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Poly(polyrotaxane): Photoreactions of 9-Anthracene-Capped Polyrotaxane

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In recent years, much attention has been focused on the construction of interlocked molecules, such as rotaxanes, catenanes, and knots, because of their unique structures and functions.[1] More recently, much effort has been directed toward design and construction of polyrotaxanes[2] and polycatenanes. Crown ethers,[3] cyclodextrins,[4] cucurbituril,[5] and cyclophanes[6] have been extensively used as cyclic components for the constructions of rotaxanes (polyrotaxanes) and catenanes. Bulky substituents, such as dinitorophenyl groups[7] and triphenylmethyl groups,[8] have been used as stoppers to prevent dethreading the above-mentioned ring compounds. If stoppers are reactive and functional, the polyrotaxanes should give polymers of polyrotaxanes, poly(polyrotaxane)s, and poly(catenane)s.

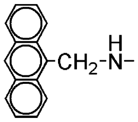
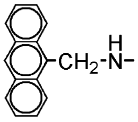
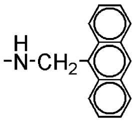
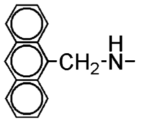
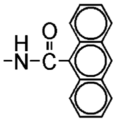
We chose cyclodextrin (CD) as a cyclic component and anthracene groups as stopper groups because anthracene groups are large enough to prevent dethreading α-CD and *β*-CD from an axle and are able to form dimers by photoirradiation.[9] In this case, poly(polyrotaxane)s and poly(catenane)s could be obtained by photoirradiation of polyrotaxanes with anthracene groups as stoppers. Now we have succeeded in obtaining polymers of polyrotaxanes by photoirradiation of polyrotaxanes having 9-anthracene groups as stoppers.

Previously, we found α-cyclodextrin (α-CD) forms inclusion complexes with poly(ethylene glycol) (PEG) having small end groups, such as amines and hydroxy groups.[10] However, PEGs with 9-anthryl (9An) groups at both ends did not form complexes with α-CD at all (Table 1). Molecular modeling studies showed that the size of 9An is larger than that of the α-CD cavity. Polyrotaxanes consisting of PEG, α-CD, and 9-anthracene groups have been prepared as shown in Scheme 1. First, we prepared PEG with an anthracene group at one end of the polymer chain. Then, the modified polymer was treated with α-CD to give the pseudo-polyrotaxane. Finally, the pseudo-polyrotaxane was capped using 9-anthracenecarboxylic acid[11] to give polyrotaxane (PR-α-9An).

PR-α-9An3350 and PR-α-9An2000 (polyrotaxanes prepared from PEG of M_w with 3350 and 2000, respectively) were characterized by SEC, UV−vis, fluorescence, powder X-ray diffraction, ^{1}H NMR, ^{13}C NMR, and FT-IR measurements.[12] The SEC results indicated that the M_w of PR-α-9An3350 is about 20 000 compared to that of standard sample. By comparing the integral of the peak of C(1)H of α-CD and that of methylene H of PEG of the ^{1}H NMR spectra, the ratio of CD and monomer units was found to be 4:1 (ethylene glycol unit: CD). PR-α-9An3350 was found to have about 19 α-CD molecules on a PEG chain. From this value, the M_n of PR-α-9An3500 was estimated to be about 22 000, which is consistent with the value obtained by SEC. Although the absorption spectra of PR-α-9An3350 are similar to that of a model compound PEG9An$_1$-9An, the intensity of 9An monomer emission of PR-α-9An3350 was much higher than that of PEG9An$_1$-9An. The motions of large PR-α-9An3350 might be inhibited, which suppress nonradiative process of excited 9An groups. The X-ray diffraction patterns (powder) of PR-α-9An3350 are similar to that of the α-CD−PEG complex, indicating a channel-type structure in which α-CD rings are stacked along a PEG chain to form cylinders.

When a DMSO solution of PR-α-9An3350 (2 × 10^{-2} mM) was exposed to visible light (λ > 340 nm) (500 W

Table 1. Complex Formation between α-CD and PEG Derivatives

	End-group			Yield / %	
Polymer	X	Y	M_w(PEG)	α−CD[a)]	β−CD[a)]
PEGNH	H_2N—	—NH_2	2000	96	0
			3350	100	0
PEG9An$_1$		—NH_2	2000	100	0
			3350	100	0
PEG9An$_2$			2000	0	0
PEG9An$_1$-9An			3350	0	0

[a] PEG derivative, 15 mg; CD saturated aqueous solution, 1 mL; sonication for 10 min and allowed to stand overnight at room temperature.

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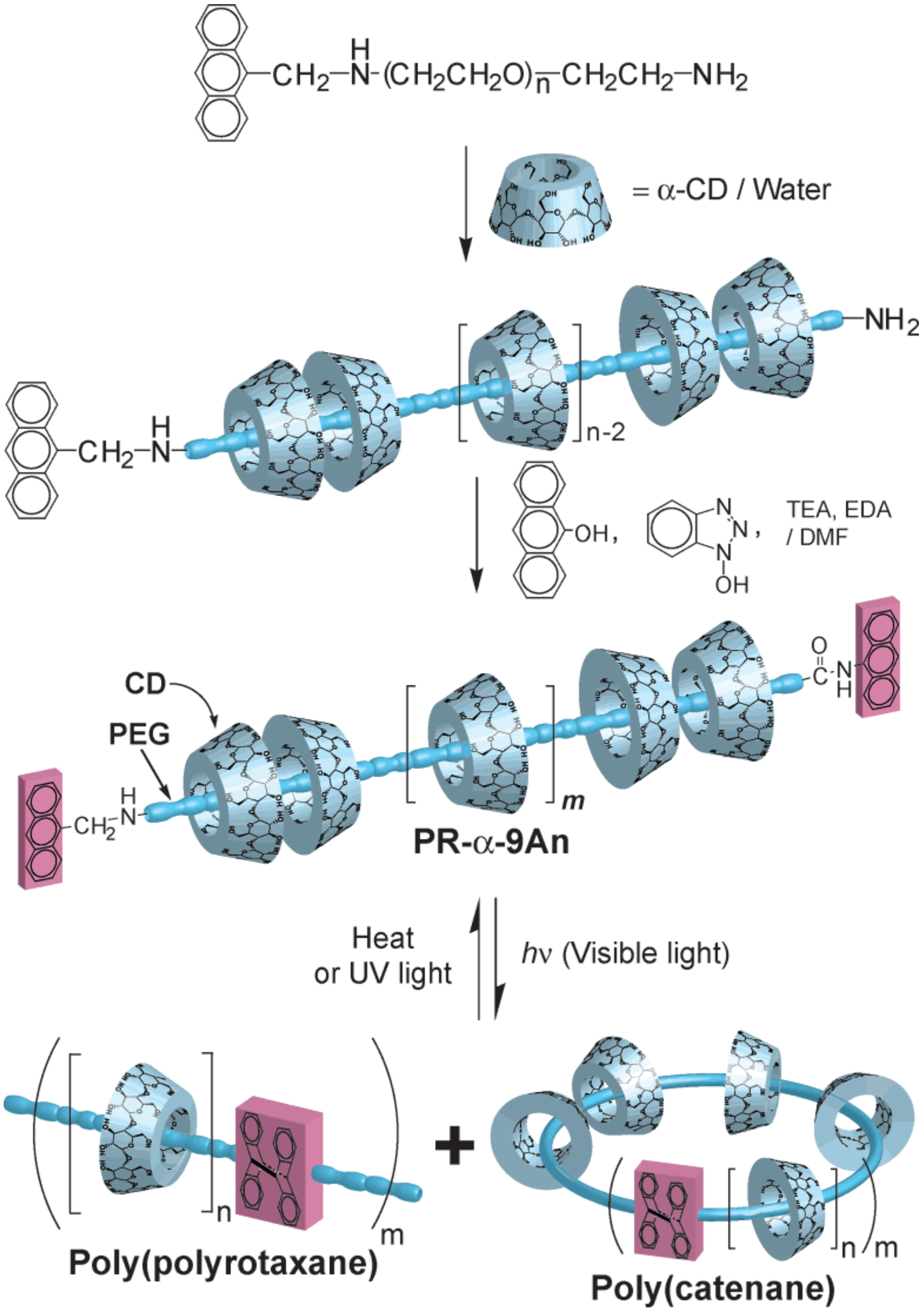
Scheme 1. Preparation of PR-α-9An and Poly(polyrotaxane) by Photoreaction of PR-α-9An



Xe lamp with UV cutoff filter) under an Ar atmosphere, the product was precipitated out. The ^{1}H NMR spectrum of the product showed broad signals of α-CD and PEG and the absence of the signals of monomeric 9An. Characteristic absorption and emission bands of 9-anthracene monomers have completely disappeared. The elution diagrams of the photoreaction product of PR-α-9An3350 showed a broad peak at the M_w of more than 1 million, indicating that photoirradiation of PR-α-9An3350 gave polymers of polyrotaxane of molecular weight higher than 1 million. When the photoreactions were carried out in dilute solution (7×10^{-3} mM), the absorption and emission bands of the 9-anthracene monomer disappeared after 3 days (Figure 1). The DMSO solution was evaporated to dryness, and the products were purified using DMSO−methanol and DMSO−water systems (yield >70%). The elution diagram of the photoreaction product of PR-α-9An3350 showed two peaks: one at the oligomers region whose polymerization degree is in the range 2−10 and the other at similar elution time to that of PR-α-9An3350. The ^{1}H NMR spectrum of the product is similar to that of PR-α-9An3350, except for the absence of the ^{1}H NMR peaks of 9An groups (Figure 2). The proposed structures of the products, poly(polyrotaxane) and poly(catenane), are shown in Scheme 1.

When the DMSO solution was kept at 120 °C after irradiation, the UV−vis and fluorescence spectra showed that the anthracene monomer came back again in more than 90% conversion. These spectral changes showed

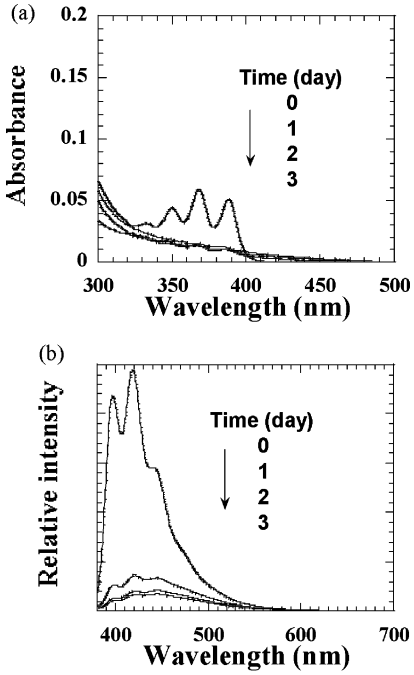


Figure 1. Changes of UV−vis (a) and flurescence (b) spectra of PR-α-9An3350 on irradiation of visible light (>340 nm). Ex = 370 nm.

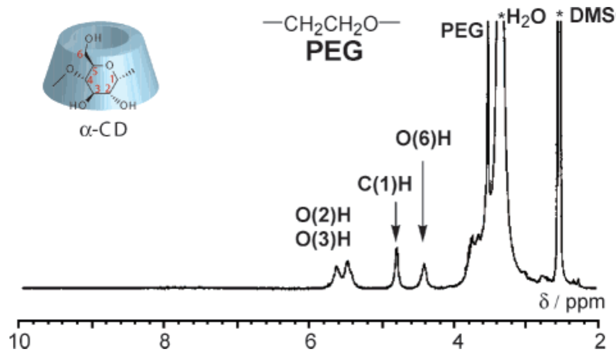


Figure 2. ^{1}H NMR spectrum of photoreaction product of PR-α-9An3350 in DMSO-d_6 at 30 °C.

that the reversible photodimerization and dissociation of 9An end groups took place.

In conclusion, we have succeeded in achieving reversible conversion of novel supramolecular structures from polyrotaxane to poly(polyrotaxanes) using both complexation between PEG and α-CD and reversible photodimerization of 9-anthracene moieties at PR-α-9An3350 ends. The detailed structures of the products are now under investigation.

Supporting Information Available: ^{1}H NMR, ^{13}C NMR, and SEC elution diagram of PR-α-9An3350 and poly(polyrotaxane). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Preparation of PR-α−9An. PEG9An$_1$ (0.26 g = 7.3 × 10^{-2} mmol = 6.0 EG unit mmol) was added to 20 mL of α-CD aqueous solution (α-CD; 2.9 g = 3.0 mmol). The mixture was sonicated for 10 min and then allowed to stand overnight at room temperature to become turbid. The heterogeneous solution was freeze-dried and then dried under high vacuum. The α-CD-PEG9An$_1$ complex (3.2 g) and 9-anthracenecarboxylic acid (0.25 g = 1.1 mmol) were introduced into a round-bottom flask, and dried DMF (5.0 mL) was added dropwise. The mixture was cooled under vigorous stirring with an ice bath, and then HOBt (0.15 g = 1.1 mmol), triethylamine (TEA) (80 mg), and EDC (0.10 g) were added. The reactant was kept to stir for a day. DMF (50 mL) was added to the heterogeneous mixture, and then the product precipitated and was collected. The product was reprecipitated from DMSO−distilled water and DMSO−organic solvents, such as methanol and dichloromethane, and washed with DMF several times. The precipitate was dried under high vacuum at 80 °C for a day to give pure PR-α-9An. PR-α-9An3350**.** Yield: 5.3% (based on PEG9An$_1$3550). ^{1}H NMR (DMSO-d_6, 270 MHz): δ 9.0−6.8 (m, 18H, H of 9-anthracene), 5.63 (s, 6H × 19, O(2)H of α-CD), 5.51−5.42 (m, 6H × 19, O(3)H of α-CD), 4.80 (s, 6H × 19, C(1)H of α-CD), 4.46−4.42 (m, 6H × 19, O(6)H of α-CD), 3.8−3.1 (m, C(2)H, C(3)H, C(4)H, C(5)H, and C(6)H of α-CD), 3.51 (s, 4H × 76, methylene H of PEG). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 101.90 (C(1) of α-CD), 82.03 (C(4) of α−CD), 73.20 (C(3) of α-CD), 72.06 (C(5) of α-CD), 69.73 (C(2) of α-CD, and methylene C of PEG), 59.93 (C(6) of α-CD). IR (KBr, cm^{-1}): 3381 (vs, νOH), 2925 (s, νCH), 1158, 1081, 1031 (vs, νCO). Anal. Calcd for $(C_{182}H_{326}O_{76}N_2)_1(C_{36}H_{60}O_{30})_{19}(H_2O)_{45}$: C, 45.12; H, 6.80; N, 0.12. Found: C, 45.12; H, 6.78; N, 0.48. PR-α-9An2000**.** Yield: 0.30% (based on PEG9An$_1$2200). ^{1}H NMR (DMSO-d_6, 270 MHz): δ 9.0−6.8 (m, 18H, H of 9-anthracene), 5.63 (s, 6H × 22, O(2)H of α-CD), 5.50−5.42 (m, 6H × 22, O(3)H of α-CD), 4.80 (s, 6H × 22, C(1)H of α-CD), 4.45−4.43 (m, 6H × 22, O(6)H of α-CD), 3.8−3.1 (m, C(2)H, C(3)H, C(4)H, C(5)H, and C(6)H of α-CD), 3.51 (s, 4H × 45, methylene H of PEG). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 101.91 (C(1) of α-CD), 82.04 (C(4) of α-CD), 73.35, 73.21 (C(3) of α-CD), 72.07, 71.57 (C(5) of α-CD), 69.74, 69.51 (C(2) of α-CD, and methylene C of PEG), 59.94, 59.51 (C(6) of α-CD). IR (KBr, cm^{-1}): 3411 (vs, νOH), 2925 (s, νCH), 1154, 1078, 1027 (vs, νCO). Anal. Calcd for $(C_{120}H_{202}O_{45}N_2)_1(C_{36}H_{60}O_{30})_{22}(H_2O)_{107}$: C, 42.58; H, 6.80; N, 0.11. Found: C, 42.57; H, 6.45; N, 0.54.

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