# Synthesis of Vinylic Macromolecular Rotaxane Cross-Linkers Endowing Network Polymers with Toughness

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S *Supporting Information*

ABSTRACT: Macromolecular rotaxane cross-linkers having two radically polymerizable vinyl groups (RCs) were first synthesized and used to prepare network polymers. A crown ether/*sec*-ammonium-type pseudorotaxane initiator having an OH terminal-containing axle and a crown ether wheel with a vinyl group was subjected to the living ring-opening polymerization of δ-valerolactone followed by end-capping with a bulky isocyanate to yield a polyester axle-tethering macromolecular [2]rotaxane cross-linker (RC). Rotaxane cross-linked polymers (RCPs) were prepared by the radical polymerization of *n*-butyl acrylate in the presence of RCs (0.25, 0.50 mol %). The properties of the RCPs and covalently cross-linked polymers (CCPs) were characterized mainly by mechanical properties. Both fracture stress and strain values of RCPs were much higher than those of CCPs, probably owing to the increased network homogeneity by the rotaxane cross-link. The hybrid-type RCPs obtained from a mixture of RC and covalently connected cross-linker (CC) showed poorer mechanical properties similar to that of CCPs, indicating the importance of RCs in increasing the toughness of the network polymers.
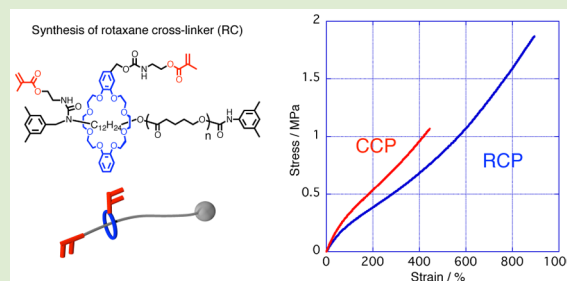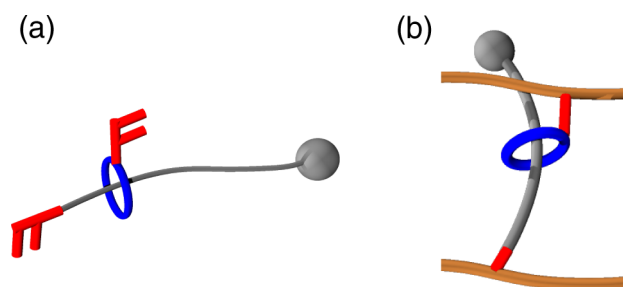
Rotaxane cross-linked polymers (RCPs) are characterized by the high mobility of the polymer chains at the cross-link points or the movable cross-link points due to the mechanically linked components that have attracted great interest of polymer scientists from both scientific and practical viewpoints.[1-18] In association with de Gennes's theoretical prediction of the unique properties of "sliding gels",[19] Ito et al. actually found unique properties of cyclodextrin (CD)-based RCPs[3,6,7,9,12,13] obtained by connecting the CD wheels of main-chain-type polyrotaxanes.[20-22] Previously, we prepared CD-based RCPs[8] using a vinylic supramolecular cross-linker having radically polymerizable vinyl groups, which were added to the radical polymerization systems of various monomers because of the diversity and versatility of vinyl polymers, especially those obtained by radical polymerizations. We also obtained various RCPs[2,5,11] using crown-ether-containing rotaxane cross-linkers with low molecular weight axles to clarify the effect of the rotaxane cross-link in typical elastic and plastic polymers but not in solvent-containing gels. However, the effect of the rotaxane cross-link on physical properties such as mechanical properties was not studied. Since longer axles can directly contribute to higher polymer chain mobility at the cross-link points in RCPs, RCs with a polymer axle and crown ether wheel seem to effectively display this essential function when applied to RCPs.

Recently, we have developed a method for efficiently synthesizing a macromolecular [2]rotaxane that comprises one wheel and one polymer axle.[23] This study has inspired us to design a macromolecular RC with a definite structure by introducing two polymerizable groups into its two components. This type of RC should satisfy the above-mentioned diversity

and generality in addition to the versatility of monomers and large-scale synthesis of RCPs enabling a wide range of applications. This paper describes the synthesis of macromolecular RCs with different axle lengths, their application to RCP synthesis, and the evaluation of mechanical properties of RCPs that is directed toward the clarification of the true nature of a rotaxane cross-link (Figure 1).

Utilizing our recently reported method for the synthesis of macromolecular [2]rotaxanes by the rotaxane-from method, the macromolecular RCs with one crown ether wheel and one polymer axle were prepared (Scheme 1a). Initial complexation of an OH-terminated *sec*-ammonium-type axle[24-31] and a methacryloyl group-tethering crown ether wheel[32] to
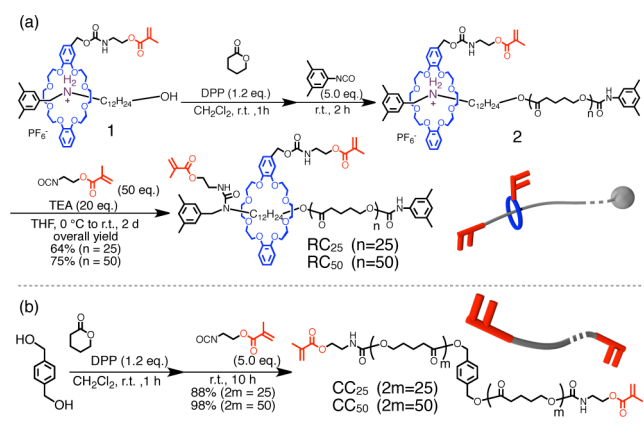
(a)   (b)

Figure 1. Schematic diagrams of (a) macromolecular rotaxane cross-linker and (b) rotaxane cross-linked polymer.

Scheme 1. Syntheses of (a) Macromolecular [2]Rotaxane Cross-Linkers and (B) Covalent Cross-Linkers

pseudo[2]rotaxane **1** was undertaken. This was followed by living ring-opening polymerization of δ-valerolactone (δ-VL, 25 equiv) catalyzed by diphenylphosphate (DPP) at room temperature in CH₂Cl₂. Finally, a successive end-capping reaction of the OH-terminal of the polyester axle chain with 3,5-dimethylphenylisocyanate to give macromolecular [2]-rotaxane **2** was performed. Modification of the ammonium moiety of **2** with an excess amount of methacryloyloxyethyl isocyanate and triethylamine in THF resulted in macro-molecular [2]rotaxane cross-linkers **RC₂₅** containing two vinyl groups with high overall yield (64% for three steps).

In a similar manner, **RC₅₀** with a longer polymer axle was obtained with 75% yield. The cross-linkers **RC₂₅** and **RC₅₀** were purified by precipitation and successive preparative gel permeation chromatography (GPC). The structures of the RCs were characterized using ¹H NMR, GPC, and MALDI-TOF-MS (Figure S1, Table S1, Supporting Information). The degree of polymerization of δ-VL, i.e., the length of the axle component of the RCs, was determined by ¹H NMR. The covalently connected cross-linkers (CCs) having the same degrees of polymerization as the RCs were also synthesized for comparison by the same method using 1,4-dihydroxymethyl-benzene instead of the pseudorotaxane initiator **1** (Scheme 1b). Table 1 summarizes the results of the syntheses of RCs and CCs.

Table 1. Syntheses of Cross-Linkers RC and CC via Scheme 1

cross-linker	yield [%]	M_{nGPC}[a] [kDa]	M_w/M_n[a]	DP_n[b]	M_{nNMR}[b] [kDa]
RC₂₅ ($n = 25$)	64	6.0	1.19	23	3.5
RC₅₀ ($n = 50$)	75	8.3	1.13	50	6.2
CC₂₅ ($2m = 25$)	88	5.2	1.25	20	2.4
CC₅₀ ($2m = 50$)	98	9.5	1.20	52	5.6

[a]Determined by GPC eluted with CHCl₃ on the basis of polystyrene standards. [b]Determined by ¹H NMR.

To evaluate the effect of the cross-linker more clearly or sensitively, *n*-butyl acrylate (BA) was chosen as a vinyl monomer because BA gives a typical elastic polymer poly(BA) (PBA). The syntheses of RCPs and CCPs were conducted by the radical polymerization of BA in the presence of a small amount of RCs and CCs. Namely, a mixture of BA, 0.50 mol % cross-linker, and a photoinitiator (IRGACURE 500) was degassed, UV irradiated for 5 min under ambient conditions,

and kept at room temperature for 12 h to afford a solid product. This product was purified by swelling in CHCl₃ and MeOH to remove the unreacted and soluble materials and gently dried *in vacuo* for 12 h at 80 °C to yield RCPs and CCPs as elastic polymers with good yields (46%−81%). To evaluate the cross-linked structures of RCP and CCP, swelling tests were conducted with chloroform as a good solvent. The swelling ratio of **RCPs** was higher than that of **CCPs**, whereas **RCP₅₀** with a longer axle chain showed slightly higher propensity to swell than **RCP₂₅** but not for **CCPs** (Figure 2). These results
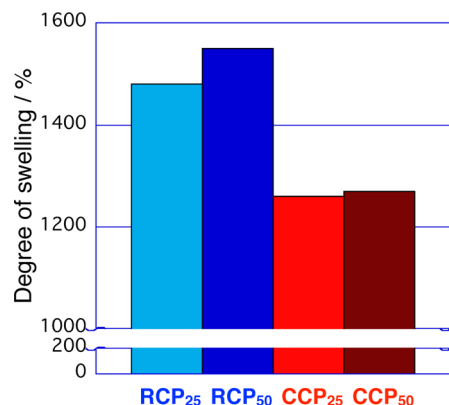
**Figure 2.** Degree of swelling of RCPs and CCPs with CHCl₃.

may be explained by the higher homogeneity of the network derived from the rotaxane cross-links. All RCPs and CCPs were amorphous polymers showing a glass transition temperature T_g around −50 °C, which originated from PBA. Meanwhile, no melting point based on polyVL (PVL) of RCs or CCs was observed, presumably because only 0.50 mol % of RC or CC was used, although PVL is a crystalline polymer.[33] Thus, all RCPs and CCPs hold the essential property of PBA as a matrix polymer (Figure S13, Supporting Information).

Figure 3a shows the stress−strain curves of RCPs and CCPs, and their mechanical property data are summarized in Figure 3b. Note that the enhanced toughness of RCPs was much more than that of CCPs. Fracture stress and strain of **RCPs** (**RCP₂₅**, **RCP₅₀**) were larger than those of **CCPs** (**CCP₂₅**, **CCP₅₀**). As for the polymer chain length of the cross-linkers, **CCP₅₀** had larger Young's modulus than **CCP₂₅**. This may be attributed to the difference in the amount of the PVL segment acting as a hard segment because the molar ratio of the cross-linkers was kept at 0.50 mol % in each case. Meanwhile, **RCPs** displayed a contrary behavior to **CCPs** in this regard. The results can be explained by the relaxation effect originating from the movable linkage on the axle chain, although the reason for this is unclear at present. Thus, it is very interesting that only a small amount of RC certainly endowed a vinyl polymer with toughness in comparison with CC, which is a prominent property of RC. The effect of the RC's concentration was evaluated with 2-ethylhexyl acrylate (EHA) because EHA affords the corre-sponding polymer with low T_g (poly(EHA), ca. −50 °C), similarly to PBA. The radical polymerizations of BA or EHA in the presence of RCs and CCs (0.25, 0.50 mol %) afforded the corresponding **RCPs** and **CCPs** (Figures S6−S8, Table S2, Supporting Information). The stress−strain curves of those derived from EHA showed a trend similar to those of BA, while the effect of the concentration of the **RCs** and **CCs** was reasonable, i.e., the higher the concentration, the larger the modulus (Figures S9−S12, Table S2, Supporting Information).
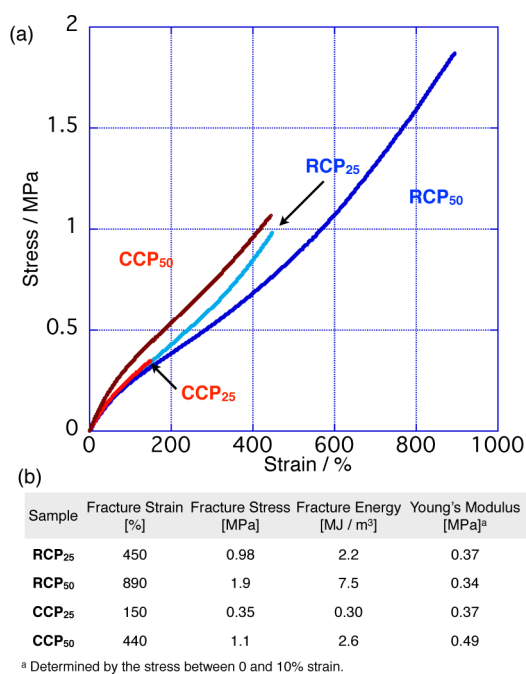
Figure 3. Results of tensile tests on **RCPs** and **CCPs**. (a) Stress—strain curves. (b) Summary of the tensile tests.

To further describe the behavior of RCs, the properties of network polymers prepared using mixtures of RC_{50} and CC_{50} were investigated (Figure 4, Table S3, Supporting Information). In a similar way, hybrid cross-linked polymers HCP_{75}, HCP_{50}, and HCP_{25} were synthesized using BA, RC_{50}, CC_{50}, and a photoinitiator. Figure 4a shows the stress—strain curves of the hybrid cross-linked polymers, including those of RCP_{50} and CCP_{50}, and the corresponding data are summarized in
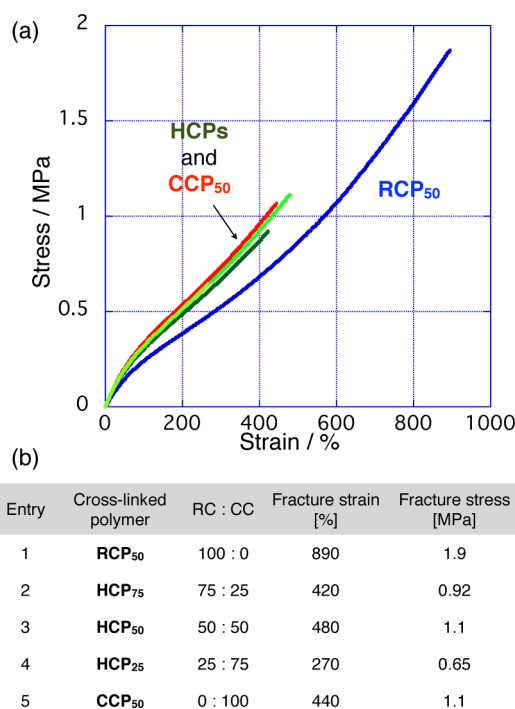
Figure 4b. Interestingly, all hybrid cross-linked polymers showed similar behaviors (entries 2—4) to that of the native **CCP** (CCP_{50}) (entry 5) independent of the feed ratio of RC_{50} and CC_{50}. It seems reasonable that the cross-link point formed by CC_{50} among the two cross-linkers produces a fragile point for fracture when the stress was loaded before the rotaxane cross-link starts to work. The present results strongly suggest the significance of the rotaxane cross-linker RC as an effective cross-linker capable of endowing polymers with toughness as well as network structures.

In summary, we have successfully prepared macromolecular [2]rotaxane cross-linked RCs, a new type of cross-linker having two polymerizable vinyl groups in the two components. The cross-linkers were readily applied to the synthesis of RCPs using BA and EHA as the monomers of common and universal polymers, i.e., vinyl polymers obtainable by radical polymerization. The RCPs prepared with RC showed excellent mechanical properties in comparison with the CCPs obtained with macromolecular chemical cross-linkers, suggesting the prominent characteristics of the rotaxane cross-linkers. Since the present macromolecular rotaxane cross-linkers have defined structures and are easy to synthesize, we expect a wide range of applications of RCs once the detailed mechanism of toughening by RCs is clarified.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and instruments, synthesis of axle component and wheel component, synthesis of macromolecular [2]rotaxane cross-linkers, synthesis of covalently connected cross-linkers, synthesis of cross-linked polymers and swelling test, and characterization of cross-linked polymers. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00242.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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Figure 4. (a) Stress—strain curves of hybrid cross-linked polymers. (b) Condition for preparing hybrid cross-linked polymers and several values obtained by tensile tests.

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