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# Synthesis of polyurea rotaxanes using a cyclodextrin complex of α,ω-diamine

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## Summary

Polyaddition of α-cyclodextrin (α-CD) inclusion complex of ethylene glycol bis(2-aminoethyl) ether with 4,4'-methylenebis(1-isocyanatobenzene) (MDI) provided a pseudopolyrotaxane. Similar reactions of α-CD inclusion complex of poly(tetrahydrofuran) terminated with 3-aminopropyl groups with MDI and with 1-methyl-2,4-phenylene diisocyanate gave polyurea pseudorotaxane and polyrotaxane, respectively. The $^1$H NMR spectrum indicates that molar ratios of α-CD to the polyurea chain in polyrotaxanes are 55, 24, and 45%, respectively. Formation of the rotaxane structure was confirmed by X-ray diffraction analysis and GPC measurement. DSC measurement indicates that they show higher glass transition temperature than that of the corresponding CD free polymers.

## Introduction

Polyureas and polyurethanes are important class of polymers due to their unique physical properties (1). These properties of the polymers are strongly influenced by intermolecular hydrogen bonding between the N-H and C=O groups in the polymer chain. Introduction of macrocyclic compounds such as cyclodextrin and crown ether onto the polymer chain would be available to alter their properties because the macrocycle covers the functional groups and prevents intermolecular hydrogen bonding. Gibson and co-workers have reported a number of polyurethane-crown ether polyrotaxanes that involve strong NH•••O hydrogen bondings between the NH hydrogen in the polyurethane chain and crown ether oxygen, and showed their unique physical properties (2). We have also reported preparation and physical properties of polyurethane-permethyl-β-CD rotaxanes (3).

In contrast to the many reports on polyurethane rotaxanes, there has been few report on polyurea rotaxane.

Most of polyrotaxanes and pseudopolyrotaxanes have been synthesized by polycondensations or polyadditions in the presence of macrocycle (4) or by addition of macrocycle(s) to polymer solutions, followed by introduction of blocking groups at the polymer ends (5). Use of a monomer containing the macrocyclic unit(s) will be another useful method to give the polyrotaxane, however, use of such monomers in polycondensation or polyaddition giving polyrotaxanes has been limited (6). Recently, we reported a facile preparation method for α- and β-CD complexes of diepoxides and a α,ω-diamine (7). As an extension of this work, we here report usability of the α-CD complex of the α,ω-diamine for synthesis of polyurea-α-CD rotaxanes by polyaddition with diisocyanates. Physical properties of the new polyrotaxanes will also be reported.

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## Experimental

### *General procedure, materials and measurement*

All the manipulations were performed under nitrogen using standard Schlenk techniques. *N*-methyl-2-pyrrolidinone (NMP) was distilled and stored under nitrogen. α-CD complexes of ethylene glycol bis(2-aminoethyl)ether (**1**) and of poly(tetrahydrofuran) terminated by 3-aminopropyl groups (**2**) were prepared according to a previous reported method (7). Other organic chemicals were purchased and used as received. IR and NMR spectra were recorded on a JASCO-IR 810 spectrophotometer and a JEOL EX-400 spectrometer, respectively. Elemental analyses were carried out by a Yanaco MT-5 CHN autocorder. GPC analyses were performed on a Toso HLC 8120 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), using a DMF solution of LiBr (0.006 M) as the eluent with a flow rate of 1.0 mL min$^{-1}$ and with RI and UV detectors. DSC data were obtained on a Shimadzu DSC-50.

### *Polyaddition*

A Schlenk flask containing 4,4'-methylenebis(1-isocyanatobenzene) (MDI) (27 mg, 0.11 mmol) and **1** (120 mg, 0.11 mmol) was flushed with $N_2$ several times. After addition of NMP (16 mL), the mixture was heated at 20 °C for 12 h with stirring. The solvent was removed by evaporation under reduced pressure and the residue was washed with MeOH (250 mL) leading to separation of the polymer product as a colorless solid which was collected by filtration, washed with MeOH, and dried in vacuo to give **3** (86 mg, 80%). IR (KBr, cm$^{-1}$): 3328 (s), 2924 (m), 1638 (m), 1598 (m), 1544 (m), 1509 (m), 1409 (w), 1311 (w), 1240 (w), 1154 (m), 1077 (m), 1030 (s), 572 (m). $^1$H NMR (400 MHz in DMSO-$d_6$): δ 8.42 (s, 1H, NH), 7.24 (d, 4H, $J$ = 9 Hz, $C_6H_4$), 7.00 (d, 4H, $J$ = 9 Hz, $C_6H_4$), 6.10 (s, 1H, NH), 5.49 (d, $J$ = 7 Hz, 3.3H, α-CD), 5.42 (d, $J$ = 2 Hz, 3.3H, α-CD), 4.79 (d, $J$ = 3 Hz, 3.3H, α-CD), 4.46 (t, $J$ = 5 Hz, 3.3H, α-CD), 3.21-3.79 (m, 31.8H, α-CD and $CH_2$ of polymer chain). Anal Calcd. for $(C_{57}H_{86}N_4O_{34})_{0.55}(C_{21}H_{26}N_4O_4)_{0.45}$ •$4H_2O$: C = 48.72%, H = 6.73%, N = 5.57%. Found: C = 48.40%, H = 6.16%, N =5.48%.

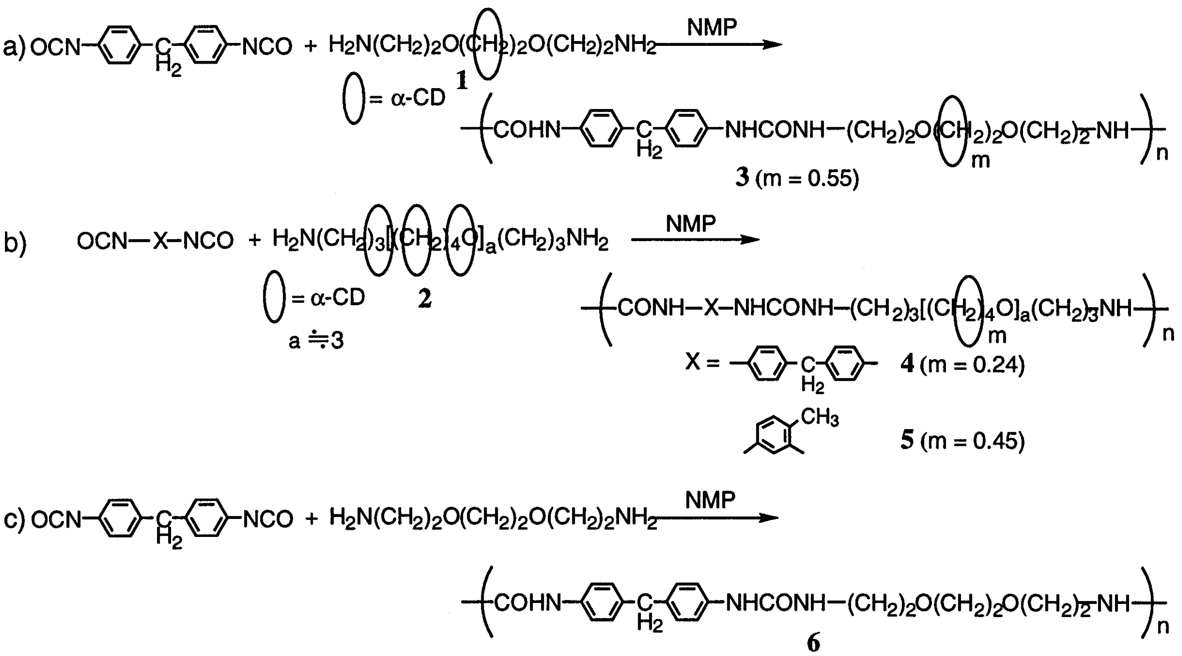
Reactions of **2** with MDI and with 1-methyl-2,4-phenylene diisocyanate were carried out in a similar manner to give **4** and **5**.

Spectroscopic and analytical data of **4**. IR (KBr, cm$^{-1}$): 3298 (w), 2930 (s), 2858 (s), 2798 (w), 1633 (s), 1591 (m), 1562 (m), 1548 (m), 1511 (m), 1365 (m), 1305 (m), 1261 (m), 1236 (m), 1100 (s), 1028 (s), 799 (m). $^1$H NMR (400 MHz in DMSO-$d_6$): δ 8.28 (s, 1H, NH), 7.26 (d, 4H, $J$ = 8 Hz, $C_6H_4$), 7.01 (d, 4H, $J$ = 8 Hz, $C_6H_4$), 6.03 (s, 1H, NH), 5.50 (d, $J$ = 7 Hz, 1.5H, α-CD), 5.42 (d, $J$ = 2 Hz, 1.5H, α-CD), 4.79 (d, $J$ = 3 Hz, 1.5H, α-CD), 4.49 (t, $J$ = 6 Hz, 1.5H, α-CD), 3.56-3.89 (m, 8.4H, α-CD), 3.09 (q, $J$ = 6 Hz, 4H, C*H*$_2$NH), 1.49-1.63 (m, 24H, $CH_2$ of polymer chain). Anal Calcd. for $(C_{69}H_{110}N_4O_{35})_{0.24}(C_{33}H_{50}N_4O_5)_{0.76}$•$3H_2O$: C = 57.47%, H = 8.15%, N = 6.44%. Found: C = 57.30%, H = 7.77%, N = 6.03%.

Spectroscopic and analytical data of **5**. IR (KBr, cm$^{-1}$): 3324 (s), 2924 (m), 2864 (m), 1652 (s), 1599 (w), 1558 (m), 1234 (m), 1151 (w), 1106 (m), 1078 (m), 1030 (s). $^1$H NMR (400 MHz in DMSO-$d_6$): δ 8.27 and 7.69 (s, 2H, N*H*$C_6H_3$), 7.47 (s, 1H, 3-position of $C_6H_3$), 7.11 and 6.90 (d, 2H, $J$ = 8 Hz, 5- and 6-positions of $C_6H_3$), 6.49 and 5.94 (t, 2H, $J$ = 2 Hz, N*H*$CH_2$), 5.51 (d, $J$ = 7 Hz, 2.7H, α-CD), 5.43 (d, $J$ = 2 Hz, 2.7H, α-CD), 4.79 (d, $J$ = 2 Hz, 2.7H, α-CD), 4.49 (t, $J$ = 6 Hz, 2.7H, α-CD), 3.38-3.78 (m, 16.2H, α-CD), 3.09 (q, $J$ = 7 Hz, 4H, C*H*$_2$NH), 1.50-1.65 (m, 24H, $CH_2$ of polymer chain). Anal Calcd. for $(C_{63}H_{96}N_4O_{35})_{0.45}(C_{27}H_{36}N_4O_5)_{0.55}\bullet 3H_2O$: C = 52.49%, H = 7.04%, N = 5.67%. Found: C = 52.19%, H = 7.98%, N = 5.51%.

## Results and discussion

Polyaddition of 4,4'-methylenebis(1-isocyanatobenzene) (MDI) with α-CD inclusion complex of ethylene glycol bis(2-aminoethyl)ether (**1**) in NMP gave a polyurea pseudorotaxane (**3**) in 80% yield (Scheme 1a).



**Scheme 1** Preparation of pseudopolyrotaxanes **3** and **4**, polyrotaxane **5**, and CD free polyurea **6**.

Polyaddition reactions of α-CD inclusion complex of poly(tetrahydrofuran) terminated with 3-aminopropyl groups (**2**) with MDI and with 1-methyl-2,4-phenylene diisocyanate gave polyurea pseudorotaxane (**4**) and polyrotaxane (**5**) in 58 and 40% yields, respectively (Scheme 1b). Polyaddition of ethylene glycol bis(2-aminoethyl)ether with MDI normally gave polyurea **6** (Scheme 1c).

Figure 1 depicts $^1$H NMR spectrum of **3**. Peaks due to NH hydrogens of the urea group were observed at δ 8.42 and 6.10. Other hydrogen peaks due to the polyurea chain and α-CD showed peaks at the essentially same positions as those of α-CD free polyurea **6** and of free α-CD. A molar ratio of α-CD to the polyurea chain was determined as 55% by the peak intensity of the $^1$H NMR spectrum. No dethreading of α-CD from the supramolecular system can be ascribed to a significant host-guest interaction and CO···NH hydrogen bond which makes the polymer conformation less flexible. Hydroxy groups of α-CD did not react with the isocyanate group during the polyaddition reaction, which is revealed from absence of $^1$H NMR peak due to urethane group. IR spectrum of **3** shows absorption peak due to ν(C=O) of the urethane unit at 1638 cm$^{-1}$ and ν(O-H) and ν(C-O) peaks characteristic of α-CD at 3228 and 1030 cm$^{-1}$, respectively.

Polyrotaxane **5** has a blocking group in the every structural unit since α-CD can not pass through the 1-methyl-2,4-phenylene group. Molar ratios of α-CD to the polymer chain of **4** and **5** were determined as 24 and 45%, respectively, from their $^1$H NMR spectra.

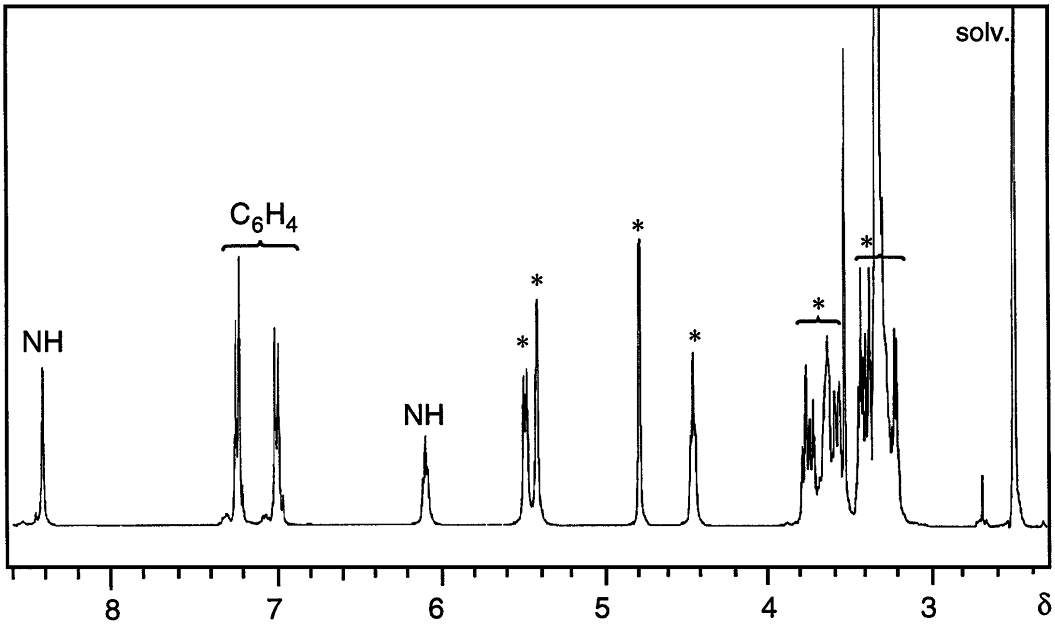


**Figure 1** $^1$H NMR (400 MHz) spectrum of **3** in DMSO-$d_6$. Peaks with an asterisk are due to hydrogens of α-CD.

A plausible reason for higher content of α-CD in **5** than **4** is that the blocking group prevents dethreading of α-CD from the polyurea chain during the polyaddition reaction.

Figure 2 compares GPC traces of **4** and α-CD. The GPC trace of **4** shows no peak assignable to free α-CD, indicating that all α-CDs in **4** are threaded by the polyurea chain. The GPC traces of **3** and **5** also show no peak due to α-CD. The GPC traces gave $M_n$ values of 1.4 x $10^4$ ($M_w$/ $M_n$ = 1.5), 1.6 x $10^4$ ($M_w$/ $M_n$ = 1.9), and 6.3 x $10^4$ ($M_w$/ $M_n$ = 1.3) for **3**, **4**, and **5**, respectively.

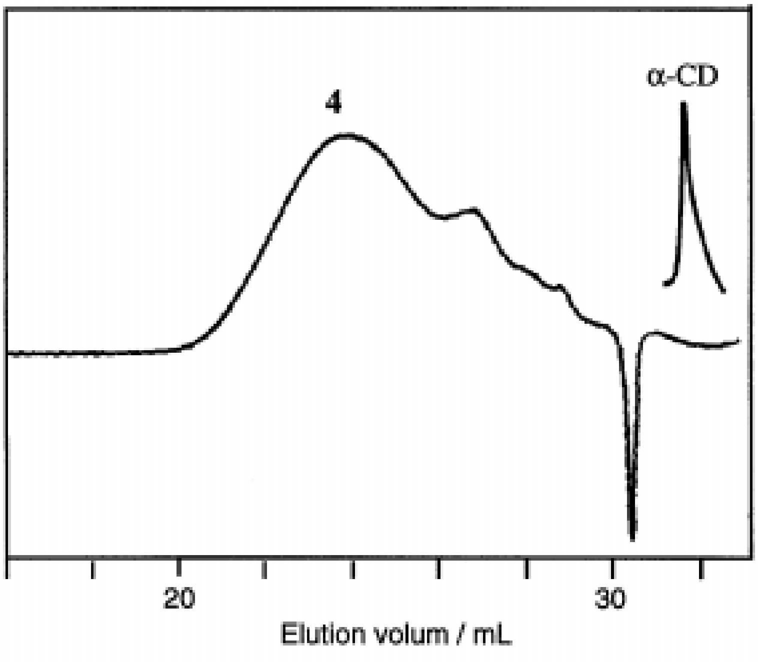


**Figure 2** GPC traces of **4** and α-CD. RI detector was used.

Figure 3 shows powder X-ray diffraction (XRD) patterns of α-CD, **4**, and **5**. The XRD patterns of **4** and **5** gave different patterns from the XRD pattern of free α-CD and suggest a channel-type array (Chart 1 (a)) of the CD molecules in the solid state, which can be distinguished from an alternative cage type structure (Chart 1((b)) (8).

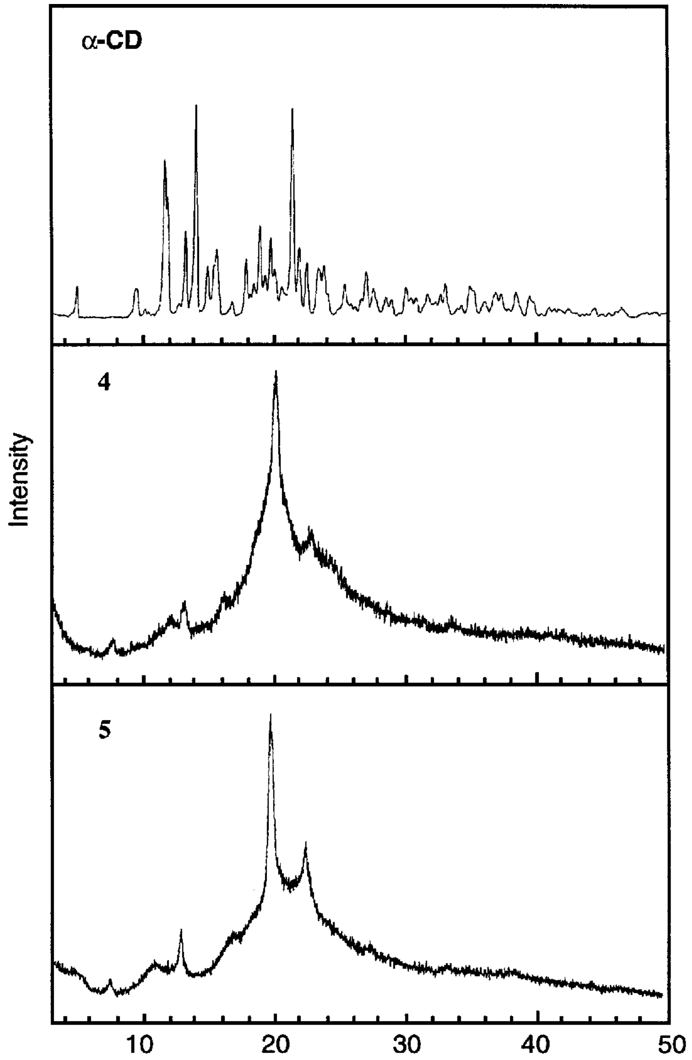


**Figure 3** XRD patterns of α-CD, **4**, and **5**.

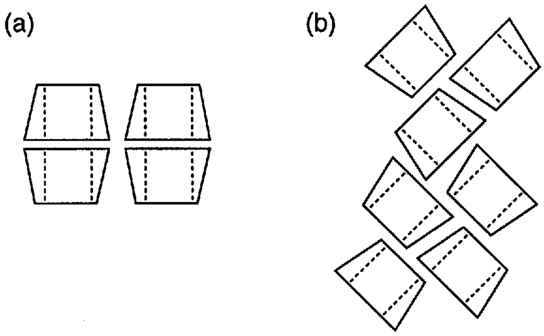


**Chart 1** Columnar structure (a) of α-CD of **4** and **5** and cage type structure (b) of CD which includes methanol.

Figure 4 depicts DSC traces of pseudopolyrotaxane **3**, α-CD free polyurea (**6**) and a physical mixture of **6** and α-CD. Pseudopolyrotaxane **3** shows a different DSC trace from that of the physical mixture of **6** and α-CD and a higher glass transition temperature ($T_g$) (19 °C) than that of **6** (8 °C).

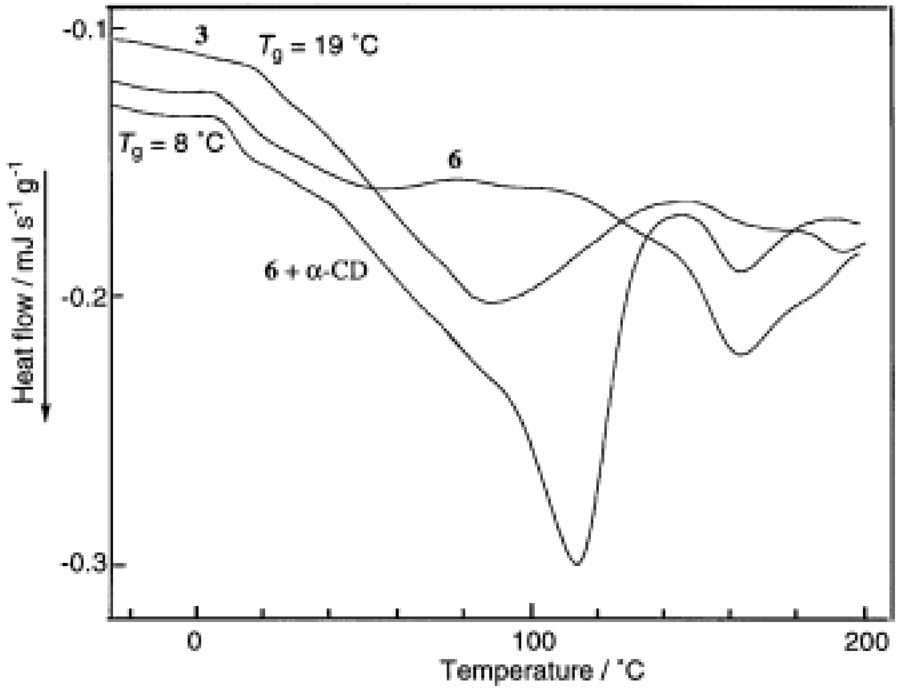


**Figure 4** DSC traces of **3**, **6**, and a physical mixture of **6** and α-CD under He atmosphere at a heating rate of 10 °C min$^{-1}$.

Pseudopolyrotaxane **4** and polyrotaxane **5** also show same $T_g$ of 40 °C higher than that of the corresponding CD free polymers (32 and 35 °C). The higher $T_g$ values of **3**, **4** and **5** than the corresponding CD free polymers seem attributable to decrease of flexibility of the polymer chain because of inclusion of α-CD onto the polyalkylene part.

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