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Synthesis of Organic-Soluble Conjugated Polyrotaxanes by Polymerization of Linked Rotaxanes

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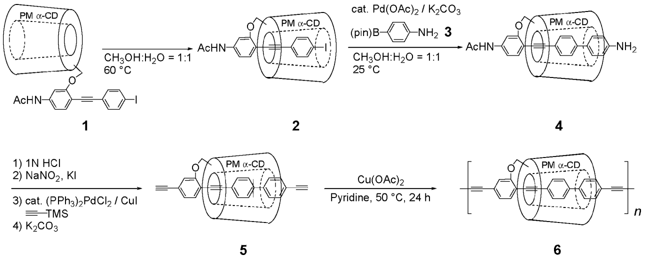
Insulated molecular wires (IMWs) have attracted considerable attention because of their potential applicability as next-generation monomolecular electronic devices.[1] Our objective is to develop organic materials for use in nanoscale molecular electronics by interconnection of nanoelectrodes via a chemical reaction with high reproducibility.[2] In order to accomplish this, we have attempted to synthesize IMWs with molecular structures that have the following ideal features: (1) a π-conjugated polymer chain with a high degree of insulation; (2) a rigid polymer chain with high linearity; (3) high solubility in organic solvents essential for simple liquid solution processes; and (4) high charge mobility. Extensive research on the use of cyclodextrin (CD) for insulating π-conjugated polymer chains has been carried out because of its commercial availability and its unique ability to form inclusion complexes with organic molecules via hydrophilic–hydrophobic interactions.[3] In one of the methods for synthesizing IMWs from CD, a solution of π-conjugated polymers is stirred in the presence of CD[4] using the method developed by Harada et al.[5] for the synthesis of a molecular necklace. Another method involves the polymerization of [2]-pseudorotaxanes generated in situ through the inclusion of conjugated monomers in CD[6] or copolymerization of [2]-pseudorotaxanes generated in situ with linker molecules.[7] However, these IMWs do not exhibit high and constant covering ratios and are generally insoluble in organic solvents.[8] Furthermore, they contain water molecules because of the hydrophilic nature of CD. Thus, their potential for use as an electronics material is reduced. Recently, we reported synthetic routes to linked rotaxanes bearing a π-conjugated system as the guest and permethylated (PM) α-CD as the host.[9] Herein, we report new methods for synthesizing polyrotaxanes (IMWs) through the polymerization of linked rotaxanes as the monomers.

An organic-soluble [1]-rotaxane **4**, also classified as a linked [2]-rotaxane, was synthesized by our previously reported method based on intramolecular self-inclusion of a π-conjugated linear guest unit into a lipophilic PM α-CD moiety in a hydrophilic solution.[9a] Intramolecular self-inclusion of **1** in 1:1 CH_3OH/H_2O formed **2**, and **4** was obtained by subsequent capping with a stopper, **3** (Scheme 1). Crystals of **4** were grown from a mixture of DMSO and H_2O. The X-ray structure (lateral and top view) of **4** is shown in Figure 1. It is apparent that the PM α-CD moiety has been displaced from the tolan core and that the π-conjugated guest is almost planar, while slight torsion is observed around its main axis. Studies performed using space-filling models revealed that the covering ratio of PM α-CD in the π-conjugated backbone of **4** was ~60%. The acetamide and amino groups of **4** were converted to ethynyl groups in four steps to yield the linked [2]-rotaxane monomer **5**. Glaser polymerization of **5** was then carried out in the presence of $Cu(OAc)_2$ in pyridine at 50 °C. Results of time-course studies and gel-permeation chromatography (GPC) revealed that **5** was completely consumed after 24 h. The mass-averaged molecular weight (M_w) and polydispersity index (PDI) of the linked [2]-rotaxane polymer **6** were estimated to be 3.88×10^4 and 2.01, respectively, using polystyrene as the calibration standard in the analysis. The average degree of polymerization (n) was found to be 25, indicating that the average contour length along the extended rodlike chain is 50 nm.

Scheme 1. Synthesis of PM α-CD-Based Polyrotaxane **6** by Polymerization of Organic-Soluble Linked [2]-Rotaxane Monomer **5**



As shown in Figure 2, the peaks in the ^1H NMR spectrum of **6** were broader than those in the NMR spectrum of **5**, indicating that the rotaxane structure was maintained during polymerization. The MALDI-TOF mass spectrum of **6** provided additional evidence for the structural authenticity of this compound. As expected, all of the

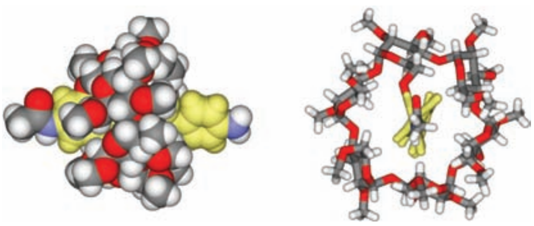


Figure 1. Lateral (space-filling model) and top (stick model) view of **4**.

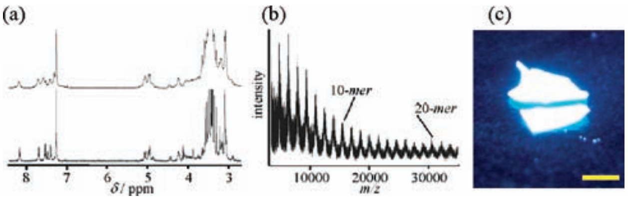


Figure 2. (a) ^1H NMR spectra (400 MHz, $CDCl_3$) of (bottom) **5** and (top) **6**. (b) MALDI-TOF mass spectrum of **6**. (c) Fluorescence micrograph of **6** (yellow scale bar: 1 mm).

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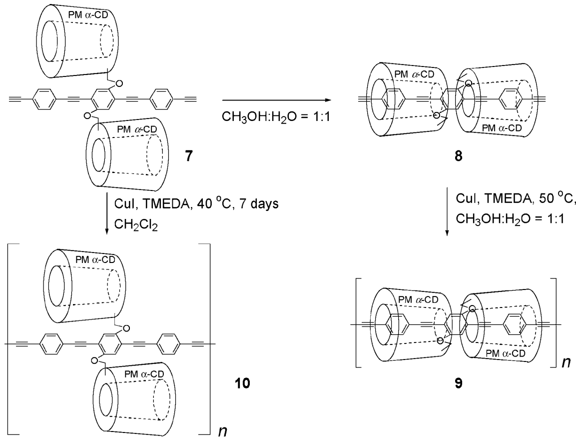
observed peaks in the mass spectrum correspond to singly charged molecular ions containing more than 20 repeating units. In addition, the rotaxane polymer was found to be soluble in various organic solvents such as ethyl acetate, chloroform, toluene, and DMF. The absolute photoluminescence (PL) efficiency of **6** in the solid state was measured to be 14% using an integrating sphere system.

In order to increase the covering ratio and structural regularity of the IMWs, we employed linked symmetrical [3]-pseudorotaxane **8** as the monomer.[9b] The formation of **8** by sequential intramolecular self-inclusion of **7**, a phenylene−ethynylene oligomer having two PM α-CDs, was confirmed from the ^{1}H NMR spectra recorded under the same conditions as in the case of the following polymerization (1:1:0.1 CD_3OD/D_2O/TMEDA, 50 °C). From the CPK model of **8**, the covering ratio was estimated to be ∼95%. Subsequently, Glaser polymerization of **8** was carried out in the presence of CuI. Although the polymerization of **8** was markedly slower than that of **5** because of the high coverage of the former, linked polyrotaxane **9** ($M_w = 5.77 \times 10^4$, PDI = 1.51, $n = 21$) was formed, as confirmed by GPC and MALDI-TOF mass spectroscopy. In order to examine the covering effect of PM α-CD, the uncovered polymer **10** ($M_w = 5.64 \times 10^4$, PDI = 1.34, $n = 21$) was synthesized as a reference via polymerization of **7** in CH_2Cl_2 instead of 1:1 CH_3OH/H_2O solution. The absolute quantum yields of **9** and **10** were determined using a calibrated integrating sphere system. The fluorescence quantum yields of **9** ($\Phi_{solution} = 0.64$, $\Phi_{solid} = 0.23$) revealed that its fluorescence efficiency was better than that of **10** ($\Phi_{solution} = 0.58$, $\Phi_{solid} = 0.06$), particularly in the solid state.

Scheme 2. Syntheses of the Fully Covered Polymer **9** and the Uncovered Polymer **10** by Polymerization of **7** in Different Solvents



Polyrotaxane **9**, in which numerous PM α-CDs are threaded onto the main chain, has the potential to exist in a chiral liquid-crystalline (LC) phase because of its rigidity and chirality, which result from the covering effect of the PM α-CDs. However, a LC polyrotaxane derived from main-chain rigidity has not been reported to date, although the LC properties of mesogenic pendants covalently linked to such a polyrotaxane have been reported.[10] In order to evaluate the rigidity of **9** and **10**, the persistence lengths (q) were estimated from the intrinsic viscosities of the solutions using the unperturbed wormlike cylinder model of the Yamakawa−Fujii−Yoshizaki theory (Figure S1 in the Supporting Information).[11] The calculated q values of **9** and **10** were 14.4 and 5.7 nm, respectively, indicating that the rigidity of the main chain in **9** can be largely attributed to the intramolecular inclusion of the polymer main chain into the PM α-CD cavity. Figure 3 shows a polarized optical micrograph of **9** in a concentrated $CHCl_3$ solution. It should be noted that **9** forms a cholesteric phase, as confirmed from its indisputably clear fingerprint texture, while **10** forms only an isotropic liquid even at high concentrations. The observed cholesteric phase can be attributed to the presence of PM α-CD in **9**, as a nematic LC phase should be observed if a polymer chain threads through achiral macrocycles. To the best of our knowledge, this is the first report of the formation of a cholesteric LC phase whose chirality originates from the inclusion of the polymer main chain into the CD cavity. Both **9** and **10** with the aforementioned global conformations successfully solidify into films upon evaporation of the solvent from the solution (Figure S2). The striking difference in the birefringence of these films indicates that **9** forms an anisotropic phase in concentrated solutions because of the rigidity of its main chain, which in turn is a result of the covering effect of PM α-CD.

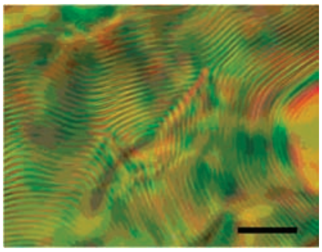


Figure 3. Polarized optical micrograph of **9** in $CHCl_3$ solution (∼15 wt %) sealed in a glass capillary tube; the micrograph was obtained at 25 °C under crossed polarizers. The LC phase was separated from the isotropic phase in equilibrium, and its cholesteric pitch was maintained for more than 3 months. Black scale bar: 50 μm.

In conclusion, we have developed a new method for synthesizing polyrotaxanes (IMWs) through the polymerization of structurally defined rotaxane monomers. The IMWs thus formed have a high covering ratio, rigidity, and PL efficiency; furthermore, they are readily soluble in a variety of organic solvents.

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Supporting Information Available: Experimental procedures, compound characterization data, and crystallographic data for **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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