Supramolecular Polymers

A Concept for Recyclable Cross-Linked Polymers: Topologically Networked Polyrotaxane Capable of Undergoing Reversible Assembly and Disassembly**

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The development of methodologies for material recycling and/or chemical recycling of cross-linked polymers such as thermosetting resins and rubbers is one of the most important issues in polymer and material science.[1] Because of the difficulty in developing suitable recycling methodologies due to the network structure of polymers, a new recycling concept has long been sought after. Reversible cross-linking–decross-linking may constitute an effective recycling protocol. We have previously shown a concept for the "recycling of cross-linked polymers" by the application of reversible acid-catalyzed ring-opening polymerization of spiroorthoester.[2] The formation and decomposition of cross-linked polymers was reversible enough to recover the original monomers in high yields.[3] Although a number of approaches to the recycling of cross-linked polymers have been reported to date,[1,4] much work remains to be done to develop new concepts and materials based on this protocol.

We have recently unveiled a new synthetic method for [2] and [3]rotaxanes based on the concept of "dynamic covalent chemistry",[5] which involves the thermodynamic control of

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the thiol-catalyzed reversible cleavage of a disulfide linkage.[6] Furthermore, the first poly[3]rotaxane in which the monomer unit is linked through topological linkages has been synthesized by using this protocol.[7]

We now report a reversible cross-linking–decross-linking system directed towards a new concept for the recycling of cross-linked polymers by utilizing a polyrotaxane network.[8] In this system, no apparent chemical bond formation or breaking takes place because the reversible disulfide bond cleavage occurring in the axle component is the only reaction during the cross-linking and decross-linking in which a polyrotaxane network is formed and disassembled.[8] Therefore, this protocol provides a novel concept for effective recycling: that is, the trunk polymer undergoes both cross-linking and decross-linking without receiving any injury because it does not participate directly in either of the two reactions.

The cross-linking reaction was carried out by treating 0.25 M of poly(crown ether) (**1**; $\bar{M}_n = 5100$, $\bar{M}_w/\bar{M}_n = 7.1$, $\bar{M}_n$ and $\bar{M}_w$ are the weight-average and number-average molar mass, respectively; 10% weight loss temperature (T_{d10}) = 256 °C and glass transition temperature (T_g) = 81 °C) based on the cyclic unit with bisammonium salt (**2**, 0.063 M), and benzenethiol (0.013 M) in a mixed solvent of acetonitrile and chloroform (1:3) at 50 °C (Scheme 1). After 20 h, a gelled product was formed quantitatively. The swelled gel, which was originally elastic and transparent, was dried under reduced pressure to form a hard solid with plasticity. Without **2** or benzenethiol, no gelation took place. The above result suggests that the gelation arises from cross-linking, especially from the formation of the [3]rotaxane-like structure composed of the dumbbell-shaped disulfide (**2**) and the crown ether units of **1**, as shown in Scheme 1.

To confirm the formation of the mechanical linkage as the cross-linking structure, the gelation process was examined by ^{1}H NMR spectra (Figure 1). The reaction was carried out in an NMR tube that contained **1** (0.10 M based on the cyclic unit), of **2** (0.040 M), and benzenethiol (0.0080 M) in CD_3CN/$CDCl_3$ (1:4) at 50 °C. Before the addition of benzenethiol, the spectrum of the mixture was almost equal to that of the simple mixture of **1** and **2**. Just after the addition of benzenethiol, a splitting of the *tert*-butyl signal and a downfield shift of the signal from the benzylic proton (a) to about 4.5 ppm were observed. Similar spectral changes were also observed with the model crown ether: that is, **2** and dibenzo-[24]crown-8 ether (see Supporting Information).[6] After 24 h, the tube was filled with the formed gelled material, which had no fluidity. The remaining small signals of the methylene protons of **2** (b, c) observed at this time imply that most of **2** had been used in the formation of the rotaxane. In fact, the association ratio between the ammonium salt moiety of **2** and the cyclic unit of **1** was calculated to be 74% by ^{1}H NMR spectrum,[6] which

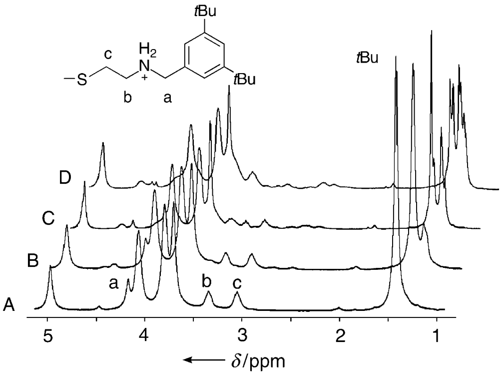
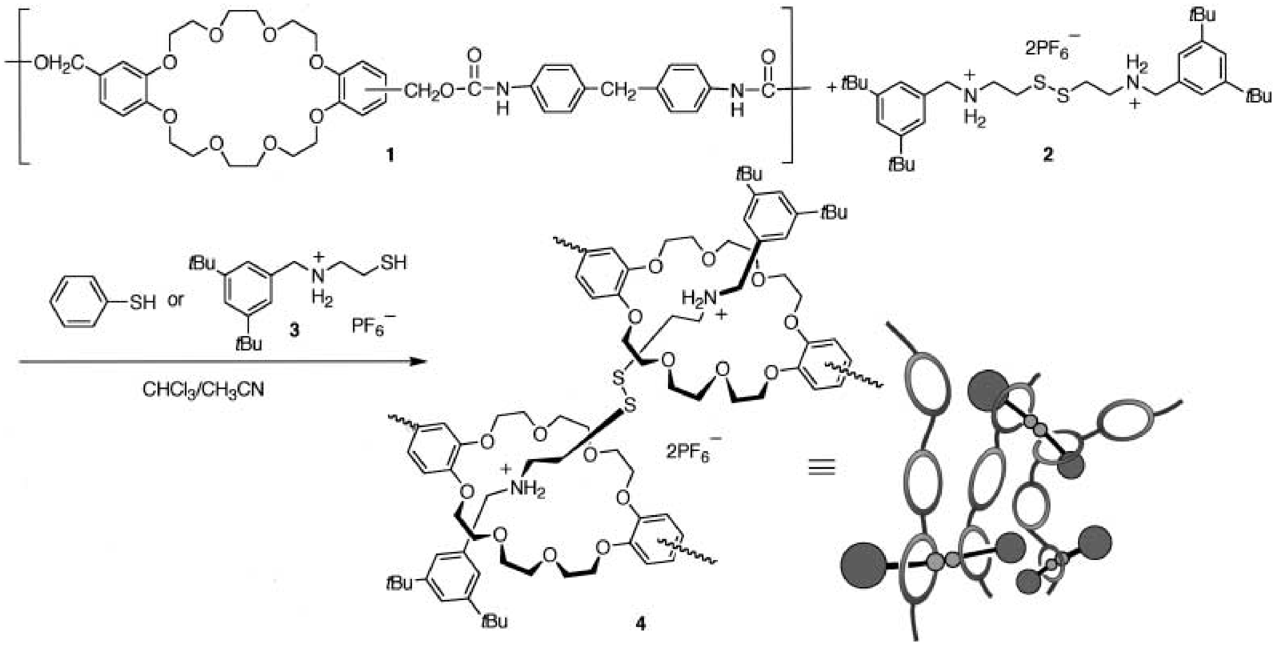


Figure 1. ^{1}H NMR spectral changes during the gelation (270 MHz, $CDCl_3$/CD_3CN 4:1, 60 °C). A) Before adding benzenethiol, B) soon after adding benzenethiol, C) after 10 h, and D) after 24 h.



Scheme 1. Polyrotaxane network **4** was synthesized from **1** and **2** by the catalysis of thiol.

suggests that the [3]rotaxane structure had been incorporated leading to cross-linking (at least 48 %). Thus, the obtained results clearly indicate that the mechanical linkage between the two caused the cross-linking of **1** with **2**.

Gel **4** swelled well in *N*,*N*-dimethylformamide (DMF; percentage swelling = 1400 % = [weight of swelled gel]−[weight of dried gel]/[weight of dried gel] × 100) and dimethylsulfoxide (DMSO; percentage swelling = 840 %). In methanol, gel **4** hardly swelled (percentage swelling = 27 %). Figure 2 depicts two pictures of gel **4** before and after swelling in DMF, revealing a colorless transparent gel. The percentage swelling and glass transition temperature of **4** were controlled by the feed ratio of [**2**] to [**1**] or by the concentration (see Supporting Information). The most characteristic feature of the cross-linking mentioned above is that both the trunk polymer (**1**) and the cross-linker (**2**) seem not to participate in any apparent chemical reaction, because their structures do not change at all besides the topological linkage produced through space between them, as shown in Scheme 1. Since the cross-linking is a reversible process, the starting materials can be perfectly recovered, if the cross-linked polymer is treated under appropriate conditions.

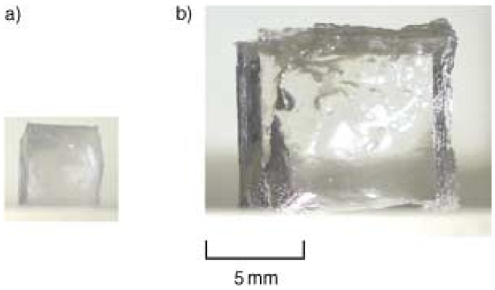


Figure 2. The pictures of gel **4** obtained, a) before swelling and b) after swelling in DMF.

To confirm this proposition, the cross-linked polymer **4** was treated with an equimolar amount of benzenethiol in DMF at 60 °C.[9] The initial heterogeneous mixture turned to a colorless clear solution within a few minutes, yielding 100 % of the original poly(crown ether) (**1**) by precipitation in methanol. Given the above effective decross-linking results, we examined the chemical recycling of cross-linked polymer **4**.

Thiol **3**[10] which is a reduced derivative of the disulfidic axle (**2**), was used instead of benzenethiol in the decross-linking. Thiol **3** (50 mol %) was added to **4**, which had been previously immersed in DMF. The mixture became a colorless homogeneous solution after 70 min at 60 °C. Precipitation in methanol gave **1** quantitatively by filtration, while a mixture of **2** and **3** was recovered in 92 % yield by the precipitation of the filtrate in water. As mentioned above, the starting materials recovered by these procedures underwent no change in chemical structure and composition before or after cross-linking and decross-linking. Therefore, the recycling of the recovered materials was accomplished.

We have succeeded in synthesizing novel polyrotaxane networks by using the reversible thiol–disulfide interchange reaction based on dynamic covalent chemistry.[5] The polyrotaxane network was readily removed by treatment with DMF that contained thiols, and the starting materials were almost quantitatively recovered when thiol **3** was used. We have thus demonstrated a new concept for recyclable cross-linked polymer based on the reversible mechanical bonding characteristic of the rotaxane system.

Supporting Information (^{1}H NMR spectra of the model rotaxanes, the effect of the cross-linking ratio on the glass transition temperature and swelling behavior of **4**, and the experimental procedures of the cross-linking and decross-linking) is available.

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