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One-Pot Synthesis of γ-Cyclodextrin Polyrotaxane: Trap of γ-Cyclodextrin by Photodimerization of Anthracene-Capped *pseudo*-Polyrotaxane

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The most significant development in supramolecular chemistry has been the efficient synthesis of interlocked molecules during decades, which could succeed in preparing new mechanically interlocked molecules such as molecular machines or molecular switches as new polymeric materials.[1] Some macrocyclic molecules currently inserted in preparing rotaxanes have a cavity of ~6 Å diameter, such as crown ether,[2,3] cucurbituril (CB-[6]),[4] α-cyclodextrin (α-CD), and β-cyclodextrin (β-CD), which make it relatively easy to prepare interlocked molecules. However, it is difficult to prepare rotaxanes or polyrotaxanes containing larger macrocyclic molecules having a cavity of more than 7.0 Å diameter by the threading method. γ-Cyclodextrin (γ-CD), cyclic oligosaccharides comprising eight α-1,4-linked D-glucopyranose rings, has a cavity of 7.5−8.3 Å diameter. To the best of our knowledge, few polyrotaxanes containing γ-CD have been reported.[5] Previously, the formation of tetraphenylcyclobutane blocking groups along the polymer main chain in the presence of both β-CD and γ-CD was achieved by irradiating an aqueous solution, which are thought to be self-assembled spontaneously by γ-CD in the polyrotaxane and be composed mainly of β-CD polyrotaxane.[6] 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.[7] Here we describe an alternative approach for the one-pot preparation of γ-CD-based polyrotaxanes using photocyclodimerization.

We found that poly(propylene glycol) (PPG) formed crystalline inclusion complexes with β-CD and γ-CD, whereas poly(ethylene glycol) (PEG) and poly(trimethylene glycol) (PTMO) did not give complexes with β-CD and γ-CD.[8] 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 isothiocyanate, etc. However, we could not obtain polyrotaxanes, probably because CDs dethreaded from the polymer axis during the process of capping reactions. On the other hand, the acceleration and the switching in the regioselectivity of the photocyclodimerization have been reported for coumarin derivatives,[9] stilbene derivatives,[10] and anthracene derivatives.[11] Although 9-anthryl groups are large enough to prevent α-CD and β-CD from dethreading, they are small enough for γ-CD to thread onto a polymer chain. However, the photocyclodimerization products of 9-anthracene groups[12,13] are large enough to prevent γ-CD from dethreading. Therefore, we chose PPG as an axle molecule and 9-anthryl groups as bulky stoppers for the PPG end, hereinafter called PPG9An. We investigated a new one-pot method to prepare polyrotaxanes containing γ-CDs by the photocyclodimerization reactions of 9-anthryl groups at the ends of the polymer chain in the presence of γ-CDs. When the precursor complex was exposed to visible light, the photocyclodimerization of the 9-anthryl group took place, and polyrotaxane could be obtained. The synthesis of novel γ-CD−PPG polyrotaxanes by photocyclodimerization of the *pseudo*-polyrotaxane complex between γ-CD and PPG9An is shown in Scheme 1, called **γ-CD−PPG9An**.

Scheme 1. Preparation of PR−γ-CDAn

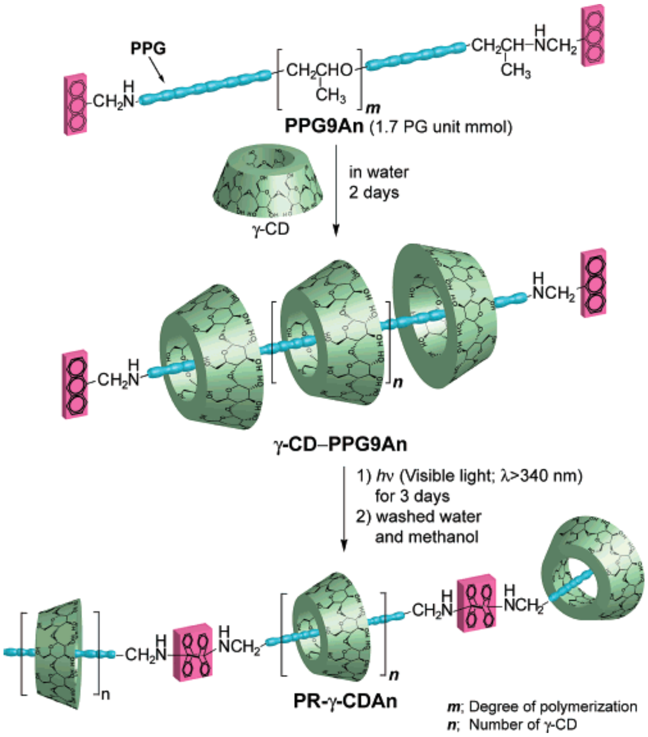
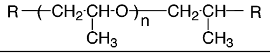
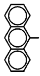


Table 1. Complex Formation between CDs and PPG Derivatives



$R-(CH_2-\underset{CH_3}{CH}-O)_n-CH_2-\underset{CH_3}{CH}-R$

	end-group R	$\overline{M_w}/10^3$ ($\overline{DP}$)	yield (%) α−CD[a]	β−CD[b]	γ−CD[c]
PPGNH	H_2N-	2.0 (35)	0	63	54
PPG9An	 $-CH_2-NH-$	2.4 (35)	0	<5	14

[a] PPG, 10 mg; α-CD saturated aqueous solution, 2.0 mL. [b] PPG, 10 mg; β-CD saturated aqueous solution, 5.3 mL. [c] PPG, 10 mg; γ-CD saturated aquous solution, 1.9 mL. The yields are calculated on the bases of 2:1 (monomer unit:CD) stoichiometry.

When PPG9An was mixed with an aqueous γ-CD solution, the solution became turbid. Table 1 lists the complex formation between CDs and PPG derivatives. β-CD did not penetrate the end groups of PPG9An, which has a bulky 9-anthryl stopper. PPG9An forms crystalline complexes with γ-CD and gave **γ-CD−PPG9An** in 14% yield.

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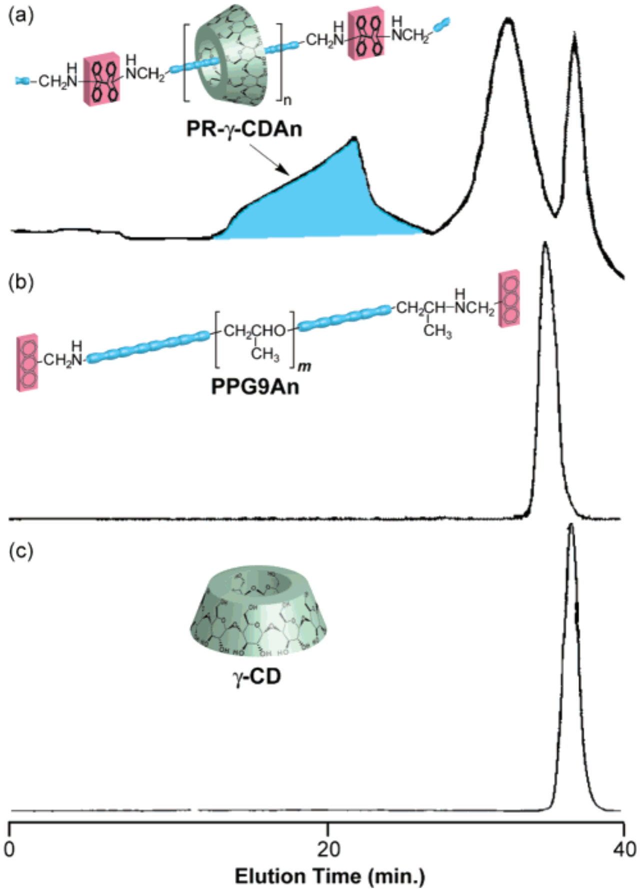

Figure 1. SEC elution diagrams of the products (a), PPG9An (b), and γ-CD (c). Column TOSOH TSKgel Toyopearl HW-55, eluent DMSO. Flow rate: 0.25 mL/min.

A suspension of γ-CD−PPG9An in water was diluted 10 times with distilled water until the solution became clear. An aqueous solution of γ-CD−PPG9An complex was irradiated under a nitrogen atmosphere at $\lambda \geq 340$ nm using a 500 W Xe lamp. The reaction mixture was evaporated to dryness. The residue was washed with water and methanol several times to give the photocyclodimerization of γ-CD−PPG9An, hereafter abbreviated as PR−γ-CDAn. PR−γ-CDAn is only partially soluble in DMSO (dimethyl sulfoxide) and insoluble in water and most organic solvents such as methanol and DMF.

Figure 1 shows the SEC (size exclusion chromatography) elution diagrams of the products in the DMSO-soluble part. The SEC results indicated that the molecular weight (M_w) of PR−γ-CDAn is higher than that of the starting materials, γ-CD and PPG9An. The M_w of PR−γ-CDAn (blue area) was found to be in the range of 10^4−10^6. The second peak of the diagram (a) could be assigned to a single unit of a polyrotaxane containing some γ-CD blocked by both polymer ends by photocyclodimerization of PPG9An and/or *pseudo*-polyrotaxane (PPG9An with some γ-CDs). These results showed that the low solubility of PR−γ-CDAn is due to the high M_w. The product was washed with water and DMF several times to remove residual γ-CD and PPG9An. PR−γ-CDAn was characterized by ^{1}H NMR and FT-IR spectroscopy. The ^{1}H NMR spectrum of PR−γ-CDAn showed the absence of the signal for 9An, and a new signal appeared at 8 ppm, which could be assignable to the photocyclodimer of 9An. The FT-IR spectrum showed CD-based bands, indicating that γ-CD molecules are interlocked in PR−γ-CDAn.

The fluorescence spectra of the γ-CD−PPG9An complex and PR−γ-CDAn are shown in Figure 2. The monomer emissions of a 9An group are observed in the γ-CD−PPG9An complex. On the contrary, the fluorescence spectrum of PR−γ-CDAn did not show a monomer emission typical for a 9An group, showing that all 9An groups in PR−γ-CDAn are dimerized by visible light.

In conclusion, we have succeeded in preparing polyrotaxane-containing γ-cyclodextrins by photocyclodimerization of precursor complexes between γ-cyclodextrin and poly(propylene glycol) having 9-anthracene groups at both ends in the presence of γ-cyclodextrin.

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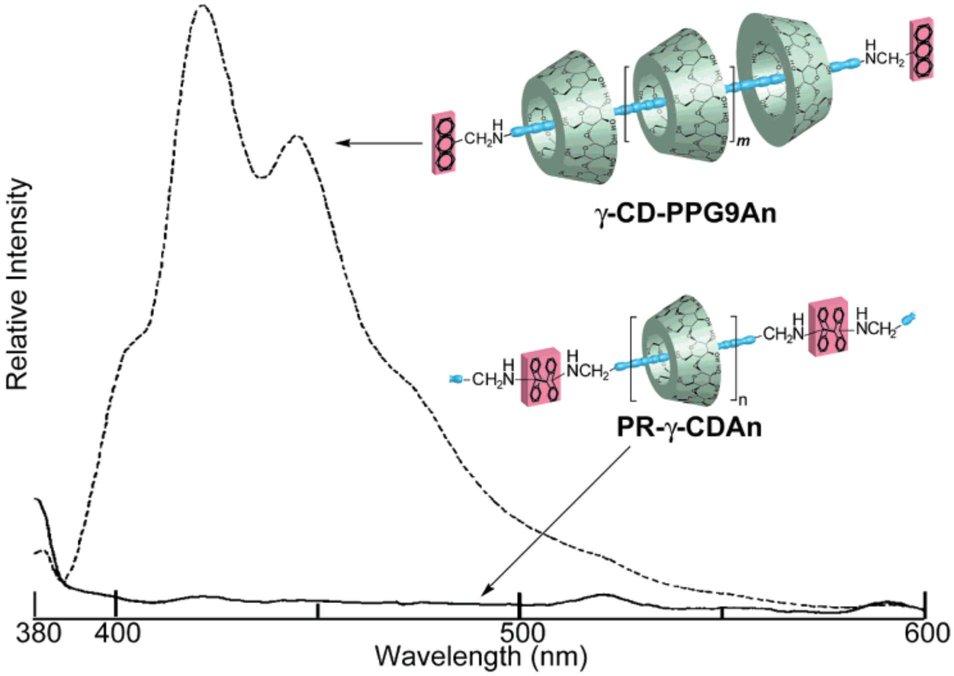

Figure 2. Fluorescence spectra of γ-CD−PPG9An and PR−γ-**CDAn** in the solid state. $\lambda_{ex} = 370$ nm.

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Supporting Information Available: Experimental procedures, characterization, and solubility of PPG9An, γ-CD–PPG9An, and PR–γ-CDAn; ^{1}H NMR and FT-IR spectra of γ-CD–PPG9An and PR–γ-CDAn. This material is available free of charge via the Internet at http://pubs.acs.org.

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