Preparation and Characterization of Polyrotaxanes Containing Many Threaded α-Cyclodextrins

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Polyrotaxanes in which many α-cyclodextrins (α-CD) are threaded on a poly(ethylene glycol) chain were prepared by the reaction of the complexes between α-CDs and poly(ethylene glycol) bisamines with 2,4-dinitrofluorobenzene which is bulky enough to prevent dethreading. The prodcts were characterized by gel permeation chromatography (GPC), UV-vis, X-ray diffraction (powder), ^{1}H NMR, ^{13}C NMR, and ^{13}C CP/MAS NMR, and 2D NOESY NMR spectra. The GPC, ^{1}H NMR, and ^{13}C NMR spectra show that the product consists of α-CDs, poly(ethylene glycol), and 2,4-dinitrophenyl groups. The ^{13}C CP/MAS NMR and 2D NOESY NMR spectra show that a poly(ethylene glycol) chain is included in cavities of α-CDs. The number of α-CDs in a polyrotaxane was calculated from the UV-vis, ^{1}H NMR spectra, and optical rotation. Four kinds of polyrotaxanes were prepared starting from poly(ethylene glycol) of various molecular weights. Fifteen to 20 α-CDs (on average) are captured in each polyrotaxane. A polyrotaxane which has about 37 α-CDs was obtained by the fractionation of the product prepared from poly(ethylene glycol) of average molecular weight 2000 using GPC.

Introduction

In recent years, much attention has been focused on supramolecular science, science of noncovalent assembly, because of the recognition of the importance of specific noncovalent interactions in biological systems and in chemical processes.[1] Rotaxanes are one of the "classical" classes of molecules consisting of a noncovalent entities, a "rotor" and an "axle" in a single molecule,[2] and have been synthesized in a statistical way; thereby, the yields were very low.[3] Recently, rotaxanes have attracted renewed interests in the field of supramolecular chemistry because of their unique structures and properties. Rotaxanes can be prepared by closing the end groups of "axle" by large groups within the ordered environments of the noncovalent templating forces in such a way as to retain the order originally imposed by the weak interactions.[4] By this method complexes containing methylated β-cyclodextrin and a thread[5] have been synthesized. Both symmetric[6] and asymmetric[7] ionic rotaxanes containing α-cyclodextrin have been reported.

We have found that α-cyclodextrin forms complexes with poly(ethylene glycol) (PEG) to give crystalline compounds in high yields which are the first example of the complexes of cyclodextrins with polymers.[8] We reported that a PEG chain is included in a tunnel formed by α-cyclodextrins. However, the complexes are soluble in water and are in an equilibrium with free cyclodextrin and polymer in solution. Now we have succeeded in preparing compounds in which many cyclodextrins are threaded on a single PEG chain and are trapped by capping the chain ends with bulky groups as shown in Scheme I. This is the first example that many rotors are imprisoned in a single molecule. We named this molecule "molecular necklace".[9] Complexes of crown ethers with polymers[10] and paraquat-hydroquinone complexes[11] have been reported. Wenz et al. also reported a rotaxane with many α-cyclodextrins.[12]

In a previous paper we reported briefly on the preparation of a polyrotaxane containing many threaded α-CDs.[9] This paper describes preparation and characterization of polyrotaxanes containing many threaded α-CDs in detail, and the structure of the polyrotaxanes is discussed.

Results and Discussion

Preparation of Polyrotaxanes. Previously we have reported that α-CD formed stoichiometric complexes with PEG of various molecular weights to give crystalline compounds in high yields.[8] Although α-CD did not form complexes with the low molecular weight analogues, such as ethylene glycol, di(ethylene glycol), and tri(ethylene

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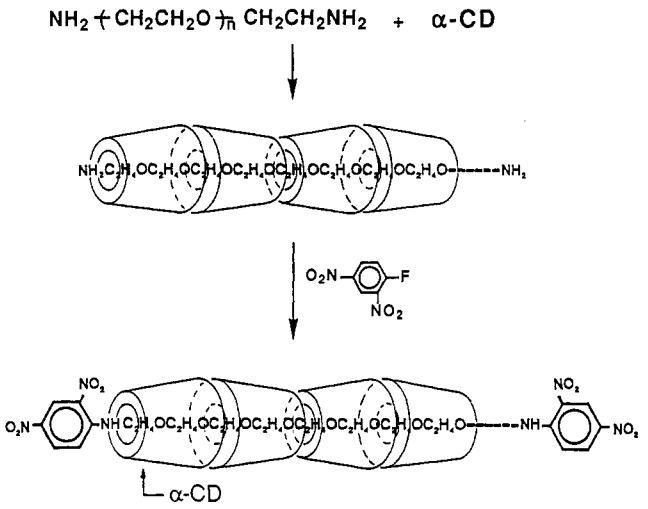
Scheme I



glycol), α-CD-formed complexes with PEG having small substituents at both ends, such as amines and methoxy groups in high yields. However, PEG carrying large substituents at both ends, such as 2,4-dinitrophenyl groups or 3,6-dinitrobenzoyl groups, did not form complexes with α-CD. PEG with a large group at one end and a small group at the other end formed complexes with α-CD. We proposed that α-CDs include a PEG chain from small end groups. Therefore, we planned to prepare rotaxanes by a method as shown in Scheme I. First, complexes of α-CDs with PEG bisamine (PEGBA) were prepared. Then the end groups (amino groups) were allowed to react with 2,4-dinitrofluorobenzene which is bulky enough to prevent dethreading to block the α-CDs on a polymer chain.[13] We chose PEG bisamine for the axle with small end groups because they can react readily with dinitrofluorobenzene to close the end groups.

The complexes between α-CD and PEG bisamine were prepared by a similar method to that previously reported for the complexes of α-CD with PEG.[8] The complexes were completely dried under vacuum with heating. The reaction of the complexes with 2,4-dinitrofluorobenzene in THF under heterogeneous conditions failed to produce polyrotaxane. α-CD and PEG bisamine derivatives could be recovered. Next, we tried this reaction in dimethylformamide (DMF). First, PEGBA (MW = 3350) complex with α-CD was suspended in DMF, and an excess (46 equiv) of 2,4-dinitrofluorobenzene together with DMF was added in the mixture. The product was precipitated from ether. The residue was dissolved in dimethyl sulfoxide (DMSO) and precipitated from methanol and water to remove unreacted α-CD, PEGBA, and water-soluble dinitrophenyl derivatives (yield 44–60%). Finally, the product was purified by column chromatography on Sephadex G-50 by using DMSO as solvent.

Characterization. The products were found to be pure and contaminated with no free α-CD, PEGBA, or dinitrophenyl derivatives. The products are insoluble in the usual organic solvents and even in neutral water and dimethylformamide (DMF). However, they are soluble in dimethyl sulfoxide (DMSO) and in 0.1 N NaOH. Hydroxyl groups of α-CD (pK_a = 12) may be ionized, so that α-CD becomes soluble in an aqueous medium.

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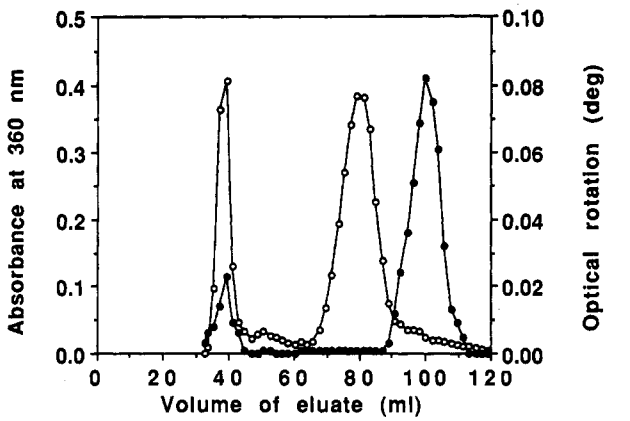

Figure 1. Elution diagram of the reaction mixture of the α-CD–PEGBA-1450 complex with dinitrofluorobenzene. The conditions are described in the text.

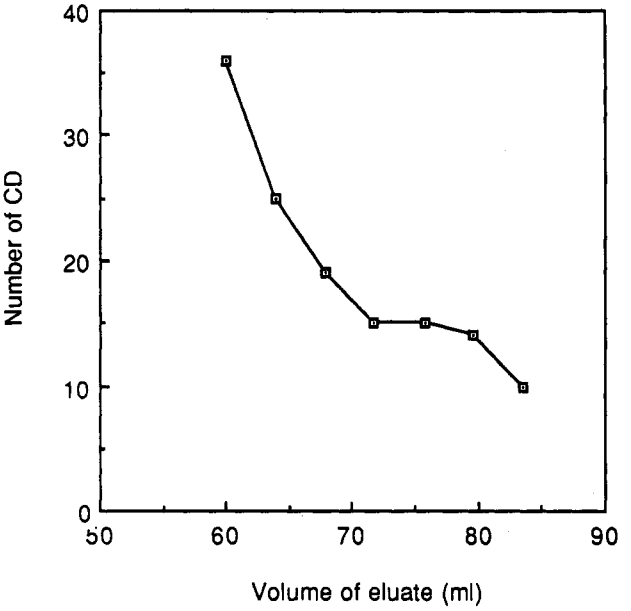

Figure 2. Fractionation of MN-2000. The number of CDs in a polyrotaxane in each fraction is shown.

Neutralizing this solution by adding 0.1 M HCl instantly produced a precipitate. This phenomenon is reversible.

The products were characterized by elemental analyses, UV–vis, X-ray diffraction (powder), ^{1}H NMR, ^{13}C NMR, ^{13}C CP/MAS NMR, and 2D NOESY NMR spectra.

Figure 1 shows the elution diagram of the reaction mixture of the α-CD–PEGBA-1450 complex with dinitrofluorobenzene. The chromatograph shows three peaks. The first peak (fraction I), which could be detected by both UV (360 nm) and optical rotation, was identified as the product, polyrotaxane. The second (fraction II), which could be detected only by UV, was identified as PEG–DNP_2. The third (fraction III), which could be detected only by optical rotation, was identified as nonreacted α-CD. The number of molecules (half of the number of the end groups) can be calculated from the absorbance at 360 nm (dinitrophenyl group). The number of CDs can be calculated from the optical rotation. Therefore, the number of CDs in a polyrotaxane can be calculated.

Figure 2 shows the number of CDs in a polyrotaxane (MN-2000), which was prepared from PEG of average molecular weight of 2000, in each fraction. The diagram shows that the product can be fractionated according to

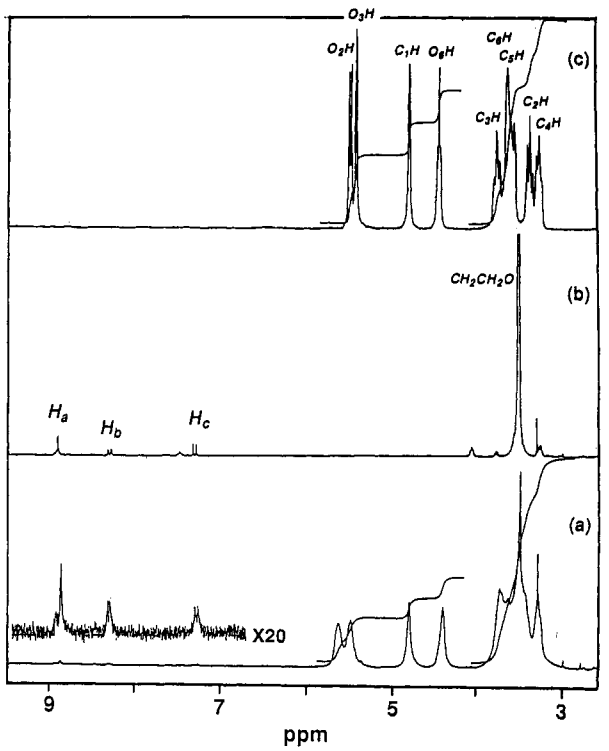

Figure 3. ^{1}H NMR spectra of fraction I (MN-3350) in DMSO-d_6 (a) that of fraction II (PEG–DNP_2) (b), and fraction III (α-CD) (c).

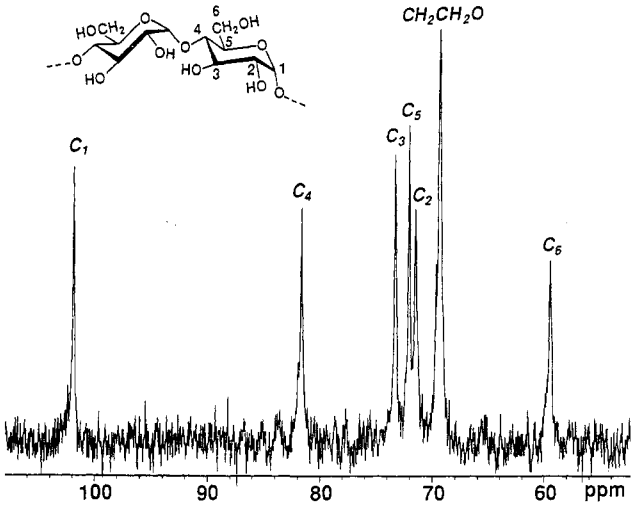

Figure 4. ^{13}C NMR spectrum of MN-3350.

the molecular weights, that is, the number of CDs per rotaxane molecule. The highest molecular weight of the polyrotaxane obtained is 38 000, which corresponds to about 37 cyclodextrins in a single rotaxane molecule.

Figure 3 shows the ^{1}H NMR spectra (in DMSO-d_6) of the product (fraction I) (a), MN-3350, which was prepared from PEG of average molecular weight 3350, together with that of the fraction II (PEGBA–DNP_2) (b) and that of the fraction III (α-CD) (c). The spectrum of the product shows that the product is composed of α-CD, PEGBA, and dinitrophenyl groups. The peaks of CD, PEG, and dinitrophenyl groups of MN-3350 are broadened. This result suggests that α-CDs are difficult to move on a PEG chain and/or the polyrotaxane is polydisperse.

Figure 4 shows the ^{13}C NMR spectrum of MN-3350. Both α-CD peaks and ethylene glycol peaks were observed. The resonances of ethylene glycol of PEG split into two

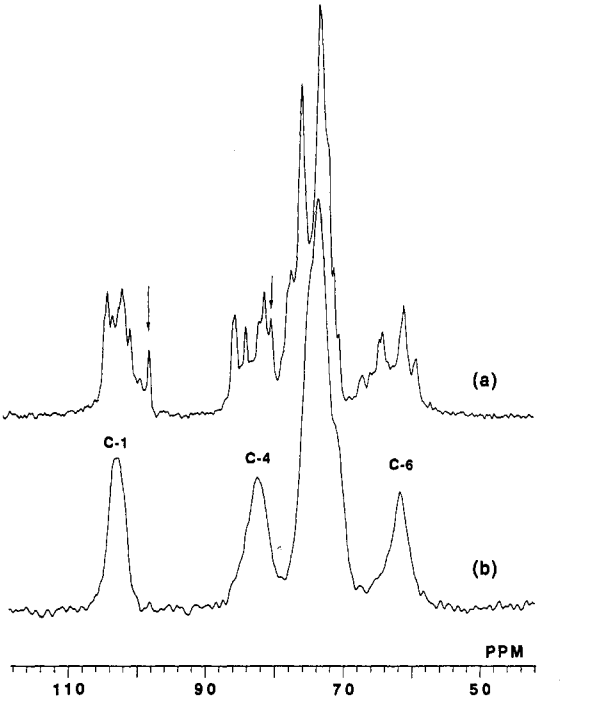

Figure 5. ^{13}C CP/MAS NMR spectrum of α-CD (a) and that of MH-3350 (b). Arrows show C-1 and C-4 peaks adjacent to a confomationally strained glycosidic linkage.

peaks, a broad peak in the higher magnetic field and a sharp one in the lower field. This indicates that the broad peak is due to the complexed part of PEG and the sharp one is assigned to a noncomplexed part of PEG. This assignment has been confirmed by measuring the ^{13}C NMR spectrum of a polyrotaxane in which a smaller part of the polymer chain is covered with CDs.

Figure 5 shows the ^{13}C CP/MAS NMR spectra of MN-3350 together with that of free α-CD.[14] Free α-CD assumes a less symmetrical conformation; that is, the C(1)–O–C(4) glycosidic linkage is distorted. Peaks at 80 and 98 ppm are assigned to C-1 and C-4 adjacent to conformationally strained glycosidic linkage, respectively. In the spectrum of free α-CD the signals of C-1, C-4, and C-6 show resolved resonances from each glucose residues because all glucose units are in different environments. On the other hand, in the spectrum of the polyrotaxane the peaks at 80 ppm and 98 ppm disappeared, and the signals of C-1, C-4, and C-6 show a single peak from each glucose unit. These results indicate that all glucose units of CD in the polyrotaxane are in a similar environment, α-CD assumes a symmetrical ring structure, and a PEG chain is included in a tunnel formed by CDs.

Figure 6 shows the 2D-NOESY-NMR spectrum of MN-3350 in NaOD. The spectrum shows that the signals of H-3 and H-5 protons of α-CD, which are directed toward the inside of the cavity, correlate with the resonance of the CH_2 of PEG, but the H-1, H-2, and H-4 protons, which are located outside the cavity, do not correlate with PEG. These results indicate that a PEG chain is included in α-CD cavities.

The X-ray powder pattern of MN-3350 shows that the polyrotaxane is crystalline and the pattern is similar to that of the complexes of α-CD with octanol or PEG, which have been reported to have extended column structure,

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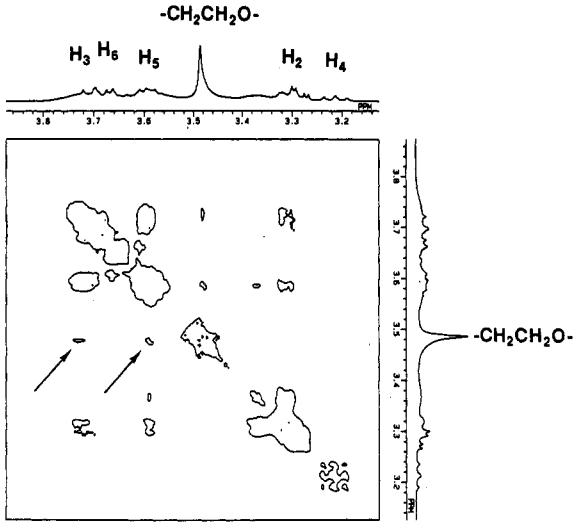

Figure 6. 2D NOESY NMR spectrum of MN-3350 in D_2O-NaOD. Arrows show correlation peaks.

Table I. Molecular Weight and Composition of Polyrotaxanes

polyrotaxane	mol wt[a]	no. of ethylene glycol units	no. of α-CD included[a]	molar ratio between ethylene glycol units and α-CD
MN-3350	23 500	77	20	3.9
MN-2000	20 000	45	18	2.5
MN*-2001[b]	19 000	45	17	2.6
MN-1450	16 500	35	15	2.3

[a] Calcd from UV–vis spectra and ^1H NMR spectra. [b] Prepared from JED-2001.

and different from those of the complexes with small molecules, such as propionic acid or propanol, which have a cage structure.[15] These results indicate that the rotaxane has a channel-type structure.

The UV absorption spectra of the polyrotaxanes show that the wavelength of the absorption maximum is 360 nm and the molar extinction coefficient is 17950 $L \cdot mol^{-1} \cdot cm^{-1}$. Although the shape of the spectrum is similar to that of 2,4-dinitro-*N*-alkylaniline, the absorption maximum is little blue-shifted. The number of molecules can be calculated from the absorbance. Then we can estimate the molecular weights of the molecular necklace.

Table I shows the results of the preparation of polyrotaxanes of various molecular weights. Four kinds of polyrotaxanes have been prepared starting from PEG of different molecular weights and JED-2001 (PEG bisamine). The number of α-CDs threaded in a polyrotaxane was calculated from UV spectra and ^1H NMR spectra or optical rotation. Fifteen to 20 α-CDs were found to be threaded on a PEG chain. The number of CDs increases with an increase in the molecular weight. The molecular weight of MN-3350 is 23 500. MN-3350 has about 20 α-CDs on a PEG chain, which corresponds to the molar ratio of ethylene glycol units to α-CDs of 3.9. More than half of the polymer chain is covered with α-CDs. The molecular weight of MN-1450 is 16 500. MN-1450 has 15 α-CDs on a PEG chain. The molar ratio of ethylene glycol units to α-CDs is 2.3. The ratio indicates that the molar ratio is almost stoichiometric; that is, CDs are almost close-packed from end-to-end of the polymer chain.

In conclusion, we have prepared polyrotaxanes in which many α-cyclodextrins are threaded on a poly(ethylene glycol) chain by the reaction of the complexes between poly(ethylene glycol) bisamine and α-CDs with 2,4-dinitrofluorobenzene which is large enough to prevent dethreading α-CDs from the polymer chain.

Experimental Section

Materials. α-Cyclodextrin (α-CD) was obtained from Nakarai Tesque Inc. and used after drying at 80 °C under vacuum. Poly(ethylene glycol) 1450 with MW 1450 (PEG-1450) and poly(ethylene glycol) 2000 with MW 2000 (PEG-2000) were purchased from Nakarai Tesque Inc. and dried under vacuum. Poly(ethylene glycol) bisamine 3350 (PEGBA-3350) with average MW of 3350 was obtained from Sigma. Jeffamine ED-2001 (JED-2001) was supplied from Texaco Chemical Co. and was purified with precipitation from diethyl ether. 2,4-Dinitrofluorobenzene (DNFB) and *p*-toluenesulfonyl chloride were obtained from Nakarai Tesque Inc. Potassium phthalimide and hydrazine hydrate were obtained from Wako Pure Chemical Ind. Methylene chloride (Nakarai Tesque Inc.) was fractionally distilled from CaH_2 under nitrogen atmosphere. Dimethylformamide (DMF) (Nakarai Tesque Inc.) was purified with reduced pressure distillation from molecular sieves (4A) under nitrogen atmosphere. DMSO-d_6, D_2O, and NaOD used as solvents in the NMR measurements were obtained from Aldrich.

Measurements. Gel chromatography (GPC) was carried out with a Sephadex G-50 column (1.7 × 70 cm) using DMSO as solvent. Fractions were collected per 1.5 mL and were detected with a Shimadzu UV-2001 UV–vis spectrophotometer at a wavelength of 360 nm and a JASCO Dip-370 digital polarimeter at a wavelength of 589 nm with a cell length of 10 cm, respectively. Proton NMR spectra were recorded at 270 MHz in DMSO-d_6 and D_2O + NaOD on a JEOL JNM GXS-270 NMR spectrometer. Chemical shifts were referenced to solvent values (δ 2.50 ppm for DMSO and δ 4.70 ppm for HOD). Carbon 13 NMR spectra were recorded at 125.65 MHz in DMSO-d_6 on a JEOL JNM GXS-500 NMR spectrometer. Chemical shifts were referenced to the solvent (DMSO-d_6) value of δ 39.50 ppm. Absorption spectra were recorded on a Shimadzu UV-2001 UV–vis spectrophotometer. Solid-state carbon 13 CP/MAS NMR spectra were measured at 67.8 MHz on a JEOL JNM EX-270 NMR spectrometer with a sample spinning rate ca. 5.5 KHz at room temperature. Chemical shifts were referenced to external standard TMS. CP spectra were acquired with a 4-ms proton 90° pulse, a 1-ms contact time, and a 5-s repetition time. 2D NOESY experiments on the polyrotaxane were obtained at 400 MHz with D_2O and NaOD as the solvent at 30 °C on a JEOL JNM GXS-400 NMR spectrometer. The 2048 experiments were performed with eight scans per experiment. X-ray diffraction powder patterns were taken by using Cu Kα radiation with a Rigaku RDA-ROC X-ray diffractometer (voltage, 40 KV; current, 40 mA; scanning speed, 3°/min).

Preparation of PEG Bisamine. PEGBA-1450 and PEGBA-2000 were prepared from PEG-1450 and PEG-2000, respectively, according to the method described by Pillai et al.[16]

PEGBA-1450. PEG-1450 (8.6 g), which had been previously dried in vacuum at 80 °C for 4 h, was dissolved in methylene chloride (60 mL). *p*-Toluenesulfonyl chloride (36 g) and pyridine (20 mL) were added to this solution, and the mixture was stirred under a nitrogen atmosphere overnight. The polymer was precipitated from this solution by addition of diethyl ether with rapid stirring. Stirring was continued for another 15 min, keeping the mixture in an ice bath. The precipitate was filtered and washed with diethyl ether. The product was crystallized from ethanol, filtered, and dried under vacuum to give PEG tosylate (9.6 g), yield 92%. GPC analysis showed that the product had the same elution time and molecular weight distribution (M_w/M_n = 1.03) as those of the PEG-1450, and the product showed absorption at 225 nm which indicated the polymer was tosylated (90% substitution from UV analysis).

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PEG tosylate (4.6 g) and potassium phthalimide (7.0 g) in DMF (60 mL) were heated under reflux in a nitrogen atmosphere for 5 h. The precipitate was then filtered off, and to the clear filtrate was added diethyl ether slowly with stirring, keeping the mixture in an ice bath. The precipitate was filtered, washed with diethyl ether, and then digested with 70 mL of methylene chloride. The insoluble impurities were filtered off, and the filtrate was then precipitated from diethyl ether. The precipitate was filtered and dried under vacuum to give PEG phthalimide (3.3 g), yield 73%. GPC analysis showed that the product had similar elution time and molecular weight distribution (M_w/M_n = 1.03) to the starting material.

PEG phthalimide (3.2 g) and hydrazine hydrate (6.0 mL) in ethanol (60 mL) were heated under reflux for 20 h. After being cooled to room temperature the product was precipitated from diethyl ether. The precipitate was filtered and redissolved in methylene chloride, and the insoluble impurities were removed by filtration. The filtrate was precipitated from diethyl ether. The precipitate was filtered, washed with diethyl ether, and dried under vacuum to give PEGBA-1450 (2.57 g, 94%). Anal. Calcd for $C_{72}H_{148}N_2O_{35}(H_2O)_2$: C, 52.80; H, 9.37; N, 1.69. Found: C, 52.57; H, 9.19; N, 1.54.

PEGBA-2000. Anal. Calcd for $C_{90}H_{184}N_2O_{44}(H_2O)_5$: C, 51.75; H, 9.36; N, 1.34. Found: C, 51.36; H, 9.04; N, 1.09.

Preparation of Polyrotaxanes. MN-3350. PEGBA-3350 (0.076 g, 2.27×10^{-5} mol) was dissolved in water (0.7 mL). A saturated aqueous solution of α-CD (8.4 mL) was added into the PEGBA aqueous solution and the mixture was irradiated with an ultrasonic wave for 10 min and allowed to stand overnight at room temperature. The precipitate was freeze-dried and then dried under vacuum at 50 °C to give the α-CD–PEGBA complex (1.29 g).

The α-CD–PEGBA complex and DNFB (0.39 g, 2.1×10^{-3} mol) were introduced into a 100-mL round-bottom flask. DMF (25 mL) was subsequently introduced, and the mixture was stirred in a nitrogen atmosphere overnight at room temperature. The mixture was heated to 80 °C for a few hours. After being cooled to room temperature the product was precipitated by dropwise addition of diethyl ether to the reaction mixture. The precipitate was filtered and washed with diethyl ether. The residue was dissolved in DMSO and then precipitated from methanol (three times) to remove unreacted DNFB, PEGBA, and dinitrophenyl derivatives of PEGBA and from water (three times) to remove free α-CD. The product was collected, washed with diethyl ether, and dried under high vacuum to give the molecular necklace-3350 (MN-3350) (0.32 g). The yield based on PEGBA was 60%. Finally, the gel filtration of the product was carried out. The product was found to be pure and contained no free α-CD, PEGBA, or dinitrophenyl derivative of PEGBA. ^{1}H NMR (DMSO-d_6) (270 MHz): δ 8.87 (s, 2H, meta H of phenyl), 8.30 (d, 2H, meta H of phenyl), 7.26 (d, 2H, ortho H of phenyl), 5.63 (s, 6H × 20, O(2)H of α-CD), 5.48 (s, 6H × 20, O(3)H of α-CD), 4.80 (s, 6H × 20, C(1)H of α-CD), 4.40 (s, 6H × 20, O(6)H of α-CD), 3.64–3.74 (m, 24H × 20, C(3)H, C(6)H, and C(5)H of α-CD), 3.51 (s, 4H × 82, CH_2 of PEG), 3.24–3.29 (m, 12H × 20, C(2)H and C(4)H of α-CD). ^{1}H NMR (D_2O + NaOD) (270 MHz): δ 8.93 (s, 2H, meta H of phenyl), 8.17 (d, 2H, meta H of phenyl), 7.05 (d, 2H, ortho H of phenyl), 4.74 (d, 6H × 20, C(1)H of α-CD), 3.59–3.75 (m, 24H × 20, C(3)H, C(6)H, and C(5)H of α-CD), 3.50 (s, 4H × 82, CH_2 of PEG), 3.19–3.32 (m, 12H × 20, C(2)H and C(4)H of α-CD). ^{13}C NMR (DMSO-d_6) (125.65 MHz): δ 101.93 (C(1) of α-CD), 81.69 (C(4) of α-CD), 73.33 (C(3) of α-CD), 72.08 (C(5) of α-CD), 71.53 (C(2) of α-CD), 69.38 (CH_2 of PEG), 59.74 (C(6) of α-CD). Anal. Calcd for $C_{888}H_{1520}N_6O_{651}(H_2O)_{40}$: C, 45.13; H, 6.66; N, 0.36. Found: C, 44.86; H, 6.69; N, 0.38.

MN-1450, NM-2000, and MH*-2001 were prepared from PEGBA-1450, PEGBA-2000, and JED-2001, respectively, with a similar method.

MN-1450. Yield: 27%. ^{1}H NMR (DMSO-d_6) (270 MHz): δ 8.88 (s, 2H, meta H of phenyl), 8.26 (d, 2H, meta H of phenyl), 7.27 (d, 2H, ortho H of phenyl), 5.64 (s, 6H × 15, O(2)H of α-CD), 5.45 (m, 6H × 15, O(3)H of α-CD), 4.80 (d, 6H × 15, C(1)H of α-CD), 4.41 (m, 6H × 15, O(6)H of α-CD), 3.60–3.78 (m, 24 H × 15, C(3)H, C(6)H, and C(5)H of α-CD), 3.52 (s, 4H × 35, CH_2 of PEG), 3.20–3.40 (m, 12H × 15, C(2)H and C(4)H of α-CD). ^{1}H NMR (D_2O + NaOD) (270 MHz): δ 9.04 (s, 2H, meta H of phenyl), 8.25 (d, 2H, meta H of phenyl), 7.12 (d, 2 H, ortho H of phenyl), 4.90 (d, 6H × 15, C(1)H of α-CD), 3.66–3.86 (m, 24H × 15, C(3)H, C(6)H, and C(5)H of α-CD), 3.59 (s, 4H × 35, CH_2 of PEG), 3.33–3.54 (m, 12H × 15, C(2)H and C(4)H of α-CD). ^{13}C NMR (DMSO-d_6) (125.65 MHz): δ 101.90 (C(1) of α-CD), 81.64 (C(4) of α-CD), 73.31 (C(3) of α-CD), 72.06 (C(5) of α-CD), 71.46 (C(2) of α-CD), 69.35 (CH_2 of PEG), 59.71 (C(6) of α-CD). Anal. Calcd for $C_{618}H_{1040}N_6O_{490}(H_2O)_{30}$: C, 43.83; H, 6.55; N, 0.50. Found: C, 43.96; H, 6.68; N, 0.55.

MN-2000. Yield: 30%. ^{1}H NMR (DMSO-d_6) (270 MHz): δ 8.86 (s, 2H, meta H of phenyl), 8.24 (d, 2H, meta H of phenyl), 7.25 (d, 2H, ortho H of phenyl), 5.63 (s, 6H × 18, O(2)H of α-CD), 5.44 (d, 6H × 18, O(3)H of α-CD), 4.78 (d, 6H × 18, C(1)H of α-CD), 4.40 (s, 6H × 18, O(6)H of α-CD), 3.58–3.78 (m, 24H × 18, C(3)H, C(6)H, and C(5)H of α-CD), 3.53 (s, 4H × 45, CH_2 of PEG), 3.30–3.44 (m, 12H × 18, C(2)H and C(4)H of α-CD). ^{13}C NMR (DMSO-d_6) (125.65 MHz): δ 102.01 (C(1) of α-CD), 81.63 (C(4) of α-CD), 73.38 (C(3) of α-CD), 72.01 (C(5) of α-CD), 71.43 (C(2) of α-CD), 69.25 (CH_2 of PEG), 59.45 (C(6) of α-CD). Anal. Calcd for $C_{750}H_{1340}N_6O_{628}(H_2O)_{36}$: C, 43.96; H, 6.59; N, 0.41. Found: C, 43.61; H, 6.77; N, 0.41.

MN*-2001. Yield: 19%. ^{1}H NMR (DMSO-d_6) (270 MHz): δ 8.88 (s, 2H, meta H of phenyl), 8.28 (d, 2H, meta H of phenyl), 7.26 (d, 2H, ortho H of phenyl), 5.42 (s, 12H × 17, O(2)H and O(3)H of α-CD), 4.81 (d, 6H × 17, C(1)H of α-CD), 4.20 (s, 6H × 17, O(6)H of α-CD), 3.59–3.79 (m, 24H × 17, C(3)H, C(6)H, and C(5)H of α-CD), 3.53 (s, 4H × 45, CH_2 of PEG), 3.17–3.48 (m, 12H × 17, C(2)H and C(4)H of α-CD). ^{13}C NMR (DMSO-d_6) (125.65 MHz): δ 102.02 (C(1) of α-CD), 81.61 (C(4) of α-CD), 73.31 (C(3) of α-CD), 72.04 (C(5) of α-CD), 71.51 (C(2) of α-CD), 69.29 (CH_2 of PEG), 59.64 (C(6) of α-CD). Anal. Calcd for $C_{714}H_{1208}N_6O_{560}(H_2O)_{34}$: C, 44.09; H, 6.68; N, 0.43. Found: C, 43.98; H, 6.61; N, 0.54.

Determination of Molecular Weight. The molecular weights of the products were determined by the end group assay using the UV–vis absorption spectra

$$MW = 2c/c' = 2c/A/eL = 2ceL/A$$

where c' (mol/L) = concentration of end groups determined by UV–vis specturm, $c' = A/eL$, A = absorbance, e = molar extinction coefficient of the dinitrophenyl group, L = cell length (1 cm), and c (g/L) = concentration of the product, the weight of the polyrotaxane dissolved in solvent. So the number (or the concentration) of the polyrotaxane is half of the end groups. The molecular weight of polyrotaxane is twice as large as c/c'.