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Communications to the Editor

Bridged Polycatenane

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Polycatenane (Figure 1a) is a polymer consisting exclusively of macrocyclic components interlocking each other.[1] Several strategies to prepare polycatenane have been proposed, but none has so far been successful, although various poly[2]catenanes and oligocatenanes have been reported.[2,3] The synthesis of polycatenane is quite a challenging task because polymerization needs to proceed through cyclization. There is currently no known polymer with a polycatenane skeleton.[4] Most previous synthesis attempts were based on the polycyclization of preorganized macrocycle precursors,[1a,e] where cyclization is carried out by kinetic control and through which polycatenane production is impossible due to the unavoidable formation of noncyclized byproducts. Recently, simple [2]- and oligocatenanes have been synthesized using the thermodynamic control approach.[5,6] However, the expansion of the thermodynamic approach to polycatenane synthesis has so far also been unsuccessful because linear polymer is not in the most thermodynamically stable form under cyclization conditions. For the synthesis of polycatenane to be successful, continuous reactions of quantitative cyclization at high concentrations are necessary. We therefore chose a concerted cyclization reaction, i.e., the Diels−Alder reaction, which is suited for the construction of a polycatenane skeleton. In this paper, we wish to report the synthesis of "bridged polycatenane" that is a polycatenane in which each ring component was bridged by covalent bonds (Figure 1b). The bridged polycatenane obtained in this paper is the first polymer with a polycatenane skeleton.

For Diels−Alder polymerization, the catenane monomer should possess both a diene and a dienophile functional group on each ring. We reported previously that macrocycle **1** is a good precursor for the synthesis of catenane and rotaxane.[7] Two secondary amide groups of **1** assist the formation of the interlocked structure by drawing on the intermolecular hydrogen bonding interaction, whereas the sulfolene group acts as a masked diene moiety providing 1,3-diene via the elimination of SO_2 on heating.[8]

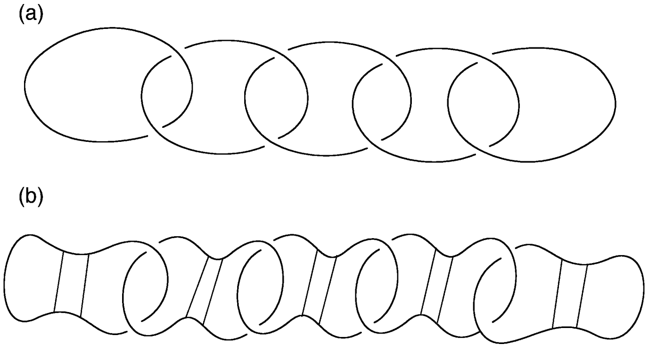

Figure 1. Schematic representation of (a) polycatenane and (b) bridged polycatenane.

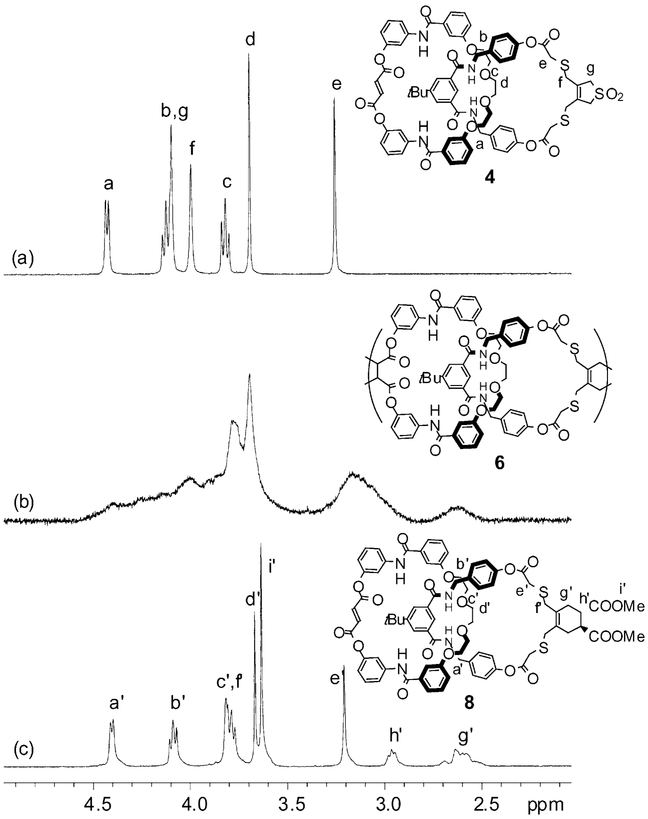

Figure 2. Partial ^1H NMR spectra (270 MHz, $CDCl_3$) of (a) [2]catenane monomer **4**, (b) bridged polycatenane **6**, and (c) Diels−Alder product **8**. The ^1H NMR spectrum of **6** was obtained at 60 °C to sharpen the signals.

Macrocyclizations using various diacid chlorides and diamines in the presence of **1** were investigated for the construction of a novel catenane monomer. As a result, **2** was found to be the most suitable diacid chloride in combination with an aromatic diamine. Therefore, the synthesis of a catenane monomer was investigated using **2** and diamine **3** having a dienophile moiety. The

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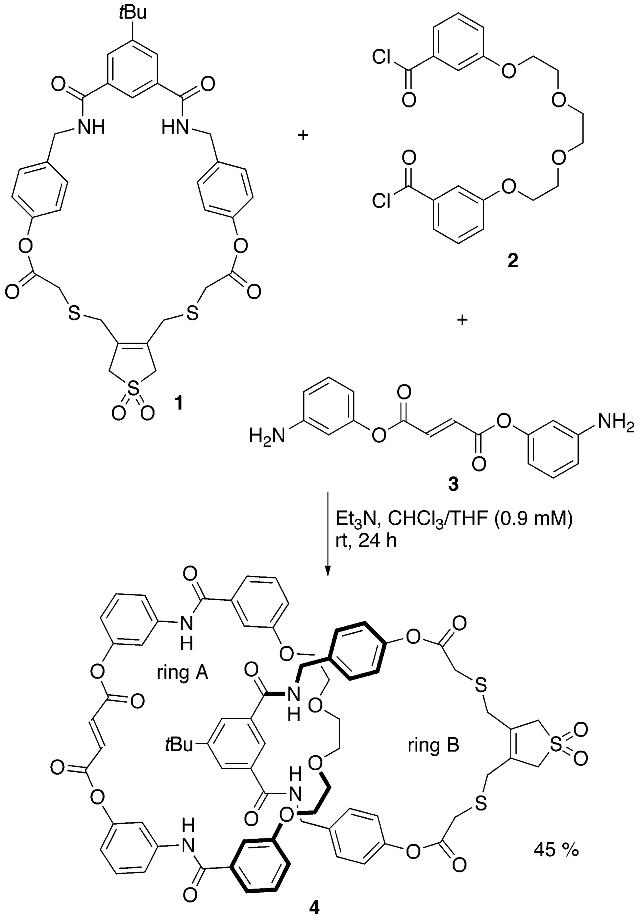
Scheme 1



macrocyclization of **2** and **3** was carried out in a chloroform−THF mixed solvent in the presence of **1** to give the desired [2]catenane **4** in 45% yield. The exceptionally high yield of **4** compared with that of similar secondary amide-based catenanes[9] seems to be the result of the effective hydrogen bonding ability of **1** and the flexible structure of **2**.

The catenane structure was fully confirmed by means of spectroscopic methods. The peak intensity of the ^{1}H NMR spectrum of **4** clearly suggests that **4** consists of rings A and B in 1:1 ratio (Figure 2a), which was supported by the elemental analysis. Some of the signals of rings A and B show characteristic upfield shifts as a result of the shielding effect by the aromatic rings on each macrocycle. The amide protons of ring A shifted to downfield due to hydrogen bonding. The sharp ^{1}H NMR signals observed in $CDCl_3$ suggest a rapid circumrotation of each catenane ring at the NMR time scale even in a nonpolar solvent.[10] The FAB-MS signals were also characteristic of a catenane structure: there was no fragment peak between $[M + H]^+$ (1375) and $[\text{ring A} + H]^+$ (653) (see Supporting Information). It should be noted that catenane **4** is very soluble in nonpolar organic solvents such as $CHCl_3$ and THF, although the component macrocycles are only slightly soluble in these solvents. This is because hydrogen bonding between the secondary amide groups of **4** takes place intramolecularly in the catenane structure.[9b,11]

The Diels−Alder polymerization of **4** was carried out by heating in 1,2-dichlorobenzene (1 M) or without solvent. On heating **4** at 140 °C for several hours, polymer **6** with a polycatenane skeleton was produced.

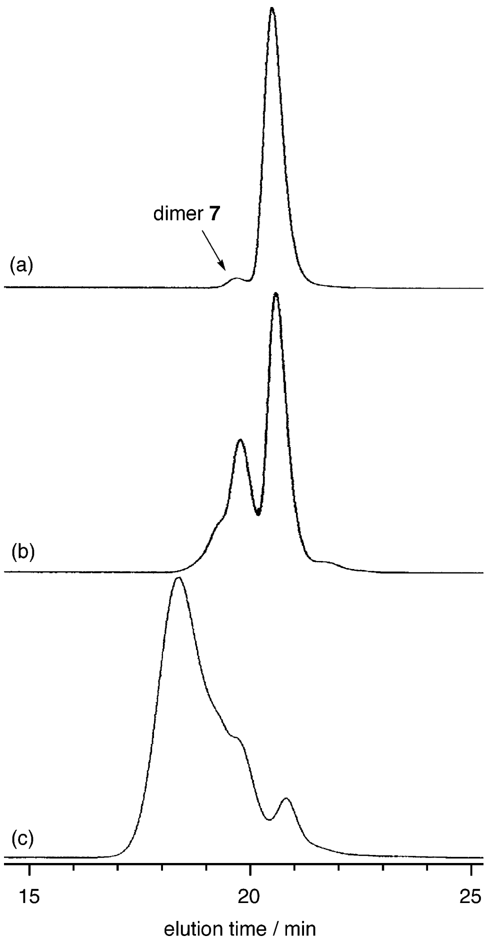
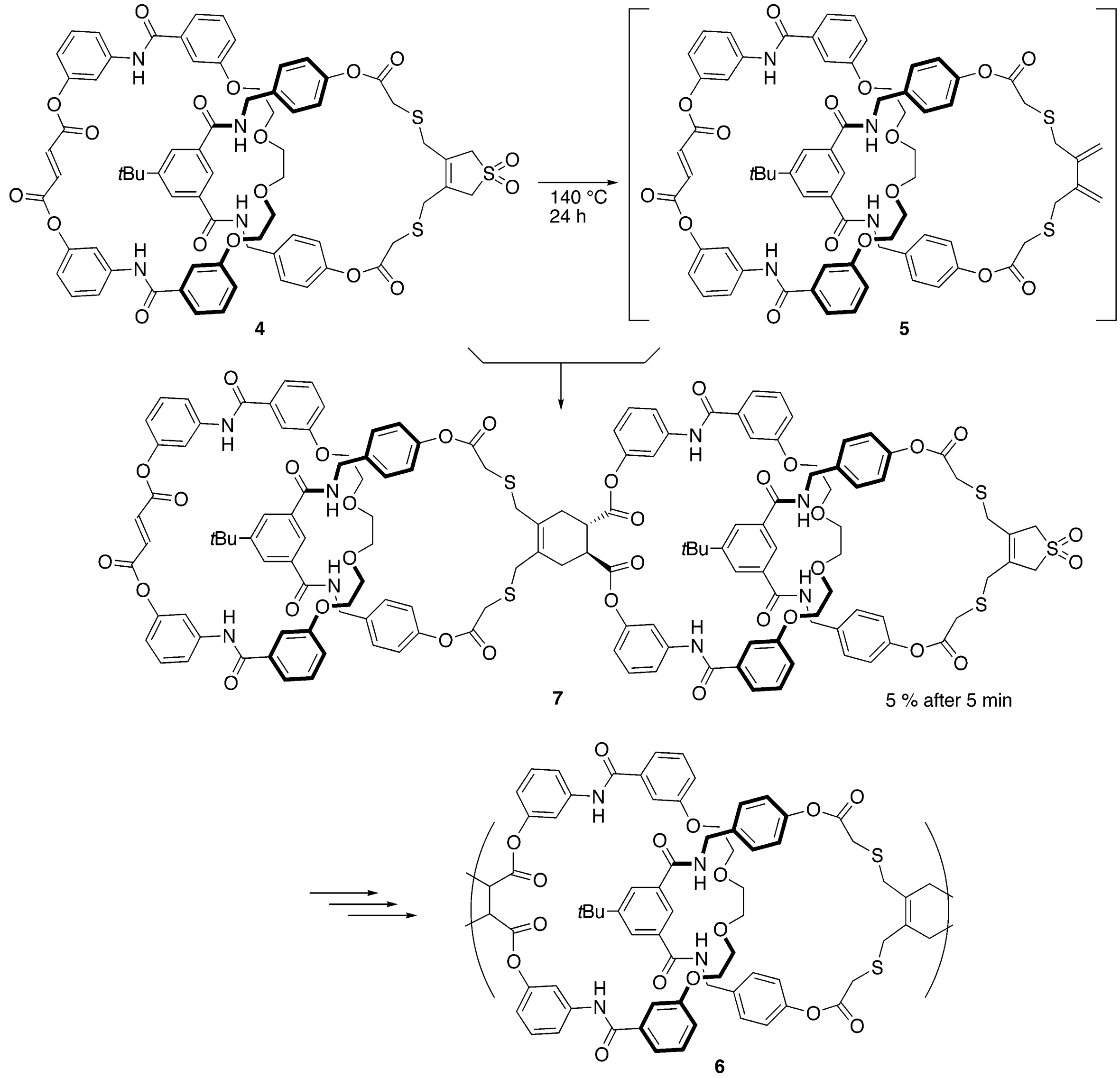


Figure 3. GPC profile ($CHCl_3$, PSt standards) in the course of the solid-state polymerization of **4** at 140 °C: (a) after 5 min at 140 °C, (b) after 10 min at 140 °C, and (c) after 24 h at 140 °C.

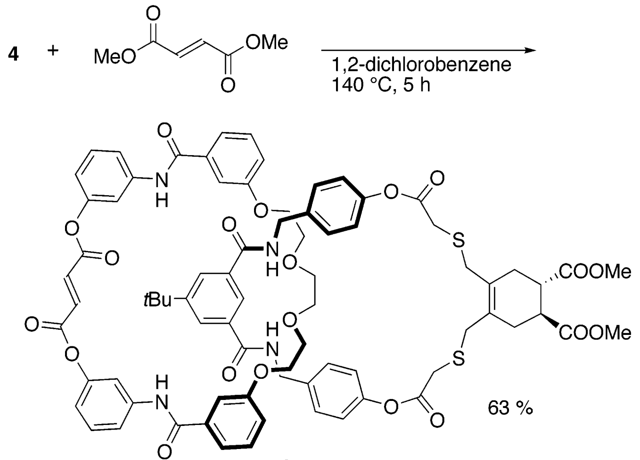
Polymerization involves the initial decomposition of the sulfolene moiety followed by the Diels−Alder reaction, as shown in Scheme 2. The elimination of SO_2 was easily confirmed by TGA analysis; when **4** was heated at a rate of 10 °C/min, the weight loss that started at 140 °C attained 5.0%, which was consistent with the theoretical value (4.7%). Polymer **6**, obtained in the form of a translucent solid, is equally soluble as **4** in various organic solvents.

The GPC analysis of the reaction mixture clearly indicates the progress of the polymerization, as shown in Figure 3. After heating at 140 °C without solvent for 5 min, a new peak appeared on GPC at a higher molecular weight region (Figure 3b). This fraction was isolated by preparative GPC and characterized as dimer **7**. Since a dimer with diene structure was not detected, it is clear that the Diels−Alder reaction was much faster than the elimination of SO_2 under polymerization conditions. After heating at 140 °C for 24 h, high molecular weight polymer was directly obtained (Figure 3c). The GPC profiles were characteristic of typical step polymerization, ruling out thermal polymerization of the diene moiety. Since each peak corresponds to a particular oligmer, the peak top of the GPC curve corresponds to a 6−7-mer whose molecular weight is approximately 8000. However, calculated molecular weight based on PSt standards (M_n 3100, M_w/M_n 1.98) was lower than the value expected from the GPC profile. Since **6** consists exclusively of cyclic components, molecular

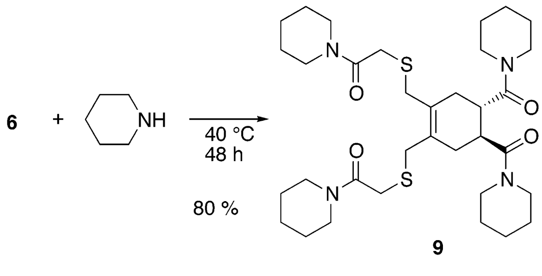
Scheme 2



Scheme 3



Scheme 4



weight was underestimated. When polymerization was carried out in a solution state, a large molecular weight distribution (M_w/M_n 6.86) was observed, indicating that bulk polymerization is more effective than solution polymerization to obtain pure polymer **6**.

To confirm the structure of **6**, the model reaction of **4** with a dienophile was investigated. When **4** was heated in 1,2-dichlorobenzene in the presence of excess dimethyl fumarate, the diene intermediate was trapped by the Diels–Alder reaction to afford [2]catenane **8** in 63% yield (Scheme 3). In the ^{1}H NMR spectra of **8** (Figure 2c), signals of cyclohexene moiety were observed around 2.9 ppm. Meanwhile, the olefinic signals of **4** disappeared by polymerization, and instead a broad signal at 2.5–3.3 ppm appeared with the appropriate integral value. These observations indicate that the polymerization occurred via the formation of a cyclohexene ring by the Diels–Alder reaction. Finally, direct evidence of Diels–Alder polymerization was obtained from the aminolysis of polymer **6** with piperidine to afford tetraamide **9** in 80% yield (Scheme 4). The yield of **9** corresponds well to the degree of polymerization of **6** estimated from the GPC profile.

In this work, we have succeeded in synthesizing a polymer with a polycatenane skeleton, i.e., “bridged polycatenane”, by the Diels–Alder polymerization. Our results provide substantial grounds to explore the possibility of constructing a true polycatenane without any structural defect by the cleavage of two carbon–carbon bonds bridging the catenane rings of **6**.[12] We have already reported that a double bond introduced into the catenane structure by the Diels–Alder reaction can be cloven by ozonolysis without destroying the interlocked structure.[7a] Thus, active progress is being made toward the synthesis of polycatenane.

Acknowledgment. We gratefully acknowledge the financial support by JSPS Research Fellowships for Young Scientist (N.W.), JSPS Grant-in-Aid for Scientific Research (C) (N.K.), and the Mazda Foundation’s Research Grant (N.K.).

Supporting Information Available: Experimental procedures for the preparation of **4**, **7**, and **8** with the spectroscopic data, polymerization, and the aminolysis of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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