Synthesis of Main-Chain-Type Polyrotaxane by Polymerization of Homoditopic [2]Rotaxane through Mizoroki−Heck Coupling

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Introduction

Polyrotaxanes,[1–18] a novel class of polymers containing mechanical linkages consisting of wheel and axle components, are expected to display unique properties such as mechanical and rheological ones. A variety of main-chain-type polyrotaxanes with the polymer axles as the main chains have been reported so far.[19–23] We have also studied main-chain-type polyrotaxanes[24–26] in addition to side-chain-type ones.[27,28] Meanwhile, little is known about polyrotaxanes having the polymacrocycle main chains among a lot of main-chain-type polyrotaxanes, although networked polyrotaxanes involving the wheel components in the main chains have been reported.[29–34] Gibson et al. first proposed the structures of such main-chain-type polyrotaxanes and the approaches to their syntheses.[1] It is of significance to synthesize novel types of polyrotaxanes for the pioneering development of novel polymer properties. There are two ways of synthesizing this kind of main-chain-type polyrotaxane: one goes through initial rotaxanation followed by its polymerization (route A), and the other undergoes initial polymerization of wheel followed by rotaxanation of the resulting polymer (route B), as shown in Figure 1.[3,10,15] We have recently succeeded in synthesizing a polyrotaxane and a polyrotaxane network with polymacrocycle main chains by the polymerization−rotaxanation protocol (route B).[35]

We describe herein the synthesis of main-chain-type poly[2]-rotaxanes by polycondensation via the Mizoroki−Heck coupling[36] of a homoditopic diviynyl-functionalized [2]rotaxane and dihaloarenes, according to the rotaxanation−polymerization protocol (route A).

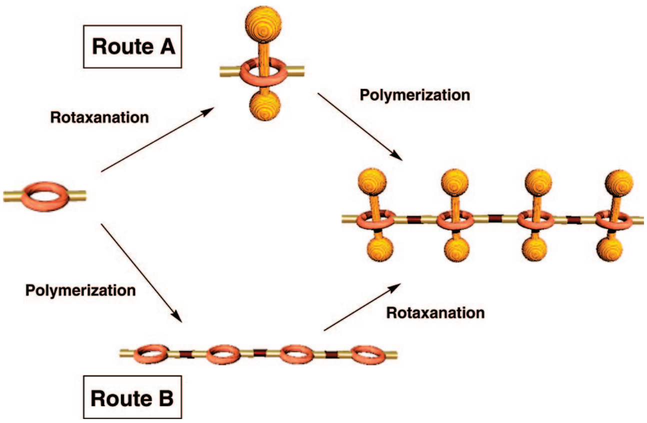

Figure 1. Synthetic strategy for main-chain-type polyrotaxanes.[1]

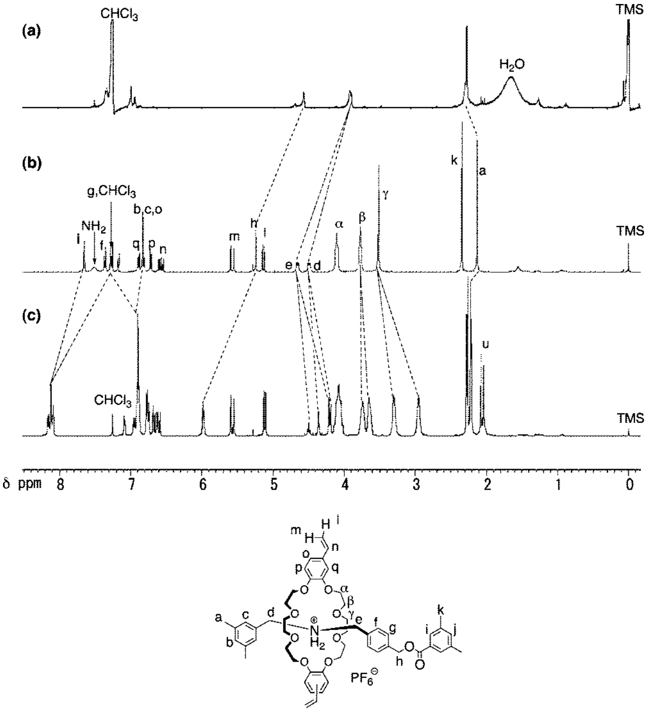

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Figure 2. ^{1}H NMR spectra (400 MHz, CDCl$_3$, 298 K) of (a) axle component **2a**, (b) [2]rotaxane **3**, and (c) *N*-acetylated [2]rotaxane **4**. The signal u denotes that of *N*-acetyl methyl protons of **4**.

Synthesis of [2]Rotaxane Monomer 4

Divinyl-functionalized dibenzo-24-crown-8-ether wheel **1** was prepared from diformyl DB24C8[37] by the Wittig reaction. Treatment of diformyl DB24C8 with triphenylphosphonium methylide in CH$_2$Cl$_2$ afforded **1** as a regio-isomeric mixture in 87% yield. The structure of **1** was fully characterized by IR, ^{1}H NMR, ^{13}C NMR, and MS spectra.

[2]Rotaxane **3** was synthesized according to the acylative end-capping protocol[38,39] by treating a mixture of **1** as a wheel component and *sec*-ammonium salt **2a** as an axle component with 3,5-dimethylbenzoic anhydride as an end-capping agent in the presence of a catalytic amount of tributylphosphine (Scheme 1). White solid product **3** was obtained in 72%. Comparison of the ^{1}H NMR spectrum of **3** in CDCl$_3$ with that of the axle component **2a** (Figure 2) confirms the interlocked structure of **3**. The most significant characteristics in the spectra are the signals of the benzylic protons neighboring the *sec*-ammonium group of the axle (H$_d$ and H$_e$), which are largely downfield-shifted (from 3.91, 3.90 to 4.67, 4.51 ppm) by the rotaxanation. The clear downfield shift can be explained by the generation of the CH−O interaction of the benzylic protons[39–43] by the complexation with the crown ether wheel. The signal of methyl protons on the phenyl ring of the axle (H$_h$) is shifted upfield because of the shielding effect of the benzene ring of the crown ether wheel.

The treatment of **3** with acetic anhydride and triethylamine gave *N*-acetylated [2]rotaxane **4**, a divinylic monomer, in 71% yield (Scheme 1), in good accordance with the reported result.[39,44–47] In the ^{1}H NMR of **4** (Figure 2), the signal of the ester benzylic methylene protons (H$_h$) showed a large downfield

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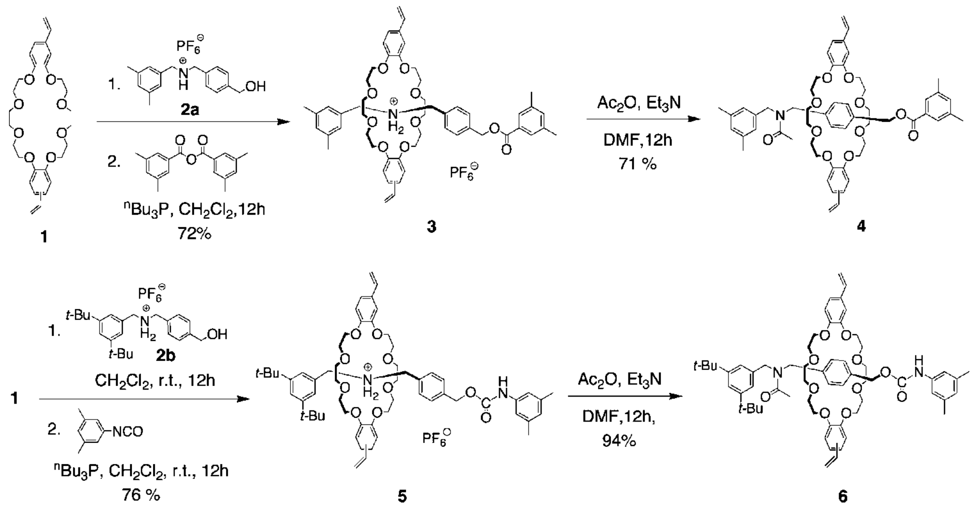
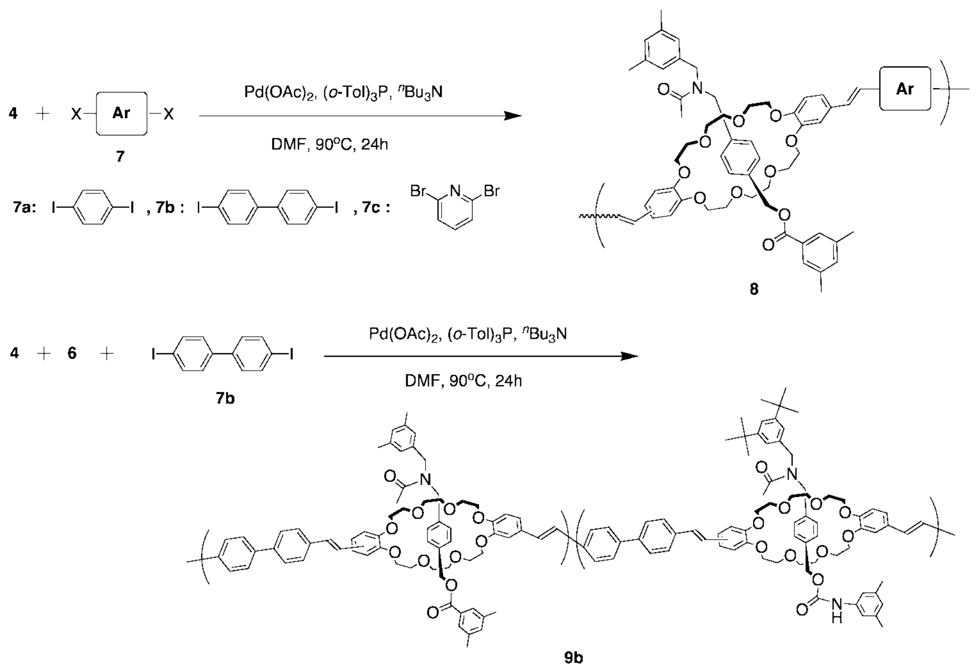
Scheme 1. Synthesis of [2]Rotaxane Monomers



Scheme 2. Polymerization and Copolymerization of [2]Rotaxane Monomer with Dihaloarene



shift from 5.24 to 5.98 ppm, being most indicative of rotaxane structure, because the crown ether wheel moved from being around the ammonium group to the ester bonding site. Two split signals of benzylic protons (H$_d$ and H$_e$) neighboring to the nitrogen would be attributed to the *syn*−*anti* stereoisomerism of the amide group formed by the acetylation, but not to the diastereotopic relation caused by the asymmetric nitrogen atom. Thus, all proton signals including vinylic signals of **4** other than the aromatic signals are assignable as those consistent with the proposed rotaxane structure.

tert-Butyl-substituted rotaxane monomer **6** was similarly obtained in 70% yield from *tert*-butyl-substituted *sec*-ammonium salt **2b** as an axle and **1** via the urethane end-capping of **5** using 3,5-dimethylphenyl isocyanate, which was developed by Takata et al. (Scheme 1).[48]

Polymerization

Since the Mizoroki−Heck coupling[36] is a widely used carbon−carbon bond forming reaction catalyzed by Pd^0 between aryl halides and olefinic compounds in the presence of a hindered amine, this coupling reaction was chosen for the present polymerization. The main-chain-type polyrotaxane **8** was derived by the polycondensation through the Pd^0-catalyzed polycoupling of a homoditopic divinyl-functionalized [2]rotaxane monomer **4** and dihaloarenes **7** in DMF for 24 h in the presence of ^{n}Bu$_3$N (Scheme 2). The results are summarized in Table 1. Poly[2]rotaxanes **8** were obtained as solids in 83–98% yield by polymerization at 90 °C, but no polymer was formed at 60 °C. Each **8** showed a unimodal GPC profile, and the molecular weight of **8** was in a range of M_w 10–14 kDa with the molecular weight distribution of 2.1–4.5. Both the molecular weight and yield were not seriously dependent on the structure of the dihaloarenes, indicating the rather high reactivity of 2,6-dibromopyridine **7c** similar to other diiodoarenes **7a** and **7b**.

The structure of **8** was characterized by IR and ^{1}H NMR spectra other than GPC. In the FT-IR spectra it was confirmed that the characteristic vinyl absorption peak at 3075 cm^{-1} clearly decreased after the polymerization.[49] The ^{1}H NMR spectrum

Table 1. Polycondensation of [2]Rotaxane 4 and/or 6 with Dihaloarene 7 under the Mizoroki−Heck Coupling Condition[a]

entry	dihaloarene	[2]rotaxane monomer	temp (°C)	polymer	yield (%)	M_w[b] (kDa)	M_n[b] (kDa)	M_w/M_n[b]	T_g[c] (°C)	T_{d5}[d] (°C)	T_{d10}[e] (°C)
1	**7a**	**4**	60	**8a**	n.r.						
2	**7a**	**4**	90	**8a**	83	13	3.9	3.5	110	265	282
3	**7b**	**4**	90	**8b**	98	10	5.0	2.1	115	260	274
4	**7c**	**4**	90	**8c**	85	14	3.1	4.5	98	240	250
5	**7b**	**4**+**6**[f]	90	**9b**	76	9.8	3.5	2.8	59	245	263

[a] Polymerization conditions: [[2]rotaxane] = [dihaloarene] = 0.1 M, 48 h, 90 °C, in DMF. [b] Determined by GPC ($CHCl_3$, polystyrene standards). [c] Glass transition temperature obtained at a heating rate of 10 °C/min under nitrogen (N_2 flow rate: 50 mL/min) in the second scan. [d] 5% weight loss temperature obtained at a heating rate of 10 °C/min under nitrogen (N_2 flow rate: 50 mL/min). [e] 10% weight loss temperature obtained at a heating rate of 10 °C/min under nitrogen (N_2 flow rate: 50 mL/min). [f] The feed ratio of **4**:**6** was 50:50.

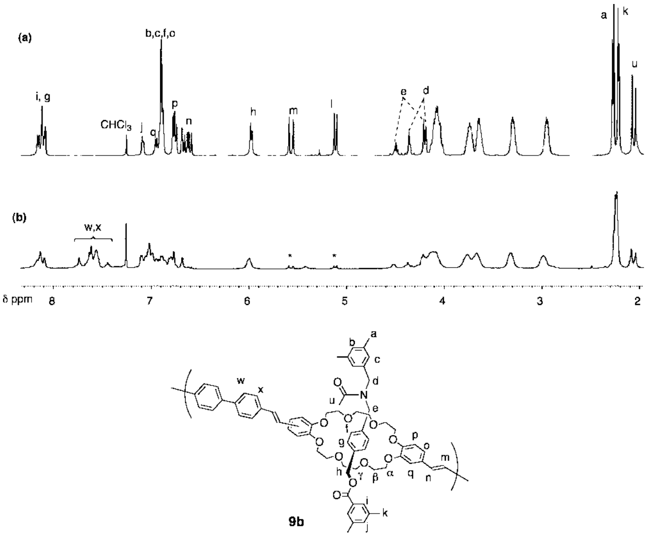


Figure 3. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) [2]rotaxane **4** and (b) poly[2]rotaxane **8b**. The signals * around 5.6 and 5.2 ppm denote the terminal vinyl proton signals of the polymer chain.

(Figure 3) is quite similar to that of the rotaxane monomer **4** except for the aromatic and vinylic signals, although most signals are broadened. Small vinylic methylene signals l and m appeared around 5.57 and 5.13 ppm and were attributed to the vinyl group of the polymer terminal end, which were significantly decreased by the progress of the polymerization. Detailed information on the DPs was obtained by the end-group analysis using ^{1}H NMR integration (Figure 3). The signal integration of the terminal vinyl protons (5.56 and 5.14 ppm) was compared with that of the methyl protons (2.26 and 2.21 ppm) of the end-capping groups. As a result, the average DPs of **8a**, **8b**, and **8c** were estimated to be 8.0, 8.0, and 10.0, i.e., M_n values of 4, 4.3, and 5 kDa, which are comparable with the GPC data of 3.9, 5, and 4.5 kDa, respectively (Table 1).

Copolymerization

From viewpoint of control of polymer structure, synthesis of copoly(phenylenevinylene) was examined using a mixture of two [2]rotaxane monomers.[49] A mixture of **4** and **6** was subjected to the poly(Mizoroki−Heck) coupling with 4,4′-diiodobiphenyl **7b** under the same conditions as the above polycondensation. The copolymer **9b** was obtained in 76% yield (Table 1, entry 5). From the IR and ^{1}H NMR spectra of **9b**, similar to those of poly[2]rotaxane **8b**, in addition to the comparison with those of **4** and **6**, it was concluded that the copolymerization successfully proceeded to give the corresponding copolymer with a composition ratio of 50:50 for **4** and **6** (Supporting Information, Figure S1). M_w of **9b** was 9.8 kDa with MWD 2.8. The similar reactivity of **4** and **6** along with the above composition ratio seems to suggest the production of a random copolymer. Since many other divinyl monomers including a macrocyclic one like **1** can be used as a comonomer in this reaction system, the present results suggest that the axle content in the repeating units (or degree of rotaxanation) of poly[2]rotaxane can be readily controlled by either use of comonomer and by change in feed ratio of comonomers.

Properties of Poly[2]rotaxanes 8 and 9

All main-chain-type poly[2]rotaxanes **8** and **9** thus obtained were soluble in ordinary organic solvents such as dichloromethane, chloroform, and THF but insoluble in methanol and *n*-hexane. On the basis of their high solubility, transparent polymer films could be prepared on a glass by casting from their chloroform solution, although no strong self-standing film was obtained, probably due to the low degree of polymerization. Thermal properties of these polyrotaxanes were evaluated by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC). Good thermal stability was confirmed from the 5% weight loss temperature of **9** and **10** ranging from 240 to 265 °C (Table 1). Thermal events around the temperature range of 98–119 °C as observed by DSC for **8** during the heating scans could be attributed to the glass transitions (T_g). On the other hand, the T_g of copolymer **9b** (59 °C) was considerably lower than that of **8b** (115 °C), suggesting some increase in chain mobility probably by the introduction of the urethane rotaxane axle to the comonomer unit.

Thus, this paper has demonstrated the first synthesis of poly[2]rotaxanes **8** and **9** possessing the rotaxanated polymacrocycle structure in the main chain according to the rotaxanation−polymerization protocol. The polymerization was carried out by the poly(Mizoroki−Heck) coupling of bis(vinylphenyl)-functionalized wheel-containing [2]rotaxane **4** with dihaloarenens **7** such as diiodoarenes and dibromopyridine in the presence of a catalytic amount of $Pd(OAc)_2$ to yield poly(phenylenevinylene)-type polymers **8**. The main-chain-type poly[2]rotaxanes **8** obtained in high yields showed a molecular weight range of M_w 10–14 kDa with molecular weight distributions of 2.1–4.5, whereas film-forming property based on their good solubility in ordinary organic solvents was confirmed, in addition to their good thermal stability. The advantage of this synthetic method made possible the preparation of copolymer **9b**, which contained two kinds of [2]rotaxane monomer units (**4** and **6**), enabling the possible control of the polymer structure. Thus, the present synthesis of the main-chain-type polyrotaxanes based on the rotaxanation−polymerization protocol provides one of the general methods for polyrotaxane syntheses.

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Supporting Information Available: Experimental details and additional NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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