© 1999 The Chemical Society of Japan

Cyclodextrin Complexes of Bisepoxide and of α,ω-Diamine in Several Molar Ratios. Preparation and Characterization in the Solid State

Isao Yamaguchi, Hidetake Ishii, Kohtaro Osakada,* Takakazu Yamamoto,* and Shin-ichi Fukuzawa†

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

†Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551

(Received January 11, 1999)

Addition of 1,4-butanediol diglycidyl ether (glycidyl = 2,3-epoxypropyl) to aqueous solutions of α-cyclodextrin (CD) leads to separation of the 2 : 1 complex from the solution. The ^{13}C CP/MAS NMR spectrum of the complex indicates the presence of diastereomeric oxirane groups formed via the complexation. 1,4-Butanediol diglycidyl ether forms the 1 : 1 or 2 : 2 complex with γ-CD similarly from the aqueous reactions of the two compounds. 2,2-Dimethyltrimethylene glycol diglycidyl ether also forms water-insoluble host–guest complexes with α-CD (2 : 1) and with γ-CD (1 : 1 or 2 : 2). Poly(propylene glycol diglycidyl ether) with an M_n of 640 reacts with β-CD to give the 1 : 4 complex. Poly(tetrahydrofuran) terminated with NH_2 groups at both ends also forms the 1 : 4 complexes both with α-CD and with γ-CD.

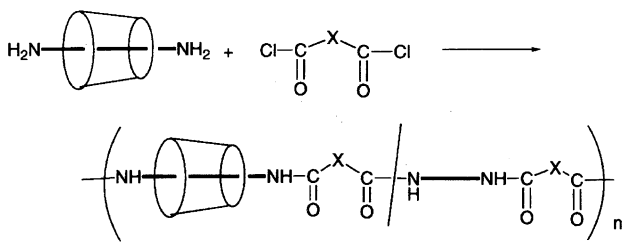
Cyclodextrins include aromatic molecules in the cavity to form various host–guest complexes. They have long been used as a host of the aromatic ring and as catalysts of organic reactions of aromatic substrates such as hydrolysis, substitution, reduction, and oxidation.[1—5] More recent interest has focused on the cyclodextrin-based supramolecules in which linear molecules and polymers penetrate the cavities of cyclodextrins.[6—12] The rotaxanes, pseudo rotaxanes, polyrotaxanes, and pseudo polyrotaxanes of cyclodextrins were applied to synthesis of novel nanotubes[13—16] and light-driven molecular shuttles,[17,18] as well as biodegradable polymer materials.[19—22]

Since the aliphatic linear molecule and cavity of cyclodextrin has a weaker attractive interaction than those observed in the host–guest complexes of aromatic compounds,[23] pseudo rotaxanes and pseudo polyrotaxanes containing the non-aromatic rod-like component often undergo degradation of the superstructure in solution. Several efforts have been made to freeze or stabilize the pseudo rotaxane geometry in solution. Introduction of negatively or positively charged terminal groups such as COO^- and pyH^+ at both ends of the rod-like molecule prevents smooth elimination of the macrocycle from the pseudo rotaxanes.[24—27] Previous synthetic studies on the cyclodextrin-based pseudo polyrotaxanes of aliphatic molecules have revealed a general tendency that a longer polymethylene or polyether chain forms a more stable supramolecule with the cyclodextrin.[24,28]

In 1976, Ogata, Sanui, et al. have reported isolation of the 1 : 1 complex of β-cyclodextrin with α,ω-diamine from an aqueous reaction of these compounds; the complex was allowed to react with diacyl chlorides to afford polyamide-cyclodextrin pseudo polyrotaxanes, as shown in Scheme 1.[29] Pseudo rotaxanes composed of macrocyclic crown ether and the rod-like molecules equipped with ammonium salt form a stable supramolecular system both in the solid state and in solution and undergo effective condensation of the terminal groups to form the corresponding polyrotaxanes.[30,31] The cyclodextrin complexes of bisepoxides and of α,ω-diamines have potential utility as the building blocks of various polyrotaxanes or pseudo polyrotaxanes but have not been studied in detail so far. Here we report synthesis of pseudo rotaxanes of oligoethers with terminal oxirane or amino groups with cyclodextrins via the aqueous reactions and their characterization in the solid state by means of X-ray diffraction and ^{13}C CP/MAS NMR spectroscopy.

Results and Discussion

Bifunctional compounds used in this study and their abbreviations are summarized in Chart 1. Stirring of aqueous solu-



Scheme 1. Preparation of Polyamide-CD Rotaxane from pseudo rotaxane.

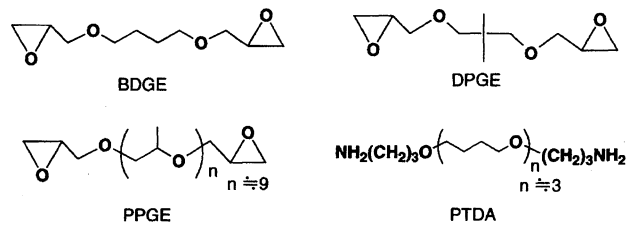


Chart 1. Compounds used as the rod part in this study.

tions of mixtures of 1,4-butanediol diglycidyl ether (BDGE; glycidyl = 2,3-epoxypropyl) with α-cyclodextrin (α-CD) and with γ-cyclodextrin (γ-CD) at 20 °C causes separation of the inclusion complexes **1a** and **1b**, respectively, from the solution. Structures of **1a** and **1b** in the solid state based on the following experimental results are proposed in Chart 2. Figure 1 shows the change of yield of **1a** as a function of the reaction time. The amount of the product increases during the initial 60 min and becomes constant after that, indicating rapid separation of **1a** from the solution. Results of elemental analyses of **1a** indicate the presence of BDGE and α-CD in a 1 : 2 molar ratio which does not vary depending on the initial molar ratio of these starting compounds. The ratio of BDGE and γ-CD in **1b** is determined as 1 : 1. Both 1 : 1 and 2 : 2 formula are possible for the complex since γ-CD has a

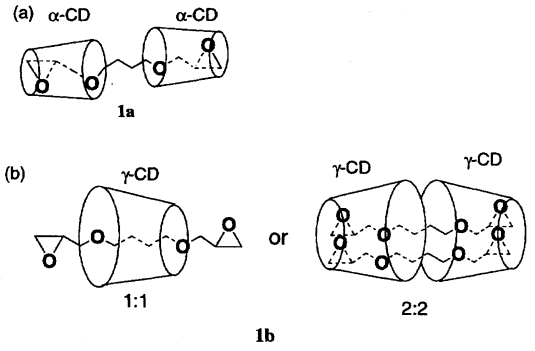


Chart 2. Structures of the inclusion complexes.

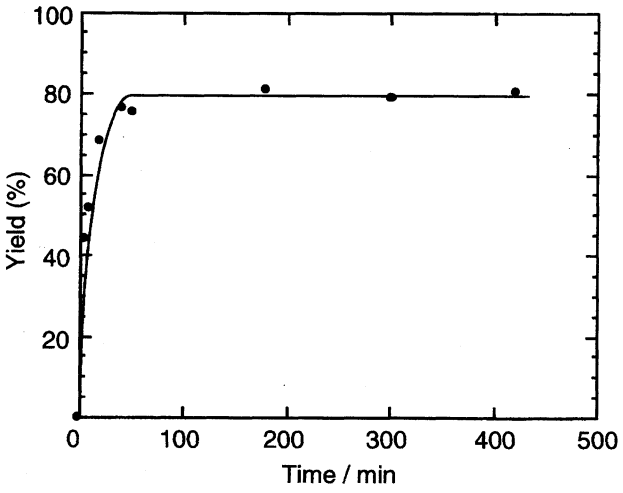


Fig. 1. Yields of **1a** as a function of the reaction time. Different final yield of the product from that in Table 1 is probably due to difference in the experimental scale and amount of water used.

cavity large enough to include two polyether chains.[32]

In order to confirm formation of the inclusion complexes, NMR measurements in the solid state and X-ray diffraction analyses were conducted. Figure 2 compares the ^{13}C CP/MAS NMR spectra of α-CD, **1a**, and **1b**. Free α-CD shows a multitude of signals for C^1 and C^4 due to the less symmetrical conformation with a strain derived from its small cavity size.[33] On the other hand, α-CD in **1a** seems to adopt a symmetrical cyclic conformation due to release of the strain by the formation of the inclusion compound, and gives rise to a simple peak pattern. Similar spectra were reported for the α-CD rotaxane of poly(ethylene glycol).[34] CH_2 and CH carbons of the oxirane rings of **1a** give the ^{13}C NMR signals at δ = 51.4 and 50.9, and 46.0 and 43.2, respectively (Fig. 2(b)), with almost equal peak intensity of each pair. The double number of signals of **1a** is attributed to coexistence of two diastereomeric oxirane groups arising from the presence of chiral centers both in BDGE and in α-CD. The oxirane carbon signals of **1b** are observed as a single resonance for each carbon because such special steric interaction between the oxirane unit and γ-CD has become

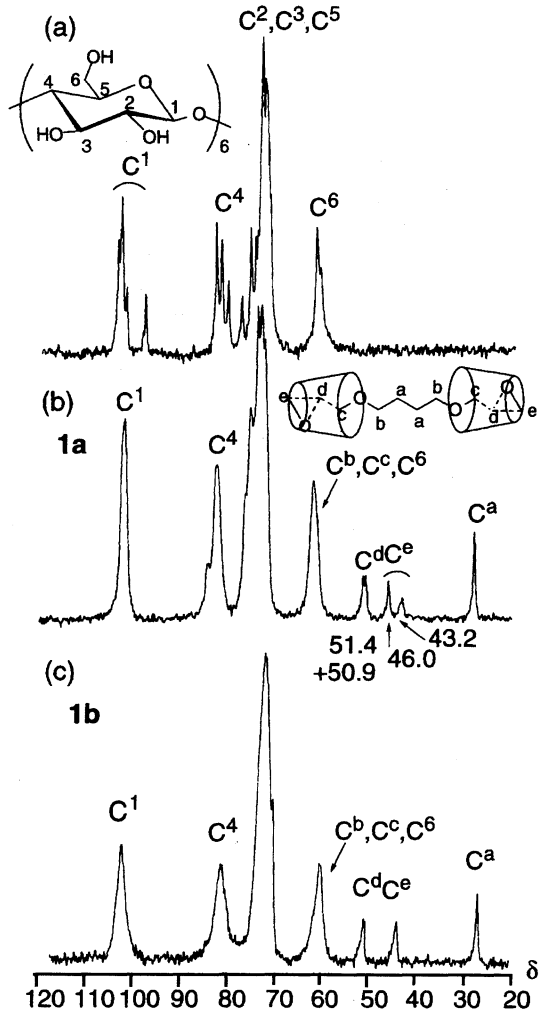


Fig. 2. ^{13}C CP/MAS NMR spectra (67.5 MHz) of α-CD (a), **1a** (b), and **1b** (c).

less significant.

The powder X-ray diffraction of **1a** gives a different pattern from free α-CD as depicted in Fig. 3 and suggests a channel-type array (Chart 3) of the CD molecules in the solid state[35,36] based on the similarity to those of reported α-CD polyrotaxanes of poly(ethylene glycol)[34] and aliphatic polyester.[37]Figure 4 compares thermogravimetric curves of **1a** and α-CD. The higher decomposition point of **1a** than that of α-CD indicates that the presence of BDGE molecule in the cavities hinders decomposition of α-CD. **1a** shows a minor degree of weight decrease below 140 °C, corresponding to elimination of the hydrated water.

The results of the above characterization of **1a** in the solid state strongly indicates formation of the 2 : 1 complexes of α-CD and BDGE. The ^{13}C CP/MAS NMR signals indicate the strong and rigid interaction of the two components and suggests the structure shown in Chart 2. Very recently, the 2 : 1 complex of cyclodextrin and a linear molecule has been determined unequivocally by single crystal X-ray diffraction.[38] Although the diffraction pattern of **1b** did not provide sufficient evidence to confirm the pseudo rotaxane structure of the 1 : 1 complex rather than the 2 : 2 complex, the composition of the complex was indifferent to the reaction conditions,

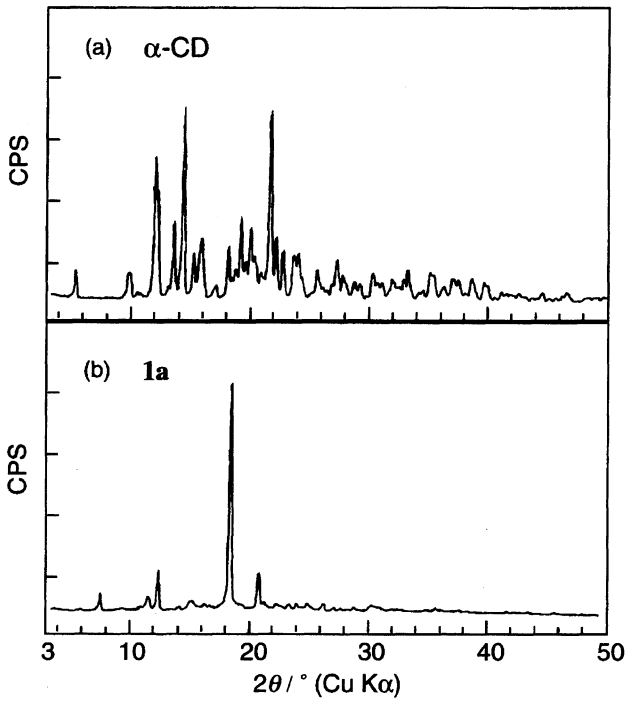


Fig. 3. Powder X-ray diffraction patterns of (a) α-CD and (b) **1a**.

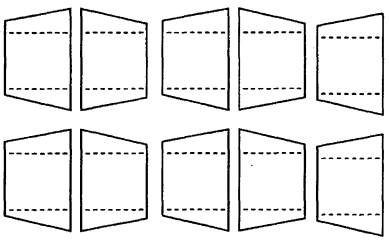


Chart 3. Channel type array of CDs.

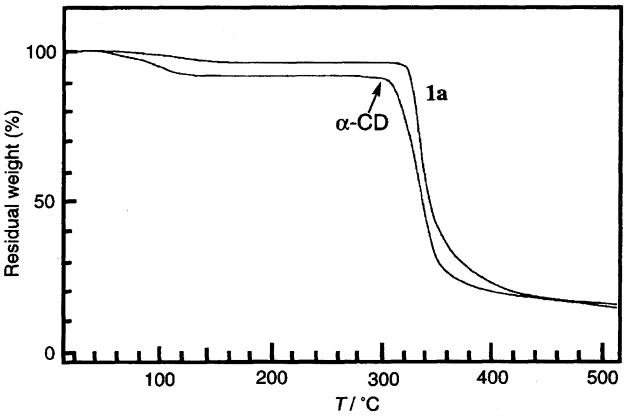


Fig. 4. Thermogravimetric curves of **1a** and α-CD. Heating was performed at 10 °C min^{-1} under nitrogen atmosphere.

which suggests either of the proposed pseudo rotaxane structures. α-CD has a suitable cavity size to include an oxirane ring, which gives a 1 : 2 inclusion complex with BDGE. On the other hand, the cavity size of γ-CD probably prevents formation of the stable 1 : 2 complex with BDGE.

The ^{1}H NMR spectra of **1a** and **1b** in DMSO-d_6 indicate the presence of the components in 1 : 2 and 1 : 1 molar ratios, respectively. The peak positions are similar to those of CDs and BDGE observed separately. This similarity is due to negligible influence of the complexation on the peak positions and/or degradation of the supramolecular system in the solution to a significant extent.

Table 1 summarizes results of the reactions of CDs with other guest molecules to form pseudo rotaxanes and pseudo polyrotaxanes. 2,2-Dimethyltrimethylene glycol diglycidyl ether (DPGE) also forms 1 : 2 and 1 : 1 (or 2 : 2) inclusion complexes with α-CD (**2a**) and with γ-CD (**2b**), respectively (Runs 3 and 4). Stirring of an aqueous solution of poly(propylene glycol diglycidyl ether) (PPGE) with an M_n of 640 and β-CD gives a pseudo polyrotaxane (**3**) as a white solid separated from the solution (Run 5). The ^{1}H NMR peak area ratio indicates the composition of **3** containing β-CD and the guest molecule in a 4 : 1 molar ratio. The polymer with

Table 1. Reactions of Bifunctional Guest Molecules with CDs[a)]

Run	Starting material		Product		
	Guest	CD		CD/guest [b)]	Yield (%)
1	BDGE	α-CD	**1a**	2.0	84
2	BDGE	γ-CD	**1b**	1.0	62
3	DPGE	α-CD	**2a**	2.0	90
4	DPGE	γ-CD	**2b**	1.0	66
5	PPGE	β-CD	**3**	4.0	53
6	PTDA	α-CD	**4a**	4.0	73
7	PTDA	γ-CD	**4b**	4.0	46

a) Reactions of guest molecules (1.0 mmol) and CDs (1.0 mmol (Runs 1, 3, 4), 0.50 mmol (Run 2), and 4.0 mmol (Runs 5—7)) were carried out in water (15 cm^3 (Runs 1—4, 6, 7), 50 cm^3 (Run 5)) at 20 °C. b) Determined by elemental analyses. Peak intensity of ^{1}H NMR spectrum in solution also supports the obtained CD/guest molar ratio although the supramolecular structure is partly degradated in the solution.

the M_n value equal to approximately four times the thickness of β-CD forms the pseudo polyrotaxane with a maximum number of β-CD molecules. Reaction of poly(tetrahydrofuran) terminated by 3-aminopropyl groups (PTDA, M_n = 350) with α-CD also gives a 1 : 4 pseudo polyrotaxane in 73% yield (Run 6). The polyether forms the 1 : 4 complex also with γ-CD. Harada et al. already prepared the complexes of CDs with poly(tetrahydrofuran) and observed a decrease in the yield of the polyrotaxane on increase of the molecular weight of the polymer.[39] The high yield of the product in Run 6 using the short chain guest compound seems to be consistent with the above observations.

In summary, the aqueous reactions of bifunctional compounds with CDs provide a convenient route for the preparation of pseudo rotaxanes with oxirane and amine terminal groups. The 1 : 1 to 1 : 4 complexes in the solid state were obtained by choosing guest molecules and size of the CD cavities. Chemical properties of the pseudo rotaxanes and pseudo polyrotaxanes containing reactive terminal groups in the rod part of the supramolecules are now under investigation.

Experimental

General Comments. Organic chemicals were purchased and used as received. IR spectra were recorded on a JASCO-IR 810 spectrophotometer. ^{1}H and ^{13}C CP/MAS NMR spectra were obtained on JEOL EX-400 and GX-270 spectrometers. X-Ray diffraction analyses were performed with Rigaku Geiger Flex RAD-1VB. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder. TG measurement was performed with a Shimadzu TG-50 under nitrogen atmosphere.

Preparation of Inclusion Complexes. Typical preparation procedure is as follows. BDGE (416 mg, 2.0 mmol) was added to an aqueous solution (15 cm^3) of α-CD (1.94 g, 2.0 mmol) at 20 °C. A colorless solid soon began to precipitate from the solution. The reaction mixture was stirred for 10 h at the temperature. The solid product was collected by filtration, washed with water, and dried in vacuo (**1a**, 670 mg, 84%).

Data of 1a: IR (KBr) 3258 (s), 2926 (s), 1632 (w), 1408 (m), 1360 (m), 1331 (m), 1153 (s), 1022 (s), 950 (m), 749 (m), 702 (m), 573 cm^{-1} (m); ^{1}H NMR (400 MHz in DMSO-d_6) δ = 5.49 (d, J = 6.8 Hz, 12H, OH of α-CD), 5.41 (d, J = 2.4 Hz, 12H, OH of α-CD), 4.78 (d, J = 3.4 Hz, 12H, CH of α-CD), 4.44 (t, J = 5.4 Hz, 12H, OH of α-CD), and 3.75 (td, J = 2.4 and 10.0 Hz, 12H, CH of α-CD), 3.62 and 3.34 (m, 8H, $CH_2OCH_2(CH_2)_2$), 3.58 (m, 60H, CH of α-CD), 3.07 (m, 2H, CH of oxirane ring), 2.70 and 2.51 (t, J = 4.9 Hz, 4H, CH_2 of oxirane ring), 1.53 (m, 4H, $(CH_2)_2$); ^{13}C CP/MAS NMR (67.5 MHz) δ = 104.3, 84.1, 82.4, 76.4, 75.2, 73.6, 72.8, and 72.1 (α-CD), 61.9 (α-CD and CH_2OCH_2 of the guest), 51.4 and 50.9 (CH of oxirane rings), 46.0 and 43.2 (CH_2 of oxirane ring), 27.8 ($(CH_2)_2$). Anal. Found: C, 44.11; H, 6.72%. Calcd for $C_{82}H_{138}O_{64}\cdot 5H_2O$: C, 44.00; H, 6.67%.

Data of 1b: IR (KBr) 3258 (s), 2928 (s), 1632 (w), 1408 (m), 1360 (m), 1331 (m), 1153 (s), 1022 (s), 940 (m), 858 (w), 750 (w), 702 (m), 573 cm^{-1} (m); ^{1}H NMR (400 MHz in DMSO-d_6) δ = 5.74 (d, J = 2.0 Hz, 8H, OH of γ-CD), 5.72 (d, J = 6.8 Hz, 8H, OH of γ-CD), 4.87 (d, J = 3.4 Hz, 8H, CH of γ-CD), 4.50 (d, J = 5.4 Hz, 8H, OH of γ-CD), 3.61 (m, 24H, CH_2 and CH of γ-CD), 3.51 (m, 8H, CH of γ-CD), 3.34 (m, 16H, CH of γ-CD), 3.32 (m, 8H, $CH_2OCH_2(CH_2)_2$), 3.07 (s, 2H, CH of oxirane ring), 2.70 and 2.51 (t, J = 4.9 Hz, 4H, CH_2 of oxirane ring), 1.53 (br, 4H, $(CH_2)_2$); ^{13}C CP/MAS NMR (67.5 MHz) δ = 104.4, 83.0, 76.5, 73.7, 73.4, and 71.5 (α-CD), 61.5 (α-CD and CH_2OCH_2 of the guest), 51.6 (CH of oxirane ring), 44.5 (CH_2 of oxirane ring), 26.9 ($(CH_2)_2$). Anal. Calcd for $C_{58}H_{98}O_{44}\cdot 6H_2O$: C, 42.86; H, 6.94%. Found: C, 42.95; H, 6.79%.

Data of 2a: IR (KBr) 3215 (s), 2928 (s), 1635 (m), 1408 (m), 1365 (m), 1301 (m), 1153 (s), 1022 (s), 940 (m), 857 (m), 750 (w), 702 (m), 533 cm^{-1} (m); ^{1}H NMR (400 MHz in DMSO-d_6) δ = 5.48 (d, J = 2.5 Hz, 12H, OH of α-CD), 5.42 (d, J = 6.8 Hz, 12H, OH of α-CD), 4.78 (d, J = 3.4 Hz, 12H, OH of α-CD), 4.45 (t, J = 5.4 Hz, 12H, CH of α-CD), 3.61 and 3.31 (m, 44H, CH_2OCH_2, CH of α-CD), 3.51 (m, 36H, CH of α-CD), 3.17 (m, 2H, CH of oxirane ring), 2.70 and 2.52 (m, 4H, CH_2 of oxirane ring), 0.83 (s, 6H, CH_3). Anal. Found: C, 44.34; H, 6.49%. Calcd for $C_{83}H_{140}O_{64}\cdot 5H_2O$: C, 44.27; H, 6.71%.

Data of 2b: IR (KBr) 3214 (s), 2926 (s), 1637 (m), 1413 (m), 1365 (m), 1301 (m), 1157 (s), 1022 (s), 940 (m), 858 (m), 756 (m), 702 (m), 533 cm^{-1} (m); ^{1}H NMR (400 MHz in DMSO-d_6) δ = 5.75 (d, J = 2.5 Hz, 8H, OH of γ-CD), 5.72 (d, J = 6.8 Hz, 8H, OH of γ-CD), 4.87 (d, J = 3.4 Hz, 8H, OH of γ-CD), 4.51 (t, J = 5.4 Hz, 8H, CH of γ-CD), 3.61 and 3.31 (m, 32H, CH_2OCH_2, CH of γ-CD), 3.51 (m, 24H, CH of γ-CD), 3.17 (m, 2H, CH of oxirane ring), 2.70 and 2.52 (m, 4H, CH_2 of oxirane ring), 0.83 (s, 6H, CH_3); ^{13}C CP/MAS NMR (67.5 MHz) δ = 104.4, 83.1, and 73.4 (γ-CD), 61.5 (α-CD and CH_2OCH_2 of the guest), 52.0 (CH of oxirane ring), 44.0 (CH_2 of oxirane ring), 32.5 ($(CH_2)_2C(CH_3)_2$), 23.0 (CH_3). Anal. Found: C, 43.75; H, 6.48%. Calcd for $C_{59}H_{100}O_{44}\cdot 5H_2O$: C, 44.19; H, 6.91%.

Data of 3: IR (KBr) 3256 (s), 2926 (s), 1636 (m), 1411 (m), 1369 (m), 1333 (m), 1156 (s), 1024 (s), 946 (m), 860 (w), 756 (m), 703 (m), 576 cm^{-1} (m); ^{1}H NMR (400 MHz in DMSO-d_6) δ = 5.71 (d, J = 6.8 Hz, 28H, OH of β-CD), 5.66 (d, J = 2.4 Hz, 28H, OH of β-CD), 4.82 (d, J = 3.4 Hz, 28H, OH of β-CD), 4.44 (t, J = 5.9 Hz, 28H, CH of β-CD), and 3.60 (m, 56H, CH of β-CD), 3.54 (m, 56H, CH of β-CD), 3.29—3.36 (m, 87H, CH_2 and CH of the guest and CH of β-CD), 3.03 (m, 2H, CH of oxirane ring), 2.70 and 2.53 (m, 4H, CH_2 of oxirane ring), 1.03 (d, J = 6.4 Hz, 27H, CH_3); ^{13}C CP/MAS NMR (67.5 MHz) δ = 104.4, 83.0, 76.5, 73.7, 73.4, and 71.5 (β-CD), 61.5 (β-CD and CH_2O of the guest), 52.5 ($CH_2CH(CH_3)$), 45.0 (CH of the guest), 20.0 (CH_3). Anal. Found: C, 43.45; H, 6.60%. Calcd for $C_{200}H_{344}O_{152}\cdot 20H_2O$: C, 43.35; H, 6.98%.

Data of 4a: IR (KBr) 3210 (s), 2926 (s), 1636 (m), 1413 (m), 1369 (m), 1241 (w), 1157 (s), 1078 (s), 1019 (s), 941 (m), 856 (w), 756 (m), 704 (m), 580 cm^{-1} (m); ^{1}H NMR (400 MHz in DMSO-d_6) δ = 5.46 (br, 48H, OH of α-CD), 4.78 (d, J = 2.9 Hz, 24H, CH of α-CD), 4.47 (br, 24H, OH of α-CD), 3.64 (t, J = 9.6 Hz, 48H, CH_2 of α-CD), 3.56—3.67 (m, 48H, CH of α-CD), 3.37—3.25 (m, 68H, CH of α-CD and CH_2OCH_2 and NCH_2 of the guest), 2.55 (t, J = 6.8 Hz, 4H, NH_2), 1.49 (m, 16H, $CH_2(CH_2)_2CH_2$ and $CH_2CH_2CH_2NH_2$). Anal. Found: C, 42.4; H, 6.6; N, 0.6%. Calcd for $C_{162}H_{280}N_2O_{124}\cdot 20H_2O$: C, 42.30; H, 7.01; N, 0.61%.

Data of 4b: IR (KBr) 3210 (s), 2928 (s), 1636 (m), 1412 (m), 1369 (m), 1241 (w), 1157 (s), 1078 (s), 1019 (s), 941 (m), 858 (w), 756 (w), 704 (m), 580 cm^{-1} (m); ^{1}H NMR (400 MHz in DMSO-d_6) δ = 5.73 (br, 96H, OH of γ-CD), 4.88 (br, 32H, OH of γ-CD), 4.47 (br, 32H, OH of γ-CD), 3.62—3.51 (m, 64H, CH of γ-CD), 3.39—3.29 (m, 116H, CH of γ-CD and CH_2OCH_2 and NCH_2 of the guest), 2.56 (t, J = 6.8 Hz, 4H, NH_2), 1.54 (m, 16H, $CH_2(CH_2)_2CH_2$ and $CH_2CH_2CH_2NH_2$). Anal. Found: C, 42.46; H, 6.54; N, 0.66%. Calcd for $C_{210}H_{360}N_2O_{164}\cdot 20H_2O$: C, 42.77; H,

6.84; N, 0.48%.

We are grateful to Dr. Yoshiyuki Nakamura for the ^{13}C CP/MAS NMR measurement and to Mr. Tohru Mori for X-ray diffraction analyses. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture and Sports.

References

1 J. Szejtli, "Cyclodextrin and Their Inclusion Complexes," Academiai Kiado, Budapest (1982).

2 "Comprehensive Supramolecular Chemistry," ed by J. Szejtli and T. Osa, Pergamon, Oxford (1996), Vol. 3.

3 "Cyclodextrin," ed by F. Toda and A. Ueno, Sangyo Tosyo, Tokyo (1995).

4 K. Takahashi, *Chem. Rev.*, **98**, 2013 (1998).

5 R. Breslow, *Acc. Chem. Res.*, **13**, 170 (1980); **28**, 146 (1995).

6 J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, **31**, 846 (1992).

7 R. Isnin and A. E. Kaifer, *Pure Appl. Chem.*, **65**, 495 (1993).

8 G. Wenz, *Angew. Chem., Int. Ed. Engl.*, **33**, 803 (1994).

9 A. Harada, *Coord. Chem. Rev.*, **148**, 115 (1996).

10 A. Harada, *Adv. Polym. Sci.*, **133**, 141 (1997).

11 N. Nakashima, *Kobunshi*, **47**, 546 (1998).

12 S. A. Nepogodiev and J. F. Stoddard, *Chem. Rev.*, **98**, 1959 (1998).

13 A. Harada, J. Li, and M. Kamachi, *Nature*, **356**, 325 (1992).

14 A. Harada, J. Li, T, Nakamitsu, and M. Kamachi, *J. Org. Chem.*, **58**, 7524 (1993).

15 A. Harada, J. Li, and M. Kamachi, *J. Am. Chem. Soc.*, **116**, 3192 (1994).

16 A. Harada, J. Li, and M. Kamachi, *Nature*, **364**, 516 (1993).

17 N. Nakashima and Y. Narikiyo, *Chem. Lett.*, **1995**, 653.

18 H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake, and N. Nakashima, *J. Am. Chem. Soc.*, **119**, 7605 (1997).

19 T. Ooya and N. Yui, *J. Biomater. Sci., Polym. Ed.*, **8**, 437 (1997).

20 N. Yui, T. Ooya, and T. Kumeno, *Bioconjugate Chem.*, **9**, 118 (1998).

21 T. Ooya, T. Kumeno, and N. Yui, *J. Biomater. Sci., Polym. Ed.*, **9**, 313 (1998).

22 J. Watanabe, T. Ooya, and N. Yui, *Chem. Lett.*, **1998**, 1031.

23 M. V. Rekharsky and Y. Inoue, *Chem. Rev.*, **98**, 1875 (1998).

24 M. Watanabe, H. Nakamura, and T. Matsuo, *Bull. Chem. Soc. Jpn.*, **65**, 164 (1992).

25 A. Toki, H. Yoneyama, and T. Matsuo, *Bull. Chem. Soc. Jpn.*, **66**, 3382 (1993)

26 A. Mirzoian and A. E. Kaifer, *Chem. Eur. J.*, **3**, 1052 (1997).

27 M. Asakawa, P. R. Ashton, V. Balzani, A. Credi, C. Hamers, G. Mattersteig, M. Montali, A. N. Shipway, N. Spencer, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White, and D. Williams, *Angew. Chem., Int. Ed. Engl.*, **37**, 333 (1998).

28 A. Harada, J. Li, and M. Kamachi, *Macromolecules*, **27**, 4538 (1994).

29 N. Ogata, K. Sanui, and J. Wada, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 459 (1976).

30 P. L. Anelli, P. R. Ashton, N. Spencer, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, **30**, 1036 (1991).

31 R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philp, H. G. Ricketts, and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, **32**, 1301 (1993).

32 A. Harada and M. Kamachi, *Nature*, **370**, 126 (1994).

33 P. C. Manor and W. Saenger, *J. Am. Chem. Soc.*, **96**, 3630 (1974).

34 A. Harada and M. Kamachi, *Macromolecules*, **23**, 2821 (1990).

35 W. Saenger, *Isr. J. Chem.*, **25**, 43 (1985).

36 K. Harata, *Chem. Rev.*, **98**, 1803 (1998).

37 A. Harada, Y. Nishiyama, Y. Kawaguchi, M. Okada, and M. Kamachi, *Macromolecules*, **30**, 7115 (1997).

38 S. Makedonopoulou, I. M. Mavridis, K. Yannakopoulou, and J. Papaioannou, *Chem. Commun.*, **1998**, 2133.

39 A. Harada, S. Suzuki, T. Nakamitsu, M. Okada, and M. Kamachi, *Kobunshi Ronbunshu*, **52**, 594 (1995).