Anionic Ring-Opening Polymerization of Cyclic Thiocarbonates Containing Norbornene and Norbornane Groups Undergoing Volume Expansion on Polymerization

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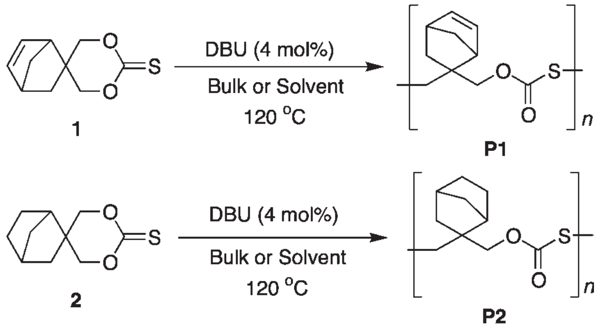
Six-membered cyclic thiocarbonate derivatives, 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxane-2-thione (**1**) and 5,5-(bicyclo[2.2.1]heptan-5,5-ylidene)-1,3-dioxane-2-thione (**2**) underwent anionic ring-opening polymerization initiated by 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) to afford polythiocarbonates accompanying 12.3 and 12.6% volume expansion, respectively.

Common vinyl monomers such as styrene and methyl methacrylate undergo polymerization with volume shrinkage.[1] Thermosetting resins such as epoxides also show 4–5% volume shrinkage during the curing process. The occurrence of the volume shrinkage of the monomers and resins induces serious problems in their industrial applications for composites, adhesives, coatings, precision castings, and sealant materials. Cyclic carbonates undergo cationic and anionic ring-opening polymerizations accompanying volume expansion, which can be accounted for by difference in strength of intermolecular dipole-dipole interactions between monomers and polymers. For example, a six-membered cyclic carbonate bearing norbornene moiety undergoes 8.2% volume expansion during anionic polymerization.[2] Recently, sulfur-containing polymers are gaining importance due to their excellent optical and thermal properties.[3] In the course of our work on ring-opening polymerization of cyclic carbonates, we have designed a sulfur analogue of cyclic carbonate, i.e., cyclic thiocarbonate, which exhibits a unique reactivity. Anionic ring-opening polymerization[3] of 1,3-oxathian-2-one proceeds via selective ring-opening with C-S bond cleavage to afford the corresponding polythiocarbonate. Cationic ring-opening polymerization[4] of 5,5-dimethyl-1,3-dioxane-2-thione proceeds accompanying isomerization of thiocarbonate group via a living process to afford polythiocarbonate.[5] We also studied cationic ring-opening polymerization of novel six-membered cyclic thiocarbonate derivatives, 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxane-2-thione (**1**) and 5,5-(bicyclo[2.2.1]heptan-5,5-ylidene)-1,3-dioxane-2-thione (**2**).[6] Unidentified products were obtained from the reaction of **1** initiated by trifluoromethanesulfonic acid (TfOH), methyl trifluoromethanesulfonate (TfOMe), boron trifluoride etherate (BF_3OEt_2), or triethyloxonium tetrafluoroborate (Et_3OBF_4); however, **1** underwent the cationic ring-opening polymerization by using methyl iodide as initiator to afford polythiocarbonate. In this study, for developing a new polymerization system with volume-expansion, we attempt anionic ring-opening polymerization of **1** and **2** as shown in Scheme 1. We report the thermal properties of the obtained polythiocarbonates and the volume change during polymerization to reveal the effect of introduction of a thiocarbonate group instead of a carbonate one.



Scheme 1.

Anionic ring-opening polymerization[7] of **1**[6] and **2**[6] was carried out with 4 mol% of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU)[2] at 120 °C as summarized in Table 1. The polymerization of **1** and **2** proceeded in all cases except run 4, wherein the high melting point (215 °C)[6] may inhibited the polymerization of run 4 in Table 1. The molecular-weight-distributions (M_w/M_n) of the obtained polymers were somewhat broad (1.40–1.48). The low polymer yields may be due to the chain-transfer reactions such as back-biting reaction. The polymer could be isolated by precipitation with methanol, and exhibited good solubility in common organic solvents such as THF, chloroform, and dichloromethane. The structures of the obtained polymers were confirmed by NMR and IR spectroscopy. **P1** and **P2** exhibited ^{13}C NMR signals at 154 ppm, which is assignable to carbonyl carbon. In addition, an absorption band based on carbonyl group was observed at 1743 cm^{-1} in their IR spectra. These data may suggest that the polymerization proceeded accompanying the isomerization of thiocarbonate group as observed in the anionic

Table 1. Anionic ring-opening polymerization of **1** and **2**[a]

Run	Monomer	Time/h	Solvent	Yield[b]/%	M_n[c]	M_w/M_n[c]
1	**1**	1	none	25	15200	1.48
2	**1**	12	toluene	38	8800	1.44
3	**1**	12	DMF	38	8600	1.47
4	**2**	1	none	no reaction		
5	**2**	12	toluene	8	7100	1.43
6	**2**	12	DMF	22	11800	1.40

[a]Temp. 120 °C, monomer 1.00 mmol, solvent 0.20 mL, initiator DBU 0.040 mmol. [b]Calculated from the amounts of the monomer and polymer isolated by preparative high performance liquid chromatography eluted with chloroform. [c]Estimated by size exclusion chromatography (SEC) eluted with THF at 40 °C based on polystyrene standards.

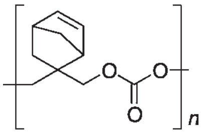
polymerization of 1,3-dioxane-2-thione.[8]

Thermal behavior of the polymers was evaluated by TGA and DSC under nitrogen as summarized in Table 2. **P1** and **P2** lost their 10% weight at 258 and 261 °C, respectively. The high thermal stability of **P1** and **P2** compared to the corresponding polycarbonate **P3**[2] may be attributable to the introduction of sulfur into the polymer backbone.

Table 2. Properties of **P1–P3**

Polymer	Volume change[a]/%	T_g[b]/°C	T_{d10}[c]/°C
P1	+12.3	82	258
P2	+12.6	82	261
P3[d]	+8.2	108	207

[a] Calculated by the densities of the monomer and polymer.
[b] Determined by differential scanning calorimetry (DSC).
[c] Determined by thermogravimetry (TG). [c] Data from reference 2.



P3

Densities of the monomers and the obtained polymers were evaluated by density gradient tubes at 25 °C. The densities of **P1** and **1** were 1.14 and 1.30, and those of **P2** and **2** were 1.11 and 1.27, respectively. These results indicated that the polymerization of **1** and **2** proceeded with volume expansion as large as 12.3 and 12.6%, respectively, due to the difference in strength of intermolecular dipole-dipole interactions between monomers and the obtained polymers.[1]

In summary, six-membered cyclic thiocarbonate derivatives, 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxane-2-thione (**1**) and 5,5-(bicyclo[2.2.1]heptan-5,5-ylidene)-1,3-dioxane-2-thione (**2**) underwent anionic ring-opening polymerization to afford the polycarbonates accompanying the isomerization of thiocarbonate group and remaining norbornene and norbornane structures, respectively. The obtained polymer showed good solubility and high thermal stability. The monomer showed volume expansion during polymerization to lead a new polymerization system with volume expansion.

This article is dedicated to Professor Teruaki Mukaiyama for his 75 th birthday.

References and Notes

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7 Typical polymerization procedure. All glass vessels were heated in vacuo before use, filled with dry nitrogen, and handled in a dry nitrogen stream. To a solution of 196 mg (1.00 mmol) of **1** in 0.20 mL of *N*,*N*-dimethylformamide (DMF) was added 6.1 mg (4.0 mol%) of DBU. Then, the tube was evacuated and sealed off. After the reaction mixture was stirred at 120 °C for 12 h, a few drops of methanol was added to the reaction mixture to quench the polymerization. The obtained polymer was purified by preparative high performance liquid chromatography with chloroform eluent.
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