

Hydrogen-bonded polymer complexes of macrocycles containing a pyridyl moiety and carboxyl-functionalized polystyrenes

An approach to H-bonded rotaxanes

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Received: 31 March 1999/Accepted: 27 April 1999

Summary

Copolystyrenes complexed with macrocyclic compounds through hydrogen bonding have been synthesized by the copolymerization of styrene with the complex of 4-vinylbenzoic acid and crown ethers containing a 2,6-pyridyl moiety. The glass transition temperatures of the copolymeric complexes are significantly lower than that of the simple copolymer, which shows that the carboxylic acid groups in the polymer backbone do not intermolecularly dimerize. The UV absorption spectra of polymeric complexes suggest that they have complex structures similar to that of the low-molecular-weight complexes of 4-ethylbenzoic acid and the crown ethers.

Introduction

Biopolymers have hydrogen bonding moieties which function for biological and chemical processes (1). Non-covalent interactions such as hydrogen bonding have also been used for the self-assembly and self-organization processes in the preparation of functional synthetic materials (2). For polymeric materials, the complexes of polymers and low-molecular-weight compounds have been built by the use of hydrogen bonding (3), which is expected to lead to the formation of dynamically-functionalized polymeric materials. For example, thermally reversible liquid-crystalline networks have been obtained through the formation of hydrogen bonding between pyridyl moieties and carboxylic acid groups (4). For topological polymer complexes, hydrogen bonding has been used for the formation of rotaxane consisting of polymers and macrocycles (5). Although a variety of methods have been employed for the preparation of polyrotaxanes (6), the formation of complexes with well-defined structures by introducing selective and stable hydrogen bonding has not yet used. Here we report the synthesis of hydrogen-bonded polymeric complexes of macrocycles containing a pyridyl moiety with carboxyl-functionalized copolystyrenes. A styrene monomer with a functional group hydrogen-bonded to the macrocyclic compounds has been copolymerized with styrene. We expected that pseudorotaxanes were obtained by using this approach (Figure 1).

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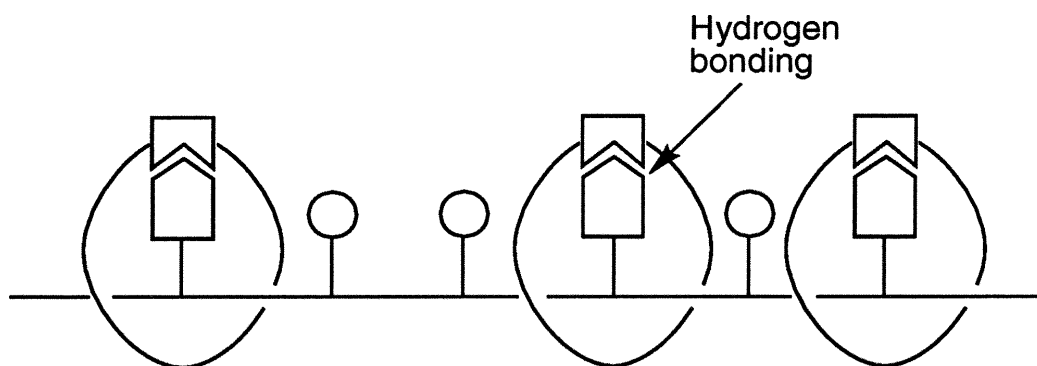


Fig. 1. A structure of a polymeric complex which is expected to be obtained in the present study.

Experimental

Thermal properties were examined using a polarizing microscope equipped with a Mettler FP82HT hot stage and a differential scanning calorimeter (Mettler DSC30). The heating and cooling rate of 10 °C/min was used for the DSC measurements. The number average molecular weights of the polyamides were determined by GPC (Tosoh) equipped with a TSK gel GMH_{HR}-N column using 0.01 M LiBr/DMF as an eluent. UV spectra were recorded on a Hitachi U-4000 spectrophotometer in THF solution. ¹H-NMR spectra were recorded on a JEOL Lambda spectrometer at 400 MHz. The following abbreviations are used to explain the multiplicity: s = singlet, d = doublet, t = triplet, and m = multiplet.

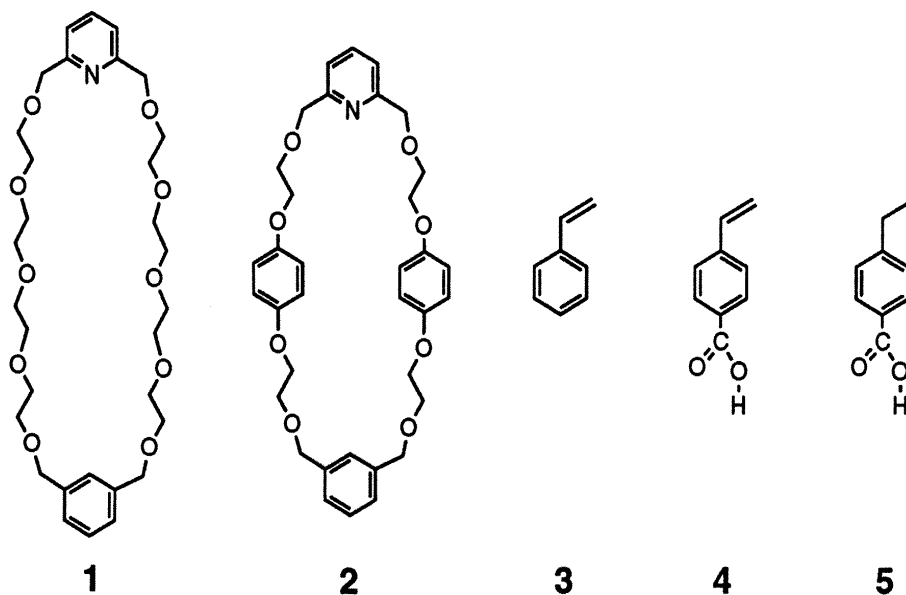


Chart 1. Components of crown ethers and the derivatives of styrene and benzoic acid.

Components used in the present paper are shown in Chart 1. They were prepared by the modification of a procedure reported previously (7). Crown ethers **1** and **2** were synthesized as follows: 1,3-Bis(bromomethyl)benzene was cyclized with the diol containing one pyridyl (Py) group which was prepared from the reaction of 2,6-bis(bromomethyl)pyridine and two monoanions from corresponding diols by KO^tBu.

1: Yield; 30.6%. ¹H-NMR δ = 3.58-3.74 (32H, m), 4.62 (4H, s), 4.70 (4H, s), 7.19 (2H, d, J = 7.4 Hz), 7.27 (2H, d, J = 6.0 Hz), 7.35 (1H, t, J = 6.0 Hz), 7.50 (1H, s), 7.60 (1H, t, J = 7.4 Hz).

2: Yield; 59.8%. ¹H-NMR δ = 3.76 (4H, t, J = 4.6 Hz), 3.86 (4H, t, J = 4.9 Hz), 4.05-4.10 (8H, m), 4.62 (4H, s), 4.70 (4H, s), 6.78 (8H, d, J = 6.8 Hz), 7.22 (2H, d, J = 7.4 Hz), 7.24-7.32 (3H, m), 7.47 (1H, s), 7.60 (1H, t, J = 7.4 Hz).

The complexes of the crown ethers and the benzoic acid derivatives were obtained from the solution in THF, followed by evaporation at moderate temperature. Simple copolymerization of styrene **3** (0.22 g, 2.1×10^{-3} mol) and 4-vinylbenzoic acid **4** (0.092 g, 6.2×10^{-4} mol) was carried out in THF (2.0 mL) with AIBN (1.0 mol%) at 60 °C for 12 h, according to previous reports (8). Initial ratio of **4** to **3** was 0.30. Polymeric complexes were synthesized by the copolymerization of **3** and preformed complexes of crown ethers and **4**. Unreacted monomers were removed by successive reprecipitations, which was confirmed by ¹H-NMR analyses.

Poly(**3-co-4**): Yield; 50-80%.

The compositions of components in the copolymerization products were estimated from integral intensities of the chemical shifts corresponding to components in ¹H-NMR spectra.

Results and discussion

The crown ethers containing a pyridyl moiety **1** and **2** were expected to function as macrocycles interacting with carboxyl-functionalized polymer through hydrogen bonding in their inner space. A variety of crown ethers containing pyridyl moieties were prepared for host molecules in the molecular recognition process (9). Crown ether **1** was designed as a host with inner cavity fitting the benzoic acid derivative which was a carboxyl-functionalized monomer. Furthermore, the phenylene-containing crown ether **2** was synthesized in order to promote the complexation with the benzoic acid by π - π stacking. A single pyridyl moiety was introduced to the crown ethers **1** and **2** for the formation of 1:1 host-guest complexes. It has been reported that the benzoic acid derivatives and pyridine compounds form stable equimolar liquid-crystalline complexes (4).

Figure 2 shows the UV absorption spectra of crown ether **2**, 4-ethylbenzoic acid **5** and their mixture. The absorption peak at 237 nm is observed in both components (Figure 2A and C), while that in the mixture seen at 229 nm (Figure 2B). These absorptions can be attributed to π - π^* transition. This result suggests that the crown ether **2** interacts with **5**. Figure 3 shows the DSC curves of 1:1 complex of **2** and **5** (**2/5**) and each of components on cooling. The glass transition of **2/5** is seen at -12 °C (Figure 3B), which is similar to that of component **2** (T_g = -16°C) shown in Figure 3A. A sharp crystallizing peak of **5** at 112°C (Figure 3C) is not seen in the DSC curve of **2/5**, which indicates the dimer form of **5** does not exist in the mixture.

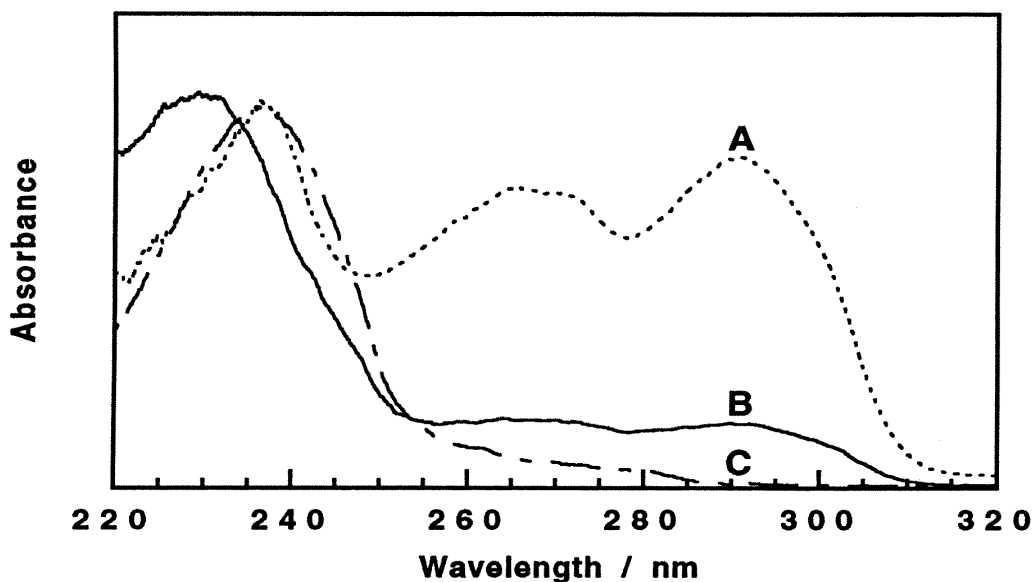


Fig. 2. UV spectra of the crown ether **2** (A), **2/5** (B) and **5** (C).

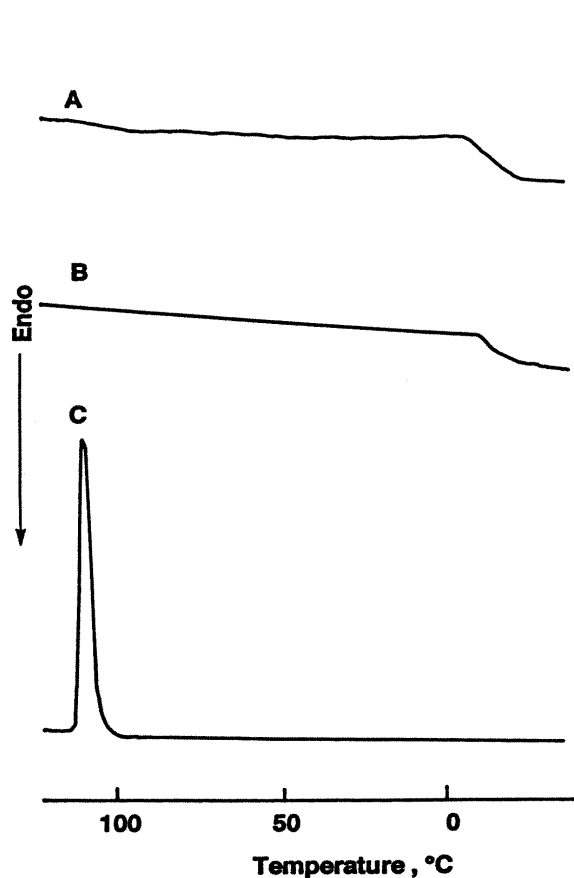


Fig. 3. DSC curves of **2** (A), **2/5** (B) and **5** (C).

We designed the preparation process for the polymeric complexes with crown ethers, which might result in the formation of pseudorotaxanes. Copolymers were prepared under the condition that the initial ratio of the complex **2/4** to compound **3** was 0.30. The results of copolymerizations of **3** and **4** in the presence and in the absence of crown ethers are listed in Table 1. The $^1\text{H-NMR}$ spectrum of the product shows that the ratio of **4** to **3** in the copolymer is 0.43 (run 3), indicating that the radical copolymerization proceeds in the presence of the hydrogen-bonded complexes between crown ethers and benzoic acids. The number average molecular weights (M_n) of the products are about 10^4 , which is similar to that of the simple copolymer obtained. The copolymeric product (run 3) contains crown ether structures. The ratio of **2** to carboxylic group is calculated to be 0.41. It suggests that 41% of **4** in this copolymeric product interacts with **2**. In the case of crown ether **1** as a host molecule the copolymeric complex (run 2) has also been obtained.

Table 1. Polymerization of the copolymers of styrene **3** and 4-vinylbenzoic acid **4** complexed with or without crown ethers^a.

Run	Crown ether	Yield	T_g	\overline{M}_n^b	Fraction of Py ^c
		%	°C		[Py]/[COOH]
1	-	80.3	174	6.5×10^4	-
2	1	64.3	120	7.7×10^4	0.18
3	2	72.0	53	7.2×10^4	0.41

^a Polymerization; temperature, 60 °C; time, 12 h; solvent, THF; initiator, AIBN (1.0 mol%); initial ratio of crown ether to **4**, 1.0; initial ratio of **4** to **3**, 0.30.

^b Determined by GPC. ^c Calculated based on ¹H-NMR. Py: Pyridyl moiety.

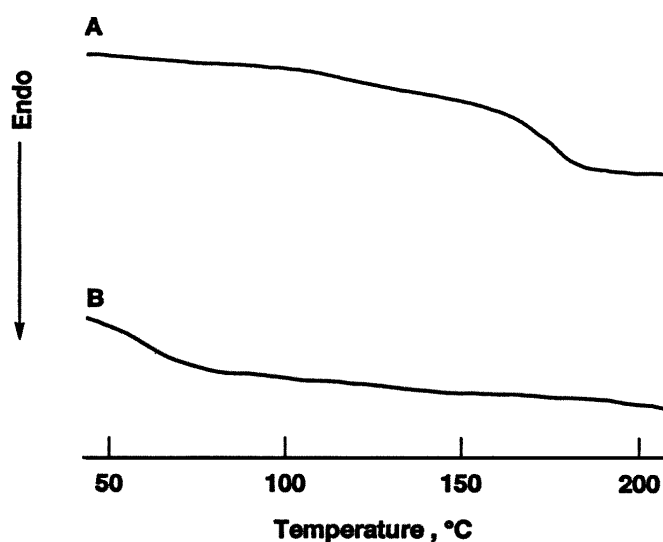


Fig. 4. DSC curves of poly(**3-co-4**) (A) and poly(**3-co-4**) with **2** (B).

Figure 4 shows the DSC curves of copolymeric products obtained in the presence and in the absence of crown ethers. The glass transition temperature of poly(**3-co-4**) (run 1) is 174 °C (Figure 4A), which is higher than that of styrene homopolymer ($T_g \sim 100$ °C). This increase can be ascribed to the interaction of copolymer chains through the dimerization of carboxylic acid groups. In contrast, the product obtained by the copolymerization in the presence of **2** (run 3) shows the glass transition behavior at 53 °C (Figure 4B). This significant decrease in T_g indicates the inhibition of the interaction of the carboxylic groups by the crown ether additives. The simple mixtures of poly(**3-co-4**) (run 1) and crown ethers after reprecipitation do not show such a large decrease of T_g , which indicates that the products (runs 2 and 3) cannot be obtained by the simple mixing of the copolymers and the crown ethers. Moreover, the successive reprecipitations of the THF solution of these polymeric products (runs 2 and 3) into 1.0 M HCl

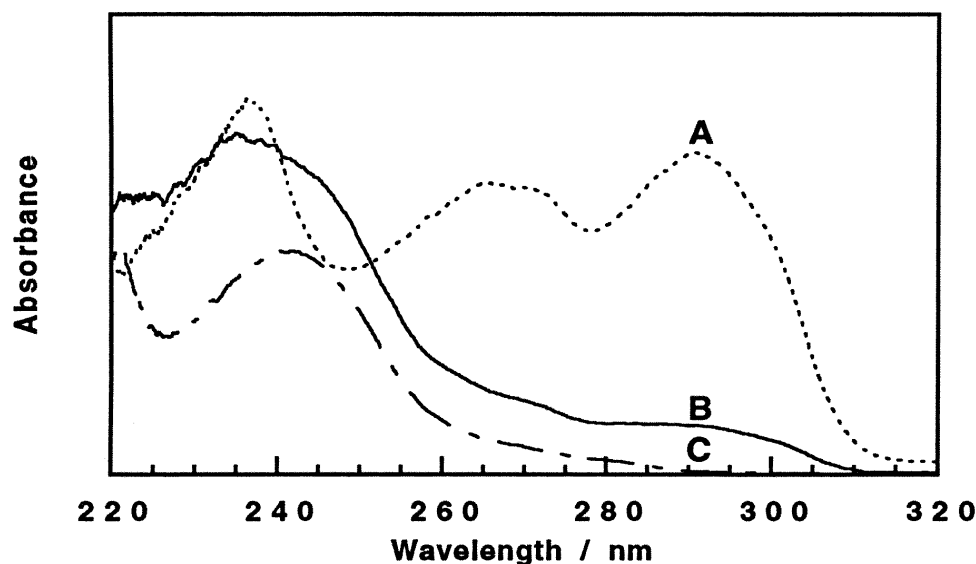


Fig. 5. UV spectra of the polymeric complex and the components. Crown ether **2** (A), poly(**3-co-4**) with **2** (B) and poly(**3-co-4**) (C).

and 1.0 M NaOH do not show the decrease of the amounts of crown ethers in these products and the glass transition temperatures.

For the UV absorption spectrum of poly(**3-co-4**) with **2** (run 3) in THF, the absorption peak is shifted by 2 nm to shorter wavelengths (Figure 5B) compared to that of the single component (Figure 5A). This is the same trend as is observed for the low-molecular-weight complex of **2** and **5** (Figure 2B). The shift is smaller compared with that of low-molecular-weight complexes, which reflects the smaller ratio of the carbonyl group interacting with the pyridine ring to the whole product.

The present results reported here suggest the polymeric complexes have pseudorotaxane structures, in which the linear copolystyrene passes through the crown ethers, as shown in Figure 1. Further examination is now underway for the characterization of the structure of these complexes.

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