Supramolecular Gels

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Size-Complementary Rotaxane Cross-Linking for the Stabilization and Degradation of a Supramolecular Network**

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As cross-linked polymers are widely used fundamental materials, their chemical recycling becomes a quite important issue.[1] A promising strategies is to utilize reversible cross-linking based on dynamic covalent chemistry (DCC).[2,3] For example, Chen et al. reported the efficient thermal reversibility of cross-linking by Diels–Alder reaction.[4] On the other hand, supramolecular gels formed by intermolecular interactions, such as hydrogen bonds,[2] can be efficiently de-cross-linked by specific stimuli without destruction of covalent bonds.[2,3d,5–7] However, supramolecular gels are naturally stable only under limited conditions that are capable of keeping the intermolecular interactions strong. A polyrotaxane network (PRN) is a supramolecular gel stabilized by not only intermolecular interactions but also mechanical restriction.[8] We previously reported a reversibly cross-linkable PRN based on DCC, consisting of poly(crown ether) backbone and bis(ammonium) cross-linker possessing a disulfide bond in its center (Figure 1 a).[9] The work gave a new impulse for the chemical recycling of cross-linked polymers, but it suffered from the disadvantage that it is a sluggish reaction. Therefore, we have developed a novel approach that enables the efficient de-cross-linking of PRNs without any cleavage of covalent bonds. Recently, we have found a novel procedure in which the axle component as a cross-linker has an end group the size of which is complementary to the macrocycle cavity placed on the trunk polymer (Figure 1 b). The end groups provide an energy barrier to slow the dissociation, thereby kinetically stabilizing the rotaxane skeleton.[10] Thus, the PRN stabilizes the network structure under normal conditions, but it can be de-cross-linked when certain conditions, such as those that accelerate the dissociation of the rotaxane skeletons, are satisfied. Because the de-cross-linking can be achieved without breaking the covalent bonds, the PRN is selectively degraded so as to not damage the trunk polymer. Furthermore, the stability and de-cross-linking capability of PRNs can be adjusted by the size of the end groups of the axle components. Herein we describe the concept of novel de-cross-linkable network polymers that utilize the size-complementary effect of the rotaxane cross-links.

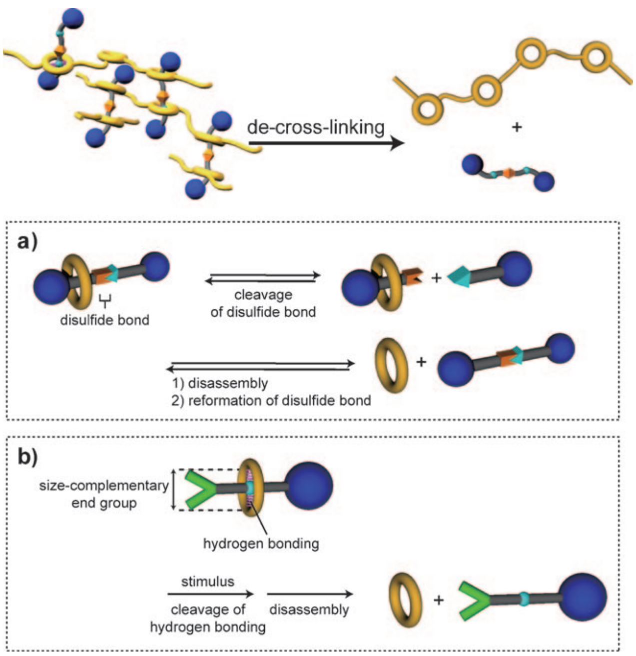

Figure 1. Strategy for de-cross-linking a PRN using a) a reversible cleavage of disulfide bond and b) characteristics of a rotaxane cross-link consisting of size-complementary components.

First, we investigated a model for the size-complementary effect using crown ether/ammonium salt [2]rotaxanes **1** (Scheme 1). According to previous reports,[10–12] roxaxanes **1** with suitable end groups (R = cyclohexyl, *t*Bu, 4-$t\mathrm{BuC_6H_4}$) were sufficiently stable to maintain its threaded structure owing to both the bulky end groups and hydrogen bonds between dibenzo [24]crown-8 ether (DB24C8) and the ammonium group.[13] However, **1** dissociated into two parts, axle and wheel, when the hydrogen bonds were disturbed by a stimulus, in accordance with reported results (R = 4-$t\mathrm{BuC_6H_4}$).[12] Details are summarized in Table 1. As we envisioned, the dissociation rate depends on both the size of the end group and the kind of the external stimulus, as discussed below.

An investigation into the dissociation behavior of **1** in dimethylsulfoxide (DMSO), a polar solvent that disturbed the hydrogen bonds, showed the decomposition of only **1a** among three derivatives. The dissociation rate of **1a** to DB24C8 and **2a** obeyed first-order kinetics. The half-life ($\tau_{1/2}$) was esti-

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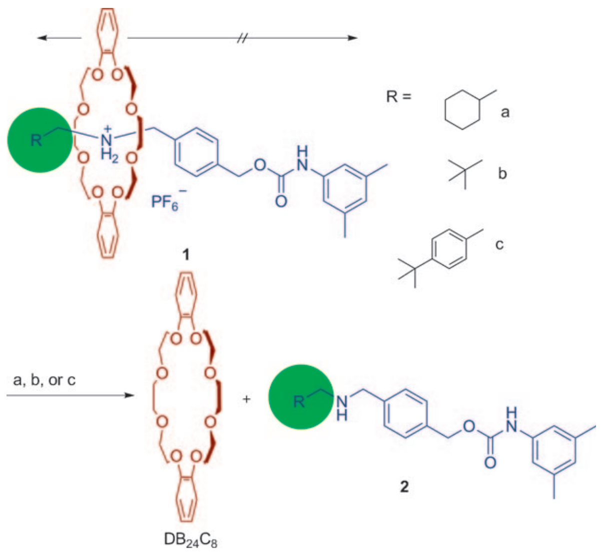


Scheme 1. Dissociation reactions of model [2]rotaxane **1**. Reagents and conditions: a) $[D_6]$DMSO, 25 °C, b) Et_3N, CD_3NO_2, 60 °C, or c) TBAF·$3H_2O$, $[D_6]$DMSO, 60 °C. DMSO = dimethylsulfoxide, TBAF = tetrabutylammonium fluoride.

Table 1: Kinetic parameters for the dissociation of rotaxanes **1a–c**.[a]

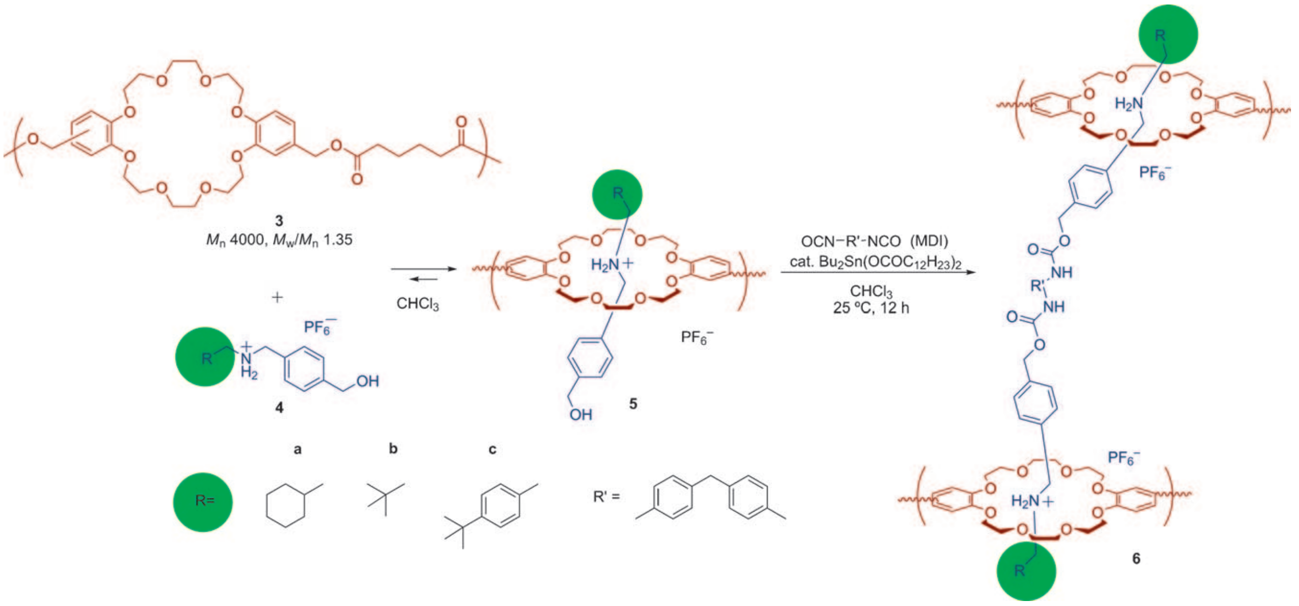
	End group[b]	$[D_6]$DMSO 25 °C[c]		Et_3N/CD_3NO_2 60 °C[d]		TBAF/$[D_6]$DMSO 60 °C[e]	
		k_{off} [s^{-1}]	$\tau_{1/2}$	k_{off} [s^{-1}]	$\tau_{1/2}$	k_{off} [s^{-1}]	$\tau_{1/2}$
1a	Cy	3.3×10^{-5}	5.8 h	7.3×10^{-5}	2.6 h	–[f]	–[f]
1b	*t*Bu	–[g]		4.4×10^{-7}	18 d	2.7×10^{-4}	0.70 h
1c	4-*t*BuC_6H_4	–[g]		–[g]		2.2×10^{-6}	88 h

[a] Determined from ^1H NMR analysis. Details are given in the Supporting Information. [b] Cy = cyclohexyl, Bu = butyl. [c] [**1**] = 10 mM. [d] [**1**] = 10 mM, [Et_3N] = 100 mM. [e] [**1**] = 10 mM, [TBAF] = 30 mM. [f] The dissociation was very rapid to give a spectrum at the intermediate state. [g] No dissociation was observed after 24 h.

mated at 5.8 h.[13] A second stimulus was the addition of a base for the neutralization of the ammonium group. The addition of triethylamine (Et_3N) caused prompt dissociation of **1a** ($\tau_{1/2} = 2.6$ h), even in CH_3NO_2 with a low donor number.[14,15] While **1b** was slowly dissociating ($\tau_{1/2} = 18$ d), the dissociation of **1c** was very slow to measure. It was found that **1b** and **1c** are kinetically much more stable than **1a**.

A third stimulus was the counteranion exchange of the ammonium salt with a fluoride ion that markedly decreases the acidity of the ammonium moiety. Recently, we found that the counteranion exchange of a similar rotaxane with tetrabutylammonium fluoride (TBAF) readily afforded the corresponding neutral rotaxane.[16] The addition of TBAF led to a rapid dissociation of all rotaxanes (**1a–c**). The dissociation of **1a** was very rapid, while **1b** smoothly dissociated ($\tau_{1/2} = 0.70$ h). Furthermore, even the most stable rotaxane, **1c**, dissociated slowly ($\tau_{1/2} = 88$ h). Thus, the present model clearly indicates that the bulkiness of the end group and the extent of the stimulus disturbing the hydrogen bonds facilitate the dissociation, which can be easily achieved by controlling these two variables to adjust the desired decomposition time.

Recognizing the results of the above model, we examined the de-cross-linking capability of PRN **6** with the size-complementary end groups at the cross-linking points. Poly(DB24C8) **3**, with an average molecular weight M_n of 4000 and polydispersity index (PDI) of 1.35, was prepared according to our previous report.[17] PRN **3** was treated with *sec*-ammonium salts **4** in $CHCl_3$ to give the corresponding pseudo(polyrotaxane) **5**,[17] which was cross-linked with a diisocyanate (MDI) to quantitatively yield **6** (Scheme 2).[17b] To equalize the degree of cross-linking, the complexation rate of the obtained pseudorotaxanes were adjusted to about 20%.[13,17] The thermal properties of **6** are shown in Table 2. The structures of **6a–c** showed similar glass transition temperatures ($T_{g,DSC}$) measured by differential scanning calorimeter (DSC) at about 5 °C, while the 5% weight loss



Scheme 2. Preparation of PRNs **6**.

Table 2: Thermal properties of PRNs **6**.

PRN	End group	T_{d5}[a] [°C]	$T_{g,DSC}$[b] [°C]	$T_{g,DMA}$[c] [°C]
3	–	279	11.3	–[d]
6a	Cy	202	5.0	12.0
6b	*t*Bu	160	5.2	14.0
6c	4-*t*BuC$_6$H$_4$	165	3.8	12.0

[a] 5% Weight-loss temperature by thermogravimetric analysis (TGA). [b] Glass transition temperature measured by differential scanning calorimetry (DSC). [c] Glass transition temperature by dynamic mechanical analysis (DMA). [d] Not measured.

temperature (T_{d5}) of **6a–c** was lower than that of **3**. The fact that DSC profiles did not show any peak up to T_{d5} suggested that the rotaxane cross-link in **6** was stable to heating. The dynamic mechanical analysis (DMA) showed similar glass transition temperatures ($T_{g,DMA}$) to $T_{g,DSC}$. Furthermore, the plateau regions of tensile storage modulus (E') between 50–110°C clearly indicated the network structure of **6**.[13]

The dissociation abilities of the various structures of **6** were examined in a manner similar to those of PRN **1** (Scheme 3). Figure 2 shows the time-dependent weight loss of **6** under various conditions. Cyclohexyl-terminated **6a** was gradually de-cross-linked in DMF at 25°C and finally gave a completely homogeneous solution after 90 min (Figure 2a). Compound **6a** was also partially de-cross-linked to afford a soluble part in other less polar solvents.[13] On the other hand, *t*Bu-terminated **6b** and 4-*t*BuC$_6$H$_4$-terminated **6c** were insoluble in any solvents but were only swollen, suggesting their kinetic stability. Treatment of **6a** and **6b** with Et$_3$N in CH$_3$NO$_2$ slowly promoted the de-cross-linking reaction, and they were finally de-cross-linked after 60 min and 360 min, respectively (Figure 2b). In contrast, **6c** maintained the cross-linked structure under these conditions. Furthermore, **6a** was perfectly dissociated within 20 min by the treatment with TBAF (Figure 2c). For **6b**, it took 75 minutes to achieve complete de-cross-linking. The drastic change in solubility is seen in Figure 3.

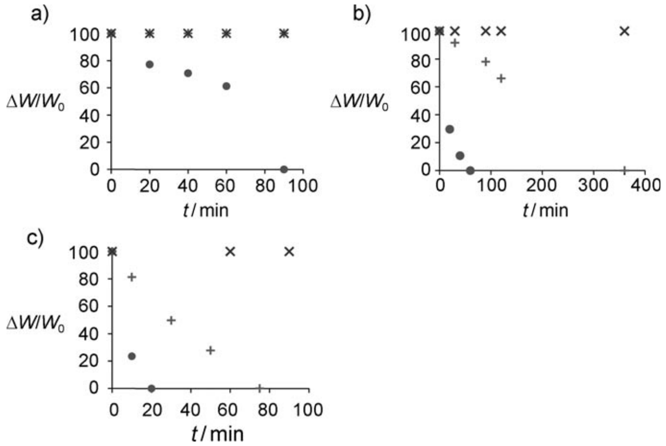
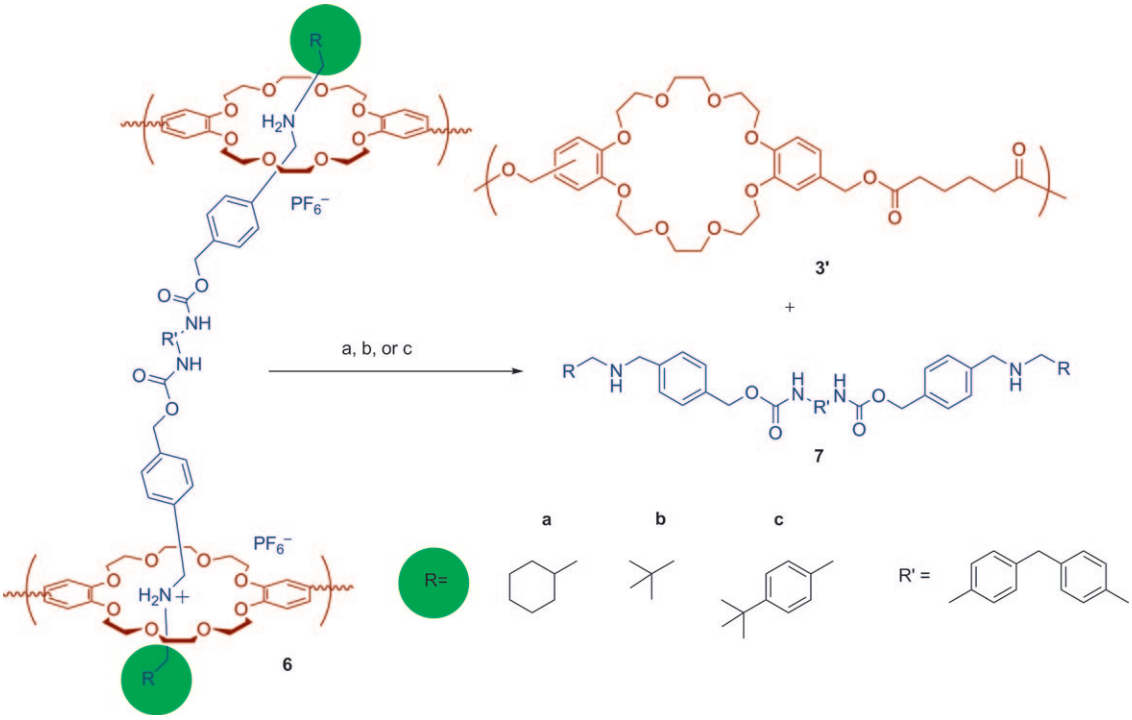


Figure 2. The time-dependent weight loss of the insoluble part of **6** under the following conditions: a) DMF, 25°C; b) Et$_3$N (100 mM), CH$_3$NO$_2$, 60°C; c) TBAF (30 mM), DMF, 60°C. ● **6a**, + **6b**, × **6c**. $\Delta W/W_0$ = (weight of dried gel)/(weight of initial dried gel) × 100%.

Although **6c** afforded little solubility after treatment for 90 minutes with TBAF, **6c** slowly decomposed to give a completely homogeneous solution after 96 h. These results were in good agreement with the results of the models using



Scheme 3. De-cross-linking reactions of PRN **6**. Reagents and conditions: a) [D$_6$]DMSO, 25°C, b) Et$_3$N, CD$_3$NO$_2$, 60°C, or c) TBAF·3H$_2$O, [D$_6$]DMSO, 60°C.

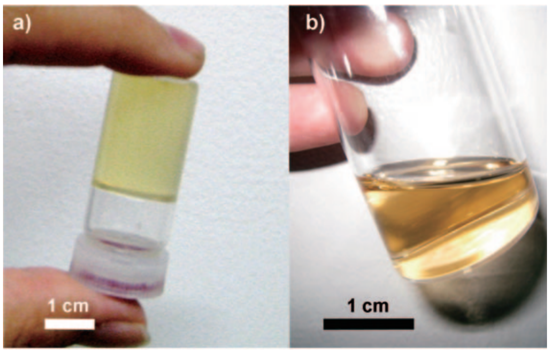


Figure 3. Photographic images of PRNs **6b**: a) In the swollen state in CH_3NO_2; b) after treatment with TBAF/DMF.

[2]rotaxane **1**: The stability of PRNs was controllable as discussed above. The fact that **6a** cannot maintain its network structure in any solvents indicates that a cyclohexyl group is too small to kinetically stabilize the rotaxane skeleton, and **6a** is not much more than a conventional supramolecular network (polypseudorotaxane network). On the other hand, **6b** and **6c**, stabilized by a bulker end-group than the cyclohexyl group, showed both good stability and suitable degradability.

To evaluate recyclability, the recovery ratio of the starting linear polymer poly(crown ether) **3′** was evaluated. From the homogeneous solution of **6a** obtained by dissolving in DMF, **3′** was recovered as a white powder in 98% yield. Similarly, a 100% yield of **3’** was obtained from mixtures of **6b** and TBAF. The very high recovery ratios of the trunk polymer strongly indicate the high efficiency of the dissociation of the present non-covalent rotaxane cross-link. The ^{1}H NMR spectrum of recovered **3′** showed no signal other than those assignable to **3**.[13] Therefore, the high recovery yield of pure **3′** clearly reveals the occurrence of the selective dissociation of the rotaxane skeleton without any destruction or damage to the polymer backbone.

In conclusion, we demonstrated a new design for degradable cross-linked polymers characteristic of rotaxane cross-links, which have sufficient stability and de-cross-linking capability depending on the structure of the cross-linker and the dissociation conditions. The PRN, and especially **6b** and **6c**, were very similar to the covalent form, thus showing the high stability as the polymer material, but it is weak relative to the hydrogen-bond-based supramolecular form, as indicated by the prompt de-cross-linking by the impediment of hydrogen bonds. Furthermore, the high recovery yield of the trunk polymer shows the potential usefulness of this concept as a way to recycle cross-linked polymers.

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