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Poly(*N*-isopropylacrylamide) hydrogels with improved shrinking kinetics by RAFT polymerization

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Abstract

Functional poly(*N*-isopropylacrylamide) (PNIPAM) hydrogels were prepared by reversible addition fragmentation chain transfer (RAFT) polymerization of *N*-isopropylacrylamide (NIPAM) in the presence of *N*,*N*-methylenebisacylamide (BIS) as a cross-linker and 4-cyanopentanoic acid dithiobenzoate as chain transfer reagent (CTA). The swelling behaviors were investigated and the hydrogels by RAFT polymerization (RAFT gels) showed accelerated shrinking kinetics and higher swelling ratio comparing with conventional hydrogel (CG). It could be attributed to the presence of dangling chains mainly caused by CTA, which could retard the crosslinking reaction rate greatly. Another CTA, 3-(trithiocarbonyl) propanoic acid, was adopted to further investigate the effect of CTA. It showed the similar effect except the different accelerated degree to the shrinking kinetics. Furthermore, the living character of the RAFT process was used to polymerize a new batch of monomer (NIPAM) from functional RAFT gels to introduce grafted structure. The PNIPAM-*g*-PNIPAM hydrogels indicted further accelerated shrinking kinetics than functional backbone hydrogels.

Keywords: Hyperbranched; *N*-Isopropylacrylamide; Reversible addition fragmentation chain transfer (RAFT)

1. Introduction

Stimuli-sensitive hydrogels show abrupt changes in their swelling behavior in response to external stimuli such as change in temperature, PH, solvent composition and electric field. They have received much attention due to their potential applications in numerous fields. 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). Due to the unique swelling properties, PNIPAM gel has been widely investigated both fundamentally and for biomedical, pharmaceutical and other applications. However, it takes more than several hours to days for completion of volume shrinking [1], 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. Okano's group [1,2] proposed a method for preparing comb-type PNIPAM hydrogels, which could collapse from a fully swollen state in less than 20 mins. They also reported comb-type grafted hydrogel composed of poly(ethylene oxide) graft chains in the cross-linked PNIPAM network [3]. Lee et al. reported alginate/PNIPAM comb-type grafted hydrogels, which were able to response rapidly to both temperature and PH changes [4]. We synthesized PNIPAM-*g*-PNIPAM comb-type hydrogels by living radical polymerization technique [5]. Such hydrogels all exhibited drastic acceleration of shrinking rate.

The formation of a porous structure has been shown to effectively enhance the deswelling rate of PNIPAM gels. Several reports in the literature describe the preparation of porous hydrogels, including the incorporation of surfactants during hydrogel preparation and their subsequent extraction [6], hydrogel preparation above its lower critical solution temperature (LCST) [7,8], hydrogel preparation by a freeze dry [9], the incorporation of silica microparticles removed by subsequent acid treatment of the silica [10], and by other means [11]. In all cases, the deswelling rate of PNIPAM hydrogels has been enhanced by the formation of porous structures.

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The conventional hydrogel (CG) need a long time to achieve full swelling, whereas micrometer-sized gel particle exhibited a more rapid response rate because of its small size and large surface area [12,13]. Some rapid responding bulk hydrogel system with microstructure has been reported. Hu et al. synthesized a new class of nanostructured polymer gels by crosslinking gel nanoparticles through covalent bonds between functional groups on the surfaces of neighboring particles in solutions, which exhibited fast shrinking rate [14]. Cai et al. have made fast responding bulk hydrogel by crosslinking poly(NIPAM-*co*-acrylic acid) microgels in a PNIPAM polymer network [15]. 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 [16]. Zhang et al. further investigated the influence of the microgels on the property of resulting PNIPAM hydrogels [17].

In recent years, some other strategies were reported to improve the response rate. Zhuo et al. synthesized PNIPAM with water/acetone as a mixed solvent during the hydrogel crosslinking reaction to obtain a faster deswelling rate [18]. Carrying out the polymerization/crosslinking of NIPAM in solid phase states also resulted in rapidly responsive PNIPAM hydrogels [19]. Zhuo et al. also reported that the response rate of the PNIPAM hydrogel could be improved via incorporating siloxane linkage [20].

As mentioned above, the synthesis of fast responsive hydrogels by new method has become an intriguing research area, motivated by both their theory and practical applications. The conventional method for the preparation of chemical crosslinked hydrogels involves the free-radical copolymerization of a monomer and a crosslinker. In this work, PNIPAM hydrogels (RAFT gels) were prepared using RAFT polymerization of NIPAM in the presence of BIS as a cross-linker and 4-cyanopentanoic acid dithiobenzoate as chain transfer reagent (CTA). To our knowledge, there is only one report about the preparation of chemical crosslinked thermoresponsive PNIPAM hydrogels by living radical polymerization [5], which described a method to prepare comb-type grafted hydrogels by two steps. The swelling property of RAFT gels was investigated and it showed accelerated shrinking kinetics compared to conventional hydrogel unexpectedly, which supplies a new and simple method to synthesize rapid responsive hydrogels. Furthermore, the living character of the RAFT process was used to polymerize a new batch of monomer (NIPAM) from functional PNIPAM hydrogels to produce grafted structure.

2. Experimental

2.1. Materials

4-Cyanopentanoic acid dithiobenzoate was prepared by McCormick's method [21]. 3-(Trithiocarbonyl) propanoic acid was prepared according to literature [22]. NIPAM (from Acros) was purified by recrystallization from the mixture of toluene and *n*-hexane. *N*,*N*-Methylenebisacylamide, 4,4′-azobis(4-cyanopentanoic acid) (ACP, from Aldrich), 1,4-dioxane and all other reagents were used as received.

2.2. Instrumentation

The optical images of the obtained hydrogels were recorded by Sony Ericsson W88c mobile phone to show their appearance. The samples were immersed in distilled water at room temperature for 48 h to reach their swollen state. For the FT-IR measurements an RFX-65A spectrometer (Analect, USA) was used. Solid samples were embedded in KBr disks after the samples were grinded into powder.

2.3. Preparation of functional PNIPAM hydrogels using RAFT polymerization

To synthesize the RAFT gels, a mixture of CTA, NIPAM, BIS, ACP and 1,4-dioxane were put into a glass tube, degassed and sealed under nitrogen. The polymerization was conducted at 60 °C. To remove unreacted monomer and linear polymers, the obtained gel was immersed in deionized water for 5 days at room temperature, and water was replaced every day. Then it was dried under ambient conditions for 24 h followed by thorough drying under vacuum at 50 °C for 24 h. Two kinds of CTA were adopted (Fig. 1). Results of the polymerization are summarized in Tables 1 and 2. For comparison, CG was synthesized with NIPAM (0.4 g), BIS (13 mg) and ACP (15 mg) at 60 °C.

2.4. Swelling and deswelling kinetics of hydrogels

Swelling and deswelling kinetics are defined as temporal weight changes for the gels. For the kinetics studies, disk-shaped PIPAM gels were first equilibrated in deionnized water at predetermined temperatures (20 °C). And the gels were weighted at each given time. After confirming no further changes in swelling ratios over time, the gels were quickly transferred into water at 40 °C. At specific time points, these gels were removed from the water and weighed. The weight data were converted to the normalized swelling which indicated the volume changes of hydrogels between equilibrium swollen (100%) and equilibrium shrunken (0%) states, which was calculated from the ratio of the wet weight of the gel at time *t* (Wt) to the equilibrium swollen weight (Wt) of the gel.

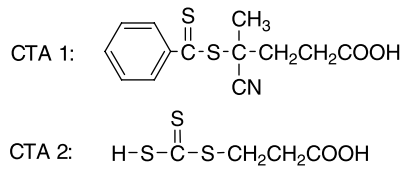

Fig. 1. The chemical structure of two kinds of CTA.

Table 1
Feed composition for preparation of hydrogels of series 1 by RAFT polymerization

Run	NIPAM (g)	CTA1 (g)	BIS (g)	ACP (g)	Dioxane (mL)	Wt of gel (g)
1	0.4032	0.012	0.0132	0.0015	1.5	0
2	0.4027	0.005	0.0291	0.0015	1.5	0.4125
3	0.4033	0.0023	0.0134	0.0014	1.5	0.3947
4	0.4029	0.001	0.0133	0.0013	1.5	0.3928
5	0.4034	0	0.0135	0.0016	1.5	0.3937

2.5. Chain extension of the functional hydrogels-synthesis of grafted hydrogels

Run 1 of series 2 that was obtained via RAFT polymerization was used as functional hydrogel to mediate the polymerization of NIPAM to prepare comb-type grafted hydrogel. Run 1 was not treated or purified further. After the 0.4041 g NIPAM, 15 mg ACP and 3 mL 1,4-dioxane were added; the mixture was immersed for overnight. The polymerizations were left for 60 h, followed the procedure above. Deswelling kinetics of comb-type grafted PNIPAM-*g*-PNIPAM hydrogel was investigated.

3. Results and discussion

3.1. Preparation of functional PNIPAM hydrogels using RAFT polymerization

Conventional PNIPAM hydrogels were synthesized by free radical copolymerization of NIPAM and BIS. In our work, hydrogels were prepared by RAFT copolymerization of NIPAM and BIS in the presence of CTA. In previous reports, Perrier et al. synthesized PMMA hyperbranched polymers via the one-pot copolymerization of MMA and ethylene glycol dimethacrylate, mediated by 2-(2-cyanopropyl) dithiobenzoate [23,24]. The different polymeric architectures (gel and hyperbranched polymer) obtained by same method were ascribed to the different ratio of CTA/crosslinker. High CTA/crosslinker ratio was unfavorable to the formation of gels because it had a retardation effect on the polymerization when the concentration of CTA was increased [25].

As given in Table 1, run 1 failed to form gel when the feed ratio of CTA/BIS was over 0.5, which could be explained by the formation of hyperbranched copolymers of NIPAM and BIS according to the reports mentioned above. Low CTA/BIS ratio is favorable to the occurrence of gelation, which could be concluded from run 2 (CTA/BIS = 0.09), run 3 (CTA/BIS = 0.09) and run 4 (CTA/BIS = 0.04). For comparison, CG (run 5) in the absence of CTA was synthesized by conventional free radical polymerization at the same reaction conditions. The conversion of the gels was approximate determined by gravimetrical method.

Table 2
Feed composition for preparation of hydrogels of series 2 by RAFT polymerization

Run	NIPAM (g)	CTA2 (g)	BIS (g)	ACP (g)	Dioxane (mL)	Wt of gel (g)
1	0.404	0.003	0.0131	0.0015	1.5	0.3817
2	0.403	0.0015	0.0132	0.0015	1.5	0.3925

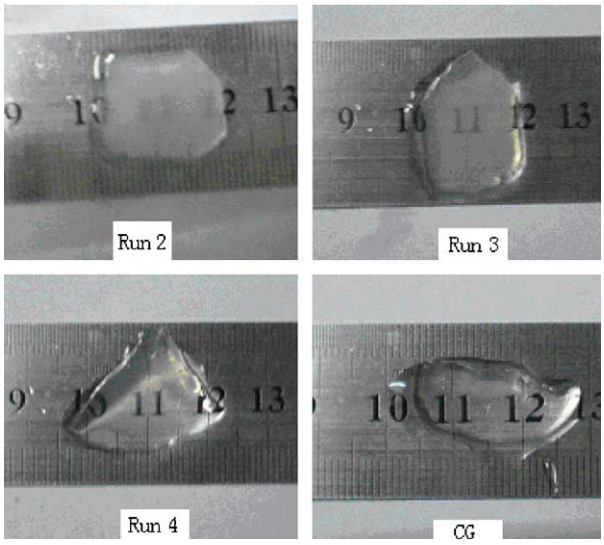

Fig. 2. Photo pictures of CG and RAFT gels of series 1 after immersed in water for 48 h.

3.2. Deswelling kinetics of the hydrogels

All of the gels are transparent and clear in 1,4-dioxane. But the appearance is different between them after the gels were immersed in water after a period of time. The transparency and clarity of the gels decreased with increased CTA/BIS ratio. As shown in Fig. 2, CG was transparent and clear but run 2 appeared turbid after immersed in distilled water. It is well known that the turbidity of a gel is a direct result of light scattered from the spatial inhomogeneities of its refractive index [26]. This indicated more inhomogeneous structure for RAFT gels than CG. But according to some studies before [27–29], the gels via living free radical technique were found to be more homogeneous than similar gels prepared by conventional free radical polymerization methods via a comparison to Flory's gelation theory.

The structural homogeneity or heterogeneity would affect the swelling property of the hydrogels. So the swelling behaviors were investigated to deepen the understanding of the structure of the hydrogels. Fig. 3 shows the deswelling kinetics. CG (run 5) shrank slowly and took long time to reach its equilibrium state. The slow deswelling of CG was attributed to the skin layer formation during the deswelling process. The surface dense and stable skin layer is impermeable and prevents the inner water from diffusing out [3]. Compared with the CG, RAFT gels showed accelerated shrinking kinetics. The accelerated degree increased with the increased CTA/BIS ratio. Among them, runs 2 and 3 showed rapid deswelling kinetics. The results are different from our prediction because homogeneous PNIPAM gels are correlated with the slow shrinking kinetics.

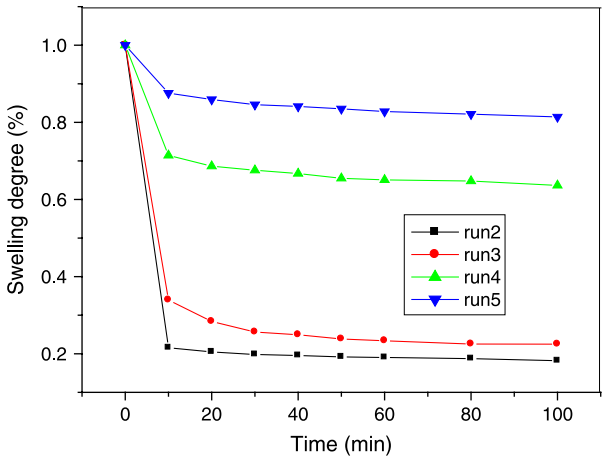

Fig. 3. Deswelling kinetics of the hydrogels of series 1 after T-jump from 20 to 40 °C.

3.3. Crosslinking polymerization mechanism

We attempt to explain the finding disclosed above. As given in Table 1, RAFT gels had the same feed composition and reaction conditions with CG except the presence of CTA. And the main difference between RAFT gels was the content of CTA. So the accelerated shrinking kinetics of RAFT gels to CG could be ascribed to the presence of CTA. There are two main effects brought by CTA. One is to introduce little hydrophobic end groups into the hydrogels; the other is retardation effect to the crosslinking reaction [23,25]. It has reported that the lower critical solution temperature (LCST) behavior of PNIPAM is scarcely affected by the presence of end groups [30]. So the effect brought by the presence of little hydrophobic groups could be neglected.

In previous report, Matsumoto et al. prepared amphiphilic network polymers by free radical crosslinking copolymerizations of monomethacrylate and dimethacrylate in the presence of lauryl mercaptan as a CTA, which led to the delayed gelation with a decrease in the primary polymer chain length. The swelling ratios of the gels obtained were high [31]. It implied that the retardation effect might affect the structure and swelling property of the gels. For RAFT polymerization the rate of polymerization decreases significantly when increasing the RAFT CTA concentration [25,32], which might lead to different intrinsic structure between RAFT gels and CG.

For CG system, as presented by Fukuda et al. [27,33], (dead) polymers of full length are formed from the beginning of the reaction [29]. It is known in a conventional free radical polymerization the monomer propagation is so quick that it gives no time to the polymer chain to relax [28]. So cross-links will be formed mostly within the same molecule, producing less expanded chains. As the reaction proceeds, intermolecular cross-linking will occur more frequently and combine these chains into larger molecules, which will absorb other chains more effectively than small molecules and leads to the generation of microgels even at relatively low conversions. At a critical conversion, these microgels will be tied up and form gel.

For RAFT system, the primary chains with living character form from the beginning of the reaction. Since in RAFT system (primary) chains grow slowly via living mechanism [25], the system will take much more time to reach gelation than conventional free radical counterpart. On the other hand, the slow growth rate permits a polymer chain to be fully relaxed, which will increase intermolecular crosslinking and reduce the intramolecular cross-linking and microgel greatly in the RAFT gels [27,28]. It has reported that the hyperbranched structure could be obtained by limiting the rate of chain growth through degradation reaction [34], chain transfer reaction [35] or living polymerization mechanism [24,36]. So during the time before gelation the living primary chains will further react with monomer and crosslinker to produce branched and hyperbranched structure [23,24,36]. Notably, the vinyl-type network polymers formed via highly branched prepolymer have abundant dangling chains as their characteristic feature because terminal parts of prepolymer chain would be dangling chains [31,37]. So some of the branched chains will remain in the network structure and lead to RAFT gels with a number of dangling chains when gelation occurs. However, it is difficult to obtain the amount (or density) of dangling chains quantitatively on the basis of the available data at this stage because the insoluble, infusible properties of network result in the lack of suitable analytical methods for their characterization [37]. Fig. 4 demonstrates the progression of gelation and the different intrinsic structure of gels by conventional radical copolymer and by RAFT polymerization.

It was well known that the gels with dangling chains would exhibit improved molecular mobility due to the existence of freely mobile graft chains, which show rapid dehydration, followed by the subsequent hydrophobic intermolecular aggregation of dehydrated graft chains [2,38]. The dehydrated graft chains create the hydrophobic cores, which can enhance the hydrophobic aggregation of the networks, resulting in drastic acceleration of shrinking kinetics of grafted PNIPAM gel. So the accelerated shrinking kinetics of RAFT gels could be attributed to the presence of abundant dangling chains. Among them, runs 2 and 3 show rapid shrinking rate, which indicated the RAFT gels with higher CTA/BIS rate have more dangling chains. Moreover, the large number of dangling chain could lead to phase separation of network because dangling chains are structurally separated from the backbone crosslinked network [2,39,40]. Hence, we believe that the turbid appearance of RAFT gels immersed in water is an evidence of the existence of abundant dangling chains.

3.4. Swelling kinetics of the hydrogels

Swelling kinetics for the CG and RAFT gels in deionized water are shown in Fig. 5. As can be seen, it all took over 10 h to reach their equilibrium state for all of the hydrogels. The presence of a number of dangling chains could not improve swelling kinetics of RAFT gels compared with CG because the swelling kinetics of the grafted-type gels was governed by

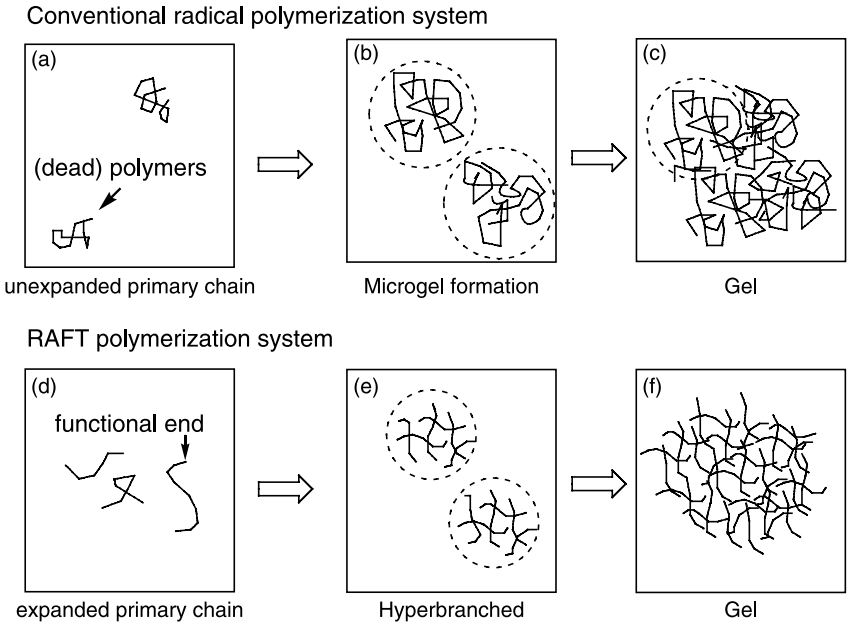

Fig. 4. Schematic presentations of the progression of gelation and different intrinsic structure of gels for (a)–(c) conventional radical polymerization system (d)–(e) RAFT polymerization system.

polymer network diffusion [2]. According to the reports before, these dangling chains in the network polymers could influence as an increase in their swelling ratios [1,2,5]. Under the measurement temperature, RAFT gels indicated a higher swelling ratio than CG, and the gels with more CTA content showed higher swelling. The order was run 3 > run 4 > CG. It was consistent with the reports before. In the case of run 2, it displayed a little lower swelling degree than CG, which was ascribed to a result of higher crossinkling density of run 2 than run 3, run 4 and CG [41]. These results could further prove the existence of abundant dangling chain in the network.

In order to further investigate the effect of CTA, another RAFT CTA, 3-(trithiocarbonyl) propanoic acid (CTA2), was adopted to prepare the RAFT gels (Table 2). 3-(Trithiocarbonyl) propanoic acid may be insufficient to control the living process according to its structure feature [42,43]. But it was an effective CTA to slower the crosslinking reaction yet and trithiocarbonyl groups could be remained after the reaction. RAFT gels of the series 2 showed different degree retardation effect, which could be observed by the gel point of counterpart of two series (series 1 > series 2 > CG). RAFT gels of series 2 also shown similar accelerated shrinking kinetics with series 1 (Fig. 6). But the accelerated degree to the shrinking kinetics was low compared with the counterpart of series 1. The reason may be less dangling chains are introduced into the gel structure by CTA2 compared with CTA1 at the same reaction condition due to the different degree of retardation effect. From the two series, it could be concluded that RAFT polymerization can lead to improved shrinking kinetics. If the proper RAFT CTA is chosen to control the reaction, rapid shrinking

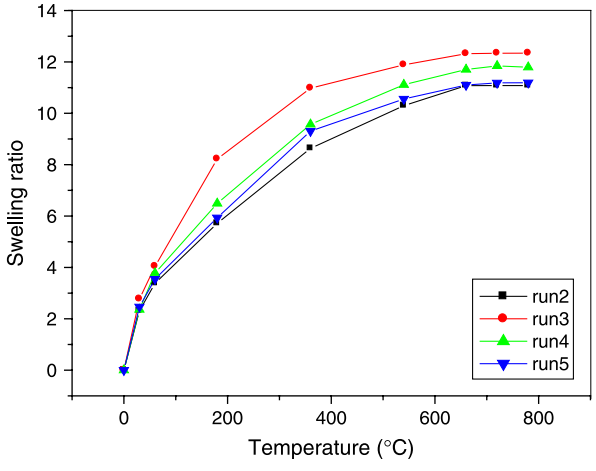

Fig. 5. Swelling kinetics of hydrogels of series 1 at 20 °C from dried conditions.

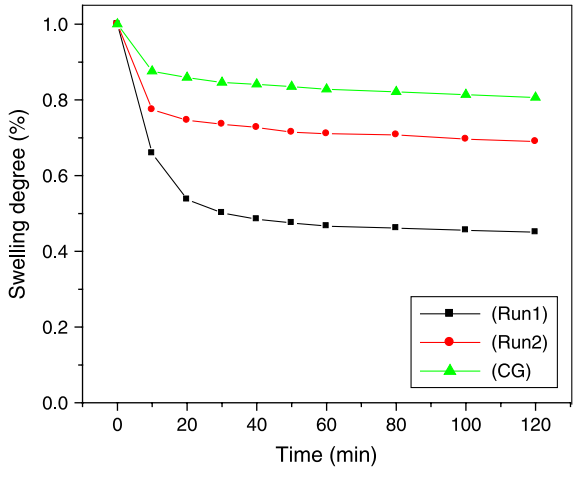

Fig. 6. Deswelling kinetics of the hydrogels of series 2 after T-jump from 20 to 40 °C.

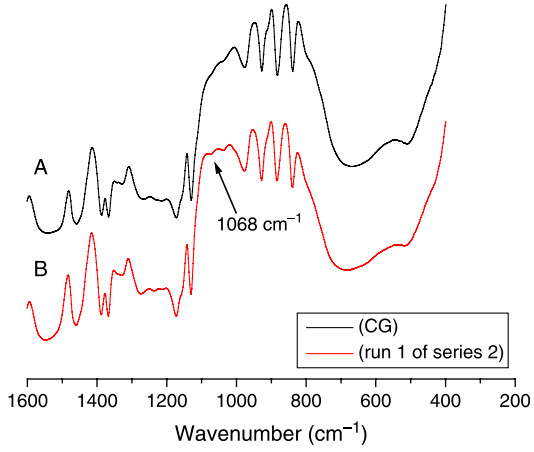

Fig. 7. FT-IR spectra of (A) CG (KBr disk); (B) run 1 of series 2 (KBr disk).

hydrogels can be prepared as shown by runs 2 and 3 of series 1, which supplies a new method to synthesize rapid responsive hydrogels.

3.5. Chain extension of the functional hydrogels-synthesis of grafted hydrogels

RAFT polymerization is a living process, which means that the reactive dithioester groups should be remained in the network at the end of the polymerization. Therefore, addition of a new batch of monofunctional monomer should lead to the chain extension of the functional hydrogels and result in a grafted structure. Run 1 of series 2 was adopted as the backbone. The living groups, trithiocarbonic bonds, could be observed by FT-IR. As shown in Fig. 7, the main difference between RAFT gels and CG was the signal at 1068 cm^{-1}, which was assigned to the presence of C=S groups in the RAFT gels. The signal 1068 cm^{-1} was not obvious due to the low content of CTA in the RAFT gel. Then the PNIPAM-*g*-PNIPAM gel was prepared by extensive reaction of the backbone.

As mentioned above, the grafted chains can improve the deswelling kinetics and can lead to the drastic acceleration of shrinking rate of the gel network From Fig. 8, we can see the

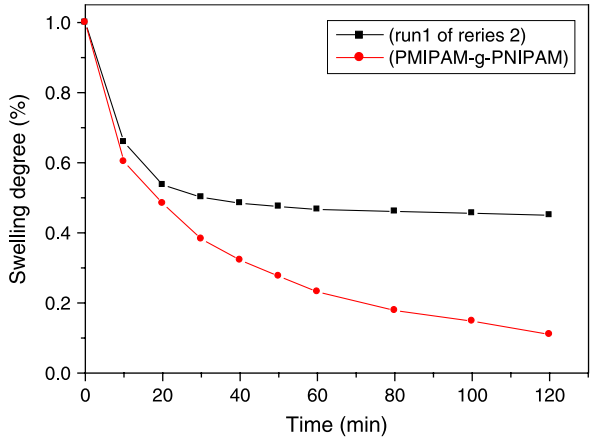

Fig. 8. Deswelling kinetics of PNIPAM-*g*-PNIPAM hydrogels after T-jump from 20 to 40 °C.

PNIPAM-*g*-PNIPAM hydrogels indicted further accelerated shrinking kinetics than functional backbone hydrogels (run 1 of series 2), which could prove the successful chain extension from the functional hydrogels. But the grafted hydrogel did not exhibited drastic acceleration of shrinking rate. The reason may be that only a little new grafted chain was introduced into the network by extension reaction because of the low content of reactive dithioester groups in the backbone and the constrained grafted efficiency. It has been reported that comb-type graft chain amount has significant influence on the gel deswelling kinetics and more freely mobile graft chains can lead to rapid shrinking [5]. So the grafted hydrogel showed further accelerated but not drastic accelerated shrinking kinetics.

4. Conclusions

In this paper, PNIPAM-*co*-BIS functional hydrogels were prepared using RAFT polymerization. And the swelling behavior was studied. It was found that the presence of CAT could lead to accelerated shrinking kinetics of RAFT hydrogels. It supplies a new method to prepare rapid responsive hydrogels, which is important for hydrogels applications in some aspects. Moreover, the functional hydrogels could initiate the grafted polymerization of a new batch of monofunctional monomer. And the derivative PNIPAM-*g*-PNIPAM hydrogels by the 'graft from' method shown further accelerated deswelling kinetics.

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