Macromolecules **2008**, *41*, 5385−5392

Synthesis of a Molecular Tube in Dimethyl Sulfoxide and Its Inclusion Complexation Behavior with Poly(ethylene oxide-*ran*-propylene oxide)

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Received September 10, 2007; Revised Manuscript Received May 22, 2008

ABSTRACT: A molecular tube was synthesized by cross-linking α-cyclodextrins (α-CDs) of a polyrotaxane with epichlorohydrin in dimethyl sulfoxide (DMSO). The obtained molecular tube was characterized with ^{1}H and ^{13}C NMR, size-exclusion chromatography, and UV−vis absorption titration with iodine. The use of DMSO afforded greater cross-linking efficiency than that with the conventional aqueous NaOH. The inclusion−dissociation behavior of the molecular tube and α-CD with poly[(ethylene oxide)-*ran*-(propylene oxide)] (PEOrPO) having a central azobenzene moiety was investigated using induced circular dichroism measurements. The PEOrPO with azobenzene was included in the tube cavity, resulting in the exhibition of induced circular dichroism. This result suggests the stable inclusion of propyrene oxide units with a molecular tube for the first time. Higher temperature and higher molecular weight of PEOrPO yielded lesser amounts of the inclusion complexes with the molecular tube. The enthalpy change of inclusion complexation of the molecular tube with the PEOrPO-Az was calculated to be −3.6 kJ mol^{-1} per PO unit, which is similar to that with a linear alkyl chain.

Introduction

In the field of polymer science, the conformation of a polymer chain is one of the most important topics for improving properties of polymer materials.[1] Although much attention has been paid to the use of external fields such as mechanical, electric, and magnetic fields,[1−5] successful control of a polymer conformation in supramolecular complexation of DNA and proteins[6] suggests that the molecular recognition of synthetic polymers is another promising route, which has been scarcely investigated. Further investigation on the molecular recognition mechanism of synthetic polymers, therefore, will enable us to produce novel intelligent polymer systems.

Typical hopeful candidates for the construction of such artificial host−guest systems are cyclodextrins (CDs), i.e., cyclic oligosaccharides with nanosized torus shapes.[7] Three kinds of CDs, i.e., α-, β-, and γ-CDs, consist of 6, 7, and 8 α-D-glucose units, respectively. They have a hydrophobic cavity, of which diameter is strongly dependent on the number of glucose units (4.7−5.3, 6.0−6.5, and 7.5−8.3 Å for α-, β-, and γ-CDs, respectively[8]), and serve as a molecular container, which allows the inclusion of small guest molecules.[9−13] Since Harada et al. found the formation of an inclusion complex of α-CDs with poly(ethylene glycol) (PEG),[14] considerable attention has been focused on cooperative inclusion complexation between CDs and polymers.[15−19] Several reports have suggested the size correlation between the inner diameters of CDs and the cross-sectional areas of guest polymer chains in the inclusion complexation.[15,17] In contrast to the remarkable water solubility of CDs, most of the CD−polymer inclusion complexes showed low water solubility and were obtained as precipitates.

Harada et al. have synthesized a novel water-soluble host macromolecule termed "molecular tube" by cross-linking the adjacent α-CDs in a single polyrotaxane and subsequent dissociation of the included PEG after hydrolysis.[20] The molecular tube has a rigid long cylindrical cavity whose inner diameter is the same as that of α-CD and includes guest molecules in its cavity analogous to CDs, while the tube forms a water-soluble inclusion complex.

The theoretical study on the inclusion−dissociation behavior of the molecular tube with a linear polymer has suggested that, in contrast to a random-coiled polymer chain in a good solvent,[1] the polymer included in the cylindrical cavity is constrained to a linear shape, leading to a drastic decrease in the conformational entropy.[21] Therefore, the inclusion−dissociation with the molecular tube enables us to control the conformational entropy of a polymer chain. Previous studies have reported the inclusion complexation of a molecular tube with various small molecules[20,22,23] or linear polymers such as PEG,[24,25] alkylated PEG,[26−28] polyaniline,[29−32] and poly(ethlyene glycol)-*block*-poly(tetrahydrofuran)-*block*-poly(ethylene glycol) triblock copolymer.[33] However, to the best of our knowledge, there is no report on inclusion complexation between a molecular tube and a linear polymer containing propylene oxide (PO) units, probably due to the previous prediction that a PO unit is too big to penetrate the α-CD cavity.[34−36]

In the present article, we investigated the inclusion−dissociation behavior of the molecular tube with poly[(ethylene oxide)-*ran*-(propylene oxide)] using induced circular dichroism measurements. We also confirmed the threading of α-CD through poly[(ethylene oxide)-*ran*-(propylene oxide)] in an aqueous solution at a low α-CD concentration without precipitation. The molecular tube used in the present study was successfully prepared from polyrotaxane in dimethyl sulfoxide (DMSO), providing greater cross-linking efficiency than that in the conventional aqueous NaOH.

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10.1021/ma702040c CCC: $40.75

Experimental Section

Materials. PEG with terminal amino groups (Sunbright DE-PA20H, MW = 2000) was kindly supplied by NOF Corp. (Tokyo, Japan). α-CD was purchased from Nihon Shokuhin Kako Co., Ltd. (Tokyo, Japan). Poly(ethylene glycol-*ran*-propylene glycol) monobutyl ethers (termed PEOrPOs) were purchased from Aldrich (Milwaukee, WI). Based on the information provided by the supplier, the number-averaged molecular weights M_n of the PEOrPOs were 970, 1700, and 3900. Azobenzene-4,4′-dicarbonyl chloride was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All the chemicals were used without further purification. Deionized water was used for optical measurements.

Synthesis of Polyrotaxane. Polyrotaxane was synthesized from α-CD, Sunbright DE-PA20H, and 2,4-dinitrofluorobenzene according to the procedure reported by Harada et al.[37,38] The yield based on PEG was 20%. The number of α-CD rings included in the single polyrotaxane was calculated to be ca. 15 by ^{1}H NMR. This value corresponds to an inclusion ratio of ca. 68%, considering that the average molecular weight of Sunbright DE-PA20H (= 2000) and the stoichiometric ratio of α-CDs to the EO units in the inclusion complexes (= 1:2[38–40]). From size exclusion chromatography (SEC) calibrated with poly(ethylene oxide) (PEO) standards, the weight-averaged molecular weight (M_w) and polydispersity (M_w/M_n) of the polyrotaxane were determined to be 9400 and 1.12, respectively.

^{1}H NMR (400 MHz DMSO-d_6, δ): 8.88 (s, 2H, *m*-H of phenyl), 8.29 (s, 2H, *m*-H of phenyl), 7.16 (s, 2H, *o*-H of phenyl), 5.71 (s, 6H × 15, O(2)H of α-CD), 5.53, 5.45 (s, s, 6H × 15, O(3)H of α-CD), 4.80 (s, 6H × 15, C(1)H of α-CD), 4.46 (s, 6H × 15, O(6)H of α-CD), 3.74 (s, 6H × 15, C(3)H of α-CD), 3.64 (s, 6H × 15, C(6)H of α-CD), 3.57 (s, 6H × 15, C(5)H of α-CD), 3.50 (s, 4H × 45, $-CH_2CH_2O-$ of PEG), 3.45 (s, 6H × 15, C(4)H of α-CD), 3.28 (s, 6H × 15, C(2)H of α-CD).

Synthesis of Molecular Tube. Polyrotaxane (4.0 g), previously vacuum-dried at 120 °C overnight, was dissolved in anhydrous DMSO (400 mL), followed by the addition of epichlorohydrin (1.48 g, 16.0 mmol) at room temperature. Finely powdered NaOH (5 g, 128 mmol) prepared by grinding granular NaOH with a Waring-type blender was added with vigorous stirring. After magnetic stirring for 18 h under nitrogen, the solution was gradually poured into cold water (400 mL) and carefully neutralized with 35 wt % aqueous HCl. After dialysis under running water for several days using dialysis tubing (BioDesign, MWCO 3500), followed by removal of precipitate by centrifugation, the solution was freeze-dried, yielding a brown solid.

The obtained solid was dissolved in 0.5 mol/L aqueous NaOH (50 g) and poured into 33 wt % aqueous NaOH (150 g) in an ice bath. After magnetic stirring for 24 h at 45 °C, the solution was cooled to room temperature and neutralized with 35 wt % aqueous HCl. After dialysis (BioDesign, MWCO 3500) under running water for a week and removal of precipitate by centrifugation, the solution was freeze-dried to yield a pale brown solid (1.78 g).

The product was fractionated by a gel permeation column (Sephadex G-100, Amersham Pharmacia Biotech) using DMSO as an eluent. Compared with the molecular weight of the starting polyrotaxane (M_{PR}), each fraction was combined into three different batches according to their molecular weights measured by SEC: (1) those with a higher average molecular weight than M_{PR} (MT-A), (2) those with a similar average molecular weight to M_{PR} (MT-B), and (3) those with considerably lower than M_{PR}. MT-A and MT-B were purified by a dialysis under running water for several days and collected as solids by freeze-drying, followed by characterization using ^{1}H and ^{13}C NMR spectroscopies, further SEC measurements, and UV−vis absorption titration with iodine. From the SEC measurements based on PEO standards, the M_w and M_w/M_n values of MT-A were 50 500 and 3.43 and those of MT-B were 14 100 and 2.66, respectively.

MT-A. ^{1}H NMR (400 MHz DMSO-d_6, δ): 6.46, 6.06 (s, s), 5.51, 5.45 (s, s, O(2)H of α-CD), 4.98, 4.90 (br, s, C(1)H of α-CD with the bridge), 4.80 (s, C(1)H of α-CD), 4.68 (s, OH of the bridge), 4.48 (s, O(6)H of α-CD), 3.96 (s), 3.3−3.8 (m, C(3)H, C(6)H, C(5)H, C(4)H, C(2)H of α-CD and CH, CH_2 of the bridge). ^{13}C NMR (DMSO-d_6, δ): 102.0 (C(1)H of α-CD), 98.3 (C(1)H of α-CD with the bridge), 82.1 (C(4)H of α-CD), 73.3 (C(3)H of α-CD), 72.1 (C(2)H, C(5)H of α-CD), 69.8 (C of the bridge), 60.1 (C(6)H of α-CD).

Table 1. Characterization of PEOrPO and PEOrPO-Az with Different Molecular Weights

	EO[a]	PO[a]	PO/EO[b]	M_n[c]	M_w/M_n[c]
$PEOrPO_{970}$	10.2	8.8	0.86	960	1.15
$PEOrPO_{1700}$	18.1	15.6	0.86	1700	1.13
$PEOrPO_{3900}$	39.4	33.9	0.86	3700	1.35
$PEOrPO_{970}$-Az	16.7	14.3	0.86	1800	1.25
$PEOrPO_{1700}$-Az	30.7	26.1	0.85	3100	1.27
$PEOrPO_{3900}$-Az	85.4	74.3	0.87	8300	1.48

[a] Calculated from the ratio of PO to EO and M_n. [b] Determined by ^{1}H NMR measurements in $CDCl_3$. [c] Determined by SEC measurements in $CHCl_3$ and calculation based on PEO standards.

MT-B. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.46, 6.06 (s, s) 5.51, 5.45 (s, s, O(2)H of α-CD), 4.98, 4.90 (br, s, C(1)H of α-CD with the bridge), 4.80 (s, C(1)H of α-CD), 4.68 (s, OH of the bridge), 4.48 (s, O(6)H of α-CD), 3.96 (s), 3.3−3.8 (m, C(3)H, C(6)H, C(5)H, C(4)H, C(2)H of α-CD and CH, CH_2 of the bridge). ^{13}C NMR (DMSO-d_6, δ): 101.8 (C(1)H of α-CD), 98.0 (C(1)H of α-CD with the bridge), 81.9 (C(4)H of α-CD), 73.2 (C(3)H of α-CD), 71.9 (C(2)H, C(5)H of α-CD), 69.6 (C of the bridge), 59.9 (C(6)H of α-CD).

Synthesis of PEOrPO-Azs. Poly[(ethylene oxide)-*ran*-(propylene oxide)] containing a central azobenzene moiety (PEOrPO-Az) was synthesized according to the following procedure (schematically illustrated in Figure 5). To the PEOrPO with an M_n value of 970 ($PEOrPO_{970}$) (5.0 g, 5.15 mmol) vacuum-dried at 80 °C overnight, azobenzene dicarbonyl chloride (0.79 g, 2.57 mmol) dissolved in anhydrous dichloromethane (20 mL) was added at room temperature under nitrogen. Activated molecular sieves (3A 1/16, Wako) were added to the mixture, followed by a dropwise addition of triethylamine (1.30 g, 12.8 mmol) and stirring for 10 min. The solution was sealed with nitrogen and stored in a refrigerator (ca. 5 °C) for a month. After additional stirring at room temperature for 2 days, the solution filtered through Hyflo supercel (Nacalai Tesque Inc.) was repeatedly washed with 0.1 mol/L aqueous $NaHCO_3$. The dichloromethane part was collected, evaporated, and further vacuum-dried to yield $PEOrPO_{970}$-Az as a red viscous liquid (5.5 g, yield 98%). Similar reactions of $PEOrPO_{1700}$ (10.0 g, 5.88 mol) with azobenzene-4,4′-dicarbonyl chloride (0.92 g, 3.0 mol) or $PEOrPO_{3900}$ (20.0 g, 5.13 mol) with azobenzene-4,4′-dicarbonyl chloride (0.79 g, 2.6 mol) yielded $PEOrPO_{1700}$-Az and $PEOrPO_{3900}$-Az, respectively, with the yields in the range of 98−99%. The synthesized PEOrPO-Azs were characterized by IR spectroscopy, ^{1}H NMR spectroscopy, and SEC measurements. The number-averaged molecular weight (M_n) and M_w/M_n of the PEOrPO-Azs and the ratios of PO to EO units are summarized in Table 1.

$PEOrPO_{970}$-Az. IR (cm^{-1}): 2990−2820, 1090−1180 ($-CH_2CH_2O-$ of PEO, $-CH_2CH(CH_3)O-$ of PPO), 1720, 1275 ($-COO-$), 1603 (aromatic ring), 1410 (azo group). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.21, 7.98 (d, d, 4H, 4H, azobenzene), 4.49, 3.97 (m, m, 2H × 2, 2H × 2, $-COO-CH_2-CH_2-$), 3.65 (d, 4H × 17, $-CH_2CH_2O-$ of PEO), 3.50 (s, 2H × 14, $-CH_2-$ of PPO), 3.41 (s, 1H × 14, $-CH-$ of PPO), 1.15 (s, 3H × 14, CH_3- of PPO), 1.55, 1.39, 0.91 (m, m, t, 2H × 2, 2H × 2, 3H × 2, $CH_3CH_2CH_2O-$ of butyl ether).

$PEOrPO_{1700}$-Az. IR (cm^{-1}): 2990−2820, 1090−1180 ($-CH_2CH_2O-$ of PEO, $-CH_2CH(CH_3)O-$ of PPO), 1720, 1275 ($-COO-$), 1603 (aromatic ring), 1410 (azo group). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.21, 7.98 (d, d, 4H, 4H, azobenzene), 4.50, 3.97 (m, m, 2H × 2, 2H × 2, $-COO-CH_2-CH_2-$), 3.65 (d, 4H × 31, $-CH_2CH_2O-$ of PEO), 3.50 (s, 2H × 26, $-CH_2-$ of PPO), 3.41 (s, 1H × 26, $-CH-$ of PPO), 1.15 (s, 3H × 26, CH_3- of PPO),

1.55, 1.39, 0.90 (m, m, t, 2H × 2, 2H × 2, 3H × 2, $CH_3CH_2CH_2O-$ of butyl ether).

PEOrPO$_{3900}$-Az. IR (cm^{-1}): 2990−2820, 1090−1180 ($-CH_2CH_2O-$ of PEO, $-CH_2CH(CH_3)O-$ of PPO), 1720, 1275 (−COO−), 1603 (aromatic ring), 1410 (azo group). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.21, 7.98 (d, d, 4H, 4H, azobenzene), 4.51, 3.97 (m, m, 2H × 2, 2H × 2, $-COO-CH_2-CH_2-$), 3.65 (d, 4H × 85, $-CH_2CH_2O-$ of PEO), 3.50 (s, 2H × 74, $-CH_2-$ of PPO), 3.39 (s, 1H × 74, −CH− of PPO), 1.15 (s, 3H × 74, CH_3- of PPO), 1.56, 1.39, 0.91 (m, m, t, 2H × 2, 2H × 2, 3H × 2, $CH_3CH_2CH_2O-$ of butyl ether).

Characterization of the Products. NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHz for ^{13}C on a JEOL JNM-AL400 spectrometer at ambient temperature. H−H COSY and C−H COSY measurements were performed at 70 °C. The chemical shifts were referenced to tetramethylsilane.

The SEC characterization of the polyrotaxane and molecular tubes was performed on a TOSOH HLC-8220GPC high-performance liquid chromatography system using an RI detector equipped with three columns in series: a TSK guard column Super AW-H and two TSK gel Super AWM-H columns (diameter 6.0 mm; length 150 mm; pore size 9 μm). DMSO containing 10 mmol/L of LiBr was used as the eluent (50 °C, 0.5 mL/min). The SEC characterization of the PEOrPO-Azs was performed on a Shimazu CLASS-VP high-performance liquid chromatography system using RI and UV detectors equipped with three columns in series: a Shodex K-800D column, a Shodex K-803L (diameter 8.0 mm; length 300 mm; pore size 10 μm), and a Shodex K-804L (diameter 8.0 mm; length 300 mm; pore size 10 μm). $CHCl_3$ containing a stabilizer (0.5% ethanol) was used as the eluent (40 °C, 1.0 mL/min). The M_w, M_n, and M_w/M_n values of the products were determined by SEC measurements based on PEO standards.

IR spectra were recorded using a Thermo Electron NICOLET 4700 FT-IR spectrometer on a single-reflection attenuated total reflection (ATR) configuration equipped with a diamond cell (DuraSampl IR II, Sens IR Technologies). The obtained spectra were corrected with an advanced ATR correction algorithm provided by the inbuilt software (OMNIC, Thermo electron Corp.).

UV−vis absorption titration spectra were recorded on a Shimazu UV-3150 spectrometer at room temperature using a 1 mm thick quartz cell. Spectra at various concentration of MT-B were measured at a fixed iodine concentration (300 μmol/L). To avoid the oxidation of iodine by atmospheric oxygen, aqueous mixtures of MT-B and iodine were prepared just before the measurements by the addition of a 50 mmol/L iodine solution (Nacalai Tesque, Kyoto Japan, containing ca. 1.3% iodine and ca. 4.0% potassium iodide) to the MT-B solutions.

Circular dichroism spectra were recorded on a Jasco J-820 circular dichroism spectrometer equipped with a Peltier temperature control unit using a 10 mm thick quartz cell. The temperature dependence of the circular dichroism spectra was recorded at a fixed wavelength of 335 nm, which is the absorption band of the azobenzene group, by increasing the temperature from 5 to 50 °C at the rate of 0.5 °C/min.

Results and Discussion

Synthesis and Characterization of Molecular Tube. There have been several reports on the synthesis of the molecular tubes, including the first one.[20] Despite a slight variation in the cross-linking conditions,[21–30,41,42] all the syntheses were carried out in aqueous NaOH (typically 5−10 wt %) using a large excess of epichlorohydrin as the cross-linking reagent. For example, Ikeda et al.[22,42] have employed epichlorohydrin with molar concentration of 20 times higher than that of the cross-linking points. The molecular weight distribution of the obtained molecular tube was in the range of 2400−23 000 by detailed analysis using SEC measurements and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy.[42] The use of excess epichlorohydrin seems to be disadvantageous due to its tendency to induce various side reactions, i.e., the cross-linking of α-CDs in different polyrotaxanes and/or the polymerization of epichlorohydrin itself. Although the reason for the use of excess epichlorohydrin is not described in the previous studies, it is speculated to be due to the hydrolysis of epichlorohydrin in aqueous NaOH.[43,44]

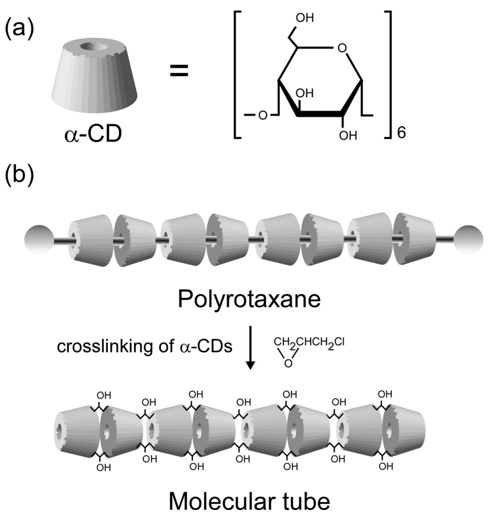

Figure 1. Schematic illustrations of (a) α-CD and (b) polyrotaxane and molecular tube.

On the basis of this hypothesis, we examined the synthesis of a molecular tube in an organic solvent. Dimethyl sulfoxide was chosen as the nonaqueous good solvent for polyrotaxane. Since the cross-linking reaction with epichlorohydrin requires an alkaline condition, the low solubility of NaOH in dimethyl sulfoxide poses a problem, while it was solved using a powerful technique of the dispersion of powdered NaOH in DMSO by vigorous stirring.[45] Powdered NaOH is widely employed in basic reactions in nonaqueous media, such as the permethylation of carbohydrates or various etherification processes of cellulose.[46]

In the first trial, a 4-fold molar amount of epichlorohydrin, compared with that of cross-linkable hydroxyls, was added to the polyrotaxane solution in DMSO. The mixture, which turned red after the addition of powdered NaOH, was stirred for 18 h, followed by dropwise dilution with a large amount of cold water. On neutralization with HCl, a large amount of precipitate was unexpectedly formed in the neutral aqueous solution; this was in contrast to the previous synthesis in aqueous NaOH, yielding a water-soluble product.[20–30,41,42] This result probably suggests the cross-linking of α-CDs not only within a single polyrotaxane but also between different polyrotaxanes and formation of a high-molecular-weight water-insoluble product. This water insolubility of the product is unsuitable for our observation of inclusion complexation in aqueous conditions.

In order to synthesize a water-soluble molecular tube by suppressing the cross-linking between different polyrotaxanes, we particularly concentrated on (1) the use of a smaller amount of epichlorohydrin and (2) a low polyrotaxane concentration at the cross-linking reaction. We employed a cross-linking condition including a stoichiometric amount of epichlorohydrin, namely half-molar amount of epichlorohydrin to that of hydroxyls, and a polyrotaxane concentration of ca. 1 wt %, which resulted in a considerable decrease in the precipitate. After the reaction, the water-soluble part was isolated from the water-insoluble part by a facile centrifugation process. Subsequently, the bulky end groups and the included PEG were removed by hydrolysis with strong alkali from both the water-soluble and water-insoluble parts, thereby obtaining water-soluble and water-insoluble tubes, respectively. The weight ratio of the former to the latter was ≈1.6, involving a slight lot-to-lot variation. The ^{1}H NMR showed almost identical spectra for both samples, and

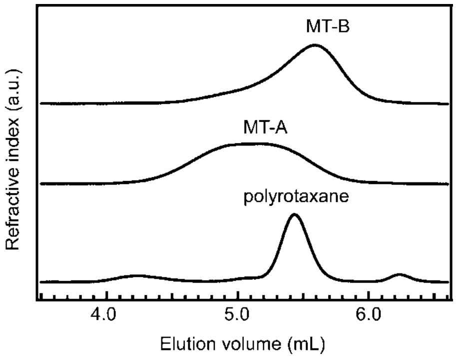

Figure 2. SEC profiles of polyrotaxane, MT-A, and MT-B.

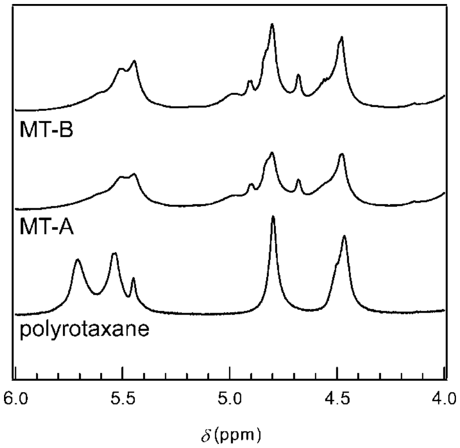

Figure 3. ^{1}H NMR spectra of polyrotaxane, MT-A, and MT-B in the range of $\delta = 4.0-6.0$.

the SEC charts showed that the water-insoluble tube had a higher average molecular weight than that of the water-soluble tube. This result supports the above interpretation that the precipitate formed just after neutralization was a cross-linked multipolyrotaxane. The obtained water-soluble tube was further fractionated, with use of a Sephadex G-100 column, into three parts: high-molecular-weight MT-A, low-molecular-weight MT-B, and a small amount of contamination. The weight percentages of MT-A and MT-B to the unfractionated sample were 33% and 53%, respectively. Although the molecular tubes were obtained in relatively good yields, complete suppression of the cross-linking between polyrotaxanes was impossible, even after several optimizations of the cross-linking conditions. Figure 2 shows the SEC charts of the starting polyrotaxane, MT-A, and MT-B. The M_w values of the polyrotaxane, MT-A, and MT-B were respectively determined to be 9400, 50 500, and 14 600. The M_w/M_n values of the tubes ($M_w/M_n = 3.43$ and 2.66 for MT-A and MT-B, respectively) were higher than that of the polyrotaxane ($M_w/M_n = 1.12$).

Figure 3a shows the ^{1}H NMR spectra of the polyrotaxane, MT-A, and MT-B in the range of $\delta = 4.0-6.0$ ppm. While sharp peaks at 4.80 and 4.48 ppm that originated from the C(1)H of α-CD and the O(6)H of α-CD were observed in all the profiles, the profiles of MT-A and MT-B showed additional peaks that are absent in that of the polyrotaxane; these peaks originated from the hydrogen atoms on the cross-linking bridge between the α-CDs: a sharp peak at 4.90 ppm and a broad peak at 4.98 ppm are from C(1)H of α-CD with the bridges, and a sharp peak at 4.68 ppm and a weak shoulder at 4.56 ppm are from the OH group of the cross-linking bridge. ^{13}C NMR spectra gave further information on the structure of the cross-linking bridge. In addition to the peaks originated from α-CD without the cross-linking bridge, the spectra of MT-A and MT-B show a peak at 98 ppm from the C(1) of α-CD with glyceryl bridges and peaks at 69−70 ppm from the carbon atoms of the glyceryl bridge.[47] These NMR results indicate that MT-A and MT-B contain glyceryl bridges between the α-CDs formed by cross-linking.

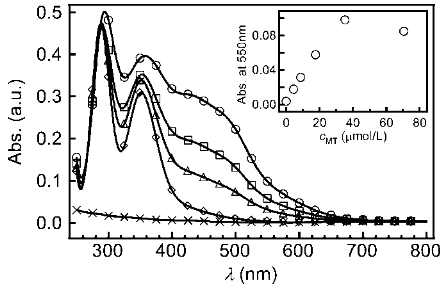

Figure 4. UV−vis spectra of iodine/MT-B solutions. The three lines from the top show the spectra for different concentrations of MT-B: 35.2 μmol/L (circles), 17.6 μmol/L (squares), and 8.8 μmol/L (triangles). The concentration of iodine was 300 μmol/L. The UV−vis spectra of iodine solution (diamonds) and MT-B solution (cross symbols) are also shown for comparison. Inset: plot of absorbance at 550 nm as a function of MT-B concentration.

While all the ^{1}H NMR peaks of MT-A and MT-B were slightly broader than that of the polyrotaxane due to the cross-linking of the α-CDs, their profiles show considerable improvements as compared with those of the sample synthesized in aqueous NaOH, showing large broad peaks at 5.0 and 4.6 ppm originating from the cross-linking bridge[20] This indicates that the cross-linking in DMSO yields a structure with higher regularity than that in aqueous NaOH. One of the reasons for this difference is presumably the formation of cross-linkages with a relatively constant length due to the less side reactions, i.e., the hydrolysis of epichlorohydrin and the subsequent bridge extension inevitable in aqueous environments.[47]

A more detailed interpretation of the NMR profiles of MT-B was carried out by H−H COSY and C−H COSY measurements, whose results are supplied in the Supporting Information. Some of the observed peaks were successfully assigned using the two-dimensional NMR analysis, although their interpretation was slightly different from that in the Experimental Section due to the difference in measurement temperature (room temperature and 70 °C for 1-D and 2-D measurements, respectively). The two-dimensional NMR analysis of the MT-B provided intriguing information on the structure of the cross-linking bridge; namely, a peak at 5.29 ppm, which was considered as un-cross-linked O(2)H and O(3)H of α-CD in the previous study,[20] was correlated only with the C(2)H of α-CD and not with the C(3)H (see the Supporting Information). This result indicates that the peak at 5.29 ppm only consists of the remaining O(2)H and suggests the preferred cross-linking of the O(3)H, at least under our reaction conditions. Although the COSY measurements of the starting polyrotaxane should be examined, ^{13}C NMR measurements in DMSO-d_6 at a high concentration (ca. 10 wt %) seems to be impossible due to severe gelation of the sample, as reported in the previous study.[48]

Although the results stated above clearly indicate the successful synthesis of the water-soluble molecular tubes, it is important to confirm the cylindrical, tubular cavity of the obtained tubes by another method. To topologically characterize the cavity of a molecular tube, Harada et al. have reported a facile technique, which was based on the experimental fact that a mixed solution of iodine and molecular tube exhibits an increase in the absorbance at wavelengths longer than 500 nm, while a mixed solution of iodine and α-CD or randomly cross-linked α-CD polymer does not exhibit such a phenomenon.[20] This technique enables us to readily distinguish the molecular

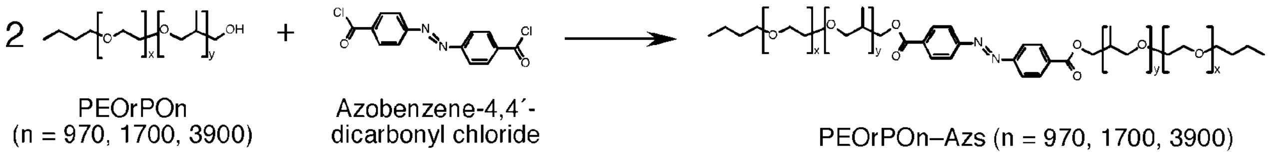

Figure 5. Scheme for synthesis of PEOrPO-Azs. For details of numbers *x* and *y*, see Table 1.

tube from a randomly cross-linked α-CD polymer. Figure 4 shows the UV−vis absorption spectra of iodine/MT-B solutions measured at a fixed iodine concentration (300 μmol/L). For comparison, the UV−vis absorption spectra of a MT-B solution and iodine solution are also shown separately. The MT-B solution showed very low absorbance without peaks in the range of 250−700 nm. The iodine solution obviously exhibited two absorption peaks at 288 and 352 nm, while the absorbance above 400 nm was low (less than 0.03 at 450 nm) and monotonically decreased with increasing wavelengths. On the other hand, the spectrum of the iodine/MT-B solution showed a significantly large broad absorbance at 400−700 nm in addition to the two peaks similar to those of the iodine solution. As shown in the inset of Figure 4, the absorbance at 550 nm intensively increased with the MT-B concentrations and showed a maximum at the concentration of 35 μmol/L. This result is qualitatively consistent with that of the previous reports[20,24] and indicates that MT-B synthesized in DMSO has a cylindrical cavity.

Inclusion Complexation Behavior of a Molecular Tube with PEOrPO. When host and guest molecules are isolated from each other, an achiral dye moiety in a guest molecule does not exhibit any dichroism because the dye is optically inactive. On the other hand, when the guest molecule forms inclusion complexes with the chiral host molecule, a dichroism is induced at the absorbance wavelength of the dye moiety because the dye is located in the chiral environment and becomes optically active.[49] Therefore, an induced circular dichroism measurement is a powerful technique to detect the inclusion complexation of a chiral host molecule (i.e., an α-CD or molecular tube in our study) with a guest dye molecule.[25,26,50–54]

For induced circular dichroism measurements, we should design a PEOrPO containing an appropriate achiral dye moiety at the center of the polymer chain (Figure 5). Choice of the azobenzene moiety as the achiral dye is indispensable due to following reasons; its favorable complexation with α-CD, which is a rare instance for visible dyes as well as viologen, is well investigated in the previous studies.[50–54] Induction of circular dichroism by complexation of a molecular tube with an azobenzene polymer is already reported[25,26] as well as its enthalpy change values,[26] which are considerably useful for our theoretical estimation of the present inclusion phenomenon in the Results and Discussion section. Introduction of azobenezene moiety at the center of PEOrPO chain was facile using commercially available reagents (Figure 5), which was resulted in high yield of the desired guest molecules (see Experimental Section). To investigate the dependence of the inclusion complexation behavior on the molecular weight of the guests, three guest polymers—PEOrPO$_{970}$-Az, PEOrPO$_{1700}$-Az, and PEOrPO$_{3900}$-Az—were synthesized (see Figure 5). The circular dichroism spectra and the corresponding UV−vis spectra of the PEOrPO$_{970}$-Az solution and PEOrPO$_{970}$-Az/α-CD mixture solution are shown in parts a and b of Figure 6, respectively. The UV−vis absorption spectra of PEOrPO970-Az and PEOrPO$_{970}$-Az/α-CD exhibited a single peak at 335 nm, which originated from the azobenzene moiety of the polymer. The circular dichroism spectrum of the PEOrPO$_{970}$-Az showed no peak due to the absence of a chiral environment; however, the spectrum of PEOrPO$_{970}$-Az/α-CD unambiguously exhibited a positive peak also at 335 nm. This result clearly indicates that the azobenzene moiety at the center of the PEOrPO chain became optically active because it was included in a chiral environment, i.e., the cavity of α-CD. A similar induced circular dichroism was observed for the inclusion complexes between α-CD and an azobenzene group.[50–53] Considering that the length of α-CD (0.79 nm[8]) is significantly shorter than the contour length of the PEOrPO chain (14 nm[55,56]) and the azobenzene moiety is located at the center of the PEOrPO chain, the above result strongly indicates that α-CD penetrated the PO units as well as the EO units, leading to inclusion of the azobenzene moiety. This interpretation appears to contradict the previous viewpoint that α-CD cannot penetrate PO units due to its smaller inner diameter than the cross-sectional area of the PO unit.[34–36] However, Li et al. have recently found the inclusion complexation of α-CDs with a PEO−PPO random copolymer[57] or a PPO−PEO−PPO triblock copolymer having 8−25 PO units.[58] To explain the findings, they have proposed that α-CDs can penetrate PO moieties and form inclusion complexes with EO moieties, resulting in the formation of a pseudopolyrotaxane. In other words, all the α-CDs that included the ends of the polymer did not stayed on the PPO moiety stably but migrated to the EO units, resulting in the formation of a stable complex with the PEO moiety.

Li's study[57,58] describes a striking observation of the formation of the crystalline precipitation, which is absent in our results. Despite this difference, our induced circular dichroism results

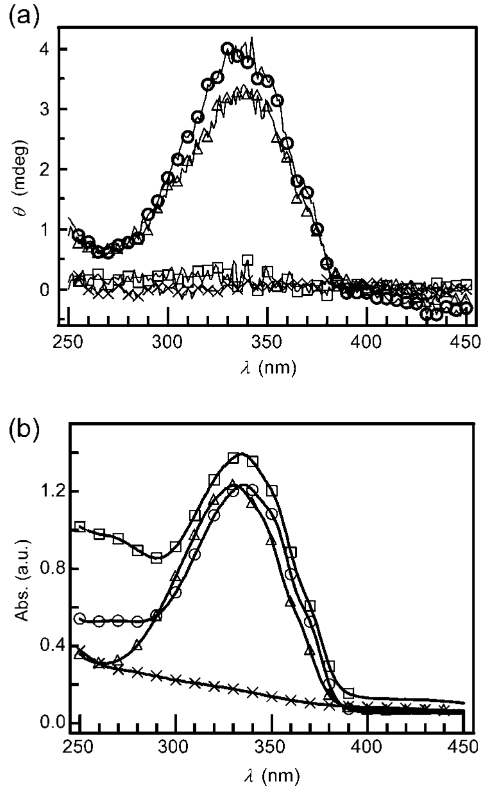

Figure 6. (a) Induced circular dichroism and (b) UV−vis absorption spectra of PEOrPO$_{970}$-Az (squares), MT-B (cross symbols), PEOrPO$_{970}$-Az/α-CD (circles), and PEOrPO$_{970}$-Az/MT-B (triangles) at 25 °C. The concentrations of PEOrPO$_{970}$-Az, α-CD, and MT-B were 71, 2.0, and 57 μmol/L, respectively.

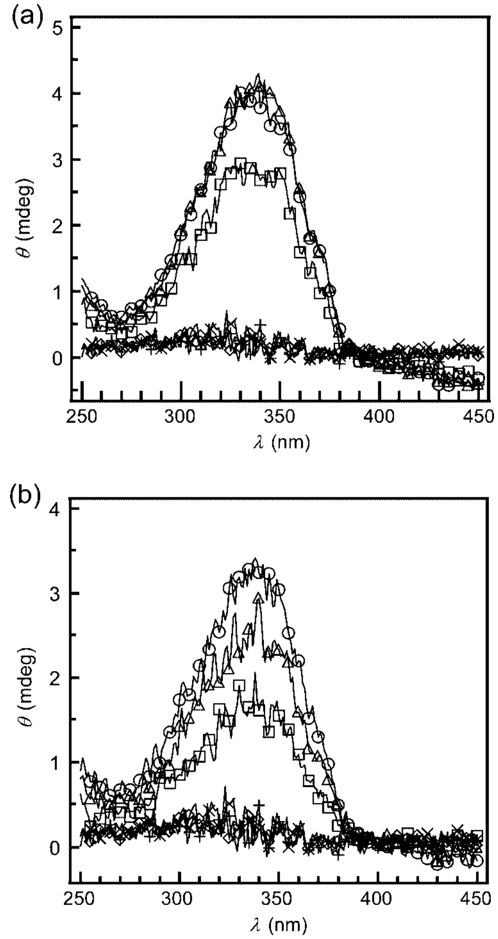

Figure 7. Induced circular dichroism spectra of (a) PEOrPO-Az/α-CD and (b) PEOrPO-Az/MT-B using three PEOrPO-Azs recorded at 25 °C. Symbols: circles, $PEOrPO_{970}$-Az (71 μmol/L); triangles, $PEOrPO_{1700}$-Az (73 μmol/L); and squares, $PEOrPO_{3900}$-Az (76 μmol/L). The concentrations of α-CD and MT-B were 2.0 mmol/L and 57 μmol/L, respectively. Induced circular dichroism spectra of $PEOrPO_{970}$-Az (plus symbols), $PEOrPO_{1700}$-Az (cross symbols), and $PEOrPO_{3900}$-Az (diamonds) are also shown for comparison.

clearly indicated the penetration of α-CDs through the PEOrPO chains. Our experimental conditions, where the α-CD concentration is considerably lower than that in Li's study, appeared to prevent the precipitation of the inclusion complex, at least within the employed measurement period (typically for a day). The inclusion complexation of the α-CDs without precipitation is also shown in our preliminary experiments, where the transparent aqueous mixture of α-CDs and PEO with a central azobenzene moiety showed induced circular dichroism at a low α-CD concentration. The precipitation of the inclusion complexes is known to be largely dominated by intermolecular interactions including hydrogen bonding between the α-CDs.[39,59–65]

Similar to the results of the $PEOrPO_{970}$-Az/α-CD, the circular dichroism spectra of $PEOrPO_{970}$-Az/MT-B exhibited a single peak at 335 nm as well as UV−vis absorption spectrum (see Figure 6). This result clearly indicates that the azobenzene moiety of the PEOrPO chain was included by MT-B. A similar induced circular dichroism was observed for a mixed solution of a molecular tube and PEO or its derivatives with an azobenzene group.[25,26] The contour length of MT-B is estimated to be 16 nm (based on the length of the α-CD (0.79 nm), the length of the cross-linking bridge (0.5 nm),[24] and the M_w value of MT-B) and is comparable to that of $PEOrPO_{970}$-Az. Therefore, we should consider an intriguing possibility that the MT-B could form stable inclusion complexes with the PEOrPO, despite no previous instance of stable complexation between α-CDs and PO units (see the above results of $PEOrPO_{970}$-Az/α-CD).

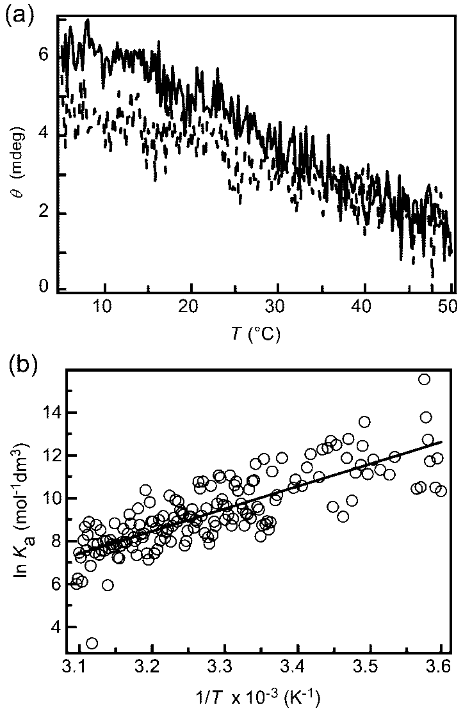

Figure 8. (a) Temperature dependence of ellipticities of $PEOrPO_{970}$-Az/α-CD (solid line) and $PEOrPO_{970}$-Az/MT-B (dashed line). (b) Natural logarithm of K_a as a function of inverse temperature (circles). The solid line represents the fitting line of eq 4.

The molecular weight dependence of the inclusion complexation of PEOrPO-Az/α-CD and PEOrPO-Az/MT-B systems was investigated, and the results are summarized in Figure 7a,b. Irrespective of the length of the PEOrPO chains, the circular dichroism spectra of PEOrPO-Az/α-CD and PEOrPO-Az/MT-B showed identical maximum peaks at 335 nm, whereas the peak intensities were slightly dependent on the molecular weight of the PEOrPO. $PEOrPO_{970}$-Az/α-CD and $PEOrPO_{1700}$-Az/α-CD showed a comparable level of peak intensity, which was ca. 1.3 times higher than that of $PEOrPO_{3900}$-Az/α-CD. The peak intensity of the PEOrPO-Az/MT-B profile monotonically decreased with an increase in the molecular weight of the PEOrPO. Although the above phenomena is not still interpreted in detail, it may be related to the stoichiometry of α-CD or MT-B with PEOrPO-Azs. Since the inclusion complexation between α-CDs and various polymers is stoichiometric,[15,17] the increase in polymer repeating units should require larger amount of α-CDs. When the molar concentrations of α-CD, MT-B, and PEOrPO-Az were fixed, the use of PEOrPO-Az with a higher molecular weight may cause a relative shortage of α-CDs or MT-B. However, a more detailed investigation is necessary to reveal the nature of the molecular weight dependence.

Figure 8a shows the temperature dependence of the ellipticities of $PEOrPO_{970}$-Az/α-CD and $PEOrPO_{970}$-Az/MT-B recorded in the range of 5−50 °C. The induced circular dichroism could not be measured above 50 °C because the solution became turbid. Since the peak wavelength for both the samples was almost identical (335 nm) over the examined temperature ranges, the ellipticity was recorded at a fixed wavelength of 335 nm. The ellipticities of the $PEOrPO_{970}$-Az/α-CD and the $PEOrPO_{970}$-Az/MT-B were monotonically decreased with increasing temperatures. The amount of the $PEOrPO_{970}$-Az/MT-B inclusion complex formed at low temperatures was larger than that formed at high temperatures; this was probably due to the dissociation of PEOrPO$_{970}$-Az from MT-B with an increase in temperature and the formation of intramolecular and/or intermolecular micellar aggregates, which is consistent with the turbidity at high temperatures. Although the theory of inclusion−dissociation between a molecular tube and a linear polymer suggests a transition-like behavior,[21] the polydispersity of the micellar aggregates and/or relatively low molecular weight of PEOrPO$_{970}$-Az may cause a gradual decrease in the ellipticity. The decrease in the induced circular dichroism of PEOrPO$_{970}$-Az/α-CD with increasing temperatures is probably due to the molecular interaction between the α-CD and azobenzene, as suggested in the previous study.[26]

Let us now theoretically consider the temperature dependence of the ellipticity of the PEOrPO$_{970}$-Az/MT-B solution. Since the azobenzene moiety is located at the center of the PEOrPO chain and the contour length of MT-B is comparable to that of PEOrPO$_{970}$-Az, we can assume 1:1 inclusion complexation of MT-B with PEOrPO$_{970}$-Az.

The reversible inclusion−dissociation reaction formula for the inclusion complexation with MT-B and PEOrPO$_{970}$-Az is given by

$$\mathrm{MT} + \mathrm{polymer} \rightleftarrows \mathrm{complex}$$

where MT, polymer, and complex represent MT-B, PEOrPO$_{970}$-Az, and the 1:1 inclusion complex of MT-B and PEOrPO$_{970}$-Az, respectively. If the total concentrations of MT-B and PEOrPO$_{970}$-Az are C_t and C_p, respectively, and the concentration of the inclusion complexes is C_c, the association constant K_a is given by

$$K_a = \frac{C_c}{(C_t - C_c)(C_p - C_c)} \tag{1}$$

To simplify the following analysis, we shall assume a linear dependence of the ellipticity on C_c. C_c is given by

$$C_c = \frac{\theta(T)}{\theta_{\max}} C_p \tag{2}$$

where $\theta(T)$ is the ellipticity expressed as a function of temperature and $\theta_{\max}$ is the maximum value of $\theta(T)$. The natural logarithm of K_a can be represented by the following equation:

$$\ln K_a = -\ln\left(C_t - \frac{\theta(T)}{\theta_{\max}} C_p\right)\left(\frac{\theta_{\max}}{\theta(T)} - 1\right) \tag{3}$$

Figure 8b shows the plot of the natural logarithm of K_a as a function of the inverse temperature. Despite slight variations in the data points, the plot of the natural logarithm of K_a is almost linear against the inverse temperature. The activation enthalpy ΔH can be derived from the following equation:[26]

$$\ln K_a = -\frac{\Delta H}{k_B T} + \ln \chi \tag{4}$$

Large negative ΔH of −87 kJ mol^{-1} is determined from the linear slope of Figure 8b. We now consider that ΔH can be represented by the summation of three main enthalpy changes: (1) enthalpy change ΔH_{azo} for inclusion complexation between MT-B and the azobenzene moiety, (2) the enthalpy change ΔH_{EO} for inclusion complexation between MT-B and the EO units, and (3) the enthalpy change ΔH_{PO} for inclusion complexation between MT-B and the PO units. As shown in the previous studies,[26,33] ΔH_{azo} has been estimated to be −36 kJ mol^{-1}, and the value of ΔH_{EO} is so small that we can neglect its contribution here. As a result, ΔH_{PO} is calculated to be −51 kJ mol^{-1}; therefore, the value of ΔH_{PO} per PO unit was calculated to be −3.6 kJ mol^{-1} based on the number of PO units of PEOrPO$_{970}$-Az (shown in Table 1). The value of ΔH_{PO} per PO unit is similar to the enthalpy change for the inclusion complexation of a molecular tube with a linear alkyl chain[22,26] and much larger than that of EO unit, which may be related to the hydrophobicity of PO unit in spite of its bulky structure.

Conclusion

A molecular tube was synthesized with powdered NaOH dispersed in DMSO. Several characterization techniques such as ^{1}H and ^{13}C NMR, SEC measurements, and UV−vis absorption titration with iodine revealed that the use of DMSO provided a greater efficiency of cross-linking between the α-CDs in a polyrotaxane than that in an aqueous NaOH. As a result, molecular tubes with higher regularity were obtained.

The circular dichroism spectrum of PEOrPO-Az/α-CD showed that α-CDs can penetrate the PO units as well as the EO units, leading to inclusion complexation with the azobenzene moiety. The circular dichroism spectrum of PEOrPO-Az/MT-B suggested a surprising possibility that MT-B can form stable inclusion complexes with PO units. The ellipticity of PEOrPO$_{970}$-Az/MT-B was monotonically decreased with increasing temperatures, indicating a greater tendency of inclusion complexation at low temperatures than that at high temperatures. A detailed analysis of the temperature dependence of PEOrPO-Az/MT-B system revealed the change in the enthalpy by inclusion complexation to be −3.6 kJ mol^{-1} per PO unit, which is similar to the enthalpy change for complexation of molecular tube with a linear alkyl chain.

Acknowledgment. We gratefully acknowledge Dr. Syunsuke Ohhashi (NOF Corporation, Japan) for the donation of PEG with terminal amino groups (Sunbright DE-PA20H). S.S. thanks Dr. B.-K. Choi (Advanced Research Laboratory, Hitachi, Ltd., Japan), Mr. Hideki Ichihara, and Mr. Takahiro Iida (Graduate School of Frontier Sciences, The University of Tokyo) for their valuable advice on the synthesis of molecular tubes. We thank Advanced Softmaterials Inc. for providing experimental support for the SEC characterization of the polyrotaxane and molecular tubes. The authors are grateful to Prof. Fumitaka Horii (Kyoto University) for his kind cooperation for COSY measurements and his valuable advice.

Supporting Information Available: H−H and H−C COSY spectra of MT-B. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA702040C