Crystal Structure of the Complex of *β*-Cyclodextrin with Bithiophene and Their Oxidative Polymerization in Water

Yoshinori Takashima,[†] Yoshihumi Oizumi,[†] Kazuya Sakamoto,[†] Masahiko Miyauchi,[†] Shigehiro Kamitori,[‡] and Akira Harada*,[†]

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, and Department of Biotechnology and Life Science, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Received February 4, 2004
Revised Manuscript Received April 5, 2004

Conducting polymers have attracted much attention as materials for sensors because they have potential use as molecular wires for the foundation to put single-molecule electronics into practical use in the future.[1] We expected to draw the interesting results from covered *π*-conjugated polymer with organic compound insulation. We chose cyclodextrins (CDs) as an insulation material for the construction of supramolecular electronics device. CDs are a series of cyclic oligosaccharides consisting of 6−8 glucose units linked by α-1,4 linkages. They are called α-, *β*-, and *γ*-CD, respectively. The remarkable property of CDs is the formation of inclusion complexes with a variety of small molecules or ions of appropriate size. We have found that CDs form inclusion complexes with a variety of polymers.[2] We chose polythiophenes as a *π*-conjugated polymer. Polythiophenes are an important representative class of *π*-conjugated polymers that form some of the most environmentally and thermally stable materials.[3] Polythiophenes can be prepared by various chemical and electrochemical polymerization techniques. Recent growing environmental concern forces industry and research laboratories to use less and less environmentally hazardous chemicals. Therefore, it is important to prepare *π*-conjugated polymers in water.[4] In this paper, we describe the synthesis and structure of *β*-CD or 2,6-dimethyl-*β*-CD (DM-*β*-CD) inclusion complexes with bithiophene (2T) and their polymerization of the corresponding inclusion complexes in a selective way to give polyrotaxanes (Scheme 1).

When 2T was added onto a saturated aqueous solution of *β*-CD, the solution became turbid and crystalline complexes were formed. When 2T was added onto a dilute *β*-CD solution, crystalline complexes suitable for X-ray studies were obtained. DM-*β*-CD also gave crystalline complexes with 2T at 40 °C. Figure 1 shows the structure of the *β*-CD−2T inclusion complex.[5] *β*-CD was found to form a 2:3 inclusion complex with 2T, regardless of the molar ratio of the host to the guest charged. Two 2Ts were included in the cavity of *β*-CD, on the other hand, another 2T was located at the center of the dimer cavity on the secondary hydroxyl side of their corresponding *β*-CDs.

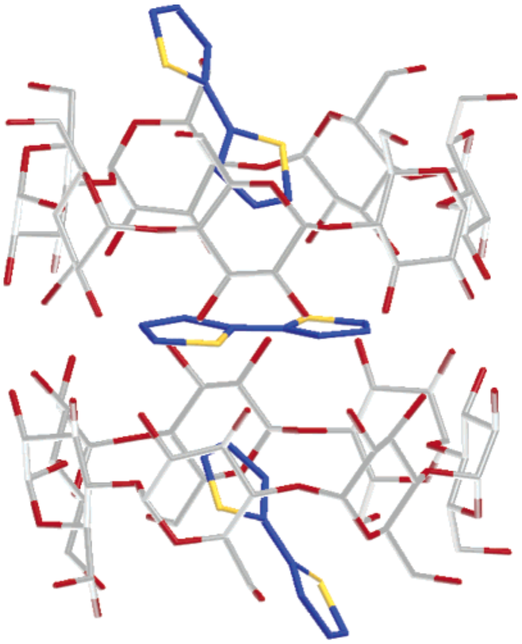


Figure 1. Crystal structure of *β*-CD−bithiophene inclusion complex. Carbon and oxygen of *β*-CD are shown in gray and red, respectively. Carbon and sulfur of bithiophene are shown in blue and yellow, respectively.

The dimer units of *β*-CD−2T are stacked to form a head-to-head channel-type structure. The *β*-CDs formed intermolecular hydrogen bonding between O2n secondary hydroxyl groups of the two *β*-CDs with an average intermolecular distance of 3.010 Å, between O3n secondary hydroxyl groups of the two *β*-CD with an average intermolecular distance of 2.828 Å, and between O6n primary hydroxyl groups of the two *β*-CDs with an intermolecular distance of 2.678 Å. These structures, which put a guest molecule with both CDs, were reported by our group[6] and the other group in metal−CDs complexes.[7] However, the crystal structure of *β*-CD−2T is relatively unusual that 2T was located horizontally between the secondary hydroxyl group sides of *β*-CD. Lagrost and co-workers reported that *β*-CD formed a 1:1 inclusion complex with 2T by ^{1}H NMR.[8] We suppose that one 2T, which is clipped by *β*-CD, was excluded by washing with diethyl ether because of unstable 2T. A single crystal of the DM-*β*-CD−2T inclusion complex suitable for X-ray study has not been obtained.

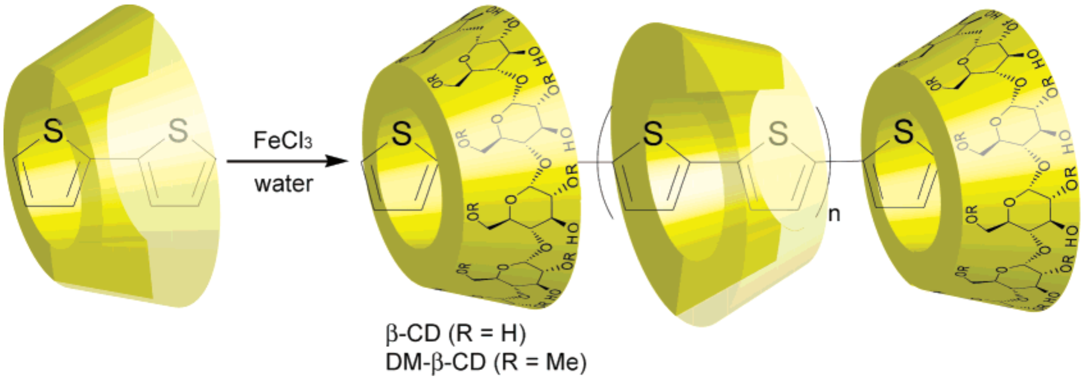
To obtain *pseudo*-rotaxane, the polymerizations of *β*-CD−2T and DM-*β*-CD−2T inclusion complexes were carried out in water using $FeCl_3$ as an oxidative initiator. The mixtures became turbid, and the polymers were obtained as a deep purple powder by centrifugation. This powder was washed with water and THF three times to remove residual DM-*β*-CD and 2T. The structure of the polymer was characterized by the IR spectrum, ^{13}C CP/MAS NMR, and the mass spectrum. Figure 2 shows the ^{13}C CP/MAS NMR spectra of DM-*β*-CD and *pseudo*-rotaxane prepared from the DM-*β*-CD−2T inclusion complex (DM-*β*-CD−poly(2T)). DM-*β*-CD−poly(2T) has a symmetrical cyclic conformation in the complex, although DM-*β*-CD assumes a less symmetrical conformation in the crystal when not

---

[†] Osaka University.
[‡] Tokyo University of Agriculture and Technology.
* Corresponding author: Tel +81-6-6850-5445; Fax +81-6-6850-5445; e-mail harada@chem.sci.osaka-u.ac.jp.

10.1021/ma049763n CCC: $27.50

Scheme 1



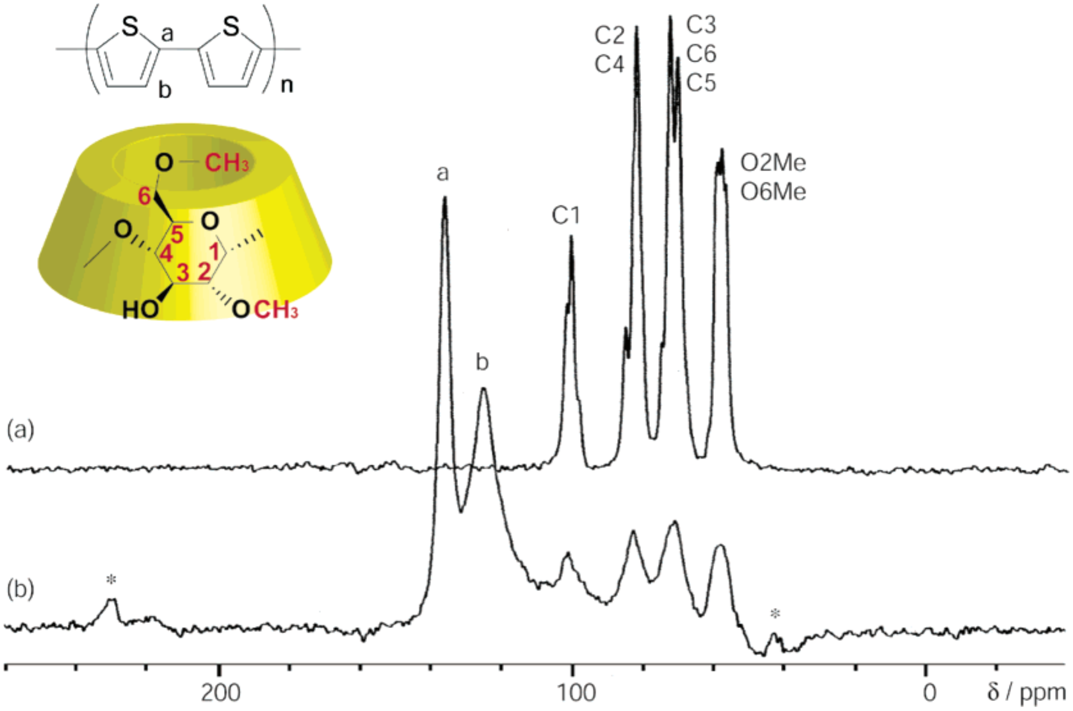


Figure 2. ^{13}C CP/MAS NMR spectra of DM-β-CD (a) and polythiophene prepared from the DM-β-CD−2T inclusion complex (b), polymerized with FeCl$_3$ initiator in water.

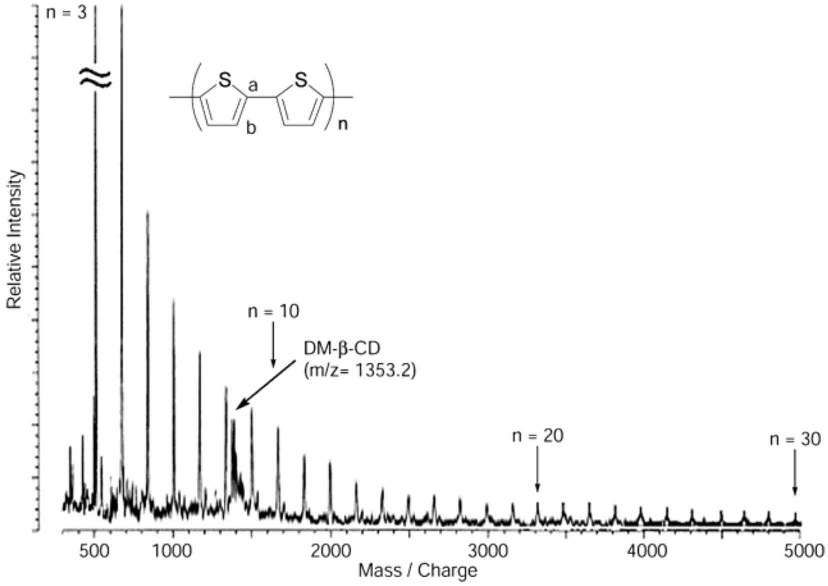


Figure 3. MALDI−TOF mass spectrum of polythiophene prepared from the DM-β-CD−2T inclusion complex, polymerized with FeCl$_3$ initiator in water.

including a guest into the cavity. A polythiophene chain is included into the cavities of DM-β-CDs. The signals in the MALDI−TOF mass spectrum of DM-β-CD−poly(2T) can clearly be assigned as proton adducts of poly(2T) and sodium or potassium cation adducts of DM-β-CD in Figure 3. The number-average molecular weight of poly(2T) was up to 5000. Although there are a few reports on the polymerization of thiophenes with CDs in water,[9] the resulting poly(ethylenedioxythiophene) did not contain any cyclodextrins, suggesting that a rotaxane-type structure was not given because CDs came off from poly(ethylenedioxythiophene) during the polymerization reaction. These results are in contrast to our results.

In conclusion, a series of novel β-CD or 2,6-dimethyl-β-CD (DM-β-CD) inclusion complexes with bithiophene (2T) were prepared, and the crystal structure of β-CD−2T was determined by X-ray crystallography. These inclusion complexes can be polymerized by $FeCl_3$ in water and give pseudo-rotaxane with high molecular weight of poly(2T).

Acknowledgment. Y.T. is a research fellow of the Japan Society for the Promotion of Science, 2003−2005.

Supporting Information Available: Experimental procedures and characterization for β-CD−2T and DM-β-CD−2T, MALDI−TOF mass spectra of β-CD−poly(2T), and FT-IR spectrum of β-CD−poly(2T) and DM-β-CD−poly(2T). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Nanostructures: Special Issue: *Chem. Rev.* **1999**, 7. (b) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T., Reynold, J., Elsenbamer, R., Eds.; Marcel Dekker: New York, 1998. (c) Shirakawa, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2574. (d) MacDiarmid, A. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2581. (e) Heeger, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2591.

(2) (a) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821. (b) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1993**, *26*, 5697. (c) Harada, A.; Kamachi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1322. (d) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406. (e) Harada, A.; Li, J.; Kamachi, M. *Chem. Lett.* **1993**, 237. (f) Harada, A.; Okada, M.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 535. (g) Michishita, T.; Okada, M.; Harada, A. *Macromol. Rapid Commun.* **2000**, *22*, 763.

(3) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley VCH: Weinheim, 1999.

(4) (a) *Aqueous-Phase Organometallic Catalysis*; Cornils, B., Herrmann, W. A., Eds.; Wiley VCH: Weinheim, 1998. (b) *Aqueous Organometallic Catalysis*; Joö, F., Ed.; Kluwer Academic Publishers: Dordrecht, 2001. (c) Rehahn, M.; Schlüer, A.-D.; Wegner, G. *Polymer* **1989**, *30*, 1060. (d) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. (e) Li, C.-J.; Slaven, W. T., IV; John, V. T.; Banerjee, J. S. *Chem. Commun.* **1997**, 1569. (f) Li, C.-J.; Slaven, W. T., IV; Chen, Y.-P.; John, V. T.; Rachakonda, S. H. *Chem. Commun.* **1998**, 1351. (g) Michels, J. J.; O'Connell, M. J.; Taylor, P. N.; Wilson, J. S.; Cacialli, F.; Anderson, H. L. *Chem. Eur. J.* **2003**, *9*, 6167.

(5) Crystal data of β-CD−bithiophene inclusion complex: formula $C_{54}H_{58}O_{45.50}S_3$, formula weight = 1531.18, monoclinic, space group $C2/c$(#15), a = 15.184(12) Å, b = 32.51(2) Å, c = 15.639(10) Å, β = 102.62(7), V = 7532(9) Å^3, Z = 4, D_{calcd} = 1.35 g/cm^3, μ(Mo Kα) = 0.1786 mm^{-1}, F(000) = 3176, T = 200(2) K, Rigaku RAXIS-RAPID imaging plate, 16850 reflections were measured (R_{int} = 0.1208). The final refinement converged at R_1 = 0.1163 and wR_2 = 0.2809 for observations with $[I > 2\sigma(I)]$ and R_1= 0.1710 and wR_2 = 0.2937 for all data. GOF = 1.589.

(6) (a) Harada, A.; Takahashi, S. *J. Incl. Phenom.* **1984**, *2*, 791. (b) Harada, A.; Takahashi, S. *J. Chem. Soc. Chem. Commum.* **1984**, 645. (c) Odagaki, Y.; Hirotsu, K.; Higuchi, T.; Harada, A.; Takahashi, S. *J. Chem. Soc., Perkin. Trans.* **1990**, *1*, 1230.

(7) Klingert, B.; Rihs, G. *J. Inclusion Phenom.* **1991**, *10*, 255.

(8) Lagrost, C.; Ching, K. I. C.; Lacroix, J.-C.; Aeiyach, S.; Jouini, M.; Lacaze, P.-C.; Tanguy, J. *J. Mater. Chem.* **1999**, *9*, 2351.

(9) Storsberg, J.; Ritter, H.; Pielartzik, H.; Groenendaal, L. *Adv. Mater.* **2000**, *12*, 567.

MA049763N