Living Ring-Opening Polymerization of Cyclic Thiocarbonate

Takeshi Endo,[1,]* *Nobukatsu Nemoto,*[2] *Fumio Sanda*[3]

[1] Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan
[2] Department of Materials Chemistry and Engineering, College of Engineering, Nihon University, Tamura-machi, Koriyama, Fukushima 963-8642, Japan
[3] Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Summary: This work deals with the cationic ring-opening polymerization of a cyclic thiocarbonate, 5,5-dimethyl-1,3-dioxane-2-thione (**1**). The polymerization was carried out with 2 mol% of trifluoromethanesulfonic acid, methyl trifluoromethanesulfonate, boron trifluoride etherate, or triethyloxonium tetrafluoroborate as an initiator to afford the polythiocarbonate with the narrow molecular weight distribution (M_n = 11200-31000, M_w/M_n = 1.04-1.15). The molecular weight of the obtained polymer could be controlled by the feed ratio of the monomer to the initiator and increased when the second monomer was added to the polymerization mixture after quantitative consumption of **1** in the first stage, supporting that the cationic ring-opening polymerization of **1** proceeded via a living process.

Introduction

It has been extensively studied that cyclic carbonates undergo ring-opening polymerization both with cationic and anionic initiators.[1] We have also found that cyclic carbonates show volume expansion during polymerization, which can be accounted for by the difference in strength of the intermolecular interaction between monomers and polymers.[2] Recently, sulfur-containing polymers such as polythioethers[3] and polythioesters[4] are gaining importance due to their excellent optical and thermal properties. In the course of the study of the ring-opening polymerization of cyclic carbonates, we have designed a sulfur analogue of cyclic carbonate, i.e., cyclic monothiocarbonate. We have reported the first anionic ring-opening polymerization of a six-membered cyclic monothiocarbonate, 1,3-oxathian-2-one, to afford poly(trimethylene thiocarbonate).[5] Polythiocarbonate with the similar structure can be obtained by the cationic ring-opening polymerization of 1,3-dioxane-2-thione as reported by

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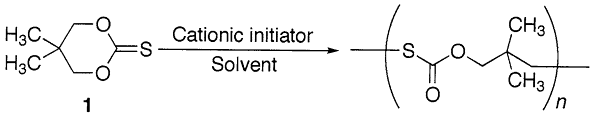
Kricheldorf et al.[6] Unfortunately, the obtained polythiocarbonate is poorly soluble in common organic solvents, therefore, the detailed polymerization behavior is not sufficiently reported. This article deals with the controlled cationic ring-opening polymerization of a six-membered cyclic monothiocarbonate, 5,5-dimethyl-1,3-dioxan-2-thione (**1**) as described in Scheme 1.



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Cationic initiator: Et_3OBF_4, TfOMe, TfOH, BF_3OEt_2
Solvent: CH_2Cl_2, $CHCl_3$, PhCl

Scheme 1.

Results and Discussion

Monomer **1** was synthesized by the reaction of 2,2-dimethylpropane-1,3-diol with an equivalent amount of thiophosgene in the presence of 2 equiv. of 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one in chloroform at 50°C for 12 h in 45% yield. The cationic polymerization of **1** was carried out with 2 mol% of trifluoromethanesulfonic acid (TfOH), methyl trifluoromethanesulfonate (TfOMe), boron trifluoride etherate (BF_3OEt_2), or triethyloxonium tetrafluoroborate (Et_3OBF_4) as an initiator at 30-80 °C under a dry nitrogen atmosphere as summarized in Table 1. The consumption of the monomer was achieved within 8 h in runs 1 and 2, and within 3 h in runs 3-5. There is no significant difference between the GPC profiles at 8 h and that at 24 h (conditions: monomer, 2.00 mmol; initiator, 0.040 mol; solvent, 2.00 mL of CH_2Cl_2; temperature, 30 °C), supporting the absence of back-biting reaction.

Table 1. Cationic ring-opening polymerization of **1**[a)]

run	Solvent	initiator	time h	temp. °C	conv. [b)] %	M_n [c)]	M_w/M_n [c)]
1	CH_2Cl_2	Et_3OBF_4	24	30	> 99	13200	1.04
2	$CHCl_3$	Et_3OBF_4	20	40	> 99	16800	1.04
3	PhCl	TfOMe	12	80	> 99	11200	1.15
4	PhCl	TfOH	12	80	> 99	13900	1.13
5	PhCl	BF_3OEt_2	12	80	> 99	31000	1.08

[a)] Monomer, 0.25 mmol; solvent, 0.25 mL; initiator, 0.005 mmol.
[b)] Determined by ^1H NMR spectroscopy measured in $CDCl_3$.
[c)] Estimated from GPC eluted with THF based on polystyrene standards.

In all cases in Table 1, polythiocarbonates with the narrow molecular-weight-distribution could be obtained, which exhibited good solubility in common organic solvents such as tetrahydrofuran (THF), chloroform, dichloromethane, and acetone.

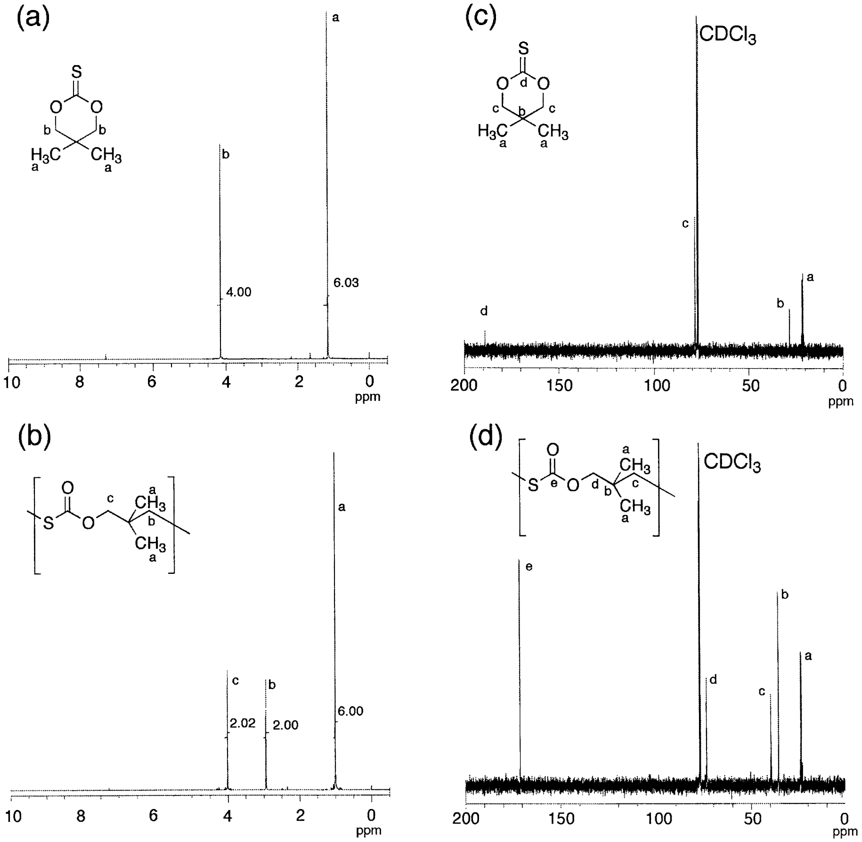
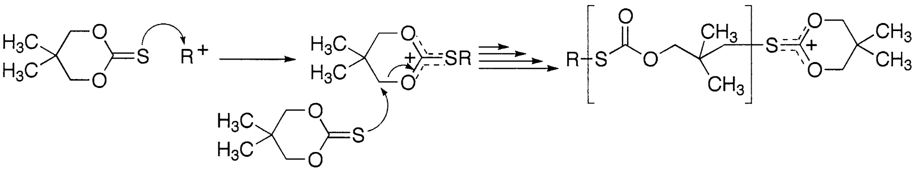


Figure 1. (a) ^{1}H NMR spectra (solvent, $CDCl_3$; 500 MHz) of **1**, (b) polymer obtained in the polymerization in run 3 in Table 1, (c) ^{13}C NMR spectra (solvent, $CDCl_3$; 125 MHz) of **1**, (d) polymer obtained in the polymerization in run 3 in Table 1.

The conversion estimated by ^{1}H NMR spectroscopy was nearly equal to the yield of the polymer. The difference in the observed M_n's among the initiators used would be due to the difference in initiation efficiency. The difference in between the observed and expected M_n's would be owing to the low initiation efficiency and/or the different solvation state in THF between the polythiocarbonate and the polystyrene standards. The obtained polymer could be isolated by precipitation with hexane and the structure was examined by ^1H NMR, ^{13}C NMR, and IR spectroscopy. Figure 1 illustrates the ^1H and ^{13}C NMR spectra of **1** and the polymer obtained in the polymerization in run 3 in Table 1. The ^1H NMR spectrum of the polymer (Figure 1b) showed three singlet signals at 1.01, 2.94, and 4.07 ppm, which were assignable to methyl group, α- and γ-methylenes of the thiocarbonate sulfur, respectively. The ^{13}C NMR spectrum of the polymer (Figure 1d) showed the corresponding three methylene carbon signals at 35.5, 39.5, and 73.6 ppm, the methyl carbon one at 23.4 ppm, and the carbonyl carbon one at 171.0 ppm. The assignments of the observed signals were confirmed by DEPT experiment. The ^{13}C NMR spectrum of **1** (Figure 1c) showed the thiocarbonyl carbon signal at 189.1 ppm, indicating the progress of the cationic ring-opening polymerization accompanying isomerization of thiocarbonyl group into carbonyl group. The isomerization was supported by a C=O absorption peak at 1717 cm^{-1} in the IR spectrum of the polymer. Scheme 2 illustrates a plausible mechanism for the ring-opening polymerization, which may proceed via the nucleophilic attack of a thiocarbonyl sulfur to a cationic initiator, followed by the nucleophilic attack of a thiocarbonyl sulfur to α-position of an ether oxygen in a cyclic carbenium ion.



Scheme 2.

The relationship between the M_n of the polymer and feed ratio of [**1**]/[Et_3OBF_4] was linear, and the M_w/M_n was around or less than 1.1 as shown in Figure 2. The living character of the present polymerization was confirmed by postpolymerization. After the first stage polymerization of **1** (20 equiv. to Et_3OBF_4) for 12 h at 0 °C, the second monomer (40 equiv. to Et_3OBF_4) was fed to react continuously for an additional 12 h at 30 °C. The M_n of the obtained polymer increased by the second monomer feed as shown in Figure 3, though a small part of the prepolymer chains did not completely grow, supporting quasi-living character of the polymerization.

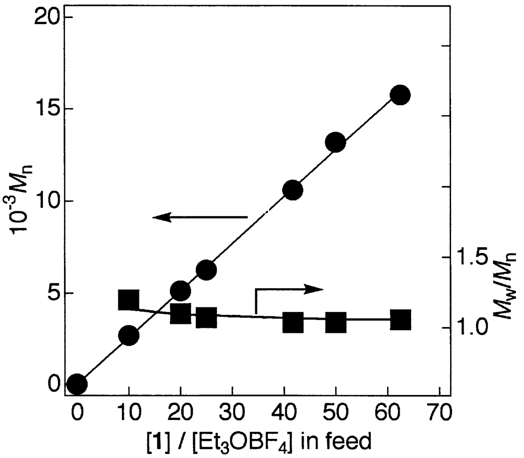


Figure 2. Relationships between M_n, M_w/M_n and feed ratio of [1]/[Et_3OBF_4]. Conditions: monomer, 0.25 mmol; solvent, 0.25 mL of CH_2Cl_2; temperature, 30 °C.

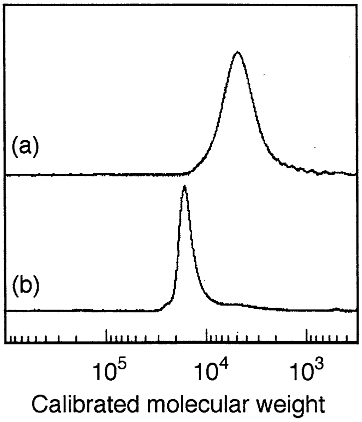


Figure 3. GPC profiles of the obtained polythiocarbonate in post polymerization: (a) after prepolymerization of **1** (20 equiv to Et_3OBF_4), M_n = 4200 (M_w/M_n = 1.16), (b) after postpolymerization of **1** (40 equiv to Et_3OBF_4), M_n = 12400 (M_w/M_n = 1.15).

Conclusions

The polymerization of 5,5-dimethyl-1,3-dioxane-2-thione (**1**) by several cationic initiators afforded polythiocarbonate with good solubility in common organic solvents and narrow molecular-weight-distribution. The molecular weight of the obtained polymer could be controlled by the feed ratio of the monomer to initiator and increased when the second monomer was added to the polymerization mixture after quantitative consumption of **1** in the first stage, supporting that the cationic ring-opening polymerization of **1** proceeded via a quasi-living process.

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