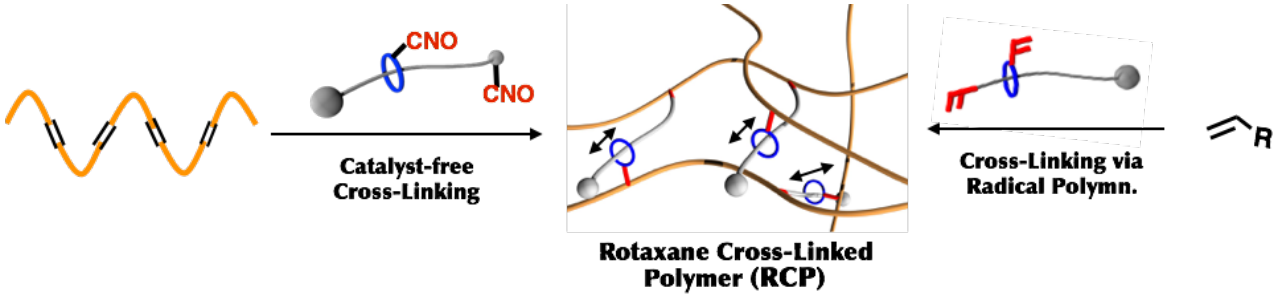
Cross-linking That Endows Rubber with Toughness Using Rotaxane Cross-Linkers

Toshikazu Takata
Department of Chemical Science and Technology, Tokyo Institute of Technology
Meguro, Tokyo 152-8552, Japan
Phone +81-3-5734-2898, Fax +81-3-5734-2888, E-Mail: ttakata@polymer.titech.ac.jp

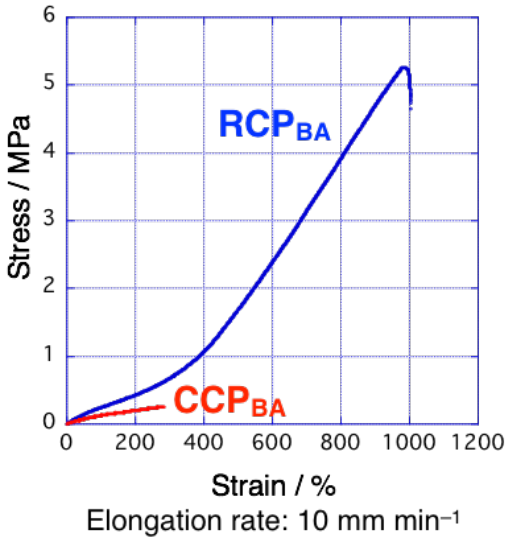
Abstract
Two novel cross-linkers for preparation of toughened rubbers are discussed. Rotaxane cross-linkers having two radically polymerizable vinyl groups in both wheel and axle components were prepared and subjected to the radical polymerization of vinyl monomers to obtain rotaxane-cross-linked polymer (RCP) which showed much higher mechanical property than covalently cross-linked polymers (CCP). Similar rotaxane cross-linkers having two nitrile *N*-oxide groups were prepared and directly used for cross-linking of NR, SBR, and so on.

Keywords: Rotaxane Cross-Linker, Vinyl Group, Nitrile *N*-Oxide, Click Reaction, Toughness, Movable Cross-Link

Network polymers having rotaxane structures at the cross-link points known as rotaxane-cross-linked polymer (RCP) are characterized by the movable polymer chains at the cross-link points and show unique properties and functions that have never been achieved with any covalently cross-linked polymer (CCP).[1-4] The movable polymer chain at the cross-link points makes possible an equalization of tension for external stimuli or stress to produce high swelling ability for solvents, high elasticity, and high stress-releasing ability. We have hitherto prepared various polymer networks showing recyclable and stimuli-responsible nature [1-4]. Herein, we would like to focus on the preparation of elastomers toughened by rotaxane cross-links using two novel rotaxane cross-linkers having vinylic and nitrile *N*-oxide functions placed on both wheel and axle components of their rotaxane structures, which were prepared based on our synthetic protocol for macromolecular [2]rotaxane consisting of one wheel and one polymer axle chain.



Direct cross-linking of NR, SBR, *etc.* using a rotaxane cross-linker having two nitrile *N*-oxide groups on its wheel and axle components [5-9] was carried out under catalyst-free or solvent-free conditions. Meanwhile, a similar rotaxane cross-linker possessing two vinyl groups in its axle and wheel components was added as a cross-linker into radical polymerization systems of vinyl monomers such as butyl acrylate to obtain solvent-insoluble polymer as rotaxane-cross-linked polymer (RCP_{BA}) [10]. Mechanical property of RCP was compared with covalently cross-linked polymer prepared from a mixture of BA and a typical covalent cross-linker. The big difference was observed as shown in the figure, suggesting the excellent cross-linker of the rotaxane cross-linkers which endow the cross-linked polymers with toughness.



[References] [1] *Angew. Chem. Int. Ed.*, **43**, 966 (2004). [2] *Macromolecules*, **41**, 8496 (2008). [3] *Angew. Chem. Int. Ed.*, **50**, 4872 (2011). [4] *Chem. Eur. J.*, **19**, 5917 (2013). [5] *ACS Macro Lett.*, **3**, 324 (2014). [6] *Angew. Chem. Int. Ed.*, **55**, in press (2016). [7] *ACS Macro Lett.*, **3**, 286 (2014). [8] *Polymer*, **54**, 4501 (2013). [9] *Chem. Commun.* **49**, 7723 (2013). [10] *ACS Macro Lett.*, **4**, 598 (2015).