

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: A Guiding Principle for Toughening Cross-Linked Polymers: Synthesis and Application of Mobility-Controlling Rotaxane Cross-Linkers

Authors: Jun Sawada, Daisuke Aoki, Hideyuki Otsuka, and Toshikazu Takata

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201813439 Angew. Chem. 10.1002/ange.201813439

Link to VoR: http://dx.doi.org/10.1002/anie.201813439 http://dx.doi.org/10.1002/ange.201813439

WILEY-VCH

10.1002/anie.201813439

WILEY-VCH

A Guiding Principle for Toughening Cross-Linked Polymers: Synthesis and Application of Mobility-Controlling Rotaxane Cross-Linkers

Jun Sawada, Daisuke Aoki, Hideyuki Otsuka, and Toshikazu Takata*

Abstract: Three component mobility-controlling vinylic rotaxane cross-linkers with two radically polymerizable vinyl groups (RC_Rs) were synthesized to prove that the mobility of the components of the RC_Rs plays a crucial role in determining the properties of rotaxanecross-linked polymers (RCPs). RC_Rs (R = H, Me, or Et) were obtained from the living ring-opening polymerization of sixmembered cyclic carbonates with two substituents R at the 5 position using pseudorotaxane initiators with a terminal OH group on the axle. A mixture of n-butyl acrylate and 0.5 mol% RC_R was exposed to UV irradiation in the presence of a photoinitiator to afford the corresponding RCPs (RCP_R; R = H, Me, or Et). RCP_Et was prepared using RC_Et, which exhibits the lowest component mobility. The low component mobility is reflected in inferior mechanical strength and stretchability in tensile stress tests compared to components with good (R = Me) and high (R = H) mobility. However, RCP_Et exhibited significantly higher stress and strain values than the corresponding covalently cross-linked polymers (CCP_Rs). These results indicate that a suitable component mobility substantially enhances the mechanical strength of RCPs. This behavior could serve as a guiding principle for the molecular design of advanced RCs

Rotaxane-cross-linked polymers (RCPs) have attracted great attention both from a fundamental and a practical perspective due to the extraordinary functionality based on the mechanically linked components with high mobility.^[1-14] Ito et al. have reported that cyclodextrin-based polyrotaxane hydrogels with rotaxane cross-links show excellent swellability and extensibility.[15] Related studies on such cross-linked cyclodextrin-based polyrotaxanes also revealed intriguing properties that cannot be attained by cross-linked polymers using covalent crosslinkers.^[16-21] Meanwhile, our group has reported a synthetic route to rotaxane-cross-linked vinyl polymers using supramolecular cross-linkers that consist of cyclodextrins and macromonomers. This study has delivered very interesting results, especially with respect to the importance of the use of small amounts of rotaxane-based materials and the generality of vinyl polymers.^{[22-} ^{23]} We have also studied the synthesis and potential applications

of crown-ether-containing vinylic rotaxane cross-linkers (RCs) for the synthesis of RCPs by radical polymerization in nonaqueous systems. RCs endow polymers with high toughness,

J Sawada, Dr. D. Aoki, Dr. H. Otsuka, and Dr. T. Takata Department of Chemical Science and Engineering Tokyo Institute of Technology 2-12-1, O-okayama, Meguro, Tokyo, Japan ttakata@polymer.titech.ac.jp

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

whereby an increasing mobile distance of the RC components improves the mechanical properties of the RCPs and induces unique properties such as high swellability, extensibility, and desirable stress-relaxing ability.^[9] As new methods for the toughening of cross-linked polymers have been developed in response to the increasing interest in RCPs, the genuine significance of the component mobility of RCs to endow RCPs with toughness should be clarified in order to firmly establish this new concept as a molecular design guideline.



Figure 1. Schematic illustration of the structures of rotaxane cross-linkers (RCs) for the evaluation of the effect of (a) the mobile distance, and (b) the mobility of the components on the (c) synthesis of cross-linked polymers toughened by RCs.

We examined the effect of the component mobility of the RCs on the physical properties of the RCPs in detail and discovered a guiding principle for the design of RCs and RCPs (Figure 1): not only the mobile distance, but also the mobility of the components of the RCs determine the properties of the RCPs (*vide infra*).

For the evaluation of the effect of the mobility of the components on the properties of the corresponding RCP_Rs, RC_Rs with different thickness, which contain two vinyl groups in the two components. were designed and synthesized. Pseudo[2]rotaxane initiator (3), prepared in situ from an hydroxyterminated sec-ammonium-type axle (1) and a methacryloyl group-tethering crown ether wheel (2), was subjected to a DPPcatalyzed living ring-opening polymerization of six-membered cyclic carbonates^[24-25] that contain two R substituents at the 5 position (R = H, Me, or Et).^[26] The polymerization was followed by the addition of 3,5-dimethylphenyl isocyanate as a bulky endcapping agent to afford a macromolecular [2]rotaxane that is comprised of one wheel and a polymeric axle chain (4).

WILEY-VCH



Scheme 1. (a) Synthesis of RCs and (b) structure of the covalent cross-linkers (CCs) synthesized for comparison.

Treatment of 4 with 2-isocyanatoethyl methacrylate for the modification of the ammonium group of the axle component afforded high overall yields of the RC_Rs, which bear two radically polymerizable vinyl groups. For comparison, macromolecular covalent cross-linkers (CC_Rs; Scheme 1b) that possess identical polymer chains, chain length, and two vinyl groups were synthesized starting from 1,4benzenedimethanol instead of 3. The structures of the RC_Rs and CC_Rs were determined using ¹H NMR, GPC, MALDI-TOF-MS, and DSC measurements (Figures S1-6). The degree of polymerization (DPn) was determined by ¹H NMR spectroscopy. Table 1 summarizes the synthetic results for these RC_Rs and CC_Rs. All cross-linkers possess a similar degree of polymerization ($DP_n = 25$) and molecular weight (3.1-5.2 kDa; ¹H NMR) as well as narrow molecular-weight distribution (M_w/M_p = 1.06–1.15; GPC), suggesting a negligible effect of the difference in molecular weight.

Table 1. Synthesis of cross-linkers (RC_Rs and CC_Rs)

Cross-linker	Yield [%]	<i>M</i> n (GPC) [kDa] ^[a]	<i>M</i> w / <i>M</i> n ^[a]	DPn ^[b]	<i>M</i> ո (NMR) [kDa] ^[b]
RC_H	87	5.1	1.12	25	3.8
RC_Me	86	4.8	1.13	25	4.5
RC_Et	88	4.2	1.15	25	5.2
CC_H	quant.	7.7	1.06	26	3.1
CC_Me	quant.	7.2	1.08	25	3.6
CC_Et	89	7.1	1.07	24	4.2

[a] Determined by GPC (eluent: chloroform; polystyrene standards). [b] Determined by ¹H NMR spectroscopy.

Prior to the synthesis of the RCPs, the mobilities of the components of the RC_Rs were evaluated based on the decomposition behavior of the corresponding macromolecular [2]rotxanes (pR Rs)(Scheme 2), which contain unprotected terminals. These were independently prepared by a protocol similar to that for the formation of precursor 4 (Scheme 1a), albeit that the end-capping reaction was not carried out. Specifically, we were interested whether the decomposition of pR_Rs occurs via an N-acetylation, which would offer valuable information on whether the wheel component can move on the axel component.^[27] The decomposition of 6 was carried out under this N-acetylation conditions by treating the ammonium moiety of the axle with a mixture of acetic anhydride and trimethylamine (TEA) in THF, which should remove the attractive interaction between the components. The structures of 6 and the N-acetylated products (pR_Rs) were characterized by MALDI-TOF-MS measurements (Figures S7-9). In case of pR_H and pR_Me, the respective wheel and axle components were obtained as the decomposition products. In contrast, pR_Et, did not afford any decomposition products, but only Nand O-acetylated products. These results clearly suggest that the wheel component of RC_H and RC_Me, whose R groups are smaller than the cavity of the crown ether wheel, exhibit sufficient mobility to freely move along their polymer axles, while the wheel component of RC_Et exhibits significantly less mobility, which renders moving along the axle component impossible.





Cross-linked polymers were obtained from the polymerization of *n*-butyl acrylate (BA) as the vinyl monomer in the presence of a small amount of cross-linker (Scheme 3). Specifically, a mixture of BA, DMF, **RC_R** or **CC_R** (0.5 mol%), and a photoinitiator (IRGACURE[®] 500) was exposed for 5 min to UV irradiation, before being left to stand overnight at room temperature to afford an insoluble gel. The gel was subsequently swollen and washed with chloroform and methanol in order to remove unreacted and soluble materials, before being dried *in vacuo* (12 h; 80 °C) to yield **RCP_R**s and **CCP_R**s as elastic polymers in moderate yield (45–70%; Table 2, S2).



Scheme 3. Synthesis of cross-linked polymers (RCP_Rs and CCP_Rs) by photo-induced radical polymerizations of butyl acrylate in the presence of 0.5 mol% of cross-linkers RC_Rs and CC_Rs, respectively.

To clarify the effect of the structure of the cross-linkers on their mechanical properties, tensile stress tests were conducted using polymer films of **RCP_Rs** and **CCP_Rs**. Figure 2 shows the corresponding stress-strain curves and the results are summarized in Table 2. Figure 2 indicates little difference in the mechanical properties of the three **CCP_Rs** (for the expanded curves, see Figure S10). This result seems reasonable, given that it should be unlikely that the thickness difference in the polymer backbone of the **CCP_Rs**, which combine two PBA polymer chains, affects the mechanical properties. On the other hand, a clear difference was observed for the three **RCP_Rs**. In addition, all **RCP_Rs** showed much higher fracture energy (both fracture stress and strain) compared to the **CCP_Rs**. This big difference is in good agreement with previously reported

results, which attributed said high fracture energy to stress dispersion originating from the movable cross-link points, even when only small amounts of RCs are used.^[9] It was also confirmed by cycle tensile tests of **RCP_R**s, that there was no hysteresis energy loss up to 300% strain with all RCPs (Figure S11).

Meanwhile, the mechanical properties of the RCP_Rs that depend on the size of the substituent (Figure 2) can be explained by the difference in mobility of the components of the RC_Rs (Scheme 2), considering the comparable thermal properties upon addition of the cross-linkers (Figure S12). Especially the lower stretchability of RCP_Et compared to RCP_H and RCP_Me coincides well with the limited component mobility, *i.e.*, the limited mobility area of the wheel component on the axle component is caused by the bulky diethyl substituent in RC_Et. This result agrees with our previous work, in which RCPs that were prepared using RCs with shorter mobility lengths showed lower extensibility than RCPs from RCs with longer mobility lengths.^[9] Although we have no clear answer for the difference in mechanical properties between RCP_Me and RCP_H at present, the notion of "molecular friction" upon translation of the wheel along the axle caused by the extension may explain it. The movement of the components at the rotaxane-cross-link point (RC_R) for a thicker axle (RCP_Me) should require more energy than that for a thinner axle (RCP_H). This explanation seems feasible, especially when considering that gemdimethyl-methylene-moiety-containing polymer chains or t-butyl groups are complementary in size to the cavity of DB24C8.^[4,]



Figure 2. S-S curves of cross-linked RCP_Rs and CCP_Rs (elongation rate: $83\% \text{ min}^{-1}$)

Table 2. Mechanical properties of RCP_Rs and CCP_Rs.

	Yield ^[a] [%]	Tensile stress test				
Cross-linked polymer		Young's modulus [MPa] ^[b]	Fracture strain [%]	Fracture stress [MPa]	Fracture energy [MJ / m ³]	
RCP_H	45	0.22 ± 0.04	1289 ± 51	2.91 ± 0.19	14.2 ± 1.5	
RCP_Me	46	0.22 ± 0.02	1351 ± 99	6.54 ± 0.95	31.9 ± 6.5	
RCP_Et	51	0.15 ± 0.02	938 ± 9	1.77 ± 0.06	5.8 ± 0.2	
CCP_H	58	0.34 ± 0.01	357 ± 9	0.68 ± 0.04	1.3 ± 0.1	
CCP_Me	53	0.41 ± 0.00	248 ± 56	0.63 ± 0.12	0.9 ± 0.3	
CCP_Et	70	0.40 ± 0.02	306 ± 28	0.74 ± 0.07	1.2 ± 0.2	

[a] Calculated based on weight. [b] Determined by the stress between 0 and 10% strain.

In summary, rotaxane cross-linkers (**RC_Rs**) that exhibit different mobilities of their components on account of the presence of axle components with different thicknesses were synthesized and used for the synthesis of the corresponding rotaxane-cross-linked polymers (**RCP_Rs**) to clarify the effect of the **RC_R** component mobility on the mechanical properties of the **RCP_Rs**. The mechanical properties of the **RCP_Rs** depend on the mobility of the components at the cross-link points, *i.e.*, on the thickness of the axle component. The results of this study clearly show that the length of the mobile area and the mobility of the rotaxane components at the cross-link point of the **RCPs** play a crucial role for the toughness of the polymer upon cross-linking with a **RC_R**. Based on these results, it should be possible to design and synthesize unprecedented cross-linked polymers with rotaxane cross-link points.

Acknowledgements

This research was financially supported by a Core Research for Evolutional Science and Technology (CREST) project from the Japan Science and Technology Agency (JST) grant number JPMJCR1522 and by JSPS KAKENHI grants 16K17910 and 16H00754.

Keywords: rotaxane • rotaxane-cross-linked polymer • vinyl polymer • mechanical property • toughening

- [1] M. Arunachalam, H. W. Gibson, Prog. Polym. Sci. 2014, 39, 1043.
- [2] Y. Koyama, *Polym. J.* 2014, 46, 315.
- [3] C. G. Gong, H. W. Gibson, J. Am. Chem. Soc. **1997**, *119*, 8585.
- Y. Kohsaka, K. Nakazono, Y. Koyama, S. Asai, T. Takata, Angew. Chem. Int. Ed. 2011, 50, 4872.
- [5] M. Ogawa, A. Kawasaki, Y. Koyama, T. Takata, Polym. J. 2011, 43, 909.
- [6] S. Tan, A. Blencowe, K. Ladewig, G. G. Qiao, Soft Matter 2013, 9, 5239.
- 7] Y. L. Cui, M. Tan, A. D. Zhu, M. Y. Guo, *Rsc Adv.* **2014**, *4*, 56791.
- [8] K. lijima, Y. Kohsaka, Y. Koyama, K. Nakazono, S. Uchida, S. Asai, T. Takata, *Polym. J.* 2014, 46, 67.
- [9] J. Sawada, D. Aoki, S. Uchida, H. Otsuka, T. Takata, ACS Macro Lett. 2015, 4, 598.
- [10] J. H. Seo, M. Fushimi, N. Matsui, T. Takagaki, J. Tagami, N. Yui, ACS Macro Lett. 2015, 4, 1154.
- [11] K. Iwaso, Y. Takashima, A. Harada, Nat. Chem. 2016, 8, 626.
- [12] T. Murakami, B. V. K. J. Schmidt, H. R. Brown, C. J. Hawker, J. Polym. Sci., Part A: Polym. Chem. 2017, 55, 1156.

- [13] J. Sawada, D. Aoki, M. Kuzume, K. Nakazono, H. Otsuka, T. Takata, *Polym. Chem.* **2017**, *8*, 1878.
- [14] Y. Sagara, M. Karman, E. Verde-Sesto, K. Matsuo, Y. Kim, N. Tamaoki, C. Weder, 2018, 140, 1584.
- [15] Y. Okumura, K. Ito, Adv. Mater. 2001, 13, 485.
- [16] Y. Noda, Y. Hayashi, K. Ito, *J. Appl. Polym. Sci.* 2014, *131*, 40509.
 [17] A. Bin Imran, K. Esaki, H. Gotoh, T. Seki, K. Ito, Y. Sakai, Y. Takeoka, *Nat. Commun.* 2014, *5*, 5124.
 [18] M. Inutsuka, K. Inoue, Y. Hayashi, A. Inomata, Y. Sakai, H. Yokoyama, V. Sakai, H. Yokoyama, K. Sakai, K. Inoue, Y. Hayashi, A. Inomata, Y. Sakai, H. Yokoyama, K. Sakai, K. Inoue, Y. Hayashi, A. Sakai, Y. Sakai, H. Yokoyama, K. Sakai, K.
- K. Ito, Polymer 2015, 59, 10.
- [19] K. Kato, K. Karube, N. Nakamura, K. Ito, Polym. Chem. 2015, 6, 2241.
- [20] K. Minato, K. Mayumi, R. Maeda, K. Kato, H. Yokoyama, K. Ito, Polymer 2017, 128, 386.
- [21] A. Yasumoto, H. Gotoh, Y. Gotoh, A. Bin Imran, M. Hara, T. Seki, Y. Sakai, K. Ito, Y. Takeoka, *Macromolecules* 2017, 50, 364.
- [22] T. Arai, K. Jang, Y. Koyama, S. Asai, T. Takata, Chem. Eur. J. 2013, 19, 5917.
- [23] K. Iijima, D. Aoki, H. Otsuka, T. Takata, *Polymer* 2017, *128*, 392.
 [24] K. Makiguchi, Y. Ogasawara, S. Kikuchi, T. Satoh, T. Kakuchi, *Macromolecules* 2013, *46*, 1772.
 [25] D. Aoki, S. Uchida, K. Nakazono, Y. Koyama, T. Takata, *ACS Macro* Lett. 2013, 2, 461.
- [26] J. Matsuo, K. Aoki, F. Sanda, T. Endo, Macromolecules 1998, 31, 4432.
- [27] N. Kihara, Y. Tachibana, H. Kawasaki, T. Takata, Chem. Lett. 2000, 29, 506.

Accepted Manuscrip

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Text for Table of Contents

