Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 8799–8804 **8799**
DOI: 10.1021/ma101811n

A Versatile Synthesis of Diverse Polyrotaxanes with a Dual Role of Cyclodextrin as both the Cyclic and Capping Components

Kazuaki Kato,* Hiroshi Komatsu, and Kohzo Ito*

Department of Advanced Materials Science, Graduate School of Frontier Sciences,
The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

Received August 9, 2010

ABSTRACT: We report herein a versatile synthesis of cyclodextrin-based polyrotaxanes (CD-PRs). Three different CD-PRs were synthesized from different linear polymers and different CDs with relatively good yields by a novel single method. This method requires no additional capping reagents, because CDs play a dual role as both the cyclic components and the end-capping groups. The end-capping is achieved by transesterification with excess CDs at both ends of pseudopolyrotaxanes activated with *p*-nitrophenyl ester. As a result of this versatile method, we also demonstrate the first synthesis of a novel CD-PR based on poly(butadiene).

Introduction

Interlocked molecules such as rotaxanes and catenanes have attracted many researchers because of the characteristic intramolecular dynamics with topological restrictions. Applications of these molecules are promising especially using cyclodextrin-based polyrotaxanes (CD-PRs) for, e.g., insulated molecular wires,[1] gene delivery,[2] drug release,[3] and cross-linked-polyrotaxane materials.[4] These technologies are built on the syntheses of CD-PRs, beginning with the first controlled synthesis of CD-PR that consists of poly(ethylene glycol) (PEG) and α-cyclodextrin (α-CD) end-capped with 2,4-dinitrobenzyl group.[5] Since then, a large number of studies has concentrated on the PEG-α-CD polyrotaxane. For example, a highly threaded PEG-based CD-PR produced a molecular tube by polymerizing the CDs.[6] CD-PRs with high filling ratio also have great advantages in solubilizing the main chain polymers. On the other hand, sparsely threaded PEG-based one was cross-linked intermolecularly to yield a peculiar material so-called slide-ring materials.[7] CD-PRs with low filling ratio allow CDs to slide along the main chain polymers, and therefore, the sliding motion affects various macroscopic properties of the materials. In this way, diverse filling ratios of the PEG-based CD-PR provided various applications.

The diversity of main chain polymers in CD-PR promises to provide a wide variety of applications. Conjugated polymers acquired insulating properties by rotaxanation with CDs.[8] A CD-PR that consists of block copolymers of PEG and polyethylenimine showed pH-induced sliding of CDs,[9] and thus, the slide-ring gel prepared from the CD-PR exhibited pH-dependent swelling.[10] A silicone-based CD-PR produced a new class of organic−inorganic materials by cross-linking of the CDs thread.[11] It has been reported that many other candidate polymers form pseudopolyrotaxanes, which are inclusion complexes without end-capping.[12] Replacing one main chain polymer with another one, however, is not at all a straightforward process, because the capping methods must meet the diverse requirements of the polymers. Unlike the water-soluble PEG, hydrophobic polymers require inhomogeneous complexations with CDs and specific techniques to achieve their subsequent end-cappings. A solvent-free complexation and the subsequent end-capping realized a polyrotaxane that consists of poly(tetrahydrofuran) and methylated α-CD.[13] Unlike PEG, which is thin enough to be accommodated with α-CD, thick polymers require larger CDs such as *β*-CD and *γ*-CD, so that larger end-capping groups are needed. At the same time, such bulky capping reagents must have enough reactivity and solubility to prevent unraveling of the CD threads. A creative photochemical coupling reaction of the both end groups of a pseudopolyrotaxane that consists of poly(propylene glycol) and *γ*-CD achieved the CD-PR.[14] Thus, various methods with a variety of capping reagents have been developed for each CD-PR to satisfy such diverse requirements of the main chain polymers.[15,16]

We report herein a versatile synthesis of CD-PRs with various main chain polymers and CDs. The synthesis started from linear α,*ω*-telechelic polymers with carboxyl end groups, which are readily prepared from bifunctionally living polymers.[17,18] The telechelic polymers were at first converted into *p*-nitrophenyl esters quantitatively by a routine method in organic chemistry. The *p*-nitrophenyl group did not prevent threading of CDs to form pseudopolyrotaxanes, and then a transesterification reaction produced CD-PRs with relatively high yield. As a result of this versatile synthesis, a novel CD-PR that consists of poly(butadiene) (PBD) and *γ*-CD was successfully prepared, while its pseudopolyrotaxane has been reported a decade earlier.[19] This synthesis method enables us to solve the problem on the end-capping process and to obtain diverse CD-PRs, as long as an axis polymer forms the pseudopolyrotaxane with CDs.

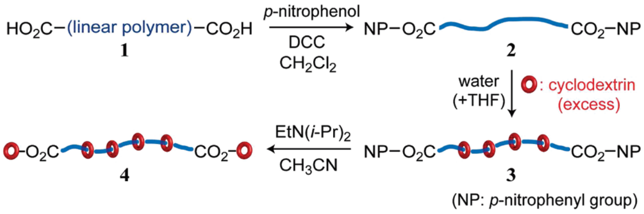
Results and Discussion

Synthesis procedures of CD-PRs generally consist of the following two steps: (1) inclusion complex (pseudopolyrotaxane) formations between main chain polymers and CDs, and (2) capping reactions at both ends of the polymers with bulky capping reagents. Since the complex formations are generally performed in saturated aqueous solution of CDs, excess CDs are then washed out before and/or after their subsequent capping reactions. Besides, an appropriate reagent for the capping reactions should be prepared with enough bulkiness, solubility and reactivity to prevent the unraveling

---

*Corresponding authors. E-mail: (K.K.) kato@molle.k.u-tokyo.ac.jp; (K.I.) kohzo@molle.k.u-tokyo.ac.jp.

Table 1. Polyrotaxanes Prepared from Various Linear Polymers and CDs[a]



polyrotaxane	4a	4b	4c
linear polymer (*M*n, *M*w/*M*n)[b]	PBD (3900, 1.59)	PDMS (10000, 1.37)	PEG (21200, 1.15)
cyclodextrin	γ-CD	γ-CD	α-CD
filling ratio (%)[c]	19	8	33
*M*n[b], *M*w[b]	12900[d], 25300[d]	30000[d], 44900[d]	89100, 125000
*M*w/*M*n	1.95	1.50	1.41
yield (%)[e]	43	80	47

[a] PBD: poly(butadiene) with *trans*:*cis*:*vinyl* = 42:37:21, PDMS: poly(dimethylsiloxane), PEG: poly(ethylene glycol). [b] Measured by GPC. [c] Estimated from ^{1}H NMR spectra, when polymer chains densely covered with CDs are defined to be 100%. [d] Values of polyrotaxanes acetylated. [e] Yields based on polymers.

Table 2. Solubility of Polyrotaxanes and Their Components[a]

solvent	4a	PBD	4b	PDMS	4c	PEG	CDs[b]
DMSO	s	i	i	i	s	s	s
DMF/LiCl[c]	s	i	s	i	s	s	s
water	i	i	i	i	i	s	s
CHCl$_3$	i[d]	s	i[d]	s	i	s	i

[a] Solubility at 20 mg/mL: s = soluble; i = insoluble. [b] α-CD and γ-CD show same results for these solvents. [c] In the presence of 8 g/100 mL of lithium chloride. [d] Solubilized by acetylation of CDs thread.

of CDs. On the other hand, in our breakthrough method shown in Table 1, excess CDs are reused as the capping groups. The end-capping was achieved by transesterification at both ends of pseudopolyrotaxanes **3** activated with *p*-nitrophenyl ester that had excess CDs. As a result, by the single method, three different CD-PRs **4** capped with CDs were obtained in relatively good yields. It is notable that this method requires no additional capping reagents, because CDs play a dual role as both the cyclic components and the capping ones. Although some CD-capped CD-PRs has been reported, activated CDs with, e.g., amino or aldehyde groups are required as the capping reagents in addition to CDs of the cyclic components.[20−22]

Our synthesis started from the bis(carboxyl)-terminated polymers **1**, which were at first converted into the *p*-nitrophenyl esters **2** quantitatively mediated by a carbodiimide as commonly used. Only **2c** was purchased and not synthesized for this study. The water-soluble **2c** was dissolved in water and then mixed with an aqueous solution of α-CD to yield the pseudopolyrotaxane **3c** as a turbid gel. On the other hand, the hydrophobic **2a** and **2b** were at first dissolved in a small amount of THF and then dropped into the stirred aqueous solutions of γ-CDs. Turbidities of the mixtures gradually increased, indicating productions of the pseudopolyrotaxanes **3a** and **3b**. These obtained gel and suspensions of **3** were simply freeze-dried without removing excess CDs and then used for their subsequent reactions. Finally, the *N*,*N*-diisopropylethylamine (DIPEA) as a base initiated transesterification reactions in the presence of excess CDs to yield polyrotaxanes **4**.

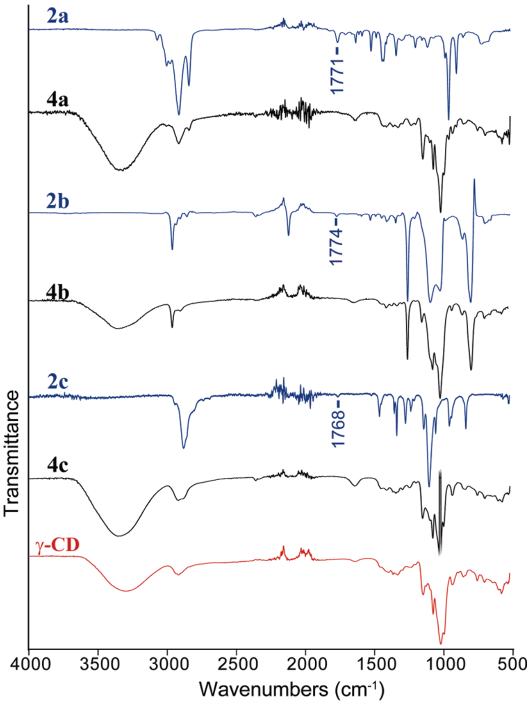


Figure 1. ATR FT-IR spectra of CD-PRs **4**, constituent polymers **2**, and CD. The spectrum γ-CD is representatively shown because that of α-CD is quite similar. Wavenumbers of carbonyl stretching of *p*-nitrophenyl esters are described.

Successful syntheses of the polyrotaxanes **4** are supported by the following evidence: (1) differences in solubility from their components, (2) coexistence of polymers and CDs with possible ratios, and (3) increases in molecular weights from their constituent polymers. Table 2 shows the solubility of **4** and their constituent polymers and CDs. The hydrophobic polymer-based polyrotaxanes **4a** and **4b** were soluble in hydrophilic solvents such as DMSO and DMF/LiCl, which are poor solvents for their constituent polymers. Thus, the insoluble polymer chains could be covered by the soluble γ-CD to form e.g. micelles. Indeed, the transparent solutions were not passed through smoothly a syringe filter with 200 nm of pore size, indicating aggregations. This kind of aggregation has also been observed in the case of our previous CD-PR based on PDMS.[11] On the other hand, the hydrophilic polymer-based polyrotaxane **4c** was insoluble in water, which is a good solvent for both **2c** and α-CD. The solubility of **4c** is quite similar to that of reported PEG-based polyrotaxanes, and therefore the insolubility may arise from an aggregation of CDs thread via hydrogen bonds.[23,24] By comparison, the pseudopolyrotaxanes **3a** and **3b** resulted in turbid solutions in DMSO and DMF/LiCl, respectively, and **3c** was soluble in hot water, indicating the reproductions of **2** as a result of the unraveling.

FT-IR spectra shown in Figure 1 indicate that each CD-PR consists of the main chain polymer and CD. Strong carbonyl stretching vibrations at 1768−1774 cm^{-1} that arise from the *p*-nitrophenyl esters of **2** disappeared after the transesterification, though those from the resultant esters of **4** were too weak to be detected. ^{1}H NMR spectra of the polyrotaxanes **4** are shown in Figure 2. It is notable that the signals of CDs and polymers are broadened, as it has been observed in other CD-PRs as a result of decreases in conformational flexibilities.[25−28] In each polyrotaxane, all signals were assigned as shown with good agreements in values of integrals within each component, except for a slight decrease in O6H of **4b**. The decrease might indicate that the primary hydroxyl group was activated in the transesterification. It is unknown which hydroxyl groups reacted preferentially in the case of the other CD-PRs, because of many more CDs coexisting as the cyclic components. From the ratios of integral values between each of the two components, filling ratios were calculated to be 8−33% (see Supporting Information). These filling

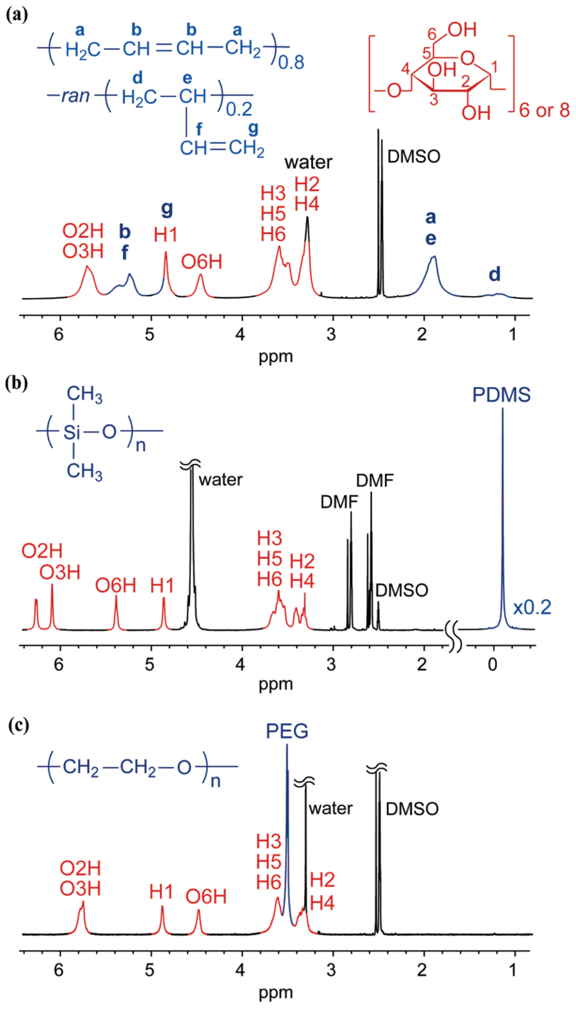


Figure 2. Partial ^{1}H NMR spectra (400 MHz, 298 K) of polyrotaxanes prepared; (a) **4a** in DMSO-d_6, (b), **4b** in DMF-d_7/LiCl and (c) **4c** in DMSO-d_6. In the case of **4b**, a reference capillary filled with DMSO-d_6 is attached as a reference.

ratios mean that the main chains of **4** are sparsely covered with CDs.

Gel permeation chromatography (GPC) is one of the decisive measurements for polyrotaxane formations, observing the apparent increases of molecular weights from their components. The CDs thread on **4a** and **4b**, which form some aggregates as mentioned above, were acetylated to dissolve themselves in chloroform, which is a good solvent for their constituent polymers. The diagrams of acetylated **4a**, acetylated **4b**, and **4c** are shown in Figure 3, with those of constituent polymers **2a**, **2b**, and **2c** for comparison. In each case, apparent molecular weights of polyrotaxanes with/without acetylation drastically increased from those of constituent polymers, though small amounts of impurities of their components were found. Molecular weights estimated from GPC roughly agreed with those calculated from the filling ratios and acetylation degrees obtained from the results of ^{1}H NMR.

Successful syntheses of these three different polyrotaxanes by the single method strongly suggest the transesterification with excess CDs, though the carbonyl stretching vibrations of resultant esters were too weak to be detected by FT-IR. Transesterification reactions are generally accelerated by adding an excess of substitutive alcohols (excess CDs, in this case) and by removing elimination alcohols (*p*-nitrophenol, in this case). Since *p*-nitrophenol can efficiently form inclusion complexes with CDs,[29] this method satisfies both the favorable conditions needed for transesterification reaction. Moreover, the excess CDs can reduce a possible side reaction, which produces cross-linked polyrotaxanes as the result of transesterification with CDs threads not excess CDs. Indeed, small amount of insoluble parts that were thought to be cross-linked **4c** were obtained, when the amount of α-CD for pseudopolyrotaxane formations was reduced. GPC trace of the soluble parts clearly showed the existence of oligomerized polyrotaxanes (see Supporting Information). The concentrations of excess CDs during the transesterification reactions were calculated to be 0.13, 0.25, and 0.09 M in the cases of **4a**, **4b**, and **4c**, respectively. The higher concentration of CDs resulted in higher production yield of CD-PRs. CD-PRs that have low filling ratios means that more free CDs existed during the capping reactions. Therefore, this method would be effective particularly in case that the main chain polymer accommodates a few CDs to produce sparsely threaded CD-PRs.

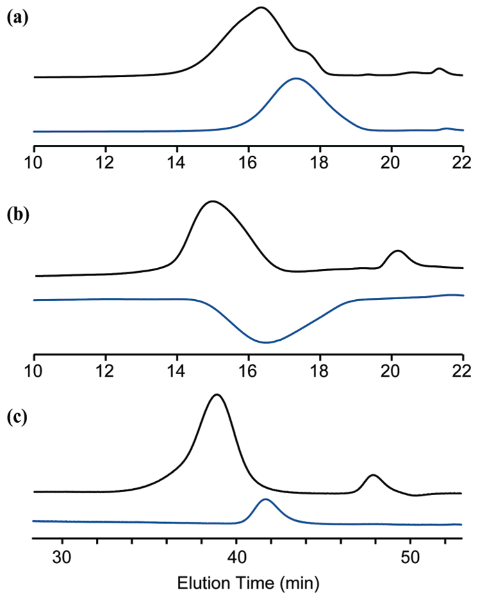


Figure 3. GPC traces of (a) acetylated **4a**, (b) acetylated **4b** and (c) **4c** (black), with that of each constituent polymer **2a**, **2b**, and **2c**, respectively (blue). Eluents for **4c** and **2c** are DMSO with 10 mM of LiBr, and those for others are chloroform; detection: differential refractive index.

Conclusion

We demonstrated herein that various CD-PRs were synthesized from different linear polymers and different CDs with relatively good yields by a novel single method. This method requires no additional capping reagents, because CDs play a dual role as both the cyclic components and the capping groups. The potential versatility regardless of the sizes of CDs and main chain polymers promise us to produce diverse CD-PRs, including unrealized CD-PRs. Indeed, as a result of this study, we succeeded in synthesizing the first CD-PR based on PBD. To the best of our knowledge, this is the first example of a CD-PR that has a reactive main chain. Since various modifications are possible on the main chain, it would enable us to, e.g., control the sliding of CDs. Controlling of the sliding mode is currently investigated, and studies on macroscopic properties of their cross-linked materials, so-called slide-ring materials, are also in progress.

Experimental Section

Materials. Biscarboxyl-terminated PBD (**1a**) was purchased from Aldrich, which has M_n = 3900 and M_w = 6220 determined by size exclusion chromatography with a calibration curve by using PEG standards purchased from Polymer Source Inc.

Unsaturation distribution was determined to be *trans*:*cis*:*vinyl* = 42:37:21 by ^{1}H NMR spectrum by reference to a literature.[30] Biscarboxypropyl terminated PDMS (**1b**) was from Gelest Inc.; M_n = 10000, M_w = 13700 based on PDMS standards purchased from Polysciences, Inc. Bis(*p*-nitrophenyl ester) terminated PEG (**2c**) was purchased from NOF Corporation as a starting material instead of biscarboxypropyl terminated PEG (**1c**). The nominal degree of end-functionalization with the active ester is 88%, and the molecular weight were determined to be M_n = 22300 and M_w = 25000 by size exclusion chromatography with a calibration curve by using the PEG standards mentioned above. α-Cyclodextrin (α-CD) and γ-Cyclodextrin (γ-CD) were purchased from Nihon Shokuhin Kako Co. Ltd. (CD content >98.5%). *N,N′*-dicyclohexylcarbodiimide (DCC) were from Aldrich. *p*-Nitrophenol was from TCI. Acetic anhydride was from Kanto Chemical Co., Inc. *N,N*-Diisopropylethylamine (DIPEA), all dehydrated solvents and other chemicals were purchased from Wako Pure Chemical Industries, Ltd. All reagents were used without further purification.

Measurements. ^{1}H NMR spectra at 400 MHz were recorded on a JEOL JNM-AL400 spectrometer at 298 or 343 K. Chemical shift was calibrated using $CHCl_3$ (7.26 ppm) or DMSO (2.50 ppm) as internal standards. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded on a Nicolet 4700 (Thermo Electron Co., Ltd.) equipped with a diamond attenuated total reflection (ATR) accessory (DurasamplIR II, SensIR Technologies) in air. Powdered samples were pressed onto a diamond window, and the obtained spectra were analyzed with the spectrometer's OMNIC software. Gel permeation chromatography (GPC) with chloroform as eluent was performed on two Shodex GPC K-803 L columns at 40 °C, using RI detection and PDMS or PEG standards. Flow rate was 1.0 mL/min. GPC with DMSO as eluent was performed on Shodex OHpac SB-G columns at 50 °C, using RI detection and PEG standards. Flow rate was 0.4 mL/min.

Bis(*p*-nitrophenyl ester)-Terminated PBD (2a). The solution of biscarboxyl-terminated PBD (**1a**) in anhydrous dichloromethane (5.00 g, 25 mL) was reacted with *p*-nitrophenol (1.91 g, 13.7 mmol) mediated with DCC (2.83 g, 13.7 mmol) at room temperature under argon for 40 h. The resultant solution was at first filtered, and then the filtrate was poured into 300 mL of methanol to precipitate the product. The obtained precipitate was again dissolved in dichloromethane (30 mL) to perform the same reprecipitation. The obtained precipitate was washed with methanol repeatedly and then dried under vacuum to yield **2a** (5.00 g) as a viscous colorless liquid. ATR-FTIR spectrum showed a shift of carbonyl stretching vibration from 1713 to 1771 cm^{-1}, indicating the successful esterification. ^{1}H NMR spectrum also showed that the carboxylic acid converted into the active ester quantitatively; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 8.29 (*meta* of nitrophenyl), 7.28 (*ortho* of nitrophenyl), 5.54 (vinyl CH), 5.4−5.3 (vinylene), 4.96 (vinyl CH_2), 2.84 (α-methylene of carboxyl), 2.1−1.9 (α-methylene and methine of alkene), 1.5−1.2 (β-methylene of alkene). IR (cm^{-1}): 3074 m, 3005 s, 2917 s, 2845 s, 1771 m, 1639 m, 1528 m, 1437 s, 1209 m, 1121 m, 968 s, 912 s, 731 br. GPC (PEG standards, $CHCl_3$ eluent): M_n = 4770, M_w = 7990, M_w/M_n = 1.67.

Pseudopolyrotaxane That Consists of PBD and γ-CD (3a). **2a** (1.927 g) was dissolved in 23 mL of THF, and then it was dropped into the continuously stirred aqueous solution of γ-CD (40 g/230 mL). The mixture was at first supersonically agitated for an hour, and then it was stirred at room temperature for 3 days to yield white turbid suspension of pseudopolyrotaxane (**3a**). The obtained suspension was freeze-dried without purification for the subsequent capping reaction.

Polyrotaxane That Consists of PBD and γ-CD (4a). Freeze-dried **3a** was replaced into a flask, and then the solution of DIPEA in acetonitrile (1.0 mL/200 mL) was added. The reaction mixture was stirred at room temperature for 4 days under argon. The resultant slurry was colored with yellow, indicating the progress of trans-esterification with elimination of *p*-nitrophenol. The slurry was at first centrifuged to remove the supernatant. Then, DMSO (200 mL) was added to dissolve the obtained precipitate, and then the solution was dropped into dichloromethane (1500 mL) to precipitate the product. The precipitate was washed with dichloromethane repeatedly (3 × 1000 mL) and then dried under vacuum to obtain a crude product as a pale yellow solid. The crude product was again dissolved in DMSO (150 mL), and then the solution was dropped into deionized water (1500 mL) to precipitate the product. The obtained precipitate was repeatedly washed with deionized water (3 × 1000 mL) and then freeze-dried to yield polyrotaxane **4a** (3.045 g) as a white powder.

The ATR-FTIR spectrum of **4a** shows signals that arise from PBD and γ-CD. Unfortunately, no signals of C=O stretching, which can emerge at 1800−1700 cm^{-1}, were observed, because the signal is too weak to be detected in the presence of γ-CD threads. The ^{1}H NMR spectrum in DMSO-d_6 was measured at 343 K to separate the signal of water from that of γ-CD (Figure S4). The ratio between the value of integrals of γ-CD at 3.9−3.2 ppm and that of PBD at 2.2−1.7 ppm shows that a single γ-CD accommodates 30 protons of methylene **a** and methine **e** of PBD. This number of protons corresponds to 5.32 times of six-carbon unit of PBD, because 5.64 protons exist on average in the unit (30H/5.64H = 5.32 unit). Thus, the filling ratio of **4a** is estimated to be 19% from the definition of the filling ratio mentioned above (1 unit/5.32 unit = 0.19). The production yield of **4a** was calculated based on the number of six-carbon unit par a single γ-CD. Since the average molecular weight of six-carbon unit is 92, the weight ratios between γ-CD and PBD is calculated to be 73:27 ($MW_{(CD)}$ = 1297: $MW_{(\text{six carbon unit})}$ = 92 × 5.32). This ratio means that 3.045 g of **4a** obtained is containing 834 mg of PBD. Therefore, the production yield on PBD basis was calculated to be 43%; ^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ 5.51 (O2H, O3H), 5.31 (vinyl CH and vinylene), 4.90 (C1H of γ-CD and vinyl CH_2), 4.24 (O6H), 3.67−3.56 (C3H, C5H, C6H), 3.40−3.37 (C2H, C4H), 1.98−1.95 (α-methylene and methine of alkene), 1.5−1.2 (β-methylene of alkene). IR (cm^{-1}): 3320 br, 2918 s, 2844 m, 1637 m, 1417 m, 1334 m, 1155 s, 1079 s, 1026 s, 967 m, 941 m, 860 m, 759 m, 705 m.

Polyrotaxane 4a Acetylated. Procedure of acetylation of **4a** followed that already reported for a PDMS-based polyrotaxane.[11] **4a** (100 mg) and *N,N*-dimethyl-4-aminopyridine (8 mg, 6.5 × 10^{-5} mol) were dried under vacuum and then dissolved in anhydrous DMF/LiCl (2 mL/160 mg). Anhydrous pyridine (0.90 mL, 1.11 × 10^{-2} mol) was added in the solution, followed by the addition of acetic anhydride (1.00 mL, 1.06 × 10^{-2} mol). The solution was stirred at room temperature overnight. Then, the reaction solution was poured into deionized water (50 mL), followed by centrifugation to obtain a precipitate. The precipitate was repeatedly washed with deionized water (3 × 50 mL) and then freeze-dried to yield **4a** acetylated (90 mg) as a white powder.

4a acetylated was soluble in chloroform (>20 mg/1 mL), and the dilute solution (1 mg/mL) was passed through a syringe filter with 200 nm of pore size smoothly. FT-IR spectrum shows a strong carbonyl stretching vibration at 1743 cm^{-1} attributed to acetyl group modified with decreasing OH signal at 3320 cm^{-1}. ^{1}H NMR spectrum also indicates the successful acetylation, and the acetylation degree was calculated to be about 45%, based on the integrations at 1.5−1.2 ppm (**d** of PBD) and 2.4−1.8 ppm (**a**, **e** of PBD and acetyl group). From the acetylation degree and the filling ratio determined, molecular weight was estimated to be 36000 based on M_w of PBD. This number is not far from M_w obtained from GPC, considering that the calibration curve was based on PEG not polyrotaxane; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.8−3.2 (CH and residual OH of γ-CD, and **b**, **f**, **g** of PBD), 2.4−1.8 ppm (**a**, **e** of PDB and acetyl group), 1.5−1.2 ppm (**d** of PBD). IR (cm^{-1}): 3456 br, 2917 s, 2845 m, 1743 s, 1639 m, 1435 m, 1370 m, 1236 s, 1159 m, 1035s, 910 m, 761 m. GPC (PEG standards): M_n = 12900, M_w = 25300, M_w/M_n = 1.95.

Pseudopolyrotaxane That Consists of PDMS and γ-CD (3b). The *p*-nitrophenyl ester (**2b**) was obtained from **1b** quantitatively as described in our previous report.[11] 500 mg of **2b** was dissolved in 2 mL of THF, and then it was dropped into the continuously stirred aqueous solution of γ-CD (4.32 g/25 mL). The mixture was stirred at room temperature for 4 days to yield a turbid suspension of pseudopolyrotaxane (**3b**). The obtained suspension was freeze-dried without purification for the subsequent capping reaction.

Polyrotaxane That Consists of PDMS and γ-CD (4b). A portion of dried **3b** (1.00 g), which should contain 104 mg of PDMS, was replaced into a flask, and then the solution of DIPEA in acetonitrile (20 μL/2.5 mL) was added and stirred at room temperature for 4 days under argon. The resultant slurry was colored with yellow *p*-nitrophenol, indicating the progress of transesterification. The slurry was at first centrifuged to remove the supernatant. Then, DMF (5 mL) and LiCl (0.40 g) was added to suspend the obtained precipitate, and then the suspension was dropped into dichloromethane (50 mL) to precipitate the product again. The precipitate was washed with dichloromethane repeatedly (4 × 50 mL) and then dried under vacuum to obtain a crude product as a pale yellow solid. The crude product was again suspended with DMF (12 mL), and the suspension was dropped into deionized water (100 mL) to precipitate the product. The obtained precipitate was repeatedly washed with deionized water (4 × 100 mL) and then freeze-dried to yield **4b** (156 mg) as a white powder.

ATR-FTIR spectrum of **4b** indicated the signals of PDMS and γ-CD, though any signals that arise from C=O stretching vibrations were not large enough to be detected. The ^{1}H NMR spectrum in DMF-d_7/LiCl (full spectrum is shown in Figure S5) indicates that PDMS monomer unit and γ-CD coexist as the ratio of 20:1. This ratio corresponds to 8% of the filling ratio, based on a reported definition that 100% of the filling ratio means 3:2 molar ratios between the monomer unit and γ-CD. The molar ratio was also correspond to 53:47 weight ratios between the monomer unit and γ-CD, meaning that 156 mg of **4b** obtained is containing 83 mg of PDMS. Therefore, the production yield on PDMS basis was calculated to be 80%; ^{1}H NMR (400 MHz, DMF-d_7/LiCl, 298 K): δ 6.26 (O2H), 6.08 (O3H), 5.38 (O6H), 4.86 (C1H), 3.8−3.5 (C3H, C5H, C6H), −0.08 (PDMS). IR (cm^{-1}): 3361 br, 2962 s, 2903 m, 1399 m, 1260 s, 1157 m, 1079 s, 1024 s, 940 m, 864 m, 800 s, 703 m.

Polyrotaxane 4b Acetylated. **4b** (40 mg) and *N*,*N*-dimethyl-4-aminopyridine (3 mg, 2.5×10^{-5} mol) were dried under vacuum and then dissolved in anhydrous DMF/LiCl (1 mL) (8 g/100 mL of LiCl). Anhydrous pyridine (0.34 mL, 4.2×10^{-3} mol) was added in the solution, followed by the addition of acetic anhydride (0.35 mL, 3.1×10^{-3} mol). The solution was stirred at room temperature overnight. Then, the solution was poured into deionized water (50 mL), followed by centrifugation to obtain a precipitate. The precipitate was repeatedly washed with deionized water, and then freeze-dried to yield acetylated **4b** (27 mg) as a white powder.

4b acetylated was soluble in chloroform (>20 mg/1 mL). FT-IR spectrum shows a strong C=O stretching vibration at 1743 cm^{-1} attributed to acetyl group modified with decreasing OH signal at 3300 cm^{-1}. ^{1}H NMR spectra also indicates the successful acetylation, and the acetylation degree was calculated to be about 75%, based on the integrations at 0.07 ppm (PDMS) and 2.2−2.0 ppm (acetyl group). From the acetylation degree and the filling ratio obtained, molecular weight was estimated to be 32200 based on M_w of PDMS. This number is not far from M_w obtained from GPC, considering that the calibration curve was based on PDMS not polyrotaxane; ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 5.6−3.2 (CH and residual OH of γ-CD), 2.1−2.3 (acetyl), 0.07 (PDMS). IR (cm^{-1}): 3477 br, 2962 s, 2908 m, 1743 s, 1370 m, 1260 s, 1238 s, 1074 s, 1024 s, 800 s. GPC (PDMS standards): $M_n = 30000$, $M_w = 44900$, $M_w/M_n = 1.50$.

Pseudopolyrotaxane That Consists of PEG and α-CD (3c). A 300 mg sample of **2c** was dissolved in 5 mL of water, and then it was mixed with an aqueous solution of α-CD (3.31 g/20 mL). The solution was left at room temperature for 48 h to yield a slightly turbid gel of pseudopolyrotaxane (**3c**). The obtained gel was freeze-dried without purification for the subsequent capping reaction.

Polyrotaxane That Consists of PEG and α-CD (4c). The obtained gel of **3c** was freeze-dried without purification, and then the solution of DIPEA in acetonitrile (150 μL/25 mL) was added and stirred at room temperature for 5 days under argon. The resultant slurry colored with yellow *p*-nitrophenol was at first centrifuged to remove the supernatant. Then, DMSO (25 mL) was added to dissolve the obtained precipitate, and then the solution was dropped into dichloromethane (500 mL) to precipitate the product again. The precipitate was washed with dichloromethane repeatedly (4 × 500 mL) and then dried under vacuum to obtain a crude product as a pale yellow solid. The crude product was again dissolved in DMSO (25 mL), and the solution was dropped into deionized water (500 mL) to precipitate the product. The obtained precipitate was repeatedly washed with deionized water (4 × 100 mL) and then freeze-dried to yield **4c** (660 mg) as a white powder.

ATR-FTIR spectrum of **4c** indicated the signals of PEG and α-CD, though the signals that arise from any C=O stretching vibrations were not large enough to be detected. The ^{1}H NMR spectrum in DMSO-d_6 was measured at 343 K to separate the signal of water from that of α-CD (Figure S6), indicating that PEG monomer unit and α-CD coexist as the ratio of 6:1. This ratio corresponds to 33% of the filling ratio, based on a reported definition that 100% of the filling ratio corresponds to 2:1 molar ratios between the monomer unit and α-CD. The obtained molar ratio was also correspond to 21:79 weight ratios between the monomer unit and γ-CD, meaning that 660 mg of **4c** obtained is containing 141 mg of PEG. Therefore, the production yield on PEG basis was calculated to be 47%. From the filling ratio obtained, molecular weight was estimated to be 113000 based on M_w of PEG. This number is not far from M_w obtained from GPC, considering that the calibration curve was based on PEG not polyrotaxane; ^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ 5.52 (O2H, O3H), 4.90 (C1H), 4.22 (O6H), 3.75−3.48 (C3H, C5H, C6H and PEG), 3.44−3.30 (C2H, C4H). IR (cm^{-1}): 3339br, 2916s, 1643 m, 1348 m, 1154s, 1081s, 1028s, 940 m, 855 m, 759 m, 705 m. GPC (PEG standards, DMSO eluent in the presence of 10 mM LiBr): $M_n = 89100$, $M_w = 125200$, $M_w/M_n = 1.41$.

Acknowledgment. This work was partially supported by Grant-in-Aid for Scientific Research (S) (No. 20221005) and for Young Scientist (B) (No. 22750099) of Japan.

Supporting Information Available: Text giving definitions and calculations of filling ratios and production yields of CD-PRs on polymer basis and figures showing characterizations of oligomerized polyrotaxane obtained from PEG and α-CD and full ^{1}H NMR spectra of CD-PRs measured at 298 and 343 K. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For a recent review, see: Frampton, M. J.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 1028–1064.
(2) For a recent review, see: Li, J.; Loh, X. J. *Adv. Drug Delivery Rev.* **2008**, *60*, 1000–1017.
(3) For a recent review, see: Yui, N.; Katoono, R.; Yamashita, A. *Adv. Polym. Sci.* **2009**, *222*, 55–77.
(4) For a recent review, see: Ito, K. *Polym. J.* **2007**, *39*, 489–499.
(5) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325–327.
(6) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516–518.
(7) Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485–487.
(8) Cacialli, F.; Wilson, J. S.; Michels, J. J.; Daniel, C.; Silva, C.; Friend, R. H.; Severin, N.; Samori, P.; Rabe, J. P.; O'Connell, M. J.; Taylor, P. N.; Anderson, H. L. *Nat. Mater.* **2002**, *1*, 160–164.
(9) Choi, H. S.; Lee, S. C.; Yamamoto, K.; Yui, N. *Macromolecules* **2005**, *38*, 9878–9881.

(10) Karaky, K.; Brochon, C.; Schlatter, G.; Hadziioannou, G. *Soft Matter* **2008**, *4*, 1165–1168.

(11) Kato, K.; Inoue, K.; Kidowaki, M.; Ito, K. *Macromolecules* **2009**, *42*, 7129–7136.

(12) For the most recent review, see: Harada, A.; Hashidzume, A.; Yamaguchi, H.; Takashima, Y. *Chem. Rev.* **2009**, *109*, 5974–6023.

(13) Liu, R.; Maeda, T.; Kihara, N.; Harada, A.; Takata, T. *J. Polym. Sci. Part A* **2007**, *45*, 1571–1574.

(14) Okada, M.; Takashima, Y.; Harada, A. *Macromolecules* **2004**, *37*, 7075–7077.

(15) Wenz, G.; Han, B. -H.; Müller, A. *Chem. Rev.* **2006**, *106*, 782–817.

(16) Loethen, S.; Kim, J. -M.; Thompson, D. H. *Polym. Rev.* **2007**, *47*, 383–418.

(17) Yurteri, S.; Cianga, I.; Yagci, Y. *Macromol. Chem. Phys.* **2003**, *204*, 1771–1783.

(18) Lima, V.; Jiang, X.; Brokken-Zijp, J.; Schoenmakers, P. J.; Klumperman, B.; Van Der Linde, R. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 959–973.

(19) Michishita, T.; Okada, M.; Harada, A. *Macromol. Rapid Commun.* **2001**, *22*, 763–767.

(20) Liu, Y.; Yang, Y.-W.; Chen, Y.; Zou, H.-X. *Macromolecules* **2005**, *38*, 5838–5840.

(21) Ooya, T.; Ito, A.; Yui, N. *Macromol. Biosci.* **2005**, *5*, 379–383.

(22) Takahashi, A.; Katoono, R.; Yui, N. *Macromolecules* **2009**, *42*, 8587–8589.

(23) Karino, T.; Okumura, Y.; Ito, K.; Shibayama, M. *Macromolecules* **2004**, *37*, 6177–6182.

(24) Araki, J.; Ito, K. *J. Polym. Sci., Part A* **2006**, *44*, 532–538.

(25) Harada, A.; Li, J.; Nakamitsu, T.; Kamachi, M. *J. Org. Chem.* **1993**, *58*, 7524–7528.

(26) Ooya, T.; Yui, N. *J. Biomater. Sci., Polym. Ed.* **1997**, *8*, 437–455.

(27) Zhao, T.; Beckham, H. W. *Macromolecules* **2003**, *36*, 9859–9865.

(28) Zhang, X. W.; Zhu, X. Q.; Tong, X. M.; Ye, L.; Zhang, A. Y.; Feng, Z. G. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5283–5293.

(29) For a review of inclusion complex formation of CDs, see: Schneider, H.-J. *Angew. Chem., Int. Ed.* **1991**, *30*, 1417–1436.

(30) Santee, E. R.; Chang, R.; Morton, M. *J. Polym. Sci., C: Polym. Lett.* **1973**, *11*, 449–452.