Kinetic Separation of Polymers with Different Terminals through Inclusion Complexation with Cyclodextrin

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Separation and purification of polymers from the complex systems such as polymer blends, functionalized polymers, and block copolymers are imperative in modern chemistry.[1] Traditionally, the purification method and technology of polymers are based on the average properties of the whole polymer chains, such as solubility parameter, hydrodynamic volume, or electrophoretic mobility.[2] However, for those polymers with identical repeat unit and molecular weight, but only difference in the terminal functionality, the purification by the conventional methods seems to be unfeasible because the end group has only a negligible contribution to the average property of whole polymer chain. Recently, the critical liquid chromatography (critical LC) has been developed greatly for separation and characterization of functional polymers.[3] At the critical condition, the polymers elute at the same time regardless of the molecular weight. The separation then only depends on the functional end groups so that the end-group separation of various polymers can be realized.[3] However, the selection of solvents, columns, detectors, and measuring conditions in critical LC for a given polymer is still a complex task, and critical conditions do not necessarily provide good end-group-based separation.[4] In this Communication, we present a new and simple supramolecular separation method based on the complexation kinetics difference between cyclodextrins (CDs) and linear polymers with different terminals.

It has been well-known for many years that CDs can be threaded by linear polymer to form the crystalline inclusion complexes which readily precipitate from aqueous or organic solvent solution.[5,6] As the first step of complexation, the molecular recognition between CD and end group of polymeric guest plays a very important role.[7,8a] Therefore, albeit the average physical and chemical characters of linear polymers with identical repeat unit and molecular weight but different end groups are very similar, the complexation kinetics for crystalline complexes might be quite different. This principle has been successfully used to separate the polymer mixture in this work, and the separation and purification processes are schematically listed in Scheme 1. As one example, the end-group separation of poly(ethylene glycol) (PEG, M_n = 2000) derivatives with propionyloxy and carboxymethyl terminals (PEG-C3 and PEG-COOH) is given below.

Scheme 1. Separation and Purification Processes

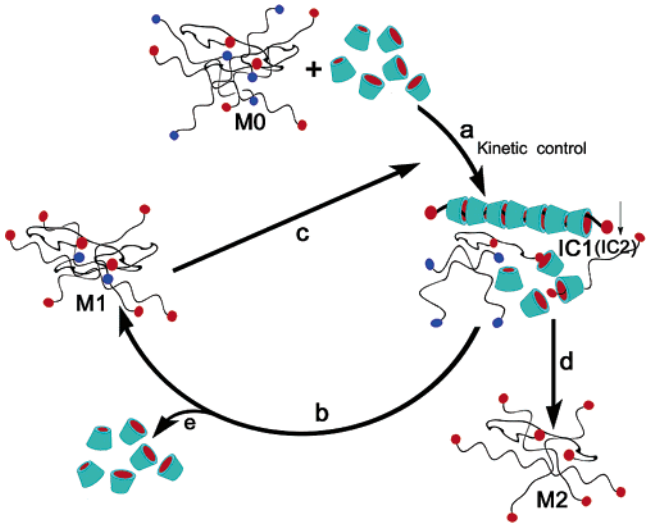

Table 1. Molecular Formula of PEG-C3 and PEG-COOH

$RO(CH_2CH_2O)_nR$	
R: (PEG-C3)	R: (PEG-COOH)
—C(=O)—CH_2—CH_3	—CH_2—C(=O)—OH

Table 1 gives the molecular formula of PEG-C3 and PEG-COOH. Mixing α-CD solution with PEG derivatives, the system becomes turbid because of the threading and sliding of CD on a linear polymer chain. Eventually, the precipitation of mass crystalline complexes is a direct evidence for the termination of complex phenomenon.[5−7] Figure 1 gives the evolution curve of transmittance vs time for different PEG derivatives. It can be found that the turbidity rate is quite different for PEG-C3 and PEG-COOH, indicating the significant influence of end groups on complexation kinetics. Because of its high hydrophobicity of the propionyloxy group, the complexation rate of PEG-C3 is much faster than that of PEG-COOH.[8] It means that in a PEG-C3/PEG-COOH mixture solution PEG-C3 can form the crystalline inclusion complexes with α-CDs very quickly in a short complexation time, while most PEG-COOH molecules are still reserved in the aqueous solution.

On the basis of the complexation kinetics difference, the polymer mixture M0 (PEG-C3:PEG-COOH = 1:1, molar ratio) was complexed with α-CD aqueous solution at ambient temperature. After 6 h (A point in Figure 1), the reaction was stopped. The abundant white precipitates appeared, indicating the formation of crystalline inclusion complexes between CDs and polymeric guests. Subsequently, the inclusion complex IC1 was collected by filtration and washed with water several times to remove uncomplexed α-CDs and unclathrated polymers. Figure 2 presents the wide-angle X-ray diffraction (WAXD) of pure α-CD and crystalline inclusion complex IC1. It can be found that the WAXD pattern of inclusion complex IC1 is quite different from that of pure α-CD. The most prominent peak for IC1 is located at approximately $2\theta = 20°$, indicating that the columnar inclusion compound has been formed with PEG

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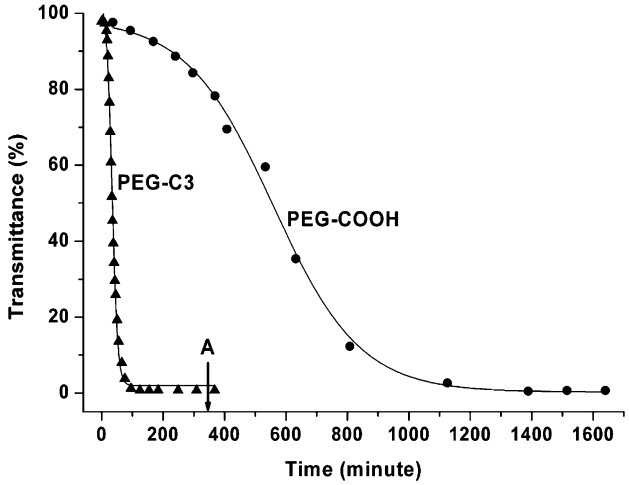

Figure 1. Turbidity rate of PEG-C3 and PEG-COOH after mixing with the α-CD solution (A point is the appropriate control time).

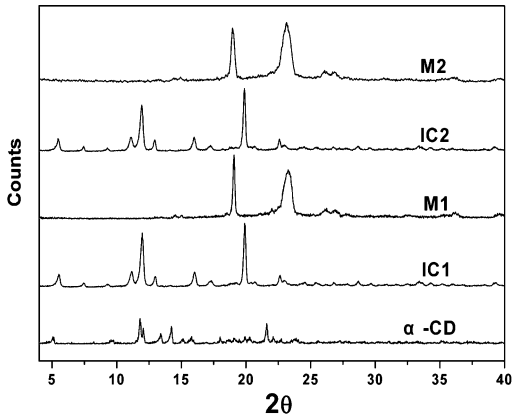

Figure 2. Wide-angle X-ray diffraction of α-CD, inclusion complexes IC1 and IC2, and purified products M1 and M2.

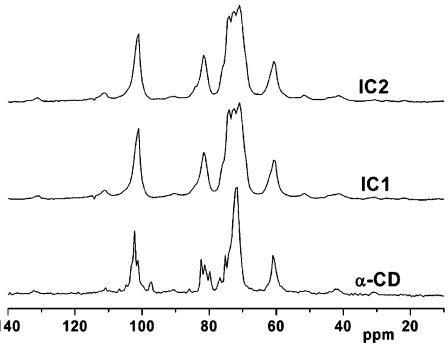

Figure 3. Solid-state CP/MAS ^{13}C NMR spectra of pure α-CD and inclusion complexes IC1 and IC2.

included inside the CD channels.[5−7] Figure 3 shows the solid-state CP/MAS ^{13}C NMR spectra of pure α-CD and crystalline inclusion complex IC1. In an uncomplexed state, pure α-CD gives two obvious signals at 80 and 98 ppm for C-1 and C-4 adjacent to conformationally strained glycosidic linkage.[9,10] The strong splitting peak demonstrates that α-CD is in a rigid and less symmetric cyclic conformation. On the contrary, in the spectra of inclusion compound IC1, each carbon of glucose gives a single peak, whereas the signals for C-1 and C-4 at 80 and 98 ppm disappear. These experimental results demonstrate that α-CD in IC1 has adopted a more symmetric cyclic conformation, further confirming the formation of crystalline inclusion compound IC1.[10] According to the ^1H NMR measurement, the molar

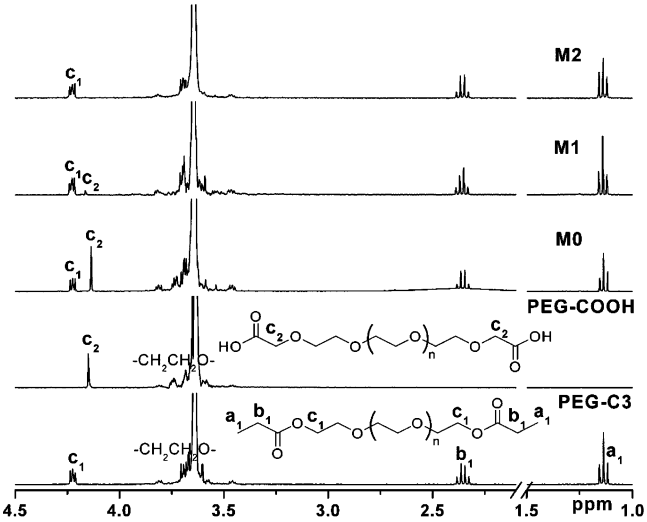

Figure 4. ^1H NMR spectra of pure PEG-C3, pure PEG-COOH, polymer mixture M0, and the purified product M1 and M2 in $CDCl_3$.

ratio of PEG-C3 to PEG-COOH in IC1 is close to 92:8 (see Supporting Information).

In order to get the pure polymer out of the CD tunnel, the urea was added into the IC1 aqueous solution to destroy the hydrogen-bonding network of the inclusion compound.[11] After the extraction by CH_2Cl_2, the PEG derivative M1 was obtained by concentration and precipitation in diethyl ether. The WAXD pattern of M1 in Figure 2 is different from both pure α-CD and inclusion complex IC1. Figure 4 gives the ^1H NMR spectra of pure PEG-C3, pure PEG-COOH, polymer mixture M0, and the purified product M1. The characteristic triplet signal at 4.22 ppm is related to $-CH_2OOC-$ of PEG-C3, while the singlet peak at 4.15 ppm can be assigned to $-OCH_2CO-$ of PEG-COOH. For polymer mixture M0, the ratio of integral areas at 4.22 and 4.15 ppm is 1:1. After the separation and purification by the inclusion complexation of polymer mixture with CDs, the PEG-C3 takes 92% in the purified product M1. Moreover, ^1H NMR shows that there is no any α-CDs in M1 (see Supporting Information). These results confirm that the end-group separation of polymers by supramolecular interaction between CDs and linear polymers with different terminals is reasonable and feasible.

The polymer mixture M1 can be further purified by repeating the kinetics-controlled complexation and subsequent extraction processes. After mixing M1 with α-CD solution for 6 h, the inclusion complex IC2 was attained by filtration and washing. Both WAXD in Figure 2 and the solid-state CP/MAS ^{13}C NMR spectrum in Figure 3 prove the formation of pseudopolyrotaxane.[5−7] Through the addition of urea and extraction by CH_2Cl_2, the purified product M2 could be finally obtained. Figure 4 exhibits the ^1H NMR spectrum of M2. It can be found that the signal at 4.15 ppm disappears completely, indicating the absence of PEG-COOH in the purified product M2. In other words, the purification of PEG-C3 has been successfully achieved by twice supramolecular purifications.

In conclusion, a supramolecular end-group separation method based on the complexation kinetics difference between CDs and linear polymers with different terminals has been developed. Since CDs (α, β, and γ) can form inclusion complexes with a wide variety of linear polymers, this method can be used to separate various kinds of linear polymers. In the meantime, the host CD is a nontoxic and environmental friendly compound[12] and can be recycled (see Supporting Information). Therefore, it is a green way to separate and purify the linear polymers

with identical repeat unit and molecular weight but different end-group functionality.

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Supporting Information Available: Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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