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ORIGINAL ARTICLE

Supramolecular end-group separation of linear polymers with different terminals through host–guest interaction

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Abstract By increasing the hydrophobicity of end group, the complexation rate between α-cyclodextrin (α-CD) and poly(ethylene glycol) (PEG) derivative speeds up greatly. Based on such a huge difference of complexation kinetics, the PEG derivative with palmityloxy terminal (PEG-C16) can be successfully separated from a carboxylic acid end-functionalized analogue (PEG-COOH) by once supramolecular purification. Adding α-CD into the aqueous solution of PEG-C16/PEG-COOH mixture, PEG-C16 is encapsulated into α-CD cavity to form the crystalline inclusion complex in a very short time, while almost all of PEG-COOH molecules are still reserved in the aqueous solution. After dichloromethane extraction, the pure PEG-C16 is obtained. Moreover, the host CD can be recycled. Thus, it is an efficient green way to separate and purify the linear polymers with different terminal functionality.

Keywords Supramolecular chemistry · Cyclodextrin · Molecular recognition · Separation and purification · Kinetic control

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Introduction

Endgroup functionality has an important influence on the final properties of polymers. For example, the performance of polyamides will be impaired greatly in the presence of cyclic end-group [1]. In coating science, the mechanical behavior (e.g. strength, brittleness) of the cross-linking network can be easily adjusted by the endgroup functionality of functional prepolymer [2–4]. Therefore, separation and purification of polymers with identical repeat unit and molecular weight, but only difference in the terminal functionality, is a remaining challenge in polymer science [5–8]. Since the end group has a negligible contribution to the whole property of polymer chain, the conventional separation methods based on the average properties of whole polymer chains, such as recrystallization, membrane separation and size-exclusion chromatography, can not be applied in this polymer blend system [9–11]. Recently, the great development of critical liquid chromatography (critical LC) provides an effective way for the separation of polymers with various terminal functionalities [2–4, 12, 13]. At the critical condition, the elution time of

polymers only depends on the functional end groups, regardless of molecular weight. Therefore, separation and purification of polymers based on the different terminal functionality can be realized. However, the selection of solvents, columns, detectors and measuring conditions in critical LC is still a complex task, which impedes its wide application [14–16].

Cyclodextrin (CD) is an important host for a great variety of guest polymers, and the molecular recognition plays a critical role in the formation of inclusion complexes [17–28]. It has been found that the complexation behavior is sensitively affected by the molecular weights of guest polymers, which has been successfully used to the polymer separation and purification [19, 26]. In a recent communication, we described a new supramolecular end-group separation method using the complexation kinetics difference between CDs and linear polymers with different terminals [17]. For example, to achieve the end-group separation of poly(ethylene glycol) derivatives with propionyloxy and carboxymethyl terminals (PEG-C3 and PEG-COOH), α-CD was added into the aqueous solution of polymer mixture (PEG-C3:PEG-COOH = 1:1, molar ratio). Because of its hydrophobicity of the propionyloxy group, PEG-C3 formed the crystalline inclusion complex with α-CD quickly, while most PEG-COOH molecules were still reserved in the aqueous solution. The linear polymers could be easily extracted from the CD channel of precipitating crystalline complex, and the PEG-C3 took 92% in the purified product. Through twice successive supramolecular separations, the pure PEG-C3 was obtained. It can be deduced that the purification of polymer blend might be completed by only once supramolecular separation, provided that the discrepancy of complexation rate between CD and different linear polymers is further magnified. Fortunately, such a speculation has been corroborated in the present work, which makes the separation and purification of linear polymers with different terminal functionality simple.

Experimental section

Materials

All reagents and solvents were provided by Rohm Hass, Acros, Alfa Aesar, and Shanghai Sinopharm Chemical Reagent Co., Ltd. (SCRC) without further purification unless especially noted. α-Cyclodextrin (α-CD) was kindly given by Rohm Hass, United States. Palmitoyl chloride and potassium tert-butoxide were purchased from Acros and Alfa Aesar, respectively. Poly(ethylene glycol) (PEG, $M_n = 2{,}000$), ethyl bromoacetate, urea, triethylamine, dichloromethane (CH_2Cl_2), and other chemicals were attained from SCRC, China. Triethylamine was freshly distilled from CaH_2 before using.

Synthesis of PEG derivative with palmityloxy end group (PEG-C16) [17, 37, 38]

Poly(ethylene glycol) ($M_n = 2{,}000$, 2 g, 1 mmol) dissolved in benzene (55 mL) was poured into a 100 mL three necked flask, and then the freshly distilled triethylamine (1.01 g, 10 mmol) was added. Prior to performing the reaction, the system was degassed using nitrogen for about 15 min. The flask was cooled to 0 °C, and palmitoyl chloride (2.75 g, 10 mmol) dissolved in benzene (5 mL) was steadily added over 1 h. Subsequently, the reaction was warmed to room temperature and stirred for an additional 24 h. After $Et_3NH^+Cl^-$ was filtered off, the solution was concentrated and precipitated into diethyl ether. The residue was collected by vacuum filtration. Repeatedly dissolving the crude product in CH_2Cl_2 and then precipitating into diethyl ether at least two times, the product was dried in a vacuum oven at 40 °C for 24 h. Finally, the PEG derivative with palmityloxy terminal (PEG-C16) was obtained. (Yield: 1.04 g, 52%)

^{1}H-NMR ($CDCl_3$): δ (ppm): 4.21 (t, –CH_2OOC– of PEG), 3.50–3.70 (m, –OCH_2CH_2O– of PEG), 2.31 (t, –CH_2COO–), 1.60 (m, –$OOCCH_2CH_2$–), 1.24 (m, –$(CH_2)_{12}$–), 0.87 (t, –CH_3).

Synthesis of PEG derivative with carboxymethyl end group (PEG-COOH) [17, 38, 39]

After PEG ($M_n = 2{,}000$, 5.2 g, 2.6 mmol) was fully dissolved in 100 mL of toluene, the potassium tert-butoxide solution (2.05 g, 18 mmol potassium tert-butoxide in 20 mL of tert-butyl alcohol) was added. Then, ethyl bromoacetate (3.2 mL, 28 mmol) was dropped slowly into the mixture over a period of 30 min. Under stirring at room temperature for 24 h, the solution was filtered, concentrated and precipitated into diethyl ether to obtain solid product. Subsequently, the residue was dissolved in 100 mL of 1 N NaOH, standing for 2 h at room temperature, and then adjusting the pH of mixture to 2. After extraction by CH_2Cl_2, the organic layer was washed with water for several times and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the concentrated solution was poured into an excess of diethyl ether to precipitate the product. Finally, the PEG derivative with carboxymethyl end group (PEG-COOH) was obtained by filtering and drying in vacuum at room temperature for 24 h. (Yield: 3.52 g, 67.7%)

^{1}H-NMR ($CDCl_3$): δ (ppm): 4.15 (s, –OCH_2CO–), 3.55–3.70 (m, –OCH_2CH_2O– of PEG).

Separation and purification of polymer mixture

An equimolar amount of PEG-C16 (38 mg, 1.88 mmol) and PEG-COOH (38 mg, 1.88 mmol) was dissolved in 5 mL water. Then, the mixture was added into α-CD aqueous solution (0.375 g α-CD dissolved in 5 mL water) at ambient temperature. After reaction for 25 min, the solution was filtered. The collected solid product was washed with water for several times to remove uncomplexed α-CD and unclathrated polymer. After drying under vacuum at 80 °C for 24 h, the crystalline inclusion complex was obtained.

To get the purified polymer out of CD channel, urea (45.5 mg) was added into the aqueous dispersion of crystalline inclusion complex (0.11 g of crystalline inclusion complex dispersed in 10 mL water). After stirred for 12 h at 40 °C, the hydrogen-bonding network between CD channels was completely destroyed [18–20]. The reaction system was cooled to room temperature and several drops of diluted HCl was added. The solution was extracted with CH_2Cl_2 for several times, and then the organic layer was dried over anhydrous magnesium sulfate, filtered, concentrated, poured into an excess of diethyl ether to precipitate the product. Finally, the purified product was obtained after drying in vacuum at room temperature.

Recycle of α-cyclodextrin

In order to remove the residual PEG derivatives, the water layer of inclusion complex was washed with CH_2Cl_2 for several times. Then, the solution was filtered and evaporated. The obtained solid was washed with anhydrous alcohol to remove the remnant urea. After drying under vacuum at 80 °C for 24 h, the pure α-CD was obtained.

Methods

The pure PEG derivatives, their mixture and purified product were analyzed by wide-angle X-ray powder diffraction (WAXD), ^{1}H-NMR and FTIR. WAXD patterns were taken by a Rigaku III Dmax 2500 diffractometer using CuK_α radiation. ^{1}H-NMR experiments were recorded on a Varian MERCURY plus-400 spectrometer. For pure PEG derivatives, their mixture and purified product, ^{1}H-NMR experiments were carried out in $CDCl_3$; while the inclusion complex between α-CD and PEG derivative was tested in DMSO-d_6. The infrared measurements were performed on a Bruker Equinox-55 FTIR spectrometer.

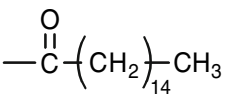
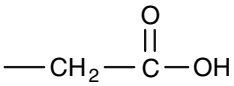
Results and discussion

It has been well demonstrated that the end groups have an important influence on the complexation kinetics of CD and linear polymer [17, 21–24, 38]. Especially, by increasing the hydrophobicity of end group, the complexation speeds up greatly [17, 38]. In order to enlarge the discrepancy of complexation rate between CD and linear polymers with different terminal functionality, the poly(ethylene glycol) (PEG, $M_n = 2{,}000$) derivatives with palmityloxy and carboxymethyl terminals (PEG-C16 and PEG-COOH) have been prepared, and the corresponding molecular formula are given in Table 1.

Mixing α-CD aqueous solution with PEG-C16 or PEG-COOH, both of the systems became turbid because of the formation of crystalline inclusion complex by threading and sliding of α-CD on a linear polymer chain [25–28]. The evolution curves of transmittance vs. time for PEG-C16 and PEG-COOH are shown in Fig. 1. It can be found that the turbidity rate is quite different, indicating the significant influence of end group on complexation kinetics. The PEG-C16 has palmityloxy terminal with extraordinary high hydrophobicity, while the PEG-COOH has carboxymethyl terminal with hydrophilicity. Therefore, the complexation rate of PEG-C16 is much faster than that of PEG-COOH [17, 29, 30, 38]. It can be inferred that in a PEG-C16/PEG-COOH mixture solution, PEG-C16 might form the crystalline inclusion complex with α-CD in a very short complexation time. In the meantime, almost all of PEG-COOH molecules remain in the aqueous solution. Thus, it should be possible to separate PEG-C16 from PEG-COOH based on the huge difference of complexation rate between CDs and PEG derivatives.

Scheme 1 illustrates the separation and purification processes of PEG derivatives. The PEG-C16/PEG-COOH mixture solution was complexed with α-CD at ambient temperature. According to Fig. 1, the reaction was stopped after 25 min (Point A in Fig. 1). A white precipitate appeared, indicating the formation of crystalline inclusion complex between CDs and polymeric guests. After filtration and washing with distilled water, the uncomplexed α-CD and unclathrated polymers were removed and the

Table 1 Molecular formula of PEG-C16 and PEG-COOH

$RO(CH_2CH_2O)_nR$	
R: (PEG-C16)	R: (PEG-COOH)
	

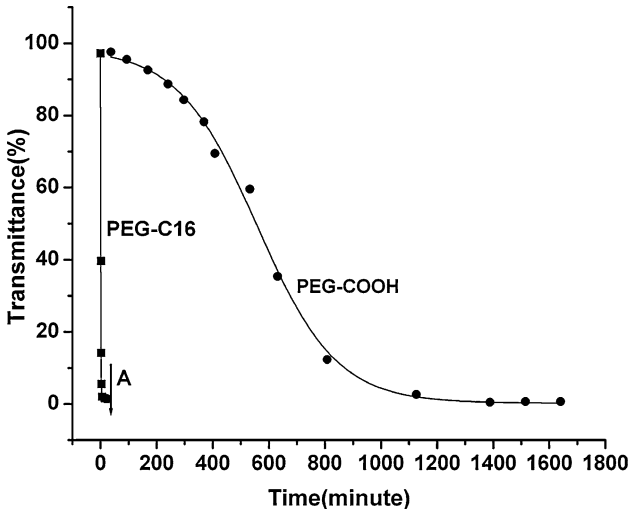


Fig. 1 Turbidity rate of PEG-C16 or PEG-COOH after mixing with the α-CD solution

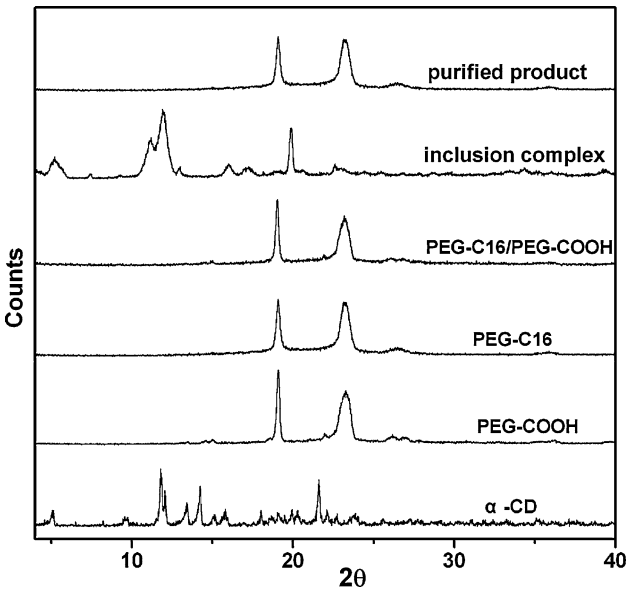
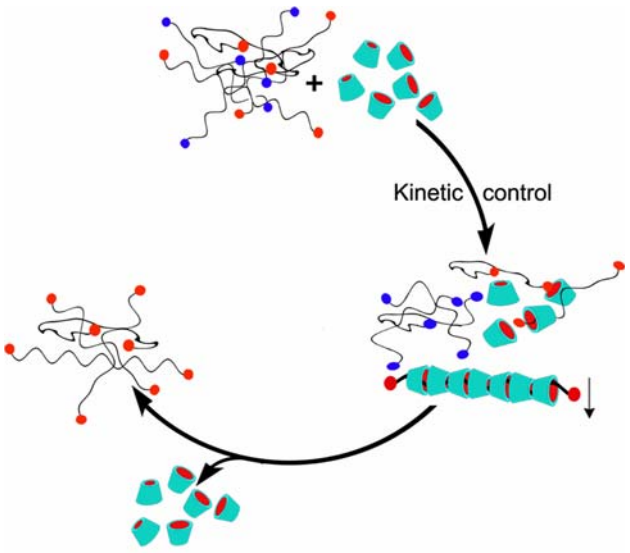


Fig. 2 Wide-angle X-ray diffractions of α-CD, pure PEG-C16, pure PEG-COOH, PEG-C16/PEG-COOH mixture, inclusion complex, and the purified product

inclusion complex was obtained. Figure 2 presents the wide-angle X-ray diffraction (WAXD) of pure α-CD, pure PEG-C16, pure PEG-COOH, PEG-C16/PEG-COOH mixture, and crystalline inclusion complex. It can be found that the WAXD patterns of pure PEG-C16, pure PEG-COOH, and PEG-C16/PEG-COOH mixture are almost the same. The characteristic diffraction peaks at $2\theta = 18.9°$ (d = 0.47 nm) and 23.0° (d = 0.39 nm) illustrate that the PEG derivatives exist in a monoclinic form [31–33]. On the other hand, the WAXD curve of crystalline inclusion complex is quite different from that of pure α-CD, PEG-C16, PEG-COOH and PEG-C16/PEG-COOH mixture. The number of reflection peaks of the inclusion complex is less than the number observed in the pure α-CD. The characteristic reflection at $2\theta = 20°$ implies that in the crystalline inclusion complex, α-CD molecules are stacked along the PEG to form the channel-type structure [22]. Figure 3 gives the ^{1}H-NMR spectra of pure α-CD, pure PEG-C16, pure PEG-COOH, PEG-C16/PEG-COOH mixture, and crystalline inclusion complex. The characteristic triplet signal at 4.21 ppm is related to –CH_2OOC– of PEG-C16, while the singlet peak at 4.15 ppm can be assigned to –OCH_2CO– of PEG-COOH. For PEG-C16/PEG-COOH mixture, the ratio of integral areas at 4.21 and 4.15 ppm is 1:1. However, in the ^{1}H-NMR spectrum of inclusion complex, the singlet peak at 4.15 ppm assigned to –OCH_2CO– of PEG-COOH disappears and only the characteristic triplet signal of PEG-C16 at 4.21 ppm for the



Scheme 1 Supramolecular end-group separation processes

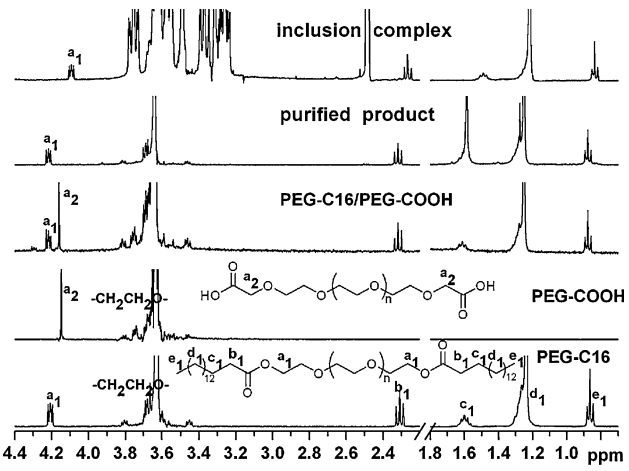


Fig. 3 ^{1}H-NMR spectra of pure PEG-C16, pure PEG-COOH, PEG-C16/PEG-COOH mixture, the purified product in $CDCl_3$, and inclusion complex in DMSO-d_6

–CH_2OOC– group remains. It means that α-CD merely complexes with the PEG-C16 in PEG-C16/PEG-COOH mixture solution under kinetic control. In other words, based on the complexation kinetics difference between CDs and polymeric guests, the supramolecular separation of linear polymers with different terminals has been realized.

Adding urea into the aqueous solution of inclusion complex, the hydrogen-bonding network between CD channels was destroyed so that the linear polymer was released from the CD cavity [18–20]. The purified PEG derivative was obtained by CH_2Cl_2 extraction, concentration and precipitation in diethyl ether. Figure 2 shows that the WAXD pattern of purified sample is different from both pure α-CD and inclusion complex, but similar to PEG derivatives (PEG-C16 and PEG-COOH). It suggests that the PEG derivative has been extracted from the tunnel of inclusion complex and all of CDs have been removed. The ^{1}H-NMR measurement in Fig. 3 shows that only the triplet signal at 4.21 ppm related to –CH_2OOC– of PEG-C16 exists in purified product, while the singlet peak at 4.15 ppm assigned to –OCH_2CO– of PEG-COOH is no longer observed. These results confirm that the purification of PEG-C16 has been successfully achieved by once supramolecular separation.

The FTIR spectra in Fig. 4 give the further evidence for the successful purification of PEG-C16/PEG-COOH mixture system. The antisymmetric stretching vibration (ν_a) of –CH_2– is located at 2,920 cm^{-1}, while the symmetric stretching vibration (ν_s) of –CH_2– appears at 2,868 cm^{-1}. For pure PEG-COOH, the ν_s of –CH_2– at 2,868 cm^{-1} is stronger than ν_a of –CH_2– at 2,920 cm^{-1}. However, for pure PEG-C16, the intensity of ν_s is similar to that of ν_a. Mixing PEG-C16 and PEG-COOH with 1:1 molar ratio,

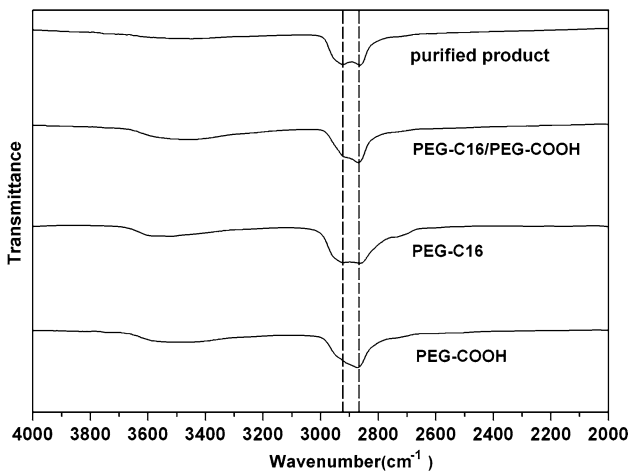


Fig. 4 FTIR spectra of pure PEG-C16, pure PEG-COOH, PEG-C16/PEG-COOH mixture, and purified product in the region of 4000 ~ 2000 cm^{-1}

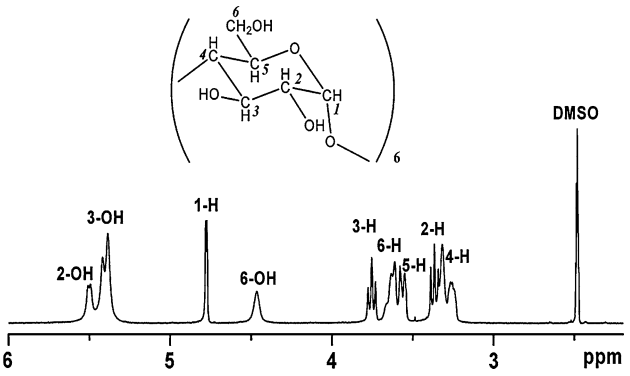


Fig. 5 ^{1}H-NMR spectrum of recycled α-CD in DMSO-d_6

the transmittance intensity of 2,868 cm^{-1} band is higher than that of 2,920 cm^{-1}. After supramolecular separation, the FTIR spectrum of purified product is identical to that of pure PEG-C16 and both 2,868 and 2,920 cm^{-1} bands have the same intensity.

It should be pointed out that the host CD can be recycled after the supramolecular purification, and the details have been described in the experimental part. Figure 5 gives the ^{1}H-NMR spectrum of recycled α-CD. Obviously, the pure α-CD is obtained. Since CD is a nontoxic and environmental friendly compound [34–36], it is a green way to separate and purify the linear polymers with different terminal functionality.

Conclusion

On the basis of the huge difference of complexation kinetics between CDs and linear polymers with different terminals, the PEG-C16 can be efficiently separated and purified from PEG-C16/PEG-COOH mixture by once supramolecular separation. Adding α-CD into the aqueous solution of PEG-C16/PEG-COOH mixture, PEG-C16 is encapsulated into α-CD cavity to form the crystalline inclusion complex in a very short time, while almost all of PEG-COOH molecules are still reserved in the aqueous solution. The linear polymeric guest can be easily obtained by CH_2Cl_2 extraction. Both ^{1}H-NMR and FTIR results indicate that only pure PEG-C16 exists in the purified product. Therefore, by increasing the hydrophobicity discrepancy of end groups, the pure component can be separated from mixing polymers with different terminal functionality by once supramolecular purification.

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