Dual Polyrotaxane: One-pot Synthesis of Topological Polymer by Using Metathesis Reaction

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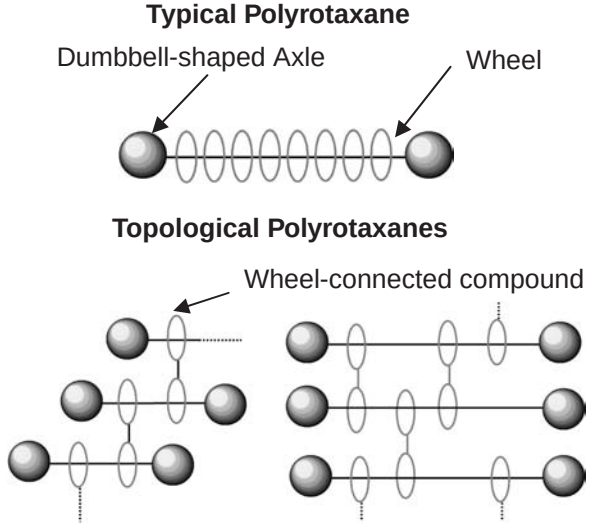
The topological polyrotaxane was built from an ammonium salt as an axle component bearing one olefin and one bulky unit at the end of chain and the derivative of dibenzo-24-crown-8 (DB24C8) as a wheel component having one terminal olefin. In this system, two kinds of reactions work at the same time as a driving force of the polymer construction. One is the inclusion reaction between the ammonium salt part of axle and the wheel, another is metathesis reaction between olefins of the axle and olefins of the wheel.

Rotaxane has many possibilities in some fields of electronic devices, medical materials, etc.[1] Moreover, interlocked polymers such as topological polyrotaxanes are capable of exercising new physical properties, in contrast with low-molecular-weight rotaxanes and rigid polyrotaxanes.[2] In these topological polyrotaxanes, the wheel-connected compound takes some axles into the interior cavities as shown in Scheme 1. Therefore, topological connections made by wheel components allow included axles to move freely, unlike the rigid and typical polyrotaxane.

This time, we paid attention to the unique and simple synthetic method of the above topological polyrotaxanes. In syntheses of reported topological polyrotaxanes, the wheel-connected compound and the dumbbell-shaped axle compound are separately synthesized, and then these components are made to react in the same container to give topological polyrotaxanes, using the slipping method or the entering method.[2b–d] The other way is that wheels in typical polyrotaxanes prepared by capping ends of pseudorotaxanes are cross-linked.[2a] In these methods, because these components have different reaction groups between a wheel and an axle, the methods demand a lot of procedures to synthesize topological polyrotaxanes.



Scheme 1. Illustration of the typical rotaxane and topological polyrotaxane structures.

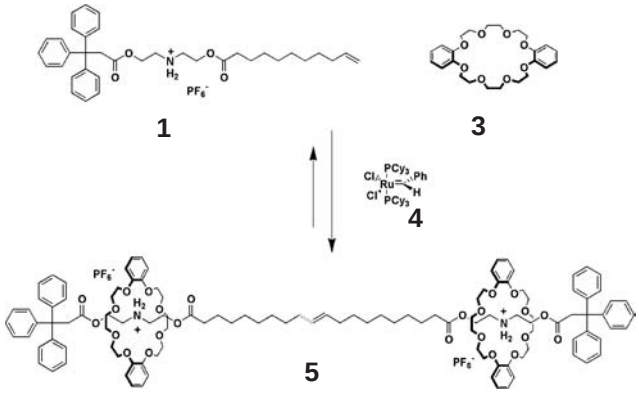
In this paper, we report on the one-pot synthesis of the topological polyrotaxane consisting of the non-dumbbell-shaped axle component, which is the ammonium salt **1** bearing one terminal olefin and one terminal bulky unit, and the modified dibenzo-24-crown-8 (DB24C8) **2** having one olefin chain as a wheel by metathesis reaction.

To understand the basic structure of our aimed polyrotaxane, we synthesized the model compound, as shown in Scheme 2.

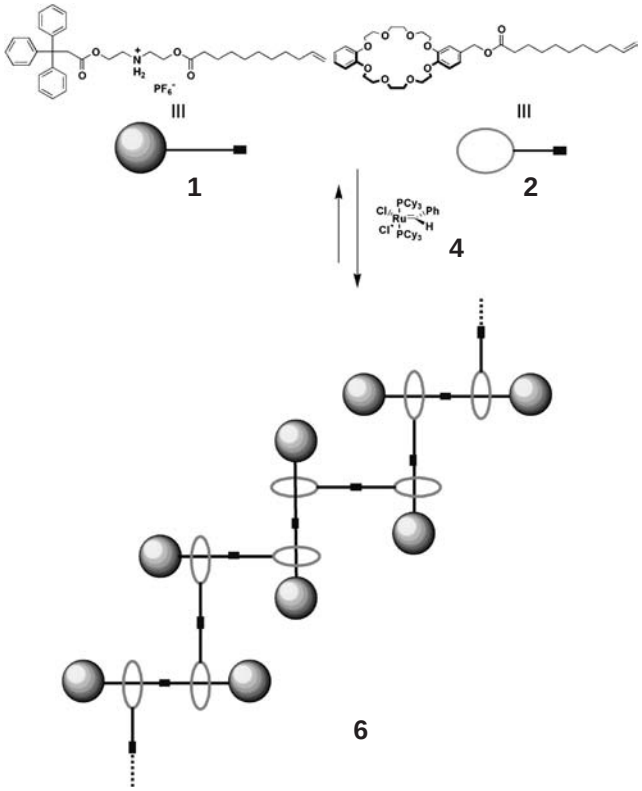
A catalytic amount of the ruthenium complex **4**[3] was added to a solution of the axle **1** and the wheel **3** in CH_2Cl_2 at room temperature. After 24 h, a few drops of ethyl vinyl ether were put in the solution, and then the solution was stirred at room temperature. The solution was evaporated and the resulting residue was purified by precipitation into MeOH to afford [3]rotaxane **5** as pale purple solid.

In a manner similar to synthesis of **5**, the desirable topological polyrotaxane **6** was synthesized by heating the mixture of **1**, **2**, and **4** in $CDCl_3$ as shown in Scheme 3.[4] After 85 h, a few drops of ethyl vinyl ether were put in the solution, and then the solution was stirred at room temperature. Then, the solution was evaporated to give the crude product as a viscous liquid. The structure of the product was analyzed by ^{1}H NMR spectroscopy and GPC measurement. The ^{1}H NMR profile of the product consisting of **1** and **2** represented broad signals. In addition, the methylene protons neighboring the ammonium salt unit displayed the downfield shift and the spectrum was similar to one of rotaxane **5** consisting of **1** and **3**.[5] These results present that a topological polyrotaxane was constructed by the inclusion reaction and metathesis reaction.

Moreover, the GPC measurement clearly revealed that the



Scheme 2. Syntehsis of [3]rotaxane **5** by metathesis reaction.



Scheme 3. Synthesis of topological polyrotaxanes **6** by metathesis reaction.

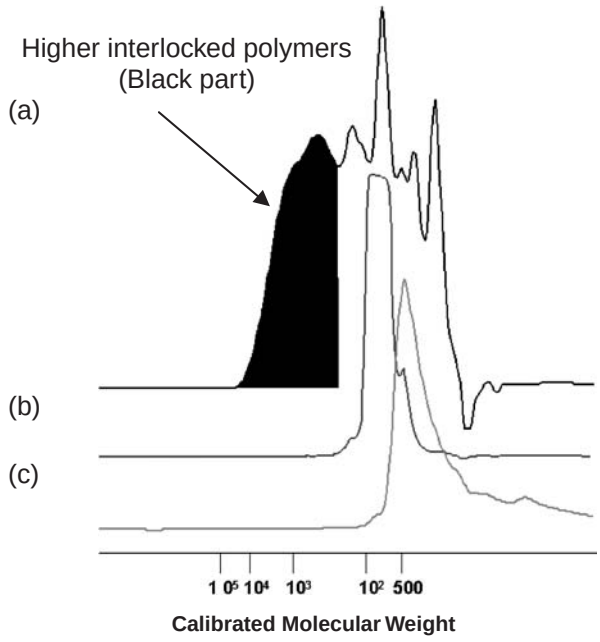


Figure 1. GPC (THF) profiles of (a) **6**, (b) **2**, (c) **1**.

system had made up a topological polyrotaxane (Figure 1). The GPC (THF) profile of the products was observed as a multimodal curve (Figure 1a).

M_n of rotaxane components **1** and **2** were respectively estimated to be ca. 330 (fw: 702) and ca. 600 (fw: 645) by polystyrene standards. Based on these data, the GPC profile of the

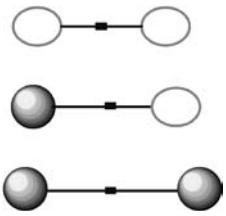


Figure 2. Illustration of proposed dimers in the topological polyrotaxane **6**.

product clearly indicates that a new compound exists besides original materials. In addition, the compound has a higher molecular weight than original materials. In particular, M_n of the black part in Figure 1 was estimated to be ca. 4800 with the polystyrene standard. The obtained value is much bigger than those of **1** and **2**. Therefore, these results suggest that the product in the higher molecular weight part surely has a topological structure, where **1** and **2** are utilized for the construction of polymer **6** by the inclusion reaction with hydrogen bonding and by the metathesis reaction.

In conclusion, we succeeded in the one-pot synthesis of a topological polyrotaxane with (1) inclusion reaction between the ammonium salt unit of the axle and the ether ring of the wheel, and (2) metathesis reaction between the terminal olefin of axle and the olefin of wheel. In this system, we think that the polyrotaxane **6** was built with three kinds of dimers (see Figure 2) consisting of **1** and **2**, which were slotted in the topological structure at random. This synthetic strategy is a new report to synthesize a topological polyrotaxane by one-pot. We are investigating on further development of the topological polyrotaxane now.

References and Notes

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4 We observed the formation complex between the axle **1** and the equimolar wheel **2** in various concentrations of the axle (0.05, 0.1, and 0.2 mol/L) by ^{1}H NMR spectroscopy. As a result, all samples showed 90–95% of the inclusion complex. In addition, to the synthesis of **6** in higher concentration (0.7 mol/L), an insoluble product separated out from the homogeneous solution. The resulting product may be a large cyclic polymer consisting of **1** and **2**.

5 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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