Polypseudorotaxanes

Block-Selected Molecular Recognition and Formation of Polypseudorotaxanes between Poly(propylene oxide)-Poly(ethylene oxide)-Poly(propylene oxide) Triblock Copolymers and α-Cyclodextrin[**]

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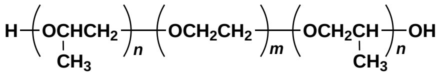
Inclusion complexes (ICs), particularly the ones leading to supramolecular assemblies, continue to be a fascinating topic in modern organic chemistry as they serve as models for understanding molecular recognition and as materials for biological applications. Polyrotaxanes, which are formed by multiple macrocycles threading over a polymer chain, are such an example.[1,2] Cyclodextrins (CDs) constitute a series of cyclic oligosaccharides composed of six, seven, or eight D(+)-glucose units linked by α-1,4-linkages, and named α-, β-, or γ-CD, respectively. The geometry of CDs gives a hydrophobic cavity having a depth of approximately 7.0 Å, and an internal diameter of about 4.5, 7.0, and 8.5 Å for α-, β-, and γ-CD, respectively.[3] Various molecules can fit into the cavity of CDs to form ICs, which have been extensively studied as models for understanding the mechanism of molecular recognition.[3,4] Recently, polypseudorotaxanes,[5] namely, ICs with necklacelike supramolecular structures formed by cyclodextrins and polymers, have attracted special interest.[6–12]

The correlation between the cross-sectional area of the polymer chains and the internal diameter of the CD cavities has been a key factor in the formation of ICs. Poly(ethylene oxide) (PEO) and oligoethylene of various molecular weights form ICs with α-CD, but not with β-CD and γ-CD, to give crystalline polypseudorotaxanes in high yields.[7] Conversely, poly(propylene oxide) (PPO) can form ICs with β-CD and γ-CD in high yields, but not with α-CD.[8] The assumption is that the PPO chain is too large to penetrate the inner cavity of α-CD.



$$H{\left(OCH\underset{CH_3}{}CH_2\right)}_n{\left(OCH_2CH_2\right)}_m{\left(OCH_2\underset{CH_3}{CH}\right)}_nOH$$

There were also studies performed on the formation of ICs between CDs and pluronic PEO-PPO-PEO triblock copolymers, in which thinner PEO blocks flank a middle PPO block; β-CD could selectively thread the middle PPO block to form a polypseudorotaxane,[9] while α-CD selectively includes the flanking PEO blocks.[10] Recently, we reported the formation of an IC between poly[(ethylene oxide)-*ran*-(propylene oxide)] and α-CD, and demonstrated that α-CD can pass over a PO unit randomly placed in the PEO chain to form ICs with EO units.[11] Herein, we report the unexpected observation that PPO-PEO-PPO triblock copolymers, in which two thicker PPO blocks flank a middle PEO block, can form ICs with α-CD to give polypseudorotaxanes in high yields. We demonstrate that α-CD can slide over the flanking bulky PPO blocks to selectively form stable complexes with the middle PEO block of the triblock copolymers.

The molecular characteristics of the PPO-PEO-PPO triblock copolymers used in this study are presented in Table 1. The PPO-PEO-PPO triblock copolymers are known as "reverse" pluronic (pluronic-R) copolymers.[13] The terminal secondary hydroxy groups of pluronic-R have lower reactivity and acidity than the terminal primary hydroxy groups of pluronic PEO-PPO-PEO triblock copolymers. We found the PPO-PEO-PPO triblock copolymers formed ICs with α-CD as well as with β-CD and γ-CD to give polypseudorotaxanes. The α-CD/PPO-PEO-PPO ICs were formed in very high yields, thus indicating that the IC formation is not the result of any contamination of the copolymers. The polypseudorotaxanes dissolved slowly when they were resuspended in a large amount of water, which indicates that the formation of the IC is reversible, and the polypseudorotaxanes are in equilibrium with their components in solution.

Figure 1 shows the X-ray powder diffraction patterns of α-CD/PPO-PEO-PPO and other ICs formed with α-CD. The pattern obtained for the α-CD/propionic acid IC (Figure 1a) is consistent with the α-CD ICs having a cage-type structure.[14] The pattern of the α-CD/PEO IC, with a number of sharp reflections and the main one at $2\theta = 19.4°$ ($d = 4.57$ Å) in Figure 1b, represents the channel-type structure of crystalline necklacelike polypseudorotaxanes of α-CD and PEO,[11,14] which is totally different from that of α-CD/propionic acid IC. The patterns of α-CD/PPO-PEO-PPO ICs (Figure 1c–e) are similar to that of α-CD/PEO IC, but different from that of the α-CD/propionic acid IC, which suggests that the α-CD/PPO-PEO-PPO polypseudorotaxanes are isomorphous with the channel-type structure formed by the α-CD/PEO IC.

The α-CD/PPO-PEO-PPO ICs were quantitatively studied by using ^{1}H NMR spectroscopy. A comparison between the integral intensities of peaks for α-CD and those for PPO-PEO-PPO gives the compositions and molecular weights of the α-CD/PPO-PEO-PPO ICs (Table 1). There are three possible structures for the α-CD/PPO-PEO-PPO ICs: a) the α-CD molecules are selectively threaded on the middle PEO

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Table 1: Characteristics of the PPO-PEO-PPO triblock copolymers and the α-CD/PPO-PEO-PPO ICs.

PPO-PEO-PPO triblock copolymer[a]			α-CD/PPO-PEO-PPO IC[d]				
composition[b]	M_n [g mol^{-1}][c]	M_w/M_n[c]	M_n [g mol^{-1}][e]	x[e]	m/x[f]	$2n/x$[g]	$(2n+m)/x$[h]
$PO_8EO_{23}PO_8$	1.99×10^3	1.03	1.31×10^4	11.4	2.0/1	1.4/1	3.4/1
$PO_{15}EO_{24}PO_{15}$	2.74×10^3	1.03	1.38×10^4	11.4	2.1/1	2.6/1	4.7/1
$PO_{25}EO_{12}PO_{25}$	3.45×10^3	1.03	8.90×10^3	5.6	2.1/1	8.9/1	11.1/1

[a] The copolymers are denoted $PO_nEO_mPO_n$ where n and m are average block lengths in repeat units. [b] Determined by combination of ^1H NMR spectroscopic and GPC results. [c] Determined by GPC. [d] The ICs are denoted $(\alpha\text{-CD})_x\text{-}PO_nEO_mPO_n$ where x is the number of α-CD molecules per single copolymer chain. [e] Determined by ^1H NMR spectroscopy. [f] Molar ratio of EO unit to α-CD. [g] Molar ratio of PO unit to α-CD. [h] Molar ratio of total number of EO and PO units to α-CD.

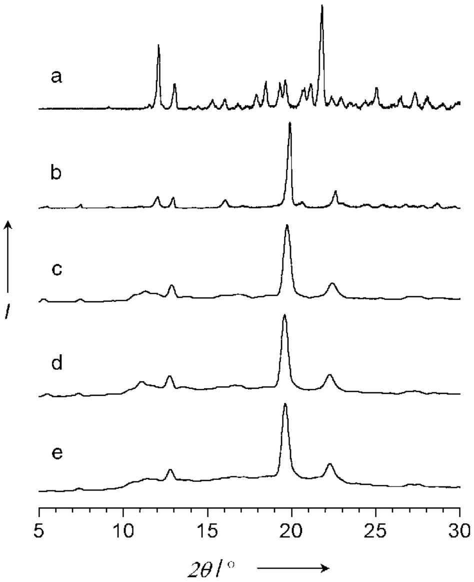

Figure 1. X-ray powder diffraction patterns for the α-CD/propionic acid IC (a), α-CD/PEO (M_n = 1000) IC (b), α-CD/$PO_8EO_{23}PO_8$ IC (c), α-CD/$PO_{15}EO_{24}PO_{15}$ IC (d), and α-CD/$PO_{25}EO_{12}PO_{25}$ IC (e). X-ray measurements: nickel-filtered $Cu_{K\alpha}$ radiation (λ = 1.542 Å), voltage: 40 kV, current: 40 mA, scanning speed: 0.6° per min.

block, while the PPO blocks remain uncovered; b) the α-CD molecules are selectively threaded on the flanking PPO blocks, while the middle PEO block remains uncomplexed; c) the α-CD molecules are threaded on both PEO and PPO blocks. As shown in Table 1, the molar ratio of EO unit to α-CD (m/x), which corresponds to the assumption (a), is 2/1 for all three polypseudorotaxanes, which matches perfectly the stoichiometry of the α-CD/PEO ICs reported previously.[7b] This result strongly suggests that only the middle PEO block in the α-CD/PPO-PEO-PPO polypseudorotaxanes is closely included by α-CD molecules, while the flanking PPO blocks are uncovered. In contrast, the molar ratios of PO unit to α-CD ($2n/x$) or total number of PO and EO units to α-CD ($(2n+m)$/x), which corresponds to the assumptions (b) or (c), show no consistency with any reasonable stoichiometry.

On the basis of these findings we can reasonably hypothesize that the IC formation is driven by the strong interaction between α-CD and the PEO segments,[15] and aided by the flexible molecular motion of α-CD and the copolymer chain. The proposed structure is also in accordance with the broadening X-ray powder patterns for the α-CD/PPO-PEO-PPO ICs (Figure 1 c–e), which show that the α-CD/PPO-PEO-PPO ICs have a lower crystallinity than the stoichiometric α-CD/PEO ICs. This effect is most likely caused by the existence of the uncovered amorphous PPO blocks. Mayer et al.[16] have performed computational studies on the IC formation between α- or β-CD and oligomers of PEO, PPO, or the PEO-PPO diblock copolymer up to EO_4PO_4. Their simulation estimated a total complexation energy of -52.4 kJ mol^{-1} for α-CD/PEO compared to -43.3 kJ mol^{-1} for α-CD/PPO, which supports our hypothesis that there is an incentive for α-CD to overcome an energy barrier to reach the middle PEO block.

The kinetics of the threading process and formation of the ICs were studied with turbidity measurements. Figure 2 shows the change in absorption during formation and precipitation of the polypseudorotaxanes formed between α-CD and PPO-PEO-PPO triblock copolymers in aqueous solution. The curves show a region where the absorption remains zero, followed by a region where the absorption sharply increases. The first region corresponds to the threading and sliding of α-CD onto the polymer chains, and so this region is defined as "threading time" (t_{th}).[8d] The stable polypseudorotaxanes are formed after time t_{th} and start to aggregate into crystalline particles. Therefore, the absorption starts to increase sharply in the second region. Figure 2 shows that the value of t_{th}

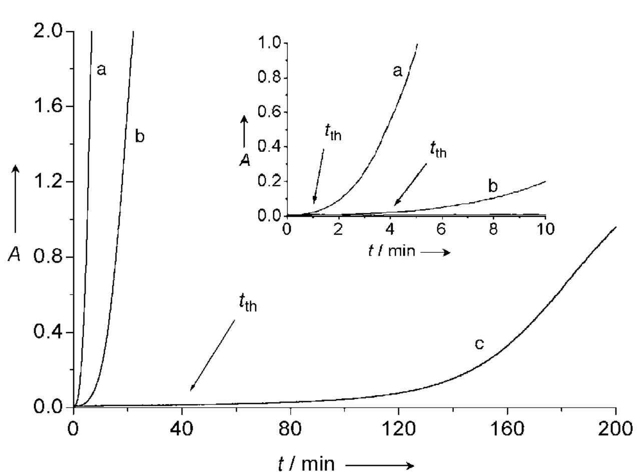

Figure 2. Plot of the absorption at 600 nm against time for aqueous solutions containing 126 mg mL^{-1} of α-CD and 6.5 mg mL^{-1} of triblock copolymer $PO_8EO_{23}PO_8$ (a), $PO_{15}EO_{24}PO_{15}$ (b), and $PO_{25}EO_{12}PO_{25}$ (c) at 20 °C. The arrows indicate the region where absorption remains zero. The inset shows an expanded plot for 0 to 10 min.

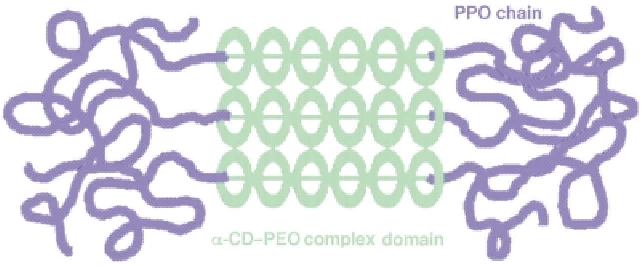

Figure 3. Schematic representation of the proposed structures of α-CD/PPO-PEO-PPO polypseudorotaxanes.

increases from about 1.0 min for $PO_8EO_{23}PO_8$ ($n = 8$), to about 4.0 min for $PO_{15}EO_{24}PO_{15}$ ($n = 15$) and about 40 min for $PO_{25}EO_{12}PO_{25}$ ($n = 25$). The value of t_{th} strongly depends on the length of the PPO blocks since the α-CD molecules have to first overcome the energy barrier of threading and sliding over the flanking PPO blocks to form a stable IC with the middle PEO block.

In summary, PPO-PEO-PPO triblock copolymers can form ICs with α-CD to give polypseudorotaxanes in high yields. It is proposed that only the middle PEO block in the polypseudorotaxanes is closely included by α-CD molecules to form crystalline IC domains with a channel structure, while flanking PPO blocks are uncovered and remain amorphous (Figure 3). The finding contradicts the conventional wisdom that α-CD would not be large enough to slip over a PPO chain. This observation may have intriguing implications in designing new cyclodextrin ICs and polypseudorotaxanes using novel functional block copolymers for molecular machines, sensors, or other interesting applications.

Experimental Section

Three PPO-PEO-PPO pluronic-R triblock copolymers ("reverse" pluronics) were purchased from Aldrich. The pluronic-R copolymers are well studied in the literature.[13] We determined the molecular characteristics of the samples by using ^{1}H NMR and GPC[17] (data shown in Table 1), which were found to be within the specifications of the supplier.

The α-CD/PPO-PEO-PPO ICs were prepared as follows. Bulk PPO-PEO-PPO triblock copolymers (75.0 mg) were added to an excess of an aqueous solution of α-CD (4.57 mL, 0.145 $g\,mL^{-1}$) in a test tube at room temperature. The dissolving of the copolymer could be facilitated by immersing the tubes in an ultrasonic waterbath or vortexing.[18] The solutions gradually became turbid, eventually producing ICs in the form of crystalline precipitates. The ICs were isolated by filtration or centrifugation, washed with a limited amount of water, and dried under vacuum. The percentage yields were calculated on the basis of the compositions of the ICs given in Table 1. α-CD/$PO_8EO_{23}PO_8$ IC: Yield, 390 mg (73%); m.p. 293–300°C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 22°C): $\delta = 5.51$ (s, ca. 68H, O(2)H of CD), 5.43 (s, ca. 68H, O(3)H of CD), 4.80 (d, ca. 68H, H(1) of CD), 4.48 (t, ca. 68H, O(6)H of CD), 3.77 (t, ca. 68H, H(3) of CD), 3.64 (m, ca. 136H, H(6) of CD), 3.58 (m, ca. 68H, H(5) of CD), 3.51 (s, ca. 92H, H of PEO block), 3.25–3.47 (brm, ca. 185H, H of PPO backbone, H(2) and H(4) of CD), 1.04 ppm (m, ca. 48H, CH_3 of PPO block); elemental analysis (%) calcd for $C_{94}H_{190}O_{40}\cdot 12\,C_{36}H_{60}O_{30}\cdot 24\,H_2O$: C 44.91, H 6.52; found: C 44.45, H 6.89. α-CD/$PO_{15}EO_{24}PO_{15}$ IC: Yield, 331 mg (83%); m.p. 293–300°C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 22°C): $\delta = 5.51$ (s, ca. 68H, O(2)H of CD), 5.43 (s, ca. 68H, O(3)H of CD), 4.80 (d, ca. 68H, H(1) of CD), 4.47 (t, ca. 68H, O(6)H of CD), 3.77 (t, ca. 68H, H(3) of CD), 3.64 (m, ca. 136H, H(6) of CD), 3.58 (m, ca. 68H, H(5) of CD), 3.51 (s, ca. 96H, H of PEO block), 3.25–3.47 (brm, ca. 227H, H of PPO backbone, H(2) and H(4) of CD), 1.04 ppm (m, ca. 90H, CH_3 of PPO block); elemental analysis (%) calcd for $C_{138}H_{278}O_{55}\cdot 12\,C_{36}H_{60}O_{30}\cdot 24\,H_2O$: C 45.87, H 6.74; found: C 45.43, H 7.21. α-CD/$PO_{25}EO_{12}PO_{25}$ IC: Yield, 146 mg (71%); m.p. 293–300°C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 22°C): $\delta = 5.51$ (s, ca. 34H, O(2)H of CD), 5.43 (s, ca. 34H, O(3)H of CD), 4.80 (d, ca. 34H, H(1) of CD), 4.47 (t, ca. 34H, O(6)H of CD), 3.77 (t, ca. 34H, H(3) of CD), 3.64 (m, ca. 67H, H(6) of CD), 3.58 (m, ca. 34H, H(5) of CD), 3.50 (s, ca. 48H, H of PEO block), 3.25–3.48 (brm, ca. 217H, H of PPO backbone, H(2) and H(4) of CD), 1.04 ppm (m, ca. 150H, CH_3 of PPO block); elemental analysis (%) calcd for $C_{174}H_{350}O_{63}\cdot 6\,C_{36}H_{60}O_{30}\cdot 12\,H_2O$: C 49.29, H 7.53; found: C 48.86, H 8.09.

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[15] The strong interaction comes from the size/steric fittings, the hydrophobic interaction between α-CD and PEO, and the intermolecular hydrogen bonding of α-CDs (also see ref. [6]), thus giving a large favorable enthalpy that becomes the driving force for α-CD to slide over the PPO segments and then form a stable complex with the PEO block.

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[18] The sonication was proved not to degrade either the copolymers or α-CD, as evident by means of ^{1}H NMR spectroscopy, GPC, and TLC. Also see ref. [6].

Lipid Nanotubes

Aligning a Single-Lipid Nanotube with Moderate Stiffness[**]

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Many types of amphiphilic molecules have been found to self-assemble into cylindrical tubules in aqueous solutions.[1–12] The synthetic lipid tubules can provide intriguing hydrophilic internal and external surfaces, unlike carbon nanotubes,[13] and therefore they have unique potential not only as cytomimetic tubules but also as hollow nanospaces for chemical reactions, the transferral of biomolecules, etc. The mechanical properties of lipid nanotubes, however, have not been investigated to date, in contrast to extensive studies on microtubules[14,15] or carbon nanotubes.[16] We have measured the Young's modulus of a single-lipid nanotube that consists of renewable-resource-based synthetic glycolipids (cardanyl-β-D-glucopyranoside)[17] by using optical tweezers. Herein we report that the Young's moduli of the present lipid nanotubes are similar to those of microtubules[15] with outer and inner diameters of the same order. Furthermore, because of the moderate stiffness, we have succeeded in aligning the single-lipid nanotube on a glass plate by microextrusion of the aqueous dispersion.

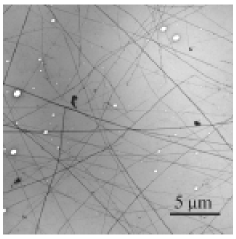

Figure 1. TEM image of lipid nanotubes in an aqueous dispersion, which were used for flexural rigidity measurements.

To measure accurately the flexural rigidity of the single nanotube, we should pay careful attention to the aggregation in an aqueous dispersion. Figure 1 is a transmission electronic microscopy (TEM) image which shows that the lipid nanotubes are completely isolated and form no bundles. TEM images of higher resolution have further shown that the outer and inner diameters are 50 and 10 nm, respectively,[17] which is similar to the values (25 and 10 nm) of microtubules.[18]

A drop of the aqueous dispersion was placed on a glass slide for optical traps, and pressed between coverslip and slide. Because some nanotubes were thereby forced to adhere firmly to the substrate, we had no difficulty in finding a target fixed well at only one end. Using optical tweezers (Sigma Koki LMS-46755), the monoattached nanotube was bent as follows: A laser beam was focused onto the target, the lipid nanotube was trapped in the focal point in a similar way to microtubules.[14,15] This trapping occurs because of the difference in refractive index between the nanotube and the surrounding medium, water. Therefore, while it is possible to manipulate the tubule in a direction perpendicular to its long axis, we cannot do this along the long axis, except by manipulation at either end. We can thus bend the nanotubes by moving the stage and capturing the tube near the free end.

The laser beam was switched off after some bending had occurred, and the resulting bow-shaped nanotube started to relax to its initial straight form. From the relaxation time τ, we can evaluate the flexural rigidity K, because the balance condition between elastic and hydrodynamic force[15] yields the time-dependence of relaxation of the free end, as shown in Equations (1) and (2). Here, y is the ordinate perpendicular to the initial straight line, L is the contour length, η is the viscosity, and d is the outer diameter.

$$y(L,t) = y(L,0)\exp(-t/\tau) \qquad (1)$$

$$\tau = \frac{11\pi\eta L^4}{60\,\mathrm{K}\ln(L/2\,\mathrm{d})} \qquad (2)$$

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