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ScienceDirect
Polymer 47 (2006) 6963–6969
polymer
www.elsevier.com/locate/polymer

Synthesis of rapid responsive gels comprising hydrophilic backbone and poly(*N*-isopropylacrylamide) graft chains by RAFT polymerization and end-linking processes

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Received 31 March 2006; received in revised form 1 August 2006; accepted 5 August 2006
Available online 28 August 2006

Abstract

A thermosensitive poly(*N*-isopropylacrylamide) (PNIPAM) grafted gel, which comprises hydrophilic backbone and freely mobile PNIPAM graft chains, was synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization and end-linking processes. Functional PNIPAM bearing dithiobenzoate end group (−C(=S)S−R) was prepared first, and then it was reacted with divinyl compounds to obtain gel. In order to adjust the composition of the gels, two divinyl compounds, *N*,*N*-methylenebisacrylamide (BIS) and poly(ethylene glycol) diacrylate (PEGDAC), were used. The cross-linking polymerization mechanism was proposed. The swelling and deswelling kinetics of the hydrogels were measured. The gels exhibit rapid deswelling kinetics. At the same time, they show rapid swelling kinetics within 30 min, whereas a conventional PNIPAM-*co*-PEG-*co*-BIS gel with the same feed composition requires more than 10 h to reach swelling equilibrium.

Keywords: End-linking processes; Poly(*N*-isopropylacrylamide); Poly(ethylene glycol)

1. Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) gels show interesting phase behavior in aqueous solution. Phase transition occurs as the temperature is increased above its lower critical solution temperature (LCST). Due to the unique properties, PNIPAM gel has been utilized in many fields [1], such as drug delivery, mass separations, biosensor and biocatalyst. But conventional PNIPAM gels are limited by their slow swelling and deswelling rates [2], and some successful strategies have been worked out to enhance the response rates.

One approach was to synthesize comb-type grafted PNIPAM gels by graft copolymerization. Comb-type grafted gels exhibited acceleration of shrinking rate due to the free mobility of the grafted chains [3–5]. And 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 PNIPAM gels, including the usage of hydrophobic additive as pore-forming agent during gel preparation [6], gel preparation above its LCST [7,8] and the incorporation of silica microparticles removed by subsequent acid treatment of the silica [9]. Some other strategies were used to improve the response rate, such as composite gels with microgels or nanoparticles [10–12], using mixed solvent [13], utilizing micelle-forming ability of surfactant [14] and adding RAFT chain transfer reagent [15]. Using these strategies we have successfully obtained PNIPAM gels with fast shrinking rate. But most of the gels have not shown fast swelling rate. The reason could be that the swelling kinetics of these gels are governed by collective diffusivity of

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doi:10.1016/j.polymer.2006.08.009

PNIPAM chains [5]. However, Lee's group [16] reported that gels composed of alginate network backbone and PNIPAM graft chains exhibited rapid swelling and deswelling kinetics, which indicate that hydrophilic backbone network and freely mobile PNIPAM chains are favorable to the rapid response of the gels.

On the other hand, the conventional methods for the preparation of gels have no control of the network architecture parameter such as the molar mass or the polydispersity of the polymer chains between cross-links [17]. But such control could be obtained by using end-linking processes, i.e., reactions between α,ω-difunctional polymer and cross-linker [18]. Recently, living radical polymerization has been used to prepare various well-defined polymers [19] and complex architectures. Some reports have demonstrated the potential of living radical polymerization technique to prepare gels with more homogeneous structure [20,21]. Connecting the two methods, Chaumont et al. synthesized poly(styrene) networks by living free radical polymerization and end-linking reactions [17,22].

Based on the discussion above, the goal of this study was to prepare a rapid responsive PNIPAM grafted gel by RAFT polymerization and end-linking processes, which comprises hydrophilic backbone and freely mobile PNIPAM graft chains. The synthetic strategy is shown schematically in Fig. 1. PNIPAM bearing dithiobenzoate end group (−C(=S)S−R) was prepared first, and then it was reacted with cross-linker to obtain gels. Two cross-linkers, PEGDAC and BIS, were used to adjust the composition of the gels. The structure of obtained gels was different from the structure of comb-type grafted gels as Fig. 1 shows [5]. We attempt to demonstrate the course of gelation and cross-linking polymerization mechanism. The swelling and deswelling kinetics of the gels were measured.

2. Experimental

2.1. Materials

4-Cyanopentanoic acid dithiobenzoate (DTE) was prepared according to literature [5]. NIPAM was purchased from Acros and used without further purification. Poly(ethylene glycol) (PEG) (Mw = 4000) was dried under vacuum for 12 h at 80 °C. Dichloromethane was treated with molecular sieve before use. *N*,*N*-Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), acrylic acid (AAc), *N*,*N*-methylenebisacrylamide, 4,4′-azobis(4-cyanopentanoic acid) (ACP, from Aldrich), 1,4-dioxane and all other reagents were used as received.

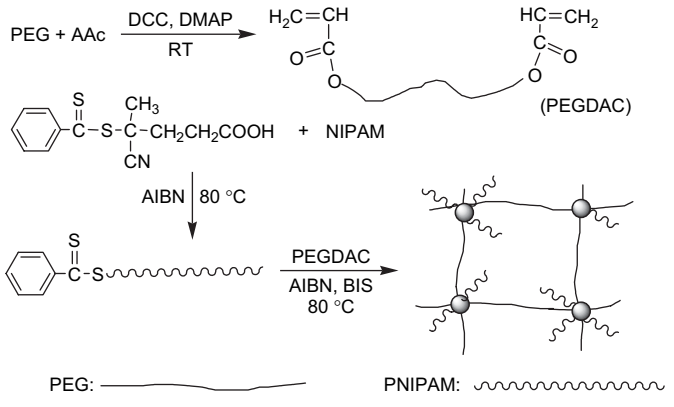

Fig. 1. Synthetic procedure for gels with PEG-*co*-BIS backbone and PNIPAM graft chains.

2.2. Instrumentation

^{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. Gel permeation chromatography (Waters 515-410) was carried out to estimate the number-average molecular weights and polydispersities of the polymers. Standard poly(styrene) was used for calibrating the molecular weight. For the FT-IR measurements, an RFX-65A spectrometer (Analect, USA) was used. Solid samples were embedded in KBr disks. The elemental analysis was performed using CHN−O−RAPID elemental analyzer (Heraeus, Germany).

2.3. Synthesis of the gels comprising hydrophilic backbone and PNIPAM graft chains (designated as HBG gels)

PNIPAM with thiocarbonylthio (−C(=S)S−R) end was prepared as follows: 0.051 g DTE, 0.012 g ACP and 2.02 g NIPAM and 15 mL 1,4-dioxane were placed in a glass tube, degassed for three times by freeze−thaw−pump cycles. Then the tube was sealed and placed in an oil bath at 80 °C. After it was cooled and diluted with acetone, it was precipitated with absolute ether for two times.

Poly(ethylene glycol) diacrylate (PEGDAC) was prepared as follows: 1 mL AAc and 5 g PEG were dissolved in 30 mL dichloromethane. Then 0.1 g DMAP was added with stirring. After cooling to 0 °C, 4 g DCC was added. The reaction mixture was further stirred at room temperature for 48 h. After filtration of undissolved impurity, the obtained polymer was precipitated into petroleum ether for three times and dried in a vacuum oven at 40 °C.

To synthesize the HBG gels, a mixture of the functional PNIPAM, PEGDAC, BIS, ACP and 1,4-dioxane was put into a glass tube, degassed and sealed under nitrogen. The polymerization was conducted at 80 °C. To remove unreacted monomer and linear polymers, the obtained gel was immersed in deionized water for three days, and water was replaced everyday. Then it was dried under ambient conditions for 48 h followed by thorough drying under vacuum at 60 °C. Results of the polymerization are summarized in Table 1. For comparison, normal PNIPAM-*co*-PEG-*co*-BIS gels with the same feed composition with run 4 was synthesized by conventional free radical copolymerization of NIPAM monomer with BIS and PEG at 60 °C.

Table 1
Feed composition for preparation of BHG gels

Run	PNIPAM (g)	PEGDAC (mg)	BIS (mg)	ACP (mg)	1,4-Dioxane (mL)	Conversion (%)
1	0.2	0	13	2	2	0
2	0.2	200	0	2	2	0
3	0.2	20	13	2	2	0
4	0.2	65	13	2	2	50
5	0.2	65	20	2	2	54
6	0.2	65	26	2	2	60
7	0.2	110	26	2	2	70

2.4. Swelling equilibria for the gels

The swelling ratio (W_{H_2O}/W_p) is defined as the weight of absorbed water (W_{H_2O}) per weight of dried gel (W_p). Equilibrium swelling weights for the gels in water at various temperatures were measured gravimetrically after wiping excess water from the gel's surface using filter paper. The gels were cut into disks (15 mm in diameter and 3 mm in thickness) and equilibrated at higher temperature (50 °C). After determining the gel mass, the temperature was lowered, and the gels were equilibrated to reach swollen conditions at this temperature. This process was repeated until the temperature reached 20 °C.

2.5. Swelling and deswelling kinetics of the gels

Swelling and deswelling kinetics are defined as temporal weight changes of the gels. For the kinetics studies, disk-shaped hydrogels were first equilibrated in deionized water at a predetermined temperature (20 °C). And the gels were weighed 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.

3. Results and discussion

3.1. Synthesis of HBG gels

Linear living polymer with active site at one or two ends can be synthesized by utilizing living radical polymerization readily. At present, there are several reports detailing the RAFT polymerization of NIPAM using different RAFT chain transfer reagents (CTAs) [23,24]. In this work, we used 4-cyanopentanoic acid dithiobenzoate as a chain transfer reagent and 1,4-dioxane as a solvent to prepare PNIPAM bearing dithiobenzoate end group (−C(=S)S−R) (1 in Fig. 2) by RAFT polymerization. The signals at 7.8–8.1 ppm in the ^{1}H NMR spectrum correspond to the aromatic protons next to dithioester group and indicate that the dithiobenzoate group remained at one end of the PNIPAM chain. The signal at 2.9–3.1 ppm is assigned to the presence of water, which could be further proved by the increased weight of PNIPAM when it was exposed to air for several days. The presence of water in PNIPAM is favorable to avoid the GPC problem due to the irreversible chain aggregation after complete drying of the sample [23]. Their number-average molecular weights and polydispersity are 12 000 and 1.3, respectively, measured by GPC (see Fig. 3A). Linear living PNIPAM could further react with divinyl compounds to obtain gel.

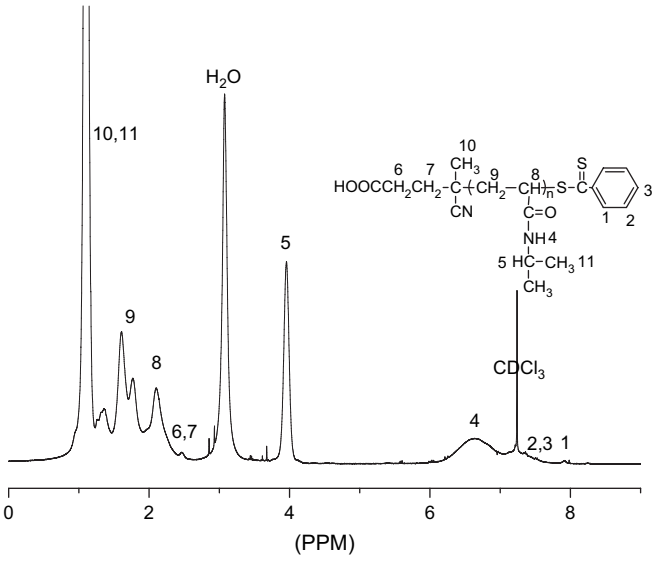

Fig. 2. ^{1}H NMR spectrum of PNIPAM obtained by RAFT polymerization.

PEGDAC was synthesized as macromolecular cross-linker (Macro-CL) (2 in Fig. 1). The ^{1}H NMR spectrum of the obtained polymer gives information on the end functionality. The peaks at and around 5–7 ppm are assigned to vinyl protons. The protons adjacent to the acrylate groups shift to around 4.3 ppm and the ratio of area of peak at a, b, c and d is about 1:1:1:2 (see Fig. 4). Moreover, FT-IR data for acryloyl-terminated PEG show an ester carbonyl peak at 1724 cm^{-1} (see Fig. 5). These results could prove that the end groups of the polymer have been converted from hydroxy group to acryloyl group quantitatively.

The results for preparation of gels are given in Table 1. When only one cross-linker was used to prepare HBG gels,

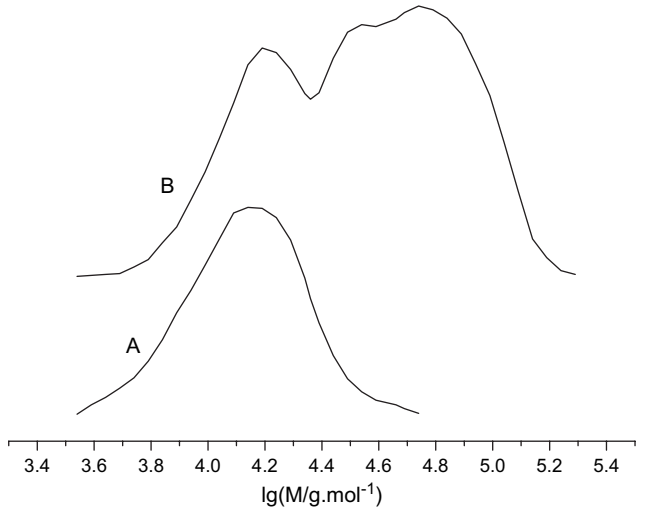

Fig. 3. GPC curves of (A) PNIPAM; (B) product of run 1 in Table 1.

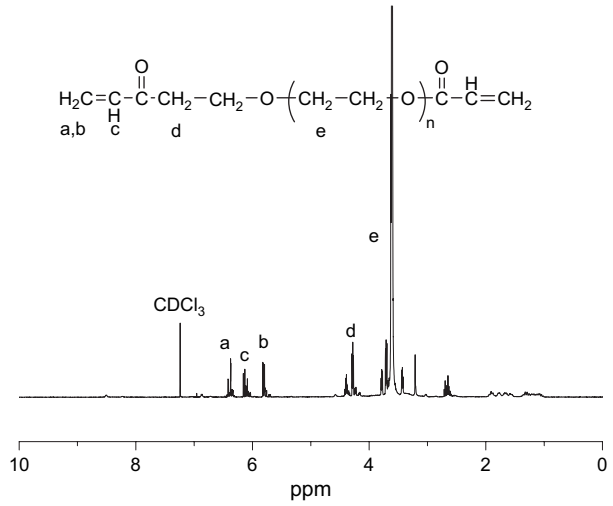

Fig. 4. ^{1}H NMR of PEGDAC.

it was unfavorable to obtain gels under reaction conditions as runs 1 and 2 indicated. Run 1 failed to obtain gel due to low ratio of BIS/PNIPAM [25]. Run 2 failed to obtain gel even when the feed of PEGDAC reached to 50% (wt%). When two cross-linkers are used together, it could be seen that the composition of gels is more adjustable than the case where only one cross-linker is used as runs 4, 5, 6 and 7 show. The PEG contents (weight ratio wt%) of runs 4, 5, 6 and 7 are 0.30 (content of feed: 0.23), 0.27 (0.22), 0.26 (0.22), and 0.34 (0.32), respectively, measured by elemental analysis. It could be seen that all of these gels have higher PEG contents than feed content of counterpart, which indicated that part of the PNIPAM was not incorporated into the gel networks. As shown in Table 1, the weight conversions of the obtained gels are not high under experimental conditions and the effects of BIS and PEGDAC content on conversion are obvious. The more BIS and PEGDAC content, the higher the weight conversion it would lead to (run 4 < run 5 < run 6 < run 7).

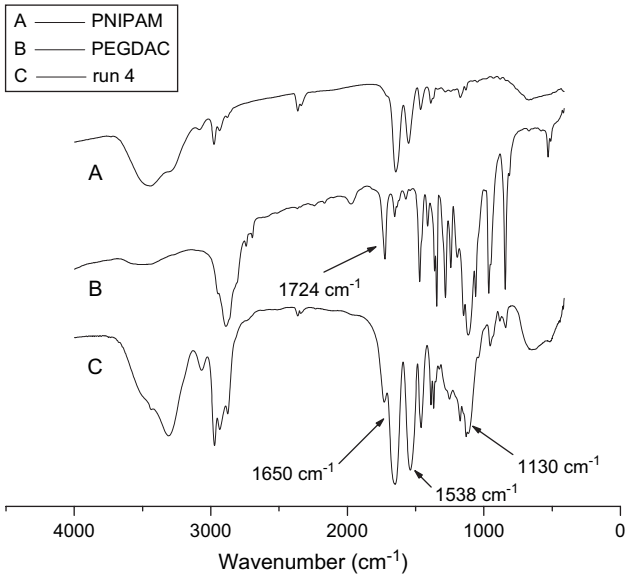

Fig. 5. FT-IR spectra of (A) PNIPAM (KBr disk); (B) PEGDAC (KBr disk); (C) gel (run 4).

3.2. Cross-linking polymerization mechanism

Here, we attempted to demonstrate the cross-linking polymerization mechanism. It was reported that reactions between linear living polymers (precursors) and divinyl compounds (cross-linker) could lead to star-shaped polymers with cross-linked core (soluble) [25–28] as shown in Fig. 6A. Initially, the divinyl compounds are added to the precursors' chain ends to form short block copolymers with unreacted pendant vinyl groups. Then the block copolymers containing the unreacted vinyl groups start to react with each other to form star polymers. During the course, end-linking reaction (see Fig. 6A, 1) between the living end of the linear polymer and the pendant vinyl groups could induce polymer linking. And the intramolecular coupling reaction (see Fig. 6A, 2) between unreacted pendant vinyl groups could induce the star polymer core formation. According to the discussion above, the product of run 1 could be star polymer when only BIS was used as cross-linker. GPC of the obtained product of run 1 (Mn = 25 000, PDI = 1.7, see Fig. 3) shows new peaks in the higher molecular weight region, indicating the star polymers formed. However, the GPC trace clearly shows the presence of unlinked block polymer. The reason is that the linear polymers are consumed slowly by RAFT mechanism during the preparation of star polymers [29], which might influence the conversions of runs 4, 5, 6 and 7 as mentioned above.

When two cross-linkers were used, the formation of gels is as proposed in Fig. 6B. The gel was produced by end-linking reaction (see Fig. 6B, 1), intramolecular coupling reaction (see Fig. 6B, 2) and by intermolecular linking reaction (see Fig. 6B, 3 and 4). As known, linear living PNIPAM could react with divinyl compounds (BIS and PEGDAC) to form the block with unreacted vinyl groups. Because PEGDAC is a divinyl compound with much longer spacers than BIS, these unreacted vinyl groups of the block copolymer would have both short and long spacers. As mentioned above, the block copolymers containing the unreacted vinyl groups could react with each other. Among them, end-linking reaction (between the living end of the block polymer and the pendant vinyl groups) could lead to polymer linking, and intramolecular coupling reaction would occur (between the pendant vinyl groups) to form the star polymer core. It is noticeable that vinyl groups of PEGDAC with the longer spacers could induce intermolecular linking to form gel [30] because part of vinyl groups of PEG could extend into another star polymer to induce intermolecular linking between star polymers during the reaction. A similar structure synthesized by end-linking processes and sequential anionic polymerization has been reported before [31].

The intermolecular linking reaction of PEGDAC can be confirmed by experimental results. As shown in Table 1, run 1 failed to obtain gel without using PEGDAC, but gel could be obtained in run 4, which had the same feed composition as run 1 except for the presence of PEGDAC. FT-IR spectrum (Fig. 5) of run 4 shows characteristic peak at 1130 cm^{-1}

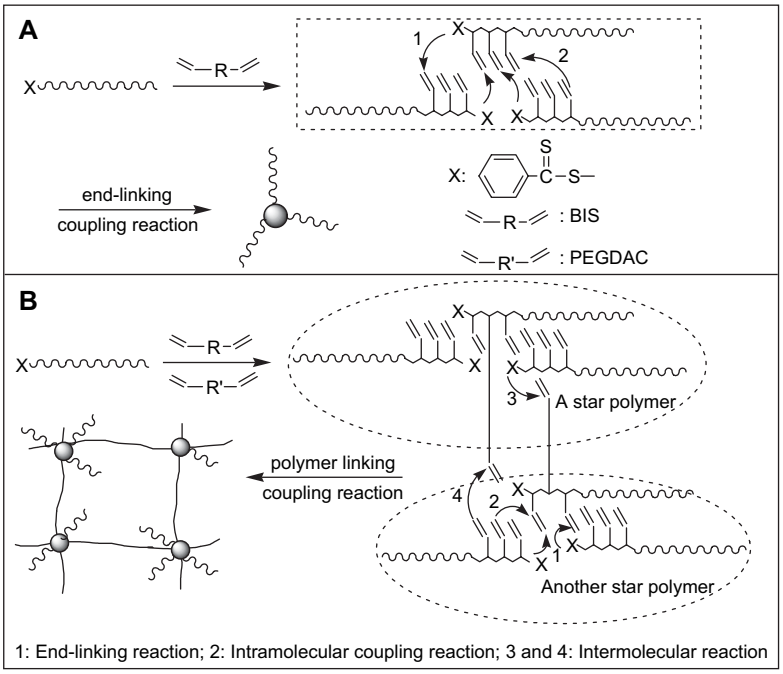

Fig. 6. The proposed mechanism for the formation of star polymers (A) and gels (B).

assigned to ether groups of PEG and absorption bands at 1650 cm^{-1} and 1538 cm^{-1} assigned to amides I and II of PNIPAM, respectively, which indicated that PEG and PNIPAM were incorporated into the HBG gels. Low PEGDAC/PNIPAM ratio is unfavorable to the gel formation as run 3 indicated. This is because only part of PEGDAC could act as intermolecular linker to link polymer, while other part of PEGDAC is consumed on intramolecular reaction or other side reactions [18,30,32]. It should be noted that the PNIPAM chains were incorporated into gel and linked at the end of PEG chains due to end-linking processes as Fig. 6 shows. And the network architecture parameter such as PEG chains between cross-links and PNIPAM graft chain is well-defined. So the structure of HBG gels was different from that of comb-type grafted gels.

3.3. Swelling equilibria, swelling and deswelling kinetics of the gels

The structure of gels would affect the swelling property of the gels. So the swelling behaviors were investigated to deepen the understanding of the relationship between the structure and property of gels. Fig. 7 shows the temperature dependence of swelling equilibrium of the gels. The resultant gels show a discontinuous volume transition between 20 and 40 °C. And the swelling ratio of gels is influenced by the content of BIS and PEGDAC. As can be seen, run 4 exhibits higher swelling ratio than runs 5 and 6, which have the same composition as run 4 except for lower contents of BIS. The reason is that the swelling rate of gels increases with a decrease in the content of BIS [33]. It was reported that high content of PEG results in the high swelling ratios of gels [34]. Run 7 exhibits higher swelling ratio than runs 5 and 6. But run 4 exhibits higher swelling ratio than run 7, which may be attributed to the much higher cross-linking density of run 7 compared with run 4.

Fig. 8 shows the shrinking kinetics of the gels after T-jump from 20 to 40 °C. They all exhibit a rapid deswelling to reach the equilibrium deswelling state within 20 min. The rapid shrinking could be mainly attributed to the freely mobile chains. When the temperature was increased up its LCST, the graft chains in the gels would show rapid dehydration, followed by the subsequent hydrophobic intermolecular aggregation of dehydrated graft chains. The dehydrated graft chains create the hydrophobic cores, which can enhance the hydrophobic aggregation of the networks, resulting in drastic acceleration of shrinking kinetics [35]. In addition, some water remained in the gels after they reached the equilibrium

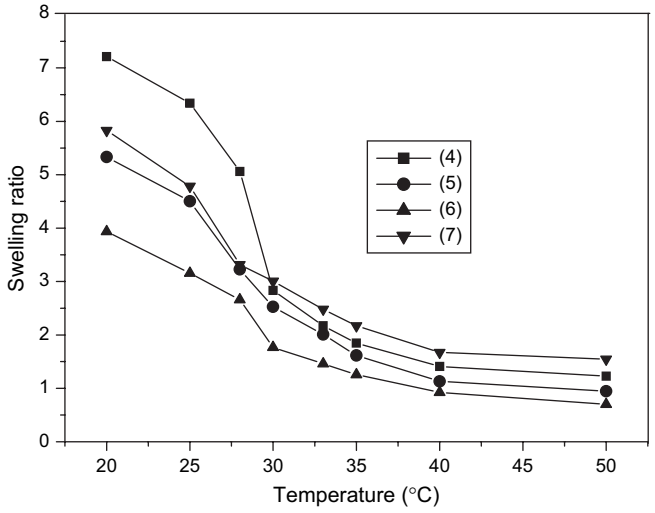

Fig. 7. Equilibrium swelling ratio for the gels as a function of temperature.

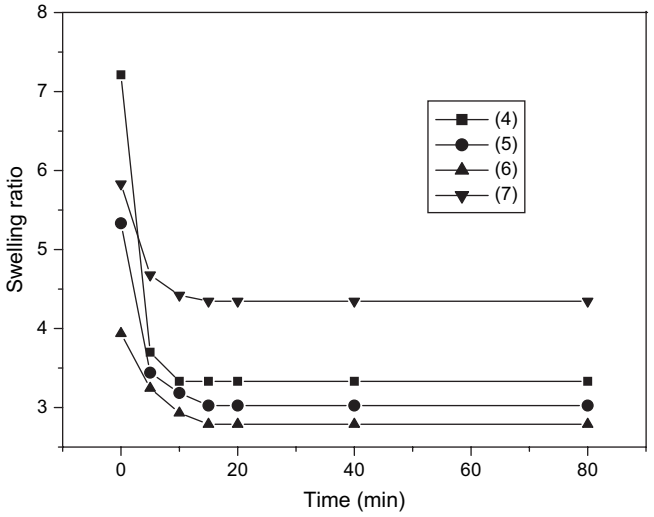

Fig. 8. Deswelling kinetics of the gels after T-jump from 20 to 40 °C.

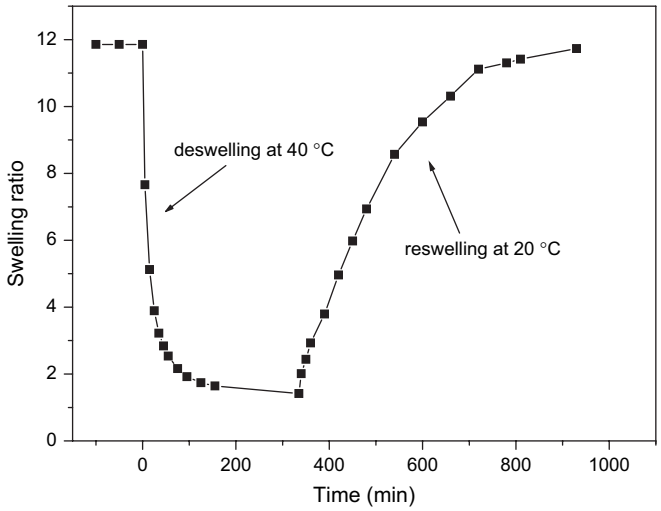

Fig. 10. Kinetics of deswelling and reswelling of normal PNIPAM-*co*-PEG-*co*-BIS gel.

deswelling state due to the hydrophilicity of the PEG. The water content maintains nearly a constant as shown in Fig. 8. Run 7 exhibits highest water content due to more PEG content. And among runs 4, 5 and 6, run 4 has the highest water content, while run 6 exhibits lowest water content because local cross-linking density increases with the content of BIS.

In previous reports, rapid swelling did not occur for comb-type grafted gels (such as PNIPAM-*g*-PEG gels) because the swelling kinetics of the gels are governed by polymer network diffusion [3,36]. But for the HBG gels, they reach their equilibrium swelling state within 30 min as shown in Fig. 9, which could be mainly ascribed to the intrinsic structure of the network. As known, the PEG-*co*-BIS backbone of HBG gels is more hydrophilic without hydrophobic groups such as isopropyl group in PNIPAM. And all PNIPAM compositions are incorporated as free chains, which would exhibit improved molecular mobility. When the temperature was decreased to its LCST, the graft PNIPAM chains could show rapid and strong hydration [37]. Both hydrophilic PEG and freely mobile PNIPAM graft chains are favorable to rapid swelling kinetics.

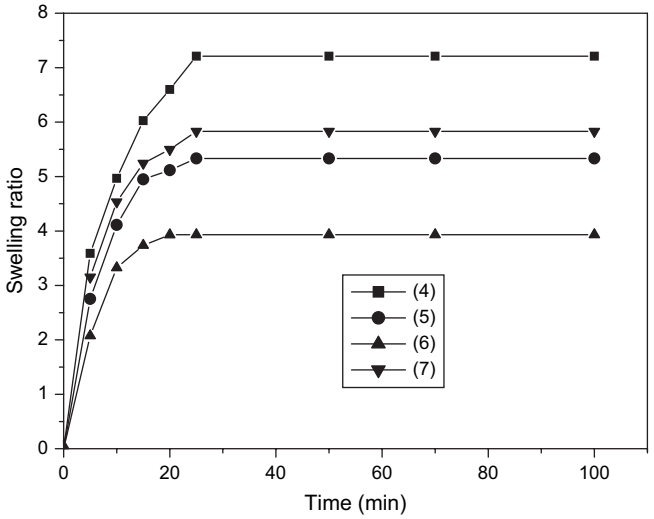

Fig. 9. Swelling kinetics of gels at 20 °C from dried gels' state.

In comparison, normal PNIPAM-*co*-PEG-*co*-BIS gel was synthesized by conventional free radical copolymerization of NIPAM monomer with BIS and PEGDAC. It has the same feed composition as run 4. Its weight conversion reached 94%. The kinetics of swelling and deswelling of normal gel are shown in Fig. 10. It shows higher swelling ratio at measurement temperature than run 4. This is because most of BIS is consumed to form compact core, which results in high local cross-linking density for run 4. It can be seen that the normal gel requires more than 10 h to reach swelling equilibrium, while run 4 can reach swelling equilibrium in only 30 min. The obvious difference of swelling kinetics is attributed to the different intrinsic structure. In normal gel, both the ends of the PNIPAM chains are cross-linked and relatively immobile. So the diffusion of PNIPAM chains towards water is governed by collective diffusivity of network during swelling. But for run 4, the diffusion of these chains is relatively free because they are immobilized only at one end. These characters of run 4 could lead to rapid hydration.

4. Conclusions

In this work, we prepared a fast-responding gel with the hydrophilic backbone and freely mobile PNIPAM graft chains by RAFT polymerization and end-linking processes. PNIPAM bearing dithiobenzoate end group could further react with divinyl compounds to obtain gels. Two divinyl compounds, PEGDAC and BIS, were used to adjust the composition of the gels. We attempt to demonstrate the mechanism of gelation. It is proposed that the content of BIS was mainly consumed to link PNIPAM chains to form the core of star polymers. But PEGDAC with longer spacer could induce intermolecular linking and result in gelation. The swelling behaviors were investigated to deepen the understanding of the structure of the gels. The obtained gels showed a discontinuous volume

transition. And they exhibit fast deswelling kinetics because of the presence of freely mobile PNIPAM graft chains. Moreover, they show rapid swelling kinetics within 30 min, whereas a conventional gel requires more than 10 h to reach swelling equilibrium. The results reflected the different intrinsic structure between HBG gels and conventional gels. In principle, the gel might find a number of applications including actuators and drug delivery systems.

References

[1] Schild HG. Prog Polym Sci 1992;17:163.
[2] Chen J, Blevins WE, Park HS, Park KN. J Controlled Release 2000; 64:39–51.
[3] Yoshida R, Uchida K, Sakal K, Kiruchi A, Sakurai Y, Okano T. Nature 1995;374:240.
[4] Kaneko Y, Nakamura S, Sakai K, Aoyagi T, Kikuchi A, Sakurai Y, et al. Macromolecules 1998;31:6099.
[5] Liu QF, Ping Z, Lu MG. J Polym Sci Part A Polym Chem 2005;43:2615.
[6] Zhang XZ, Chu CC, Zhuo RX. J Polym Sci Part A Polym Chem 2005;43: 5490–7.
[7] Kabra BG, Gehrke SH. Polym Commun 1991;32:322.
[8] Wu XS, Hoffman AS, Yager P. J Polym Sci Part A Polym Chem 1992;30: 2121.
[9] Serizawa T, Wakita K, Akashi M. Macromolecules 2002;35:10.
[10] Zhang JT, Huang SW, Xue YN, Zhuo RX. Macromol Rapid Commun 2005;26:1346.
[11] Zhang XZ, Chu CC. Polymer 2005;46:9664.
[12] Liu Y, Zhu MF, Liu XL, Zhang W, Sun B, Chen YM, et al. Polymer 2006;47:1–5.
[13] Zhang XZ, Zhuo RX, Yang YY. Biomaterials 2002;23:1313.
[14] Noguchi Y, Okeyoshi K, Yoshida R. Macromol Rapid Commun 2005;26: 1913–7.
[15] Liu QF, Ping Z, Qing AX, Lan YX, Lu MG. Polymer 2006;47:2330.
[16] Ju HK, Kim SY, Lee YM. Polymer 2000;42:6851.
[17] Asgarzadeh F, Ourdouillie P, Beyou E, Chaumont P. Macromolecules 1999;32:6996–7002.
[18] Hild G. Prog Polym Sci 1998;23:1019.
[19] Feldermann A, Toy AA, Davis TP, Stenzel MH, Barner-Kowollik C. Polymer 2005;46:8448–57.
[20] Idle N, Fukuda T. Macromolecules 1999;32:95–9.
[21] Jiang CF, Shen YQ, Zhu SP, Hunkeler D. J Polym Sci Part A Polym Chem 2001;39:3780–8.
[22] Ourdouillie P, Chaumont P, Mechin F, Dumon M, Durand D, Nicolai T. Macromolecules 2001;34:4109–13.
[23] Ganachaud F, Monteiro MJ, Gilbert RG, Dourges MA, Thang SH, Rizzardo E. Macromolecules 2000;33:6738.
[24] Ray B, Isobe Y, Matsumoto K, Habaue S, Okamoto Y, Kamigaito M, et al. Macromolecules 2004;37:1702–10.
[25] Xia J, Zhang X, Matyjaszewski K. Macromolecules 1999;32:4482.
[26] Baek KY, Kamigaito M, Sawamoto M. Macromolecules 2001;34:215.
[27] Lord HT, Quinn JF, Angus SD, Whittaker MR, Stenzel MH, Davis TP. J Mater Chem 2003;13:2819.
[28] Bosman AW, Vestberg R, Heumann A, Frechet JMJ, Hawker CJ. J Am Chem Soc 2003;125:71.
[29] Zheng GH, Pan CY. Polymer 2005;46:2802.
[30] Ma XM, Cui YJ, Zhao X, Zheng SX, Tang XZ. J Colloid Interface Sci 2004;276:53.
[31] Bastide J, Picot C, Candau S. J Polym Sci Polym Phys Ed 1979;17: 1441.
[32] Liu B, Kazlauciunas A, Guthrie JT, Perrier S. Macromolecules 2005; 38:2131.
[33] Varga I, Gilanyi T, Meszaros R, Filipcsei G, Zrinyi M. J Phys Chem B 2001;105:9071.
[34] Lee WF, Lin YH. J Appl Polym Sci 2003;90:1683.
[35] Yoshinari E, Furukawa H, Horie K. Polymer 2005;46:7741.
[36] Kaneko Y, Nakamura S, Sakai K, Kikuchi A, Aoyagi T, Sakurai Y, et al. Polym Gels Networks 1998;6:333–45.
[37] Takei YG, Aoki T, Sanui K, Ogata N, Sakurai Y, Okano T. Macromolecules 1994;27:6163.