Efficient Chemical Recycling System of Networked Polymer: De-Cross-Linking of Cross-Linked Polymer Obtained from Bis(five-membered cyclic dithiocarbonate)

Tohru Nakamura, Bungo Ochiai, and Takeshi Endo*

Department of Polymer Science and Engineering,
Faculty of Engineering, Yamagata University,
Jonan 4-3-16, Yonezawa, Yamagata 992-8510, Japan

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Ring-opening polymerization is a useful reaction to introduce functional groups into the polymer main chain, although it is often accompanied by depolymerizations including the backbiting reaction, which decrease the molecular weights of the resulting polymers to give the oligomers and broaden the polydispersities. Therefore, many researchers have studied to suppress such side reactions to control the molecular weights and the polydispersities.[1] Meanwhile, backbiting reaction may lead polymers to monomers; this means that monomers can be chemically recycled from waste polymers. That is, ring-opening polymerization can be expected as one of the most appropriate processes for chemical recycle systems based on depolymerization by backbiting reaction that efficiently generates starting monomers. A lot of studies have been conducted for depolymerizations to recycle monomers selectively without producing contaminant including oligomers, which is difficult because of the monomer−polymer equilibrium.[2] As another approach, we focused on a polymerization−depolymerization system of cyclic dithiocarbonates, 1,3-oxathiolane-2-thione derivatives. Selective cationic polymerization took place with carbocationic reagents, whereas protonic or Lewis acids selectively isomerize to afford 1,3-dithiolane-2-ones.[3] The resulting polymers can be cationically and anionically depolymerized to generate the aforementioned isomers, especially by employing *t*-BuOK.[4] The selective nature of the depolymerization prompted us to apply this reaction for cross-linked polymers. Although much effort has been made for de-cross-linking reactions of cross-linked polymers to produce linear polymers[5] or original monomers,[6] de-cross-linking of a cross-linked polymer into an isomer of the monomer has not been reported. Formation of an isomer is postulated to be an effective regeneration method because it is irrespective to the monomer−polymer equilibrium to prevent efficient depolymerization in typical polymerization−backbiting systems. This Communication herein deals with cationic cross-linking reaction of a bis(five-membered cyclic dithiocarbonate) and both cationic and anionic de-cross-linking of the cross-linked polymer, giving the isomer of the starting monomer containing 1,3-dithiolane-2-one moieties.

The bis(five-membered cyclic dithiocarbonate), 2,2-bis-[*p*-(1,3-oxathiolane-2-thione)-5-yl-methoxyphenyl]propane (**1**), was prepared by the reaction of the corresponding epoxide with carbon disulfide in the presence of lithium bromide as a catalyst according to the literature.[7] Cross-linking reaction of **1** was conducted by cationic ring-opening polymerization with ethyl trifluoromethanesulfonate (TfOEt) (Scheme 1, Table 1).

TfOEt was added to a solution of **1** (1.48 g, 3.00 mmol) in monochlorobenzene (PhCl) (2.00 mL), and the reaction mixture was stirred at 60 or 80 °C for 24 h (run 1) or 0.5 h (runs 2 and 3). This reaction mixture was quenched with pyridine. When the 4 mol % of TfOEt was used at 60 °C, an isomer of **1** (2,2-bis[*p*-(1,3-dithiolane-2-one)-4-yl-methoxyphenyl]propane (**2**)) was obtained in a high yield, and no objective cross-linked product was obtained (run 1), while carbocationic reagents predominantly polymerize monofunctional five-membered cyclic dithiocarbonates.[3] A possible reason for this differing reaction course is the steric hindrance that prevented the polymerization. The reaction at higher temperature (80 °C) gave **2** and an insoluble product (run 2). The use of more TfOEt enabled selective formation of the desired insoluble product **P2** (run 3). A similar temperature dependence of the selectivity is also observed for monofunctional dithiocarbonates, which however is not so drastic as the case of **1**.[3b] These results suggest the lower polymerizability of **1** than conventional monofunctional monomers. The cross-linked polymer was purified by Soxhlet extraction of the precipitate with THF. The resulting compound was insoluble in common organic solvents (dichloromethane, chloroform, THF, DMSO, DMF, and so forth). An IR absorption peak of a carbonyl group (1644 cm^{-1}) supported the successful isomerization polymerization. The glass transition temperature (T_g) of the cross-linked polymer obtained in run 3 was 113 °C, indicating the relatively flexible character of the product. By considering the fact that the polymerization with lesser amount of TfOEt (run 2) gave a modest amount of the isomer **2**, **P2** probably contains isomerized cyclic dithiocarbonate structure as well as the polymerized structure.

The resulting cross-linked polymer (**P2**) (obtained in run 3 in Table 1) was subjected to de-cross-linking reaction. In the de-cross-linking by cationic initiator, a suspension of **P2** (49.3 mg, 0.10 mmol unit) in PhCl (1.00 mL) was treated with 5 or 20 mol % of trifluoromethanesulfonic acid (TfOH), methyl trifluoromethanesulfonate (TfOMe), or TfOEt at 80 °C for 24 h (Scheme 2, Table 2).

Soluble products were obtained in 9−61% yields. The highest yield required 20 mol % of TfOEt (run 6). These yields are lower than those in the cationic depolymerizations of linear polydithiocarbonates,[4] probably due to the rigid structure of the cross-linked polymer **P2**. NMR and IR spectroscopic analyses suggested that the soluble products consist of the pure isomer **2**. Gel permeation chromatographic (GPC) analysis clearly showed that the oligomers were negligibly produced (see Supporting Information). In contrast, anionic de-cross-linking afforded the isomer **2** in quantitative yield (run 7). That is, when **P2** (98.5 mg, 0.20 mmol unit) in a THF suspension (2.00 mL) was treated with 10 mol % of potassium *tert*-butoxide (*t*-BuOK) at room temperature for 24 h, the suspension gradually changed to a homogeneous solution, indicating that the THF-insoluble cross-linked polymer was efficiently de-cross-linked (Scheme 2). The quantitative formation of isomer **2** was

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* To whom all correspondence should be addressed: Tel & Fax +81-238-26-3090; e-mail tendo@yz.yamagata-u.ac.jp.

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Scheme 1. Cationic Cross-Linking or Isomerization of Bifunctional Dithiocarbonate (1)

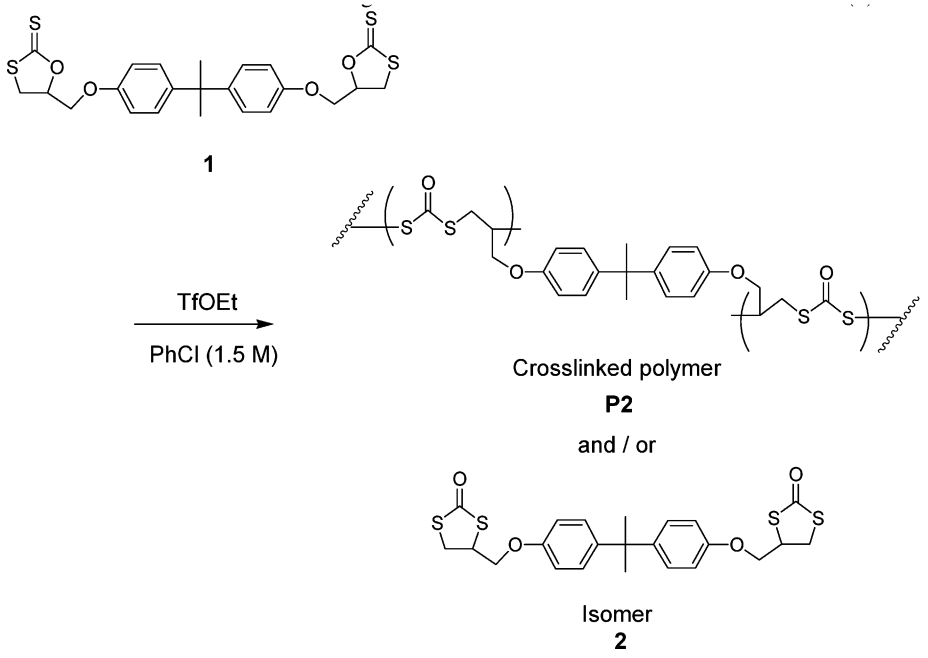

Table 1. Cationic Cross-Linking or Isomerization of Bifunctional Dithiocarbonate (1)[a]

run	[TfOEt]/ [dithiocarbonate]	reaction temp (°C)	reaction time (h)	cross-linked polymer yield[b] (%)	isomer yield[c] (%)
1	0.04	60	24	*d*	90[c]
2	0.04	80	0.5	58[b]	39
3	0.20	80	0.5	92[b]	*d*

[a] Conditions: solvent, PhCl; concentration of **1**, 1.5 M; initiator, TfOEt. [b] THF-insoluble part. [c] Hexane-insoluble part. [d] Not observed.

Scheme 2. De-Cross-Linking of Cross-Linked Polymer (P2)

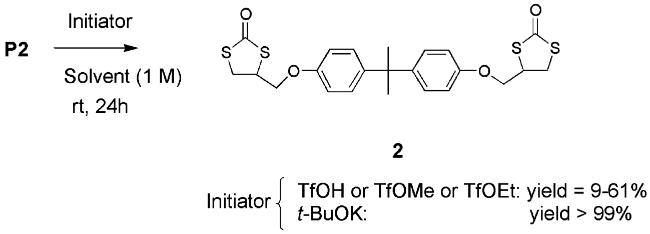

Table 2. De-Cross-Linking of Cross-Linked Polymer (P2)[a]

run	initiator (mol %)[b]	solvent	temp (°C)	isomer yield (%)
1	TfOH (5)	PhCl	80	9
2	TfOH (20)	PhCl	80	28
3	TfOMe (5)	PhCl	80	22
4	TfOMe (20)	PhCl	80	54
5	TfOEt (5)	PhCl	80	30
6	TfOEt (20)	PhCl	80	61
7	*t*-BuOK (10)	THF	rt	>99

[a] Conditions: concentration of the repeating unit of **P2**, 0.1 mol/L; reaction time, 24 h. [b] Mol % vs repeating unit of polydithiocarbonate.

confirmed by ^{1}H NMR, ^{13}C NMR, and IR measurements. GPC analysis did not show any peak assignable to oligomers, supporting the selective nature of the depolymerization (see Supporting Information). The effective de-cross-linking behavior using *t*-BuOK agreed well with the case of linear polydithiocarbonate.[4]

As mentioned above, we established an effective de-cross-linking system of a cross-linked polymer to generate an isomer of the starting monomer. The generation of the stable isomer would have enabled the complete and selective de-cross-linking, owing to the absence of the monomer−polymer equilibrium.

Supporting Information Available: Measurement conditions, ^{1}H and ^{13}C NMR spectroscopic data of isomer **2**, and a figure showing GPC profiles of the reaction mixture after cationic de-cross-linking reaction (Table 2, run 6) and anionic de-cross-linking reaction (Table 2, run 7). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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