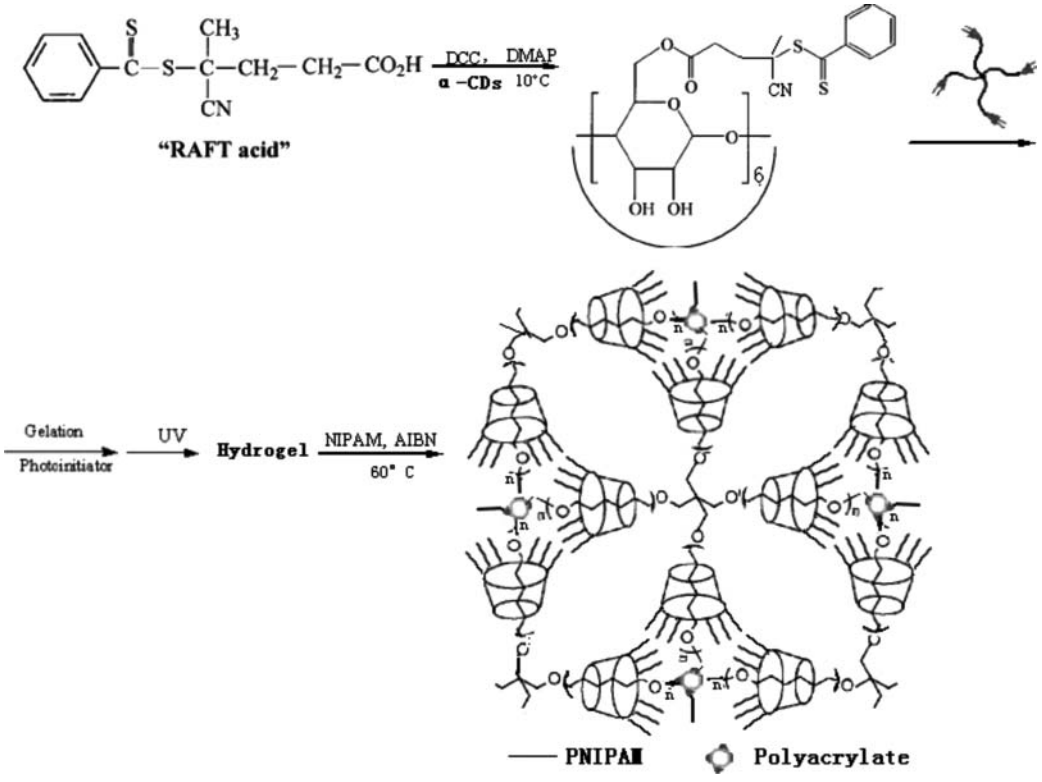

Fig. 2. Preparation of the functional hydrogels by chain extension of supramolecular structured hydrogel via RAFT polymerization.

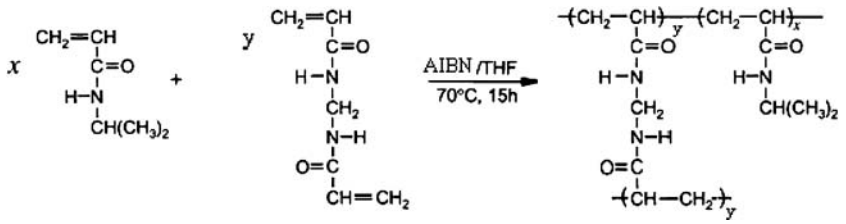

Fig. 3. The chemical formula of CG.

2.6 Characterization

The ^{1}H-NMR spectra were recorded on a 400 MHz NMR spectrometer (BRUKER, DRX-400) with chloroform-d as the solvent, and chemical shifts were obtained relative to tetramethylsilane.

FTIR spectra was measured using a RFX-65A FTIR (Analect, America) spectrometer at room temperature in the range from 4000 to 500 cm^{-1}, with a resolution of 2 cm^{-1} and 20 scans. Samples were prepared by dispersing well the complexes in KBr and compressing the mixtures to form disks.

The surface of the hydrogels was observed using a SEM (JEOL, JSM 5400, and Japan). After freeze-drying, the sample of the hydrogels was coated with gold/palladium using an Ion Sputter (JEOL, JFC-1100). Coating was provided at 20 mA for 4 min. Observation was performed at 20 Kv.

The swelling behavior of dried hydrogel was studied by a general gravimetric method. Dry films (a diameter of 10 mm and a thickness of 2 mm) were incubated in distilled water at 20°C, and the swollen weight for each sample was recorded at regular time intervals after excess surface water was blotted carefully with moistened filter paper. The procedure was repeated until there was no further weight increase. While the temperature increased gradually, the swollen hydrogel began to shrink. The temperature was maintained constant for 3 h after increasing by every 5°C, and then the weight of the shrunk hydrogel was measured. The swelling ratio (SR) was calculated by the following equation:

$$SR = (m_1 - m_0) * 100\%/m_0$$

Where m_0 stands for the initial weight of dried gel and m_1 stands for the weight of the swelling gel at a particular temperature and a prescribed time interval.

3 Results and Discussion

3.1 Preparation

In the process of preparation of supramolecular structured hydrogel, α-CDs appeared to act as a powerful gelator, and a rapid physical gelation occurred at room temperature upon a polymerizable macromer solution mixing with an aqueous solution of α-CDs. The physical gels are thixotropic and reversible, and the sol-gel transition process can be readily controlled by adjusting the α-CD concentration and the composition of the polymerizable macromers. These gels were freeze-dried to give ICs or polypseudorotaxanes.

In the step of preparing the functional hydrogels by chain extension of supramolecular structured hydrogel via RAFT polymerization, the molecular weight of PNIPAM segment increases almost linearly with respect to the increasing conversion of NIPAM. We used the α-CD-based RAFT agent to grow six-arm PNIPAM star polymers threaded onto the PEG backbones. The polymerizations proceeded as expected from Pan's experience (36). It is known that conformation and solubility of PNIPAM chains in water can change with temperature. PNIPAM chains collapse at T32°C, so the functional hydrogels that we obtained are temperature-sensitive hydrogels.

3.2 Characterization

The ^{1}H-NMR spectra of 4-Cyanopentanoic Acid Dithiobenzoate (RAFT Acid) are presented in Figure 4. In the ^{1}H-NMR spectrum, the signal (δ 7.4–8.0 ppm) represents the aromatic hydrogens of the phenyl group, the signal (δ 2.5–3.0 ppm) represents the methylene hydrogens of the cyanopentanoic acid fragment, and the signal (δ 2.0 ppm)

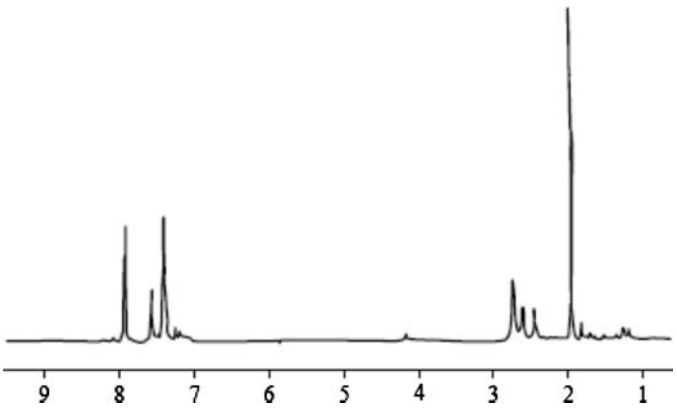

Fig. 4. 400M ^{1}H-NMR of 4-Cyanopentanoic Acid Dithiobenzoate.

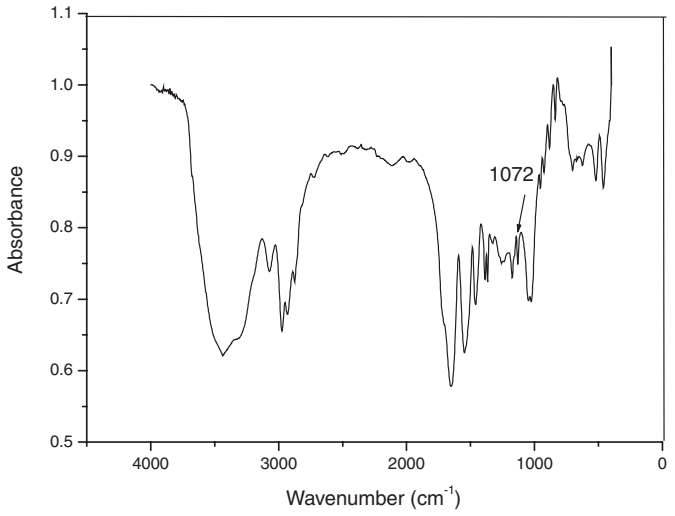

Fig. 5. FTIR spectra of supramolecular structured hydrogels.

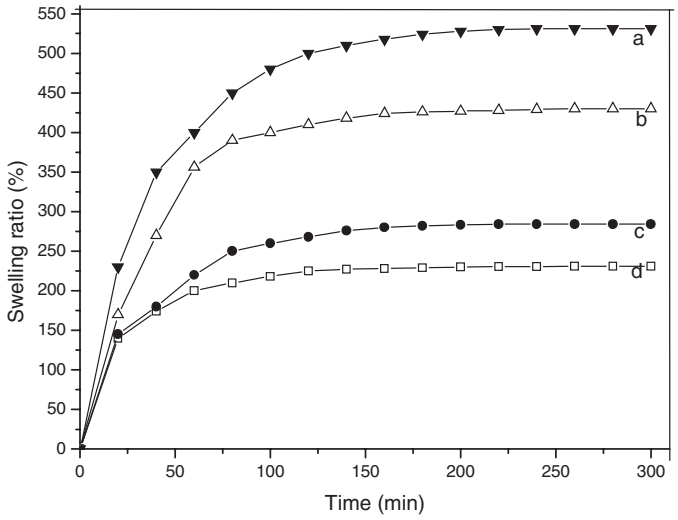

Fig. 6. Swelling ratio of a: run 5, b: run 4, c: run 2 d: run 1 of series 1.

represents the hydrogens of the methyl group on the same fragment.

FTIR spectra of the functional hydrogel are presented in Figure 5. The hydrogel spectrum exhibits bands at 1098 and 1750 cm^{-1}, which are attributed to the C-O-C stretching mode and the characteristic stretching vibration of carbonyl, respectively. Upon introducing the PNIPAM segment, the characteristic absorbance band of PNIPAM in the spectra is observed. The amide I band (C=O stretch) emerges at 1648 cm^{-1}, the amide II band (N=H vibration) at 1550 cm^{-1}, and the methyl groups (in isopropyl group) at 1359–1385 cm^{-1}. Moreover, the intensity of the amide I band increases as the NIPAM to α-CD molar ratio augments. The C=S groups were assigned to 1070 cm^{-1}. The signal 1070 cm^{-1} was not obvious due to the low content of CTA in the hydrogel.

3.3 Swelling and Deswelling Kinetics of Hydrogels

According to feed compositions shown in Table 1, two series of the functional hydrogels were prepared and their swelling ratios were measured in distilled water at 20°C.

The swelling ratios of hydrogels with different amounts of NIPAM and α-CDs are presented in Figures 6 and 7, respectively. Compared with the CG, all the samples absorbed water quickly, and equilibrium water uptakes were reached after about 200 min, but equilibrium water uptakes were reached after more than 10 h for CG (Fig. 8). We think that it is a slow process that polymer network in hydrogel absorbed or released solvent. However, for the network with the pore structure, the hydrogel absorbed or released solvent through a hole directly. This process is much faster than CG, so the formation of additional microporosity in the functional hydrogels by the introduction α-CDs can accelerate the swelling rate. In Figure 7, incorporated α-CDs apparently decreased the swelling ratio of the hydrogels. Consequently, the equilibrium water uptakes decreased with an increase in the α-CDs threaded onto the gel network chains. This result indicates that it is difficult for water to enter the matrix because of the rigidity of the network chains formed by the self-assemblies of α-CDs. With grafted chains, (PNIPAM) composition increased in the hydrogel, the swelling ratio of the hydrogels uptakes increased in Figure 6. On the other hand, the increase in the swelling rate of the functional hydrogels may be explained by the formation of additional microporosity by the introduction α-CDs, which accelerated the water diffusion into the hydrogel. Figure 9 (SEM photograph of the supramolecular structured hydrogels) confirms the above belief.

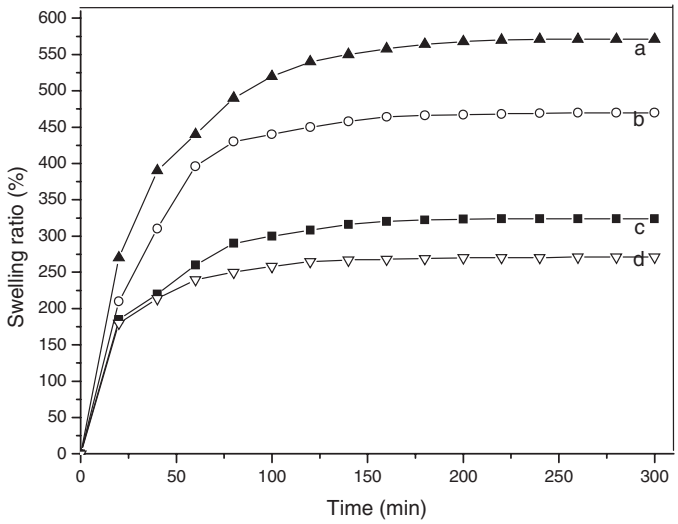

Fig. 7. Swelling ratio of a: run 1, b: run 2, c: run 4 d: run 5 of series 2.

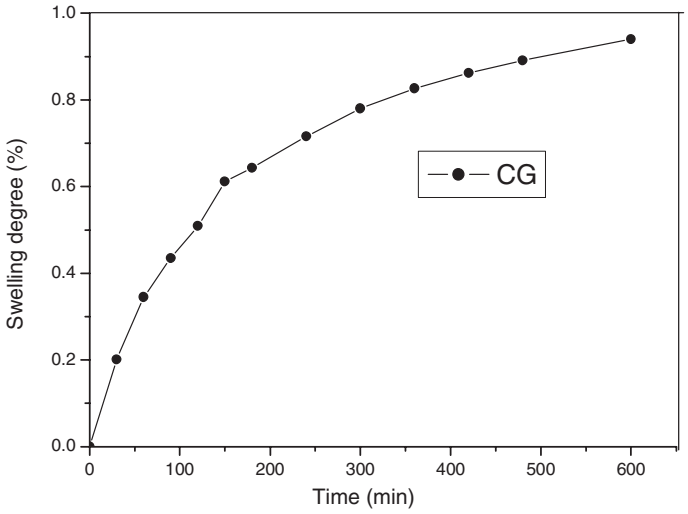

Fig. 8. Swelling kinetics of conventional hydrogel in water at 20°C.

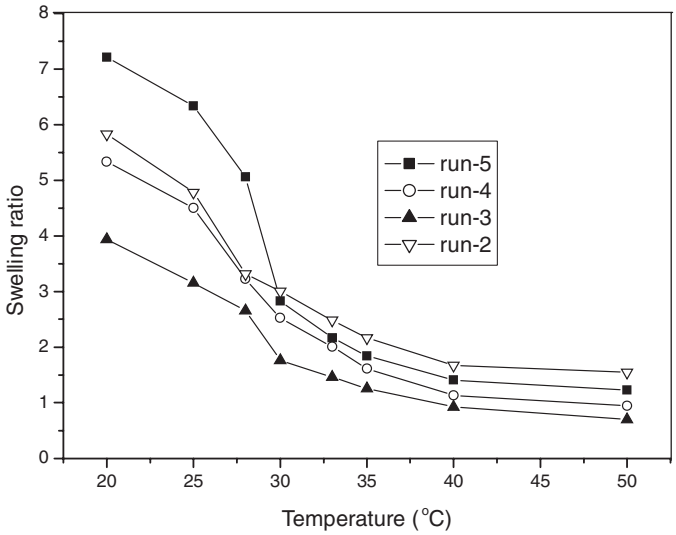

Fig. 10. Equilibrium swelling ratio for the hydrogels of series 1 as a function of temperature.

Figure 10 shows the temperature dependence of swelling equilibrium of the hydrogels. The resultant hydrogels shows a discontinuous volume transition between 30 and 40°C, and the swelling ratio of hydrogels is influenced by the content of PNIPAM. As can be seen, Run -5 exhibits higher swelling ratio than the others, which have the same composition as run-5 except for the content of PNIPAM. The reason is that the swelling rate of the functional hydrogels increased with an increase in the content of PNIPAM. We think that long grafted chains of PNIPAM result in the high swelling ratios of the functional hydrogels, so the swelling rate could be controlled to a certain degree by adjusting the content of PNIPAM.

Compared with the CG, all samples showed rapid deswelling kinetics. The slow deswelling of CG was attributed to the skin layer formation during the deswelling process. The surface dense and stable skin layer can balance the deswelling forces with internal pressure during shrinking, preventing water release from the gel (37). The functional hydrogels with more freely mobile graft chains than CG showed no skin layer formation. The reason maybe more freely mobile graft chains accumulated stronger aggregation force, which could break the balance deswelling forces and internal pressure. It could be imagined that that some of the free mobile chains would diffuse the outward surface of the gel, causing aggregation forces in the surface, which is favorable in producing no skin layer as well. In

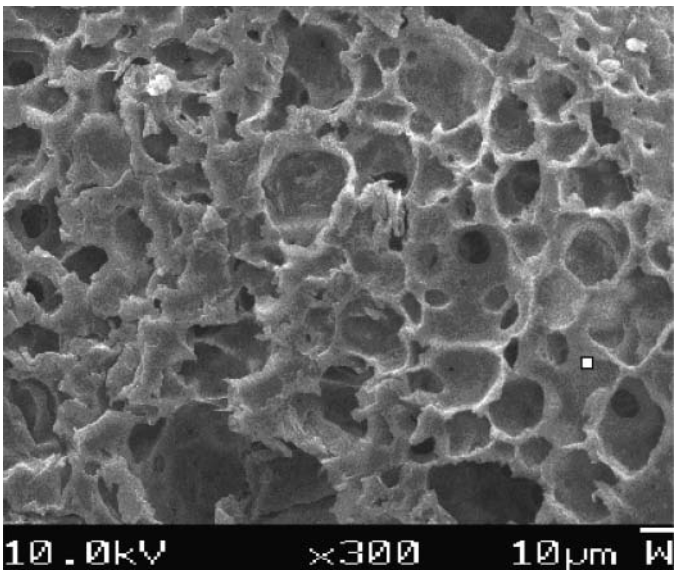

Fig. 9. The SEM photograph of the supramolecular structured hydrogels.

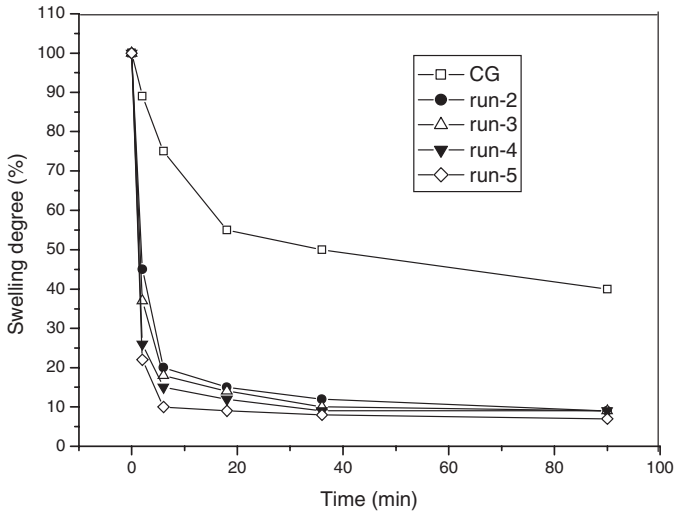

Fig. 11. Shrinking kinetics of conventional hydrogel and the supramolecular.

addition, an increasing in void volume in the gel resulting from the dehydration of graft PNIPAM chains may also facilitate the rapid release water to the gel exterior, so all the functional hydrogels exhibited rapid deswelling. Moreover, from Figure 11, with NIPAM composition increased in the hydrogel grafted chains, the functional hydrogels allowed rapid deswelling, therefore, we think that a longer chain showed no formation of skin layer and allowed rapid deswelling.

In contrast to CG, the increase in the swelling rate of the NIPAM-rich gel may be explained by the formation of additional microporosity by the introduction of PEG 4000, which accelerated the water diffusion into the gel.

4 Conclusions

In this study, new functional hydrogels were prepared by RAFT polymerization of NIPAM in the presence of 4A-PEG as backbone and 4-cyanopentanoic acid dithiobenzoate functional α-Cyclodextrin threaded onto the PEG as chain transfer reagent (CTA). The hydrogels exhibited rapid swelling and deswelling kinetics. In principle, the hydrogel might find a number of applications including on-off system and drug delivery systems.

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