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Polyrotaxane Containing a Blocking Group in Every Structural Unit of the Polymer Chain. Direct Synthesis of Poly(alkylenebenzimidazole) Rotaxane from Ru Complex-Catalyzed Reaction of 1,12-Dodecanediol and 3,3′-Diaminobenzidine in the Presence of Cyclodextrin

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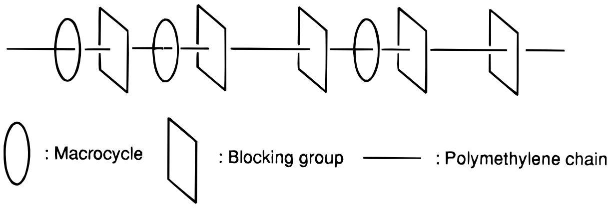
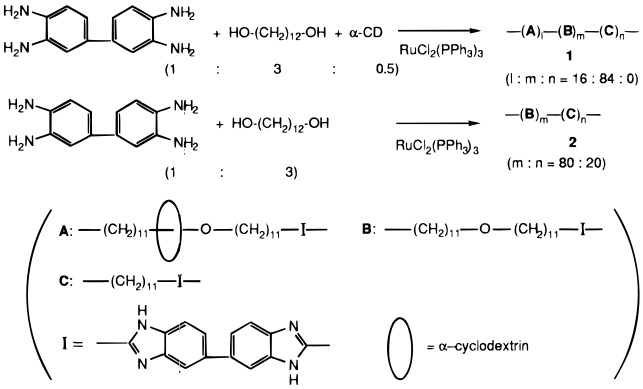
Polyrotaxanes that contain macrocyclic molecules and a linear polymer molecule[1] have attracted growing attention due to both interest in the structure and properties[2−6] and the potential utility as a molecular material for electron switching and photoswitching.[7−9] Most of the polyrotaxanes already reported contain cyclodextrin or crown ether molecules that thread onto polymers such as polyethylene, poly(ethylene oxide), and polyester. The macrocyclic molecules are able to move along the polymer chain, although bulky end-capping groups at both ends of the polymer chain prevent the macrocycles from being released from the supramolecular system. Alternating polycondensation of a bifunctional compound with the polymethylene chain and with a bulky group in the presence of a macrocycle with a suitable cavity size would give a novel type of polyrotaxane containing a blocking group in every structural unit of the main chain, as shown in Chart 1. Macrocycle rings in this system are fixed between two blocking groups. There have been only a few reports on this kind of oligorotaxane.[10]

Our approach to synthesizing this novel type of polyrotaxane involves preparation of poly(alkylenebenzimidazole) in the presence of α-cyclodextrin (α-CD), since α-CD could include the alkylene chain but has too small a cavity size (∼4.5 Å diameter) to include the benzimidazole group. Conventional preparations of poly(benzimidazole)[11] require highly acidic or severe thermal conditions, under which cyclodextrin would be decomposed, and are not suitable for this purpose. Thus, we examined the $RuCl_2(PPh_3)_3$-catalyzed condensation of a primary alcohol with 1,2-diaminobenzene to form an imidazole ring[12] for polycondensation of the α,*ω*-diol with 3,3′-diaminobenzidine in the presence of the macrocyclic compound.

Chart 1. Poly(rotaxane) Containing a Blocking Group in Every Structural Unit of the Polymer Chain



Scheme 1. Polycondensation in the Presence and Absence of α-CD



Reaction of 3,3′-diaminobenzidine, 1,12-dodecanediol, and α-CD (1:3:0.5 molar ratio) in the presence of $RuCl_2(PPh_3)_3$ catalyst gave the polymer product **1**, containing structural units **A** and **B** in a 16:84 ratio based on the analytical and spectroscopic results (Scheme 1).[13] Similar reaction in the absence of α-CD gave poly(alkylenebenzimidazole) (**2**), containing structural units **B** and **C** in an 80:20 ratio.

Figure 1 shows the ^1H NMR spectra of the products. Polyrotaxane **1** gives rise to peaks due to α-CD and those due to the polymer chain. The triplet signals at 2.80 and 3.36 ppm are assigned to hydrogens of the CH_2 group bonded to the imidazole ring and to CH_2O hydrogens, respectively. The peak intensity ratio between the above two signals is 1.0:1.0, indicating the absence of structural unit **C** in the polymer chain. Assignment of the peaks due to the hydrogens of the polymer chain is based on comparison of the spectrum with that of a model compound, $\overline{\text{NHC}_6\text{H}_4\text{N}{=}\text{C}}{-}(\text{CH}_2)_{11}\text{O}(\text{CH}_2)_{11}{-}\overline{\text{C}{=}\text{NC}_6\text{H}_4\text{NH}}$, prepared from $RuCl_2(PPh_3)_3$-catalyzed condensation of 1,2-diaminobenzene with 1,12-dodecanediol. Peaks of hydrogens due to α-CD appear at the same positions as those for polymer-free cyclodextrin, similarly to poly(ethylene oxide) rotaxane with cyclodextrin.[6] The $^{13}C\{^1H\}$ NMR spectrum and results of elemental analysis agree with the above formula. Table 1 summarizes the results of the reactions using α-CD in several molar ratios as well as those of the reaction using *β*-cyclodextrin. Yields and molecular weight of the products do not vary when

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[13] Similar reaction of 3,3′-diaminobenzidine, 1,12-dodecanediol, and α-CD in a 1:3:1 molar ratio gave the products in a composition similar to that obtained for the reaction in a 1:3:0.5 molar ratio.

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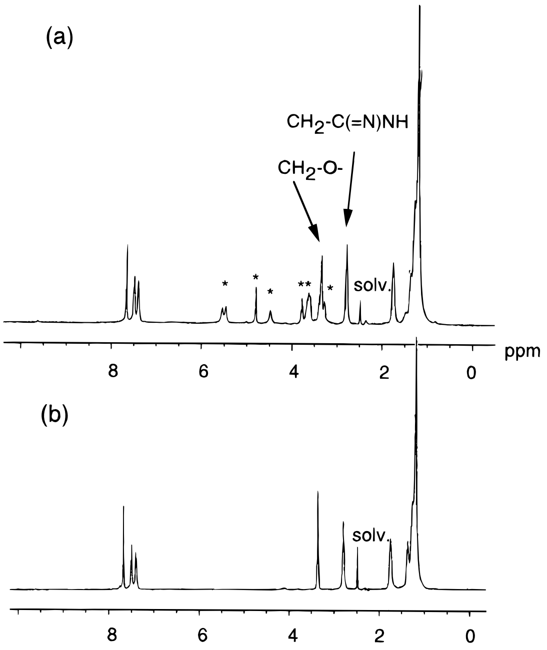


Figure 1. ^{1}H NMR spectrum of (a) **1** and (b) **2** in DMSO-d_6 (400 MHz at 25 °C). Peaks with asterisks are due to hydrogens of α-CD. NH hydrogens appear as a broad peak at ~12 ppm due to hydrogen bonding to H_2O or solvent.

Table 1. Preparation of Poly(alkylene benzimidazole) Rotaxane from 3,3′-Diaminobenzidine, 1,12-Dodecanediol, and Cyclodextrin in the Presence of $RuCl_2(PPh_3)_3$ Catalyst[a]

conditions[b]			products				
3,3′-diamino-benzidine	1,12-dodecane-diol	CD	yield (%)[c]	10^{-3} M_n[d]	10^{-3} M_w[d]	CD/monomeric unit[e]	A + B/C[f]
3.0	3.0	α-, 1.5	37	1.0	4.9	10:90	100:0
3.0	6.0	α-, 1.5	81	4.3	6.5	13:87	69:31
3.0	9.0	α-, 1.5	90	4.0	7.2	14:86	100:0
3.0	9.0	none	89	4.8	6.5		80:20
3.0	9.0	β-, 1.5	70	4.2	7.5	9:81	100:0

[a] Reactions were carried out for 19 h at 200 °C in NMP (*N*-methylpyrrolidone) using 0.1 mmol of $RuCl_2(PPh_3)_3$. [b] Amounts of the substrates (mmol) are shown. [c] Based on 3,3′-diaminobenzidine. [d] GPC using DMF containing 0.01 M LiBr as eluent. Polystyrene standard. [e] Determined by ^{1}H NMR peak area ratio. [f] Ratio between the structural units in the polymer chain. Determined by ^{1}H NMR peak area ratio.

more than 2 mol of dodecanediol per mole of diaminobenzidine is used in the preparation reaction. β-Cyclodextrin, having a larger cavity than α-CD, also forms polyrotaxane.

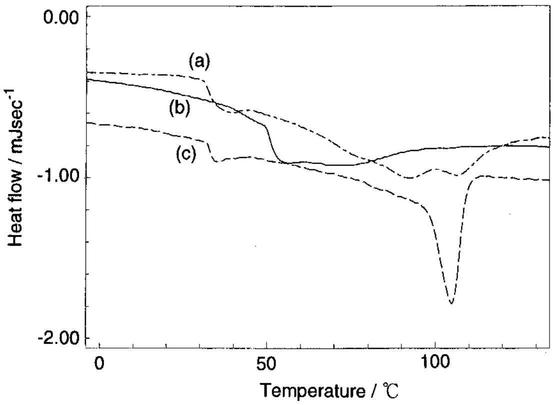
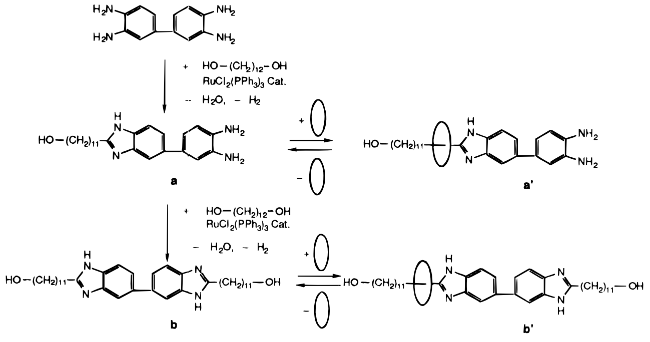


Figure 2. DSC traces of (a) a physical mixture of **2** and α-CD, (b) **1**, and (c) **2**. Temperature was increased from −50 °C at 10 °C min^{-1}.

Scheme 2. Formation of Intermediate Oligomer in Polycondensation of Diol and Tetramine



Scheme 2 shows plausible pathways for formation of **1** involving intermediates **a** from 1:2 condensation of diaminobenzidine and 1,12-dodecanediol and **b** from 1:1 condensation. In the presence of α-CD, condensation of the CH_2OH groups of **b** (or **b′**) and of **a** (or **a′**) and **b** (or **b′**) occurs exclusively, while in the absence of α-CD, the condensation of the diamino group of **a** and the OH group of **a** or **b** occurs in part during the reaction to give the polymer backbone containing structures **B** and **C**.

Figure 2 compares DSC traces of the products showing glass transition temperatures, T_g, of **1** and **2** at 51 °C and 32 °C, respectively. The difference in T_g between **1** and **2** is ascribed to less flexibility of the polymer chain of **1** than that of **2**, caused by an inclusion of a part of the main chain by an α-CD ring.

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Supporting Information Available: Full experimental procedures and ^{1}H and ^{13}C NMR and IR spectral data for the products (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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