

Effect of Temperature-responsive Solution Behavior of PNIPAM-*b*-PPEOMA-*b*-PNIPAM on Its Inclusion Complexation with α -Cyclodextrin^{*}

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Abstract The effect of temperature-responsive solution behavior of PNIPAM-*b*-PPEOMA-*b*-PNIPAM on its inclusion complexation with α -cyclodextrin was studied. The triblock polymer was prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization and formed inclusion complexes (ICs) after selective threading of the PEO segment of the triblock polymer through the cavities of α -CD units. For comparison, PPEOMA homopolymer was prepared and the inclusion complexation with α -CD was also studied. The ICs were prepared with α -CD when the polymer was in different conformations by changing the temperature, and the formed ICs were characterized by XRD, ¹H-NMR, TGA and DSC. The solutions of the ICs show temperature-responsive clear/turbid transition or fluidic emulsion/gel transition depending on the concentration of the α -CD added, and the stoichiometry determined by ¹H-NMR and TGA indicates that the stoichiometry of EO to α -CD of the resulted ICs increases with increasing of temperature.

Keywords: Temperature-responsibility; Comblike triblock polymer; Inclusion complexes.

INTRODUCTION

Recently, increasing attention has been paid to polymer inclusion complexes (ICs) formed between various polymers and cyclodextrins (CDs) due to the great potential for biological and medical applications, such as controlled drug delivery, environmental protection and pharmaceutical formulations^[1–7]. Cyclodextrins, as the most popular host molecules employed to include a wide range of guest molecules, are a series of cyclic molecules composed of 6, 7, and 8 glucopyranose units connected by α -1,4-glycosidic linkages, which are named as α -, β -, and γ -CD, respectively^[8, 9]. Harada *et al.* were the first to report that α -CD can form a crystalline ICs with poly(ethylene oxide) (PEO) in aqueous solution in 1990^[10]. After that, extensive studies have been made on ICs formation of various linear and nonlinear polymers with α -CDs such as grafted PEOs^[11–13], star polymers^[14, 15], hyperbranched polymers^[16] and block copolymers^[17–19]. The formation process of ICs can be explained that PEO chains penetrate α -CD cavities, and then the α -CD rings connect together by the hydrogen bonds to form inclusion complexes. The α -CD rings become hydrophobic because of the consumption of the hydroxyl groups and complex form aggregates by hydrophobic interaction^[20].

Up to now, most of the investigations mainly focused on the preparation techniques and the characterization of solid phase, or the solution properties such as the self-assembly behavior of the inclusion complexes with a certain ratio of EO/ α -CD. However, few reports have been found about the ratio of EO/ α -CD of the complexes under different conditions. Li *et al.* studied the relationship between molecular weight of PEO and the ratios of

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ICs, and the results showed that when the molecular weights of PEO are less than 2000, full coverage (the ratio of EO/ α -CD is at least 2:1) occurs before precipitation of the ICs, while the ratio increases for molecular weights beyond 2000 because aggregation takes place and gels are formed before each PEO chain is wholly included by α -CD^[20]. So, it is reasonable to assume that the solution behavior of the polymer has a great influence on its inclusion complexation with α -cyclodextrin.

Herein, this paper presents inclusion study between α -CD and triblock comblike polymer PNIPAM-*b*-PPEOMA-*b*-PNIPAM. The purpose of this report is to study the effect of the temperature-responsive solution behavior of PNIPAM-*b*-PPEOMA-*b*-PNIPAM on its inclusion complexation with α -cyclodextrin. It has been reported that the densely PEO grafted polymers can form ICs with α -CD^[9], and α -CD units will thread onto the PEO segment but not the PNIPAM segment because of the steric hindrance of the *N*-isopropyl amide side groups^[19]. The polymer applied in this paper with PNIPAM segments located on both sides of the polymer underwent a temperature-induced coil-to-globule phase transition in water^[21, 22], ICs were prepared with α -CD when the polymer was in different conformations. The stoichiometry was established using ¹H-NMR and TGA, and the temperature-responsive solution behavior of the resulted ICs was also studied.

EXPERIMENTAL

Materials

α -CD was obtained from Aladdin and used without any treatment. Poly(ethylene oxide) methyl ether methacrylate (PEOMA, M_n = 950 g/mol), obtained from Aldrich Chemical Co, was dissolved in tetrahydrofuran (THF) and passed through an alumina column to remove inhibitor before use. *N*-Isopropylacrylamide (NIPAM, Aladdin) was recrystallized in hexane before use. The RAFT agent, *S,S'*-bis(α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate (BDMAT) was prepared according to procedures reported in the literature^[23]. The initiator α,α' -azobisisobutyronitrile (AIBN) was recrystallized in anhydrous ethanol twice before use. The dialysis bag (cellulose tubing with cutoff molecular weight of 3500 g/mol) was produced by Beijing Solarbio Co. All other reagents were commercially available chemicals and used as received.

Measurements

Gel permeation chromatography (GPC) was performed on an Alltech 626 HPLC pump equipped with an evaporative light scattering detector, and a Jordi Gel DVB column (100 nm, 300 mm $\times$ 7.8 mm) using DMF as eluent at a flow rate of 1.0 mL/min at 60 °C. Polystyrene standards were used for calibration. ¹H-NMR spectra were recorded using a Varian INOVA-300FT-NMR spectrometer (Palo Alto, America) operating at 500 MHz using CDCl₃ or DMSO-*d*₆ with tetramethylsilane (TMS) as standard at room temperature. XRD patterns of the complexes were recorded on a Bruker D8/Advance X-ray powder diffractometer with Cu K α (0.1541 nm) radiation (40 kV, 40 mA). Powder samples were mounted on a sample holder and scanned with a step size of 0.02° between 2θ = 3° and 50°. DSC measurements were performed on a Netzsch DSC200F3 at heating rate of 10 K/min. Each sample was heated from -40 to 160 °C and scanned two times to erase thermal history. Thermogravimetric analyses (TGA) were performed on a Netzsch STA409PC instrument. Samples were heated at 20 K/min from room temperature to 1000 °C under nitrogen atmosphere with a 20 mL/min flow speed.

Preparation of PNIPAM

A typical RAFT polymerization procedure is as follows: NIPAM (4.24 g, 37.5 mmol), BDMAT (0.0663 g, 0.25 mmol), AIBN (4 mg, 0.025 mmol) and 7 mL THF were added into a 25 mL Schlenk flask, and the homogeneous solution was purged with N₂ for 30 min to remove the dissolved oxygen. Then, the flask was sealed and placed into an oil bath at 60 °C with stirring to initiate the polymerization. After a predetermined time, the polymerization was stopped by quenching the flask in cold water and exposing to air. The reaction mixture was precipitated in a large amount of diethyl ether two times to remove unreacted monomers. The final product was then dried under vacuum to a constant mass.

Synthesis of PNIPAM-*b*-PPEOMA-*b*-PNIPAM

The procedures used for the polymerization of PEOMA were similar to those used for the RAFT polymerization of NIPAM. PEOMA (0.71 g, 0.75 mmol), macro-RAFT agent PNIPAM (0.83 g, 0.054 mmol), AIBN (2 mg, 0.012 mmol) and 7 mL anhydrous ethanol were added in a 10 mL Schlenk tube. The solution was purged with N₂ for 30 min to remove the dissolved oxygen and then heated to 75 °C in an oil bath for 24 h. The experiment was stopped by quenching the flask in cold water and exposing to air. The reaction mixture was purified by dialysis in water, and water was removed by rotary evaporator.

Preparation of the Inclusion Complexes

Two types of α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM inclusion complexes were prepared with the same concentrations of polymer (10 mg/mL) but different concentrations of α -CD at different temperatures.

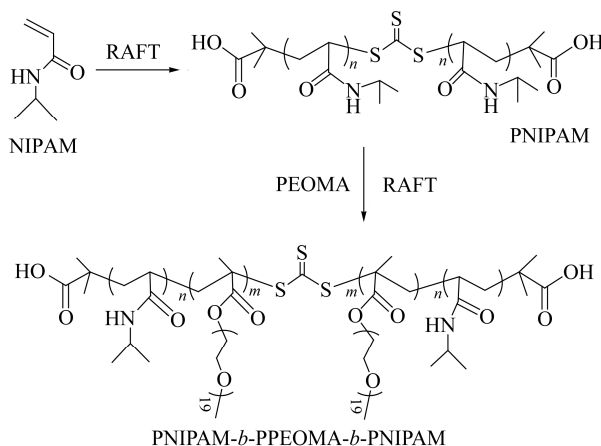
Type 1: A solution of α -CD (40 mg, 0.041 mmol) in water (1 mL) was added to the solution of PNIPAM-*b*-PPEOMA-*b*-PNIPAM (20 mg, 0.186 mmol of EO units) in deionized water (1 mL) at 25 °C and 40 °C. The resultant solutions were sonicated for 10 min and then vigorously stirred 24 h at predetermined temperature. The solid inclusion complexes were obtained after freeze-drying.

Type 2: A solution of α -CD (124 mg, 0.127 mmol) in water (1 mL) was added to the solution of PNIPAM-*b*-PPEOMA-*b*-PNIPAM (20 mg, 0.186 mmol of EO units) in deionized water (1 mL) at temperature of 25 °C, 34 °C and 40 °C. The resultant solutions were sonicated for 10 min and then vigorously stirred 24 h at predetermined temperature. The solid inclusion complexes were isolated by centrifugation, washed with a limited amount of water, and dried in vacuum at 60 °C for 24 h.

RESULTS AND DISCUSSION

Polymer Synthesis

Scheme 1 presents the procedure employed for the synthesis of PNIPAM-*b*-PPEOMA-*b*-PNIPAM. The well-defined PEO grafted polymer was synthesized by RAFT polymerization. The resulting macro-CTAs and triblock polymer were characterized by GPC and ¹H-NMR. Figure 1 displays the GPC traces of the polymers, and Table 1 summarizes the molecular weight characteristics of PNIPAM and PNIPAM-*b*-PPEOMA-*b*-PNIPAM. It is clear to see that the M_n (measured by GPC) of the PNIPAM-*b*-PPEOMA-*b*-PNIPAM is close to that of the PNIPAM homopolymer, which is probably caused by the fact that the hydrodynamic volumes of the comblike polymer differ substantially from those of the linear PS standards^[24].



Scheme 1 Synthesis of PNIPAM-*b*-PPEOMA-*b*-PNIPAM

Figure 2 shows the ¹H-NMR spectrum of PNIPAM and PNIPAM-*b*-PPEOMA-*b*-PNIPAM. In Fig. 2(A), peaks **a**, **b**, and **d** were assigned to the two methyl groups, methine protons and secondary amine of PNIPAM

respectively^[25]. Figure 2(B) shows the ¹H-NMR spectrum of PNIPAM-*b*-PPEOMA-*b*-PNIPAM. Besides the characteristic chemical shifts of PNIPAM segments, the chemical shifts at $\delta = 3.38$ (b) and $\delta = 3.5\text{--}4.2$ (a, c, d) correspond to the protons of methoxyl group ($-\text{OCH}_3$) and methylene protons ($-\text{OCH}_2-\text{CH}_2-$) of the pendant PEO brushes of PPEOMA, respectively^[26–29]. The ¹H-NMR spectrum reveals that polymers have been synthesized successfully, and the degrees of polymerization (DP) is 134 for the PNIPAM (calculated from the Eq. 1), 13 for the PPEOMA block (calculated from the ratio of the protons of methine in PNIPAM block to the protons of methylene ($-\text{OCH}_2-\text{CH}_2-$ of the PEO brushes). Thus, the obtained polymer can be referred to as PNIPAM₆₇-*b*-PPEOMA₁₃-*b*-PNIPAM₆₇.

$$\text{DP} = \frac{10I_b}{I_c + I_a - 9I_b} \quad (1)$$

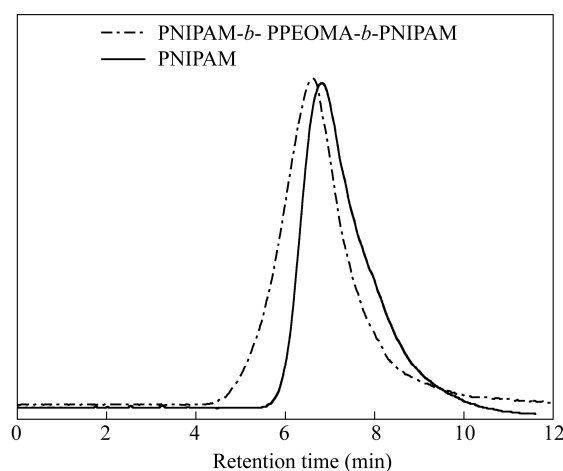


Fig. 1 GPC traces of PNIPAM and PNIPAM-*b*-PPEOMA-*b*-PNIPAM

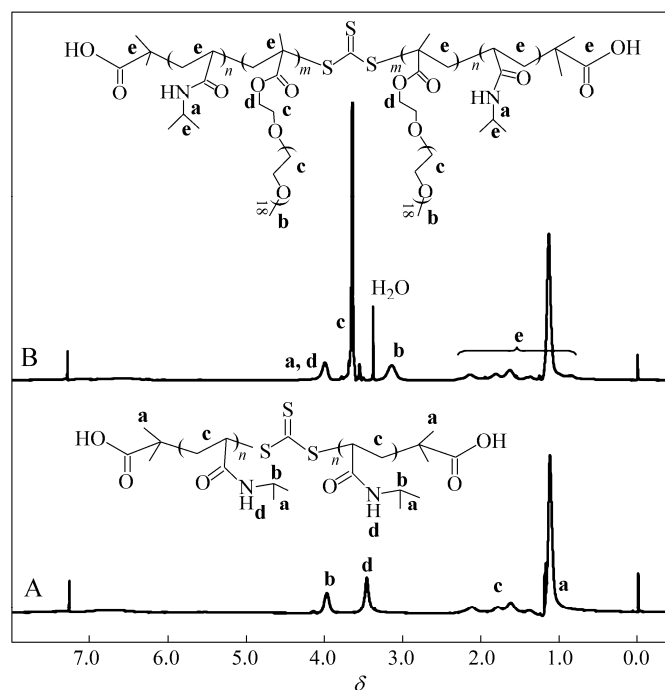


Fig. 2 ¹H-NMR of (A) PNIPAM and (B) PNIPAM-*b*-PPEOMA-*b*-PNIPAM

Table 1. Molecular weight characteristics of the macro-CTAs PNIPAM and PNIPAM-*b*-PPEOMA-*b*-PNIPAM

Polymer	M_w^a (g·mol ⁻¹)	M_n^a (g·mol ⁻¹)	M_n^b (g·mol ⁻¹)	PDI ^a
PNIPAM	12500	8800	15000	1.40
PNIPAM- <i>b</i> -PPEOMA- <i>b</i> -PNIPAM	16000	10000	27000	1.60

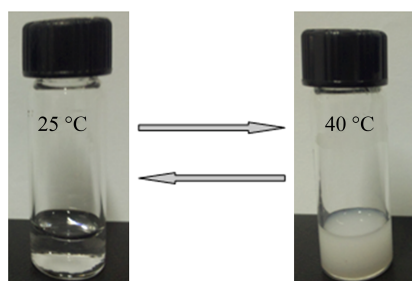
^a From GPC experiments performed using samples dissolved in DMF, $PDI = M_w/M_n$;

^b Number-average molecular weight calculated from ¹H-NMR spectroscopy results (CDCl₃)

Inclusion Complexation of PNIPAM-*b*-PPEOMA-*b*-PNIPAM with α -CD

It has been reported that the densely PEO grafted polymers can form ICs with α -CD^[9], and α -CD units will thread onto the PEO segment but not the PNIPAM segment because of the steric hindrance of the *N*-isopropyl amide side groups^[19]. And it is well-known that PNIPAM is a thermosensitive polymer that has a low critical solution temperature (LCST) in water at 32 °C^[21, 22], so PNIPAM-*b*-PPEOMA-*b*-PNIPAM with PNIPAM segment located on both sides will undergo a temperature-induced coil-to-globule phase transition in water, which means the polymer will be in different conformations by changing the temperature. The temperature-responsive solution properties and variable stoichiometry of EO to CD of the ICs prepared under different temperatures were expected.

When adding a small amount of α -CD (20 mg/mL), the solution of α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM inclusion complexes (Type 1) was clear at 25 °C, while became turbid at 40 °C as shown in Fig. 3, and the transition was reversible by only changing the temperature of the solution. The temperature-sensitivity of the complex could be attributed to the presence of PNIPAM segments. At 25 °C, the PNIPAM segments were hydrophilic because of the hydrogen bonds between water and the amide^[21], and the PNIPAM segments were long enough to inhibit the aggregation of the complexes, which could cause the complete dissolution of the α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM. While at 40 °C, the hydrogen bonds of PNIPAM and water were broken and PNIPAM expelled water molecules to form a coil-globule transition, which could cause the precipitation of the complexes^[21].

**Fig. 3** α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM complex solution (Type 1) at 25 °C and 40 °C

The water-soluble complexes between PNIPAM-*b*-PPEOMA-*b*-PNIPAM and α -CD were confirmed by XRD analysis after freeze-drying. Figure 4 gives the XRD patterns of α -CD, PNIPAM-*b*-PPEOMA-*b*-PNIPAM and α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs. The major characteristic peaks for the crystalline phase of PNIPAM-*b*-PPEOMA-*b*-PNIPAM (Fig. 4b) appear at values of 19.5° and 23.7°. The diffraction pattern of the α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs (Fig. 4c) is substantially different from those of α -CD and PNIPAM-*b*-PPEOMA-*b*-PNIPAM, the characteristic peaks at $2\theta \sim 20^\circ$ demonstrate that the complexes have column-type crystalline structure^[9, 30], strongly supporting the formation of ICs between α -CD and the triblock polymer. And there is no obvious peaks from α -CD crystals observed, indicating that most of the α -CD molecules have threaded onto the side chains of the polymer^[11]. Figure 5(b) shows the ¹H-NMR spectrum of the water-soluble ICs. The stoichiometry of EO to α -CD (4.68) can be calculated by comparing the area of the protons from PEO segments and CD ring (equation 2)^[9], close to the feed ratio of EO to α -CD (4.54). The precipitate at 40 °C was collected and analyzed too, and the same results were achieved.

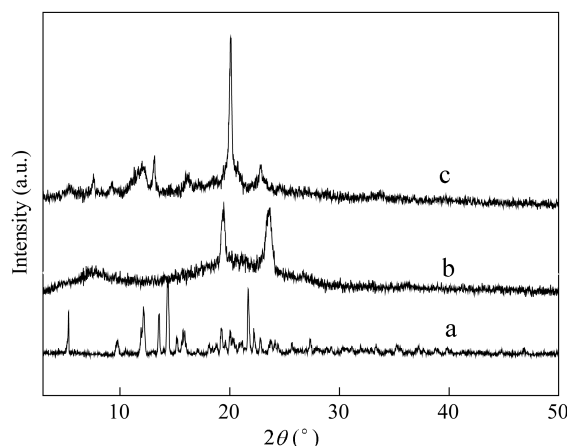


Fig. 4 X-ray diffraction patterns of (a) α -CD, (b) PNIPAM-*b*-PPEOMA-*b*-PNIPAM and (c) α -CD/ PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs (Type 1) after freeze-drying

$$\frac{\text{EO}}{\text{CD}} = \frac{6 \times I_{\text{H}(-\text{OCH}_2-\text{CH}_2)}}{4 \times I_{\text{H1}}} \quad (2)$$

The results above showed the temperature-responsive solution properties of the ICs prepared when the polymer was in different conformations, while the stoichiometry of EO to α -CD was not affected probably because the amount of α -CD was not enough. So to prepare ICs with variable stoichiometry of EO to α -CD, a series of mixtures with same concentrations of polymer (10 mg/mL) but higher concentrations of α -CD (62 mg/mL) at different temperatures were prepared and equilibrated (Type 2). At the same time, the inclusion complex of homopolymer PPEOMA with α -CD was prepared for comparison. All the solutions became turbid immediately after the addition of α -CD, indicating the rapid formation of the inclusion complexes. The temperature-dependent behavior of ICs was characterized by solution property and the stoichiometry of EO to α -CD (calculated by comparing the area of the protons from PEO segments and CD ring^[9]). Figures 6(a)–6(c) show the solution property of the ICs, and the results suggest that the solutions of ICs undergo a fluidic emulsion to gel transition, which can be attributed to the increasing of temperature. Figures 5(c)–5(e) show the ¹H-NMR spectra of the ICs. Table 2 lists the stoichiometry of the ICs and the results indicate the stoichiometry increase with the increasing of the temperature. The PNIPAM segment can increase the solubility of the pseudopolyrotaxane in water at 25 °C, while reduce the solubility and accelerate the precipitation of the pseudopolyrotaxane from its aqueous solution above 32 °C. Thus, the inclusion complexes became gel at 34 °C and 40 °C while the solution remained fluidic emulsion at 25 °C when PNIPAM is hydrophilic. The stoichiometry of EO to α -CD values listed in Table 2 are greater than 2:1, which means that fewer α -CD were threaded by grafted PEO chains compared to that of linear PEO. It demonstrated that some of EO units are difficult to be threaded by α -CDs due to the repulsion of side chains and the steric hindrance between backbone and side chains^[9]. Compared with α -CD/PPEOMA ICs, the α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs at 34 °C and 40 °C showed higher stoichiometry of EO to α -CD because of the hydrophobic character of PNIPAM segments, while at 25 °C, the hydrophilic PNIPAM can improve the water-solubility of complexes and prevent the formation of gel, resulting in the stoichiometry lower than 3.12. The results indicated that the water-solubility of ICs can change the amount of inclusion to a certain extent.

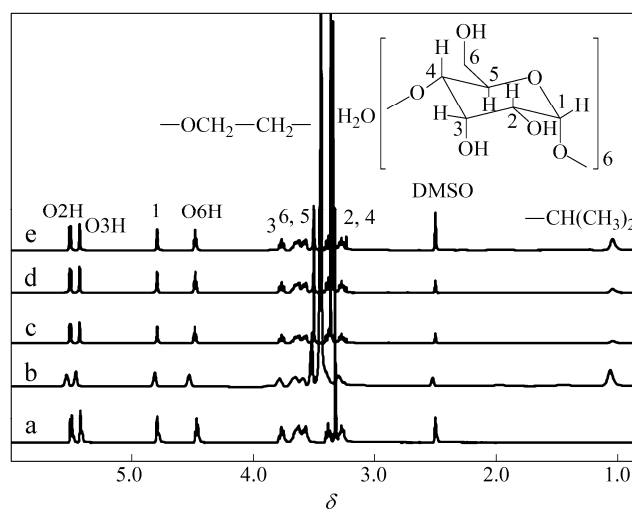


Fig. 5 ^1H -NMR spectrum of (a) α -CD, (b) ICs (Type 1) and ICs (Type 2) at 25 °C (c), 34 °C (d) and 40 °C (e)

Table 2. Preparation conditions and characterization of temperature-dependent ICs (Type 2)

Polymer	Temperature (°C)	Solution state	EO/ α -CD	
			^1H -NMR	TGA
PNIPAM- <i>b</i> -PPEOMA- <i>b</i> -PNIPAM	25	fluidic emulsion	2.66	2.56
PNIPAM- <i>b</i> -PPEOMA- <i>b</i> -PNIPAM	34	gel	3.10	3.18
PNIPAM- <i>b</i> -PPEOMA- <i>b</i> -PNIPAM	40	gel	3.34	3.54
PPEOMA	25	gel	3.12	3.19

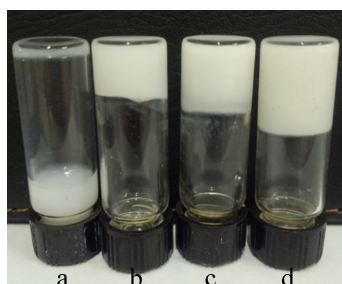


Fig. 6 Photographs of α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs (Type 2) at 25 °C (a), 34 °C (b), 40 °C (c) and α -CD/PPEOMA ICs (d)

The crystalline structure of the inclusion complexes was established by XRD studies. Figure 7 shows the XRD patterns of α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs at different temperatures, α -CD/PPEOMA ICs and α -CD. The characteristic peak at 20° demonstrates that the CD rings were stacked along the PEO side chain axis to form the necklace structure, therefore, the XRD results confirm the ICs possess a column structure^[30].

The thermal properties of α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs were studied by TGA and compared with uncomplexed α -CD and the triblock polymer. Figure 8 displays TGA measurements of PNIPAM-*b*-PPEOMA-*b*-PNIPAM, α -CD and the ICs. Unlike the α -CD and the polymer, the α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs undergo two-step thermal degradation. The first and second steps can be attributed to the decomposition of the α -CD and the PNIPAM-*b*-PPEOMA-*b*-PNIPAM, respectively^[19]. The stoichiometry of EO to α -CD in the α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs estimated from the two-step weight loss of the thermogram is in quite good agreement with that calculated using ^1H -NMR, and the results are shown in Table 2.

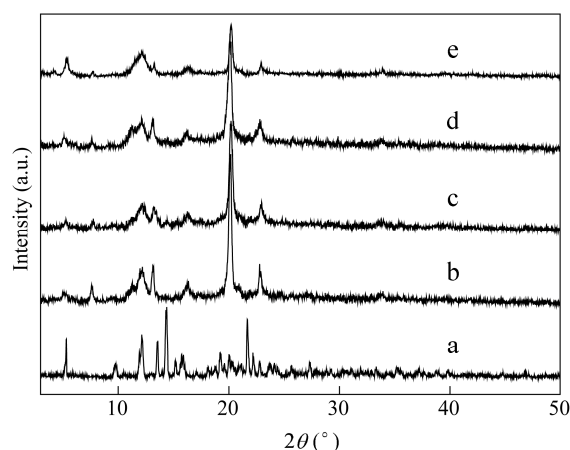


Fig. 7 XRD patterns of (a) α -CD, α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM ICs (Type 2) at 25 °C (b), 34 °C (c), 40 °C (d) and α -CD/PPEOMA ICs (e)

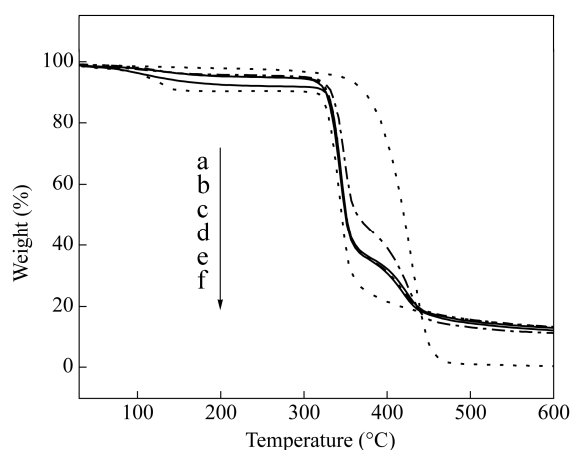


Fig. 8 Thermogravimetric curves of PNIPAM-*b*-PPEOMA-*b*-PNIPAM (a), ICs (Type 1) (b), ICs (Type 2) at 25 °C (c), 34 °C (d), 40 °C (e) and α -CD (f)

Figure 9 shows the conventional second run DSC thermograms of PNIPAM-*b*-PPEOMA-*b*-PNIPAM, α -CD and the ICs. For the thermogram of PNIPAM-*b*-PPEOMA-*b*-PNIPAM, a distinct endothermic peak at 38 °C corresponds to the melting temperature (T_m) of the crystalline PEO. However, the ICs showed no melting peak, demonstrating that the PEO side chains are confined in the α -CD channels and their original crystalline properties are lost owing to the formation of inclusion complexation^[9].

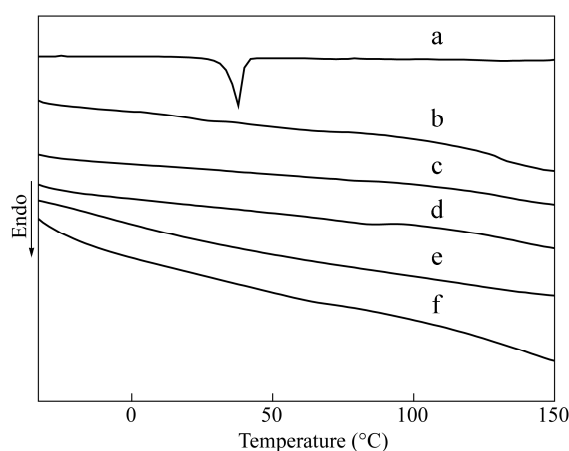


Fig. 9 DSC thermograms of (a) PNIPAM-*b*-PPEOMA-*b*-PNIPAM, ICs (Type 1) (b) and ICs (Type 2) at 40 °C (c) 34 °C (d), 25 °C (e) and α -CD (f)

CONCLUSIONS

This paper described the temperature-responsive inclusion complexation of PNIPAM-*b*-PPEOMA-*b*-PNIPAM with α -CD. The PNIPAM-*b*-PPEOMA-*b*-PNIPAM triblock polymer was successfully synthesized through RAFT polymerization and characterized by GPC and ^1H -NMR spectroscopy. ICs prepared using the triblock polymer with α -CD when the polymer was in different conformations were used to study whether the stoichiometry of EO to α -CD of the resulted ICs can be altered when the molecular weight of PEO is fixed. The formed ICs were characterized with XRD, ^1H -NMR, TGA and DSC measurements. When adding a small amount of α -CD (20 mg/mL), the inclusion complexes of α -CD/PNIPAM-*b*-PPEOMA-*b*-PNIPAM are water-soluble because the PNIPAM segments are long enough to prevent the precipitation of ICs at 25 °C. The

inclusion complexes formed hydrogels when a large amount of α -CD (62 mg/mL) was added. The stoichiometry of EO to α -CD given by $^1\text{H-NMR}$ ranged from 3.34 to 2.66 with the temperature decreased. XRD measurements indicate that all ICs have a channel-type crystalline structure. The results indicate that temperature-responsive solution behavior of PNIPAM-*b*-PPEOMA-*b*-PNIPAM has a great influence on the solution properties and the stoichiometry of EO to α -CD of the resulted ICs.

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