ORGANIC LETTERS

2004
Vol. 6, No. 3
361−364

Preparation of *β*-Cyclodextrin Polyrotaxane: Photodimerization of *pseudo*-Polyrotaxane with 2-Anthryl and Triphenylmethyl Groups at the Ends of Poly(propylene glycol)

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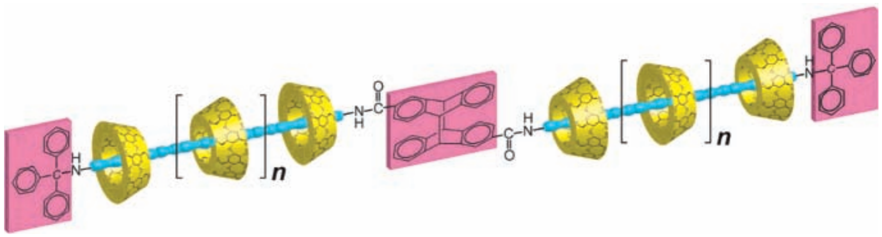
Received November 5, 2003

ABSTRACT



A polyrotaxane containing *β*-cyclodextrins has been prepared by photoreactions of a precursor complex between *β*-cyclodextrin with poly(propylene glycol) having a triphenylmethyl group at one end and a 2-anthryl group at the other end.

In recent years, polyrotaxanes have attracted much attention as new polymeric materials in which many cyclic molecules are mechanically incorporated onto a polymer chain.[1] However, only a few groups have succeeded in preparing new polyrotaxanes because of the synthetic difficulty. Gibson,[2] Ritter,[3] and Stoddart[4] et al. prepared crown-ether-based or cyclodextrin (CD)-based polyrotaxane using polymerization of 1:1 or 1:2 inclusion complexes, whereas we prepared α-CD-based polyrotaxanes by capping ends of α-CD-poly(ethylene glycol) complexes, in a *pseudo*-polyrotaxane structure, with covalently bound stoppers.[5] The incorporation of CDs into polyrotaxane is important, because CDs have well-defined cyclic structures and thereby polyrotaxane-containing CDs should have distinct functions. However, it is difficult to prepare polyrotaxanes containing

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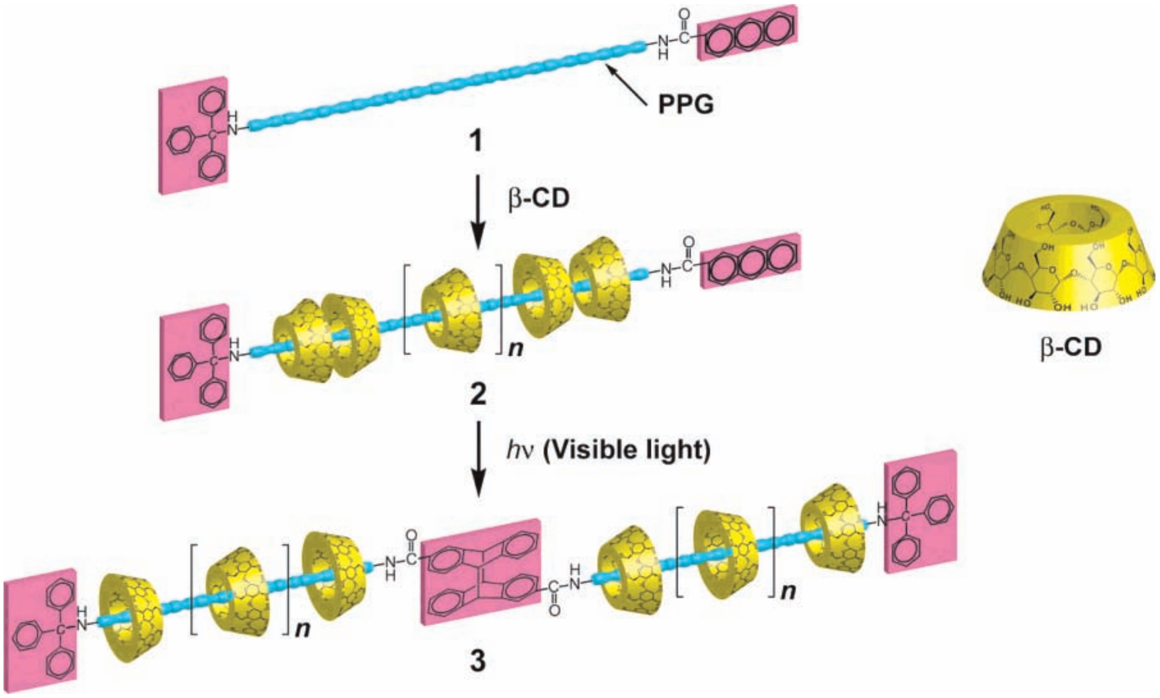
10.1021/ol0361608 CCC: $27.50 © 2004 American Chemical Society
Published on Web 01/15/2004

Scheme 1. Preparation of β-CD-Based Polyrotaxane Using Photoreactions

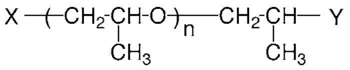


β-CD or γ-CD, because their cavities are so large that it is difficult to find suitable stopper groups to prevent dethreading β-CD or γ-CD.

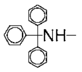
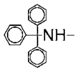
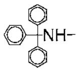
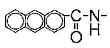
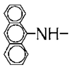
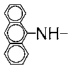
Now an alternative approach for the preparation of CD-based polyrotaxane using photoreactions is described (Scheme 1). We had found that poly(propylene glycol) (PPG) formed crystalline inclusion complexes with β-CD.[6] If the ends of CD-PPG complexes are able to be covalently blocked with bulky stoppers, novel β-CD or γ-CD based polyrotaxanes will be obtained. First, we tried to attach bulky stoppers to CD-PPG ends using triphenylmethyl derivatives, fluorescamine, fluorescein isocyanate, etc. However, we could not obtain polyrotaxanes, probably because CDs dethreaded from the polymer axle during the capping reactions. Therefore, first we prepared a precursor complex of β-CD with a derivative of PPG having a triphenylmethyl group at one end and a 2-anthryl group as the other end. When the precursor complex was exposed to visible light, the photodimerization of the 2-anthryl group[7,8] took place and a polyrotaxane could be obtained.

Molecular modeling studies showed that the size of 2-substituted anthracene (**2A**) is smaller than that of the β-CD and γ-CD cavity. A triphenylmethyl group (**T**) does not penetrate β-CD and γ-CD rings, showing that **T** is suitable for stoppers of CD-PPG complexes as far as the size is concerned. We planned to prepare CD-PPG polyrotaxanes by photodimerization of complexes (Scheme 1). Table 1 lists the complex formation between CDs and PPG derivatives. β-CD did not slip over end groups of **PPGT** as a result of having the very bulky **T** stopper. Compound **1**, which has a bulky **T** stopper and a **2A** photoreactive moiety, forms crystalline complexes with β-CD.

Table 1. Complex Formation between CDs with PPG Derivatives



$$\mathrm{X}\!-\!\left(\mathrm{CH_2}\!-\!\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\!-\!\mathrm{O}\right)_n\!-\!\mathrm{CH_2}\!-\!\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\!-\!\mathrm{Y}$$

	end-group		$M_w/10^3$	yield (%)	
	X	Y		α–CD[a]	β–CD[b]
PPGNH	H_2N-	H_2N-	2.0	0	63
PPGT			2.5	0	<1
1			2.4	0	15
PPG9An			2.4	0	<5

[a] PPG, 10 mg; α-CD saturated aqueous solution, 2.0 mL. [b] PPG, 10 mg; β-CD saturated aqueous solution, 5.3 mL. The yields are calculated on the bases of 2:1 (monomer unit:CD) stoichiometry.

When **1** was mixed with aqueous β-CD solution, the solution became turbid. The heterogeneous solution was

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diluted with distilled water and then exposed for 5 days to visible light ($\lambda \geq 340$ nm) using a 500 W Xe lamp and appropriate cutoff filter. The solution was evaporated to dryness, and the residue was precipitated from DMSO into water and DMSO into methanol to remove free β-CD and PPG derivatives. The solubility of **3** in DMSO is lower than those of starting materials; **3** is insoluble in water and methanol, whereas β-CD is soluble in water and **1** is soluble in methanol.

Figure 1 shows the SEC elution diagrams of **1**, **3**, and β-CD. The *Y*-axis on the left shows the degree (α) of the optical rotation with the open blue circles. The *Y*-axis on the right shows the absorbance at 370 nm with the closed red squares. Compound **3** was monitored by both optical rotation (CD active) and absorption (aromatic groups at PPG ends), showing that **3** consists of CD and end-labeled PPG. In addition, the elution volume of **3** is smaller than that of the starting material, indicating that the size of **3** is larger than that of the component. Figure 2 shows the fluorescence spectrum of the **2** complex. Compound **3** did not show anthracene emission, showing that **2A** groups in **3** are dimerized by visible light.

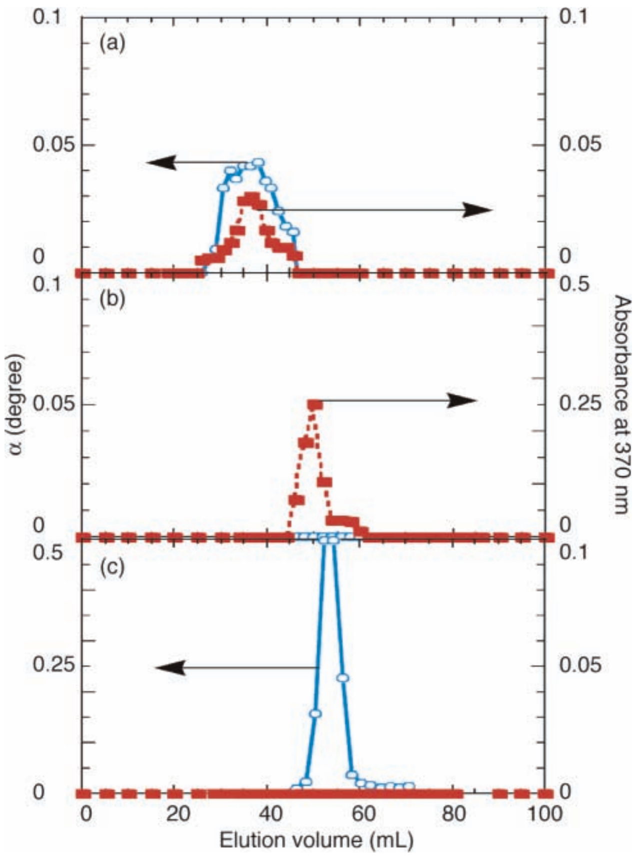

Figure 1. SEC elution diagrams of **3** (a), **1** (b), and β-CD (c). Column TOSOH TSKgel Toyopearl HW-55, eluent DMSO. (○) *Y*-axis on the left. (■) *Y*-axis on the right).

Figure 3 shows the ^{1}H NMR spectrum of **3** in DMSO-d_6 at 30 °C. By comparison of the integral of the C(1)H signal of β-CD with that of the methyl H of PPG, the stoichiometry of **3** was estimated to be about 1:7 (β-CD:PG unit), showing that about 10 β-CD molecules are interlocked in **3**.[9]

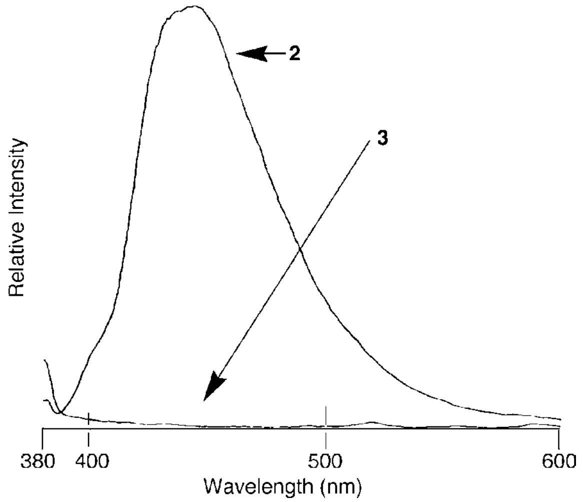

Figure 2. Fluorescence spectra of **2** complex and **3**. $\lambda_{ex} = 370$ nm.

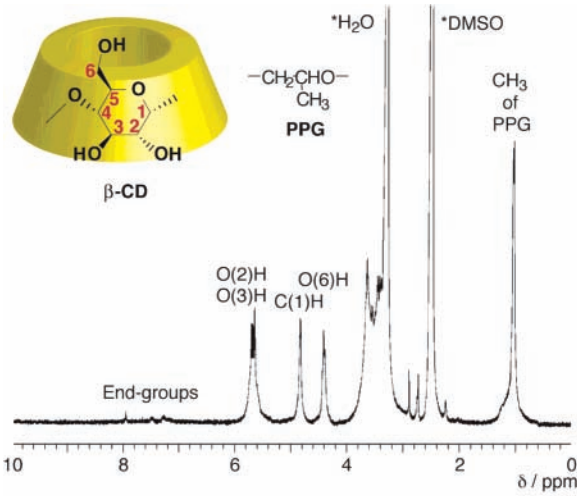

Figure 3. ^{1}H NMR spectrum of **3** in DMSO-d_6 at 30 °C.

In conclusion, we have succeeded in preparing a polyrotaxane containing β-cyclodextrins by photoreactions of a

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[9] **Preparation of 3.** Compound **1** (0.10 g = 1.7×10^{-3} PG unit mol) was added to a β-CD saturated aqueous solution, 53 mL (β-CD; 0.86 mmol). The mixture was stirred for 3 days to become turbid. Distilled water (250 mL) was added, and the heterogeneous solution was exposed to visible light ($\lambda > 360$ nm) under vigorous stirring for 5 days. Precipitates were collected by centrifugation, washed with methanol and distilled water, and then reprecipitated from DMSO/water and DMSO/methanol to give pure **3**. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 5.71−5.65 (m, 14H, O(2)H and O(3)H of β-CD), 4.83 (s, 7H, C(1)H of β-CD), 4.41 (m, 7H, O(6)H of β-CD), 3.64−3.30 (m, C(2)H, C(3)H, C(4)H, C(5)H, and C(6)H of β-CD), 1.04 (m, 3H × 7, methyl H of PPG). IR (KBr, cm^{-1}): 3412(vs, ν_{OH}), 2922, 2853(s, ν_{CH}), 1154, 1078, 1027(vs, ν_{CO}).

precursor complex between β-cyclodextrin with poly(propylene glycol) having a triphenylmethyl group at one end and a 2-anthryl group at the other end. Dynamic behavior of the polyrotaxanes is now under investigation. This may open the way for interesting copolymers consisting of α-CD/PEO and β-CD/PPG in which the two cyclics are confined to their respective segments.

OL0361608