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Notes

Preparation and Characterization of Polyurethane−Cyclodextrin Pseudopolyrotaxanes

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Introduction

There has been considerable interest in the physical properties of aromatic polyurethanes containing soft and flexible polymethylene or polyether chains in the diol part[1] and of copolymers of the elastomeric polyurethanes[2] because coexistence of a hard aromatic urethane group and the soft segment in the polymer chain leads to changes of thermal properties and occurrence of microphase separation depending on the molecular structures. Studies on motions and domains within the polymer systems have been carried out by the use of X-ray diffraction, thermal analyses, and spectroscopic measurements. Recently we have prepared polyurethanes from the reaction of aromatic diisocyanates and α,ω-diols with long carbon chains and reported lowering the melting point of the polymer by introducing longer polymethylene groups.[3]

Introduction of macrocyclic compounds such as cyclodextrin and crown ether onto the polyurethane chain to form pseudopolyrotaxanes[4] would also alter their properties because the macrocycle covers the polar urethane group and prevents intermolecular hydrogen bond between urethane functions in part.[5] Gibson and co-workers have reported a number of polyurethane−crown ether polyrotaxanes that involve strong NH···O hydrogen bonding among the polyurethane chain and crown ether oxygen and show several unique physical properties.[6] Polyurethane−cyclodextrin polyrotaxanes or pseudopolyrotaxanes have attaracted much less attention.[7] In this paper we describe formation of cyclodextrin pseudopolyrotaxane of the polyurethanes having a long diol part in the structural unit of the polymer chain and results of NMR measurements and of thermal analyses.

Experimental Section

General Considerations, Materials, and Measurements. 1,4-Bis(7-hydroxy-1-oxaheptyl)benzene (BHHB) and permethyl-β-cyclodextrin (PM-β-CD) were prepared according to the literature methods.[3,8] Other chemicals were obtained from commercial suppliers. Solvents were dried over CaH_2 and distilled under reduced pressure prior to use. IR and NMR spectra (^{1}H and ^{13}C) were recorded on a JASCO-IR 810 spectrophotometer and a JEOL EX-400 spectrometer, respectively. GPC analyses were carried out by a Toso HPLC 8120 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), using a DMF solution of LiBr (0.02 M) as the eluent with a flow rate of 1.0 mL min^{-1} and with RI and UV detectors. DSC analyses were performed on a Shimadzu DSC-50. Elemental analyses were carried out on a Yanaco MT-5 CHN autocorder.

Preparation of Pseudopolyrotaxanes. To a DMF (5 mL) solution of BHHB (165 mg, 0.50 mmol) was added PM-β-CD (715 mg, 0.50 mmol) and methylenediphenyl-4,4′-diisocyanate (MDI) (125 mg, 0.50 mmol) in this order at room temperature with stirring. After 24 h, a mixture of BHHB (165 mg, 0.50 mmol) and MDI (125 mg, 0.50 mmol) was added to the solution. Heating of the reaction mixture was continued for 20 h at 120 °C. The products were slowly poured into distilled water (300 mL) with vigorous stirring. The solid separated from the solution was collected by filtration, washed with water, and then dried in vacuo (608 mg, 90% as **1a**). IR (KBr, cm^{-1}): 3322 (ν(NH)), 2936 and 2862 (ν(CH)), 1702 (ν(C=O)), 1596, 1535 (ν(CN)), 1514, 1472, 1412, 1229, 1074, 1034. ^{1}H NMR (400 MHz in DMSO-d_6): δ, 9.48 and 8.51 (2H, NH), 7.31 (m, 4H, C_6H_4), 7.08 (m, 4H, C_6H_4), 6.78 (s, 4H, C_6H_4), 5.02 (d, 7H, $J = 3$ Hz), 4.36 (t, 4H, OH, $J = 6$ Hz), 4.02 (t, 4H, CH_2-OCO, $J = 6$ Hz), 3.84 (t, 4H, $PhOCH_2$, $J = 6$ Hz), 3.75 (s, 2H, CH_2), 3.76−3.65 (m, 14H, CH_2), 3.47 (s, 21H, OCH_3), 3.43−3.31 (m, 14H), 3.35 (s, 21H, OCH_3), 3.22 (s, 21H, OCH_3), 3.05 (dd, 7H, $J = 10$ and 3 Hz), 1.65−1.39 (m, 16H, CH_2). ^{13}C NMR (100 MHz in DMSO-d_6): δ, 153.6, 152.6, 152.5, 137.6, 137.1, 135.3, 134.9, 134.8, 129.0, 128.8, 118.2, 115.2, 113.9, 97.7, 81.6, 81.2, 79.6, 71.1, 70.4, 67.8, 67.7, 64.0, 60.7, 60.6, 58.1, 57.8, 32.5, 28.8, 28.7, 28.5, 25.4, 25.3, 25.2, 25.1. Anal. Calcd for **1a**, $C_{33}H_{40}N_2O_6(C_{63}H_{112}O_{35})_{0.08}$: C, 67.68; H, 7.31; N, 4.15. Found: C, 67.72; H, 7.09; N, 4.33.

Other pseudopolyrotaxanes were prepared analogously, and polymers obtained with a different PM-β-CD/monomer ratio (**1b**) and with a different kind of cyclodextrin, permethyl-α-cyclodextrin (PM-α-CD) (**2a** and **2b**), were obtained. ^{1}H NMR and IR data of the products were similar to those of **1a** except for the peak area ratio of the ^{1}H NMR spectra. Anal. Calcd for **1b**, $C_{33}H_{40}N_2O_6(C_{63}H_{112}O_{35})_{0.20}$: C, 64.73; H, 7.38; N, 3.30. Found: C, 64.58; H, 7.39; N, 3.53. Anal. Calcd for **2a**, $C_{33}H_{40}N_2O_6(C_{54}H_{96}O_{30})_{0.14}$: C, 66.57; H, 7.30; N, 3.83. Found: C, 66.49; H, 7.66; N, 4.07. Anal. Calcd for **2b**, $C_{33}H_{40}N_2O_6(C_{54}H_{96}O_{30})_{0.25}$: C, 64.46; H, 7.39; N, 3.23. Found: C, 64.71; H, 7.34; N, 3.38.

Results and Discussion

Polyaddition of BHHB with MDI in the presence of PM-α-CD or PM-β-CD proceeds smoothly at 120 °C to result in formation of the pseudopolyrotaxanes in high yields as shown in Scheme 1 and summarized in Table 1. Figure 1 depicts the GPC trace of **2b** which shows unimodal elution pattern. Comparison of it with that of PM-β-CD (Figure 1b) indicates that **2b** is the pseudopolyrotaxane rather than a physical mixture of polyurethane and PM-β-CD. Ratios of the cyclodextrin to the repeating units of the polyurethanes were determined by ^{1}H NMR peak area ratios and the results of

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Scheme 1

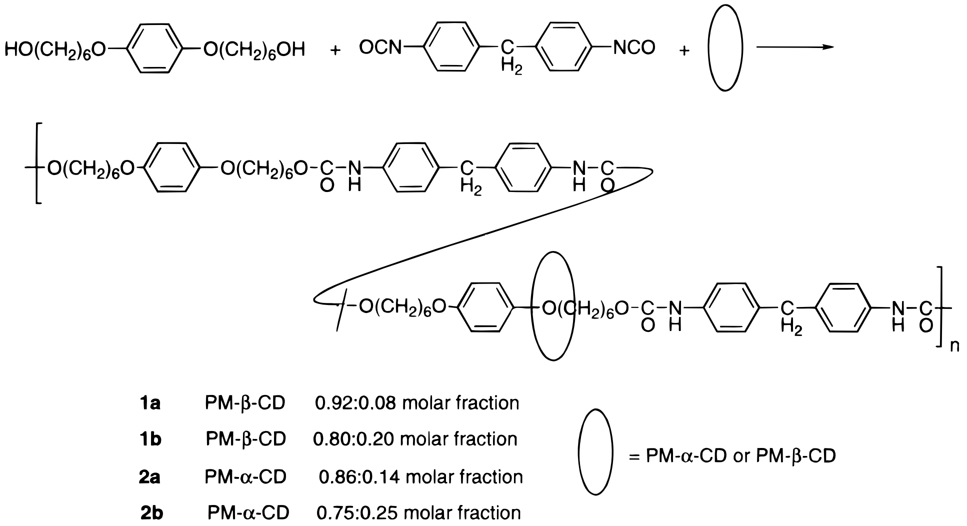

Table 1. Results of Polyaddition of BHHB and MDI in the Presence of Permethylcyclodextrins (PM-CD)

preparation[a]			product			
run	PM-CD	PM-CD/MDI[b]	yield (%)	CD content[c]	$10^{-3}M_n$[d]	$10^{-3}M_w$[d]
1	*β*	0.5:1.0	**1a** (90)	0.08	3.9	7.3
2	*β*	1.0:1.0	**1b** (95)	0.20	5.6	9.7
3	α	0.5:1.0	**2a** (83)	0.14	12.9	16.0
4	α	1.0:1.0	**2b** (96)	0.25	28.3	42.3

[a] Reaction conditions: 20 h (Run 1 and 3), 120 h (Run 2), and 84 h (Run 4) at 120 °C in DMF under Ar. [b] Molar ratio of PM-CDs to MDI or BHHB used in the reactions. [c] Molar ratio of cyclodextrin to the repeating unit of polyurethane chain in the pseudopolyrotaxanes. [d] Determined by GPC using DMF containing LiBr (0.02 M) as the eluent and polystyrene standards.

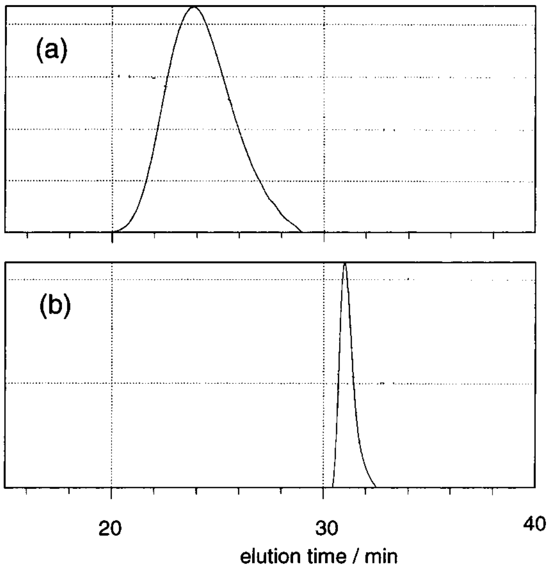

Figure 1. GPC traces of (a) **2b** and (b) permethyl-*β*-cyclodextrin (PM-*β*-CD). Elution was carried out by using a DMF solution of LiBr (0.02 M) with a flow rate of 1.0 mL min^{-1}, and with RI detector

elemental analyses. The initial molar ratio of PM-CDs and monomers influences the PM-CD content in the produced pseudopolyrotaxane. The polyaddition in the presence of equimolar PM-CD to the monomers gives the products containing PM-CD and the repeating unit in the ratios of 0.20 (**1b**) and 0.25 (**2b**), while the reaction using a smaller amount of PM-CDs causes the content of the PM-CD to become smaller in pseudopolyrotaxane.

The ^{1}H NMR spectra of the products contain the signals of PM-CD and the polyurethane chain. Figures 2a and 3a depict the ^{1}H NMR spectra of **1b** and **2b**, respectively. Signals of hydrogens of the polymer chain part are observed at positions similar to those of the corresponding polyurethane reported previously.[3] The ^{13}C{^{1}H} NMR spectrum of **2b** also shows most signals of PM-*β*-CD part at the same positions as free PM-*β*-CD, although a signal due to C^5 (δ 79.6) is shifted slightly from the corresponding signal of PM-*β*-CD (δ 81.0). The ^{1}H NMR spectra using the ROESY technique[9] (Figures 2b and 3b) provided not only evidence for the pseudopolyrotaxane formation but also information about its structure. Irradiation at the signals of the CH hydrogens which are on the inside of cavity of PM-*β*-CD of **1b** (δ 3.43−3.31) leads to appearance of positive signals at aromatic hydrogen regions (δ 7.31, 7.08, and 6.78), indicating significant NOE between the aromatic hydrogens of polyurethane chain and the above hydrogens of PM-*β*-CD. Signals due to nonaromatic hydrogens of the polyurethane chain (δ 4.1−1.2) become almost negligible on the irradiation. These results imply that the PM-*β*-CD is situated on the aromatic ring of the polyurethane chain arising from formation of a stable inclusion complex. The ROESY ^{1}H NMR spectrum of **2b** (Figure 3b) indicates the presence of NOE between the signals of the CH hydrogens and both aromatic and aliphatic hydrogens. The presence of a close contact (ca. 6 Å) between the hydrogens of PM-α-CD and polymethylene group is suggested. A physical mixture of PM-α-CD and the polyurethane do not show such signals by NOE. The different NMR results of **1b** and **2b** can be accounted for by assuming the structures of the pseudopolyrotaxanes as described below. PM-*β*-CD in **1b** can include a benzene ring of the polymer chain similarly to many already reported inclusion complexes of *β*-CD and aromatic compounds and is positioned on the aromatic group of the polymer chain. PM-α-CD has too small of a cavity size to include a benzene ring fully, and the macrocycle of **2b** is mainly situated on the polymethylene group of the polymer chain.

Thermal properties of **1b** and **2b** were compared by DSC scanning as shown in Figure 4. The polymer free from macrocycle gives a glass transition at 50 °C, whereas pseudopolyrotaxane **1b** exhibits a significantly

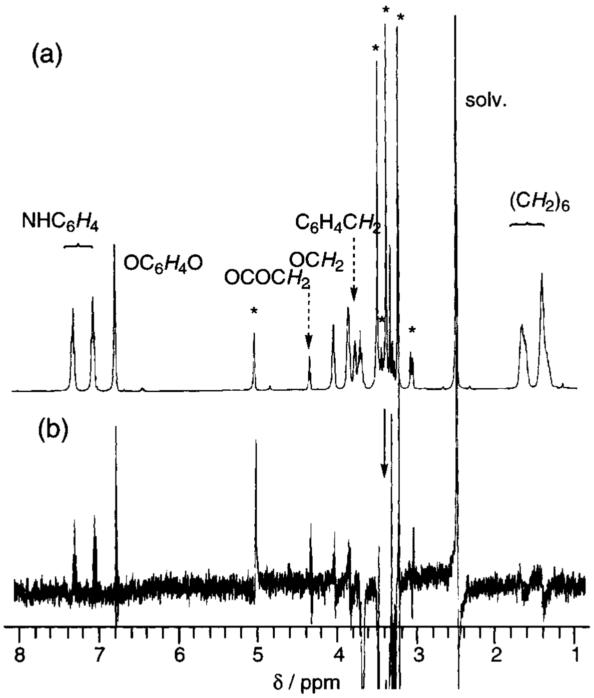

Figure 2. (a) ^{1}H (400 MHz) NMR spectrum and (b) the spectrum under ROESY conditions with irradiation at the hydrogens on the inside of PM-β-CD cavity of **1b**. Signals of NH hydrogens (δ 8.51 and 9.48) are omitted. Signals with an asterisk are due to PM-β-CD. An arrow in part b indicates the irradiated position.

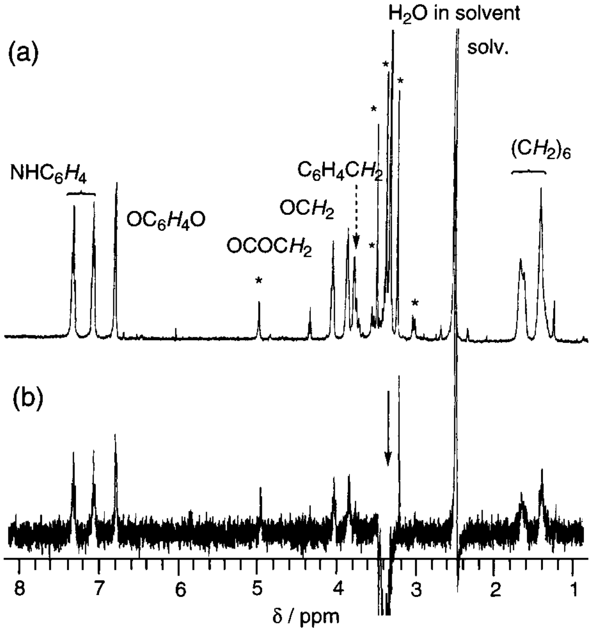

Figure 3. (a) ^{1}H (400 MHz) NMR spectrum and (b) the spectrum under ROESY conditions with irradiation at the hydrogens on the inside of the PM-α-CD cavity of **2b**. Signals of NH hydrogens (δ 8.51 and 9.48) are omitted. Signals with an asterisk are due to PM-α-CD. An arrow in part b indicates the irradiated position.

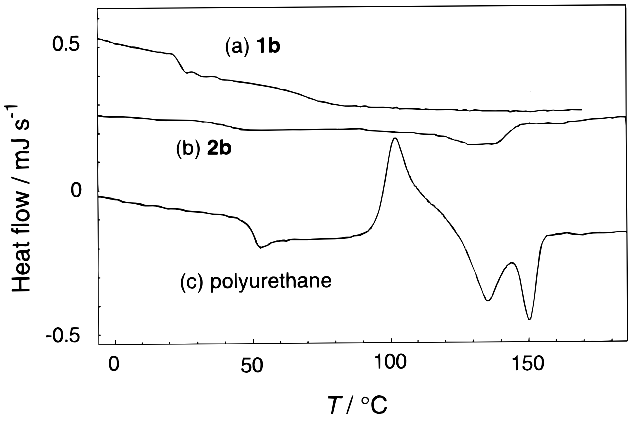

Figure 4. DSC scans of (a) **1b** and (b) **2b** and (c) polyurethane from BHHB and MDI (M_n = 42.4 kg mol^{-1}; M_w = 59.9 kg mol^{-1}; see ref 3). Second scans are shown.

lower T_g, 24 °C. The pseudopolyrotaxane **2b** also shows a weak transition at approximately 40 °C, which may be assigned to T_g. The transitions of CD free polyurethane at higher temperatures (130 and 150 °C) are not observed or are obscure in the pseudopolyrotaxanes. These results suggest that thermal properties of the polyurethane were altered by introduction of the cyclodextrins to form pseudopolyrotaxanes.[10]

The present study has provided several new aspects on the structure and properties of the polyurethane–cyclodextrin pseudopolyrotaxanes. PM-β-CD of the pseudopolyrotaxane is fixed onto aromatic ring of the polymer chain, whereas PM-α-CD is not localized at the aromatic polyurethane group and possibly moves along the polymethylene chain. These pseudopolyrotaxanes show lower T_g values than the parent polyurethane because of weaker intermolecular hydrogen bonding between the urethane functions than the corresponding polyurethane.

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(10) Although the pseudopolyrotaxane has a lower molecular weight than the polyurethane analyzed by DSC, the difference in the T_g values seems to be larger than that expected from different molecular weights.

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