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Cationic Ring-Opening Polymerization of Cyclic Monothiocarbonates: Varying the Polymer Main Chain by Neighboring Group Participation

Nobukatsu Nemoto,[†,‡] Xiaoyu Xu,[§] Fumio Sanda,[§] and Takeshi Endo*[,‡]

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan; and Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226−8503, Japan

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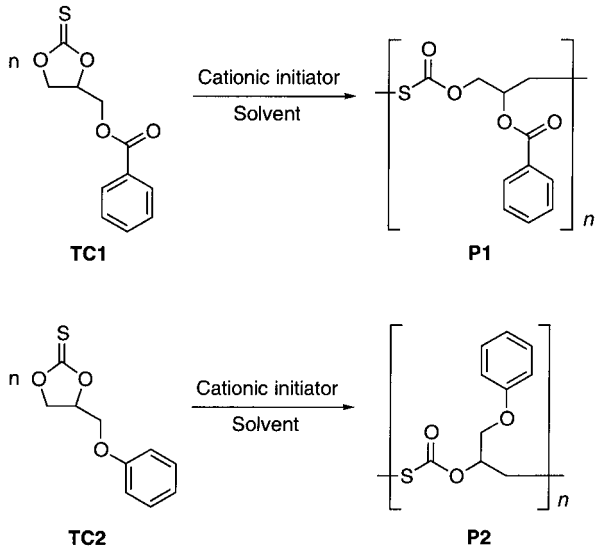
ABSTRACT: Novel five-membered cyclic monothiocarbonate derivatives, 4-benzoyloxymethyl-1,3-dioxolane-2-thione (**TC1**) and 4-phenoxymethyl-1,3-dioxolane-2-thione (**TC2**), were synthesized by reaction of the corresponding diols and thiophosgene in the presence of 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (antipyrine) in chloroform. The cationic ring-opening polymerization of **TC1** and **TC2** using several cationic initiators afforded polythiocarbonate with good solubility in common organic solvents accompanying isomerization of thiocarbonate group. The polymerization of **TC1** proceeded involving the neighboring group participation of the ester group. The main chains of the polymers obtained from **TC1** and **TC2** were different. The main chain structure depends on the substituent on the thiocarbonate ring, i.e., whether neighboring ester group participation was involved or not.

Introduction

Six-membered cyclic carbonates undergo anionic ring-opening polymerization to yield the corresponding polycarbonates; [1] cationic polymerization is generally accompanied by partial elimination of carbon dioxide to afford polycarbonates containing an ether unit. In contrast, polymerization of five-membered cyclic carbonates affords mainly polyethers rather than polycarbonates through competitive elimination of carbon dioxide independent of the polymerization mode.[2] We recently found that a dimethyl-substituted six-membered cyclic monothiocarbonate, 5,5-dimethyl-1,3-dioxane-2-thione, undergoes living cationic ring-opening polymerization to afford a polymonothiocarbonate.[3] Kricheldorf et al. also reported that cationic ring-opening polymerization of 1,3-dioxane-2-thione affords polymonothiocarbonate.[4] The obtained polythiocarbonate is poorly soluble in common organic solvents, therefore, the detailed polymerization behavior was not sufficiently analyzed. Jones et al. have reported the cationic ring-opening polymerization of a five-membered monothiocarbonate without a substituent; [5] however, the polymerization mechanism and polymer structure are still unclear because of the poor solubility of the polymer and the limitations of analytical methods at that time. We recently reported that a five-membered cyclic dithiocarbonate having an ester group undergoes living cationic ring-opening polymerization due to the neighboring group participation of the ester group.[6] In this case, neighboring group participation is effective to stabilize the propagating polymer end, resulting in a living polymerization. Miyamoto et al. and Kanoh et al. have also reported the control of polymerization by neighboring group participation in the cationic ring-opening polymerization of ester-substituted oxiranes[7] and imide-substituted oxetanes.[8] We would like to generalize the living polymerization involving neighboring group participation from the viewpoint of both polymer and organic chemistry. This article describes the synthesis and cationic ring-opening polymerization behavior of a five-membered cyclic monothiocarbonate bearing an ester group (**TC1**), as shown in Scheme 1. This work also studies the cationic ring-opening polymerization behavior of a five-membered cyclic monothiocarbonate having a phenoxy group (**TC2**) to clarify the effect of an ester group.

Scheme 1



Experimental Section

Materials. 1,2,3-Propanetriol (glycerol) (Kanto Chemical Co., Inc., > 99%), benzoyl chloride (Tokyo Kasei Kogyo Co., Inc., > 99%), dimethyltin dichloride (Tokyo Kasei Kogyo Co., Inc., 98%), 3-phenoxypropane-1,2-diol (Tokyo Kasei Kogyo Co., Inc., 95%), thiophosgene (Tokyo Kasei Kogyo Co., Inc., 95%), and 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (antipyrine) (To-

* To whom all correspondence should be addressed. Telephone and fax: +81-238-26-3090. E-mail: tendo@poly.yz.yamagata-u.ac.jp.
† Japan Chemical Innovation Institute
‡ Yamagata University.
§ Tokyo Institute of Technology.

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Table 1. Cationic Ring-Opening Polymerization of TC1 and TC2

run	monomer	solvent[a]	initiator[b]	time (h)	temp (°C)[c]	convn[d] (%)	yield[e] (%)	$10^{-3}M_n$[f]	M_w/M_n[f]
1	**TC1**	PhCl	TfOMe	8	rt	>99	94	6.4	1.21
2	**TC1**	PhCl	TfOMe	8	80	>99	92	9.6	1.16
3	**TC1**	PhCl	TfOMe	1	80	>99	90	8.5	1.24
4	**TC1**	PhCl	TfOH	1	80	>99	94	12.9	1.31
5	**TC1**	PhCl	BF_3OEt_2	1	80	>99	95	22.4	1.32
6	**TC2**	CH_2Cl_2	TfOMe	8	rt	>99	85	12.3	1.48
7	**TC2**	PhCl	TfOMe	1	80	>99	84	11.0	1.39
8	**TC2**	PhCl	TfOH	1	80	97	86	7.6	1.33
9	**TC2**	PhCl	BF_3OEt_2	1	80	>99	84	25.1	1.53

[a] Concentration of monomer, 1 mol/L. [b] 2 mol % to the monomer. [c] rt = room temperature. [d] Determined by ^{1}H NMR spectroscopy measured in $CDCl_3$. [e] Insoluble part in hexane. [f] Estimated from GPC eluted with THF based on polystyrene standards. M_n's expected from $[M]_0/[I]_0$ are 11 900 for **TC1** and 10 500 for **TC2** ($DP_n = 50$).

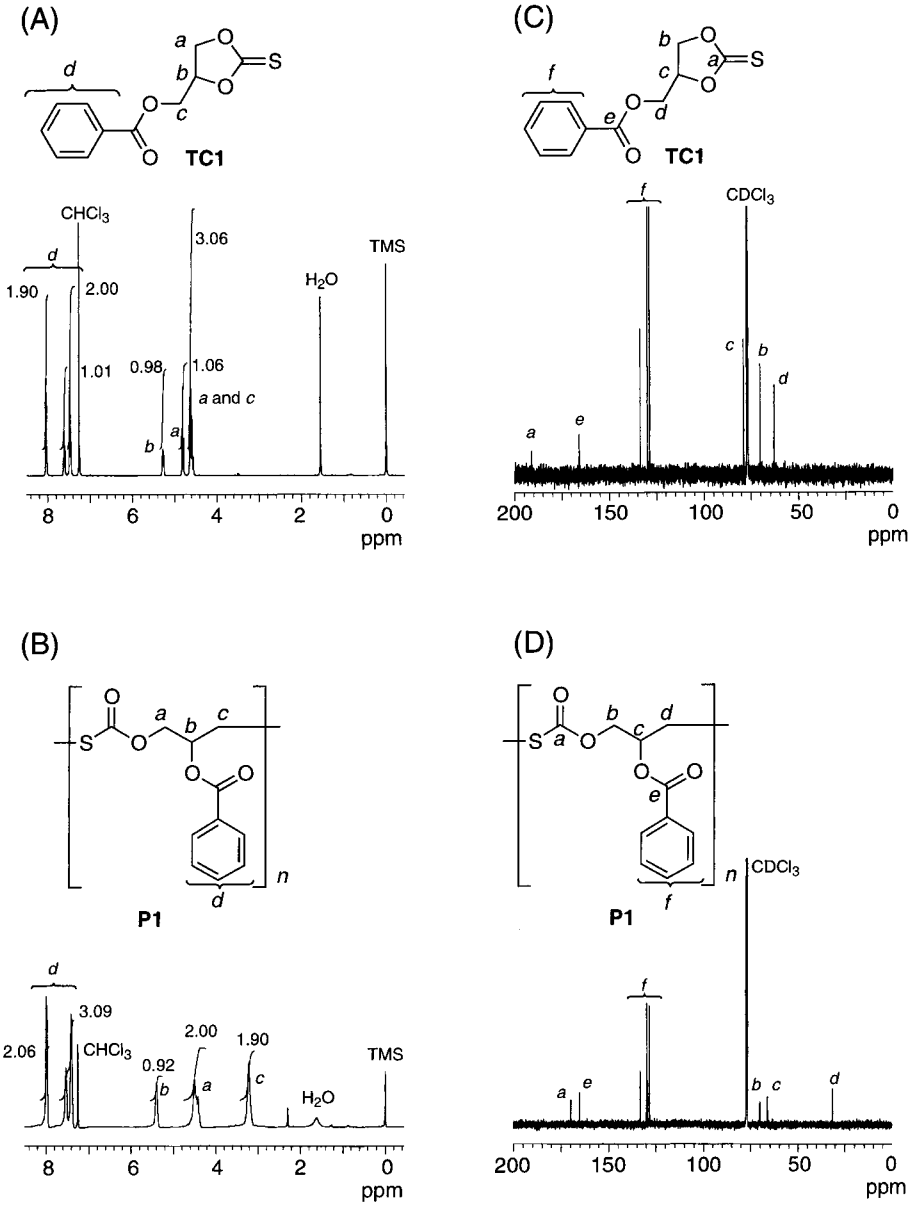


Figure 1. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of (A) **TC1**, and (B) **P1** obtained from the polymerization in run 3 in Table 1. The numbers at the resonance lines represent the integration ratios of the signals. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of (C) **TC1**, and (D) **P1** obtained from the polymerization in run 3 in Table 1.

kyo Kasei Kogyo Co., Inc., 99%) were commercially available and used as received. Triethylamine (TEA) (Tokyo Kasei Kogyo Co., Inc., > 99%), boron trifluoride etherate (BF_3OEt_2) (Kanto Chemical Co., Inc., 95%), methyl trifluoromethanesulfonate (TfOMe) (Kanto Chemical Co., Inc., 97%), chloroform, dichloromethane and chlorobenzene were distilled over CaH_2 before use. Tetrahydrofuran (THF) was distilled from sodium. Trifluoromethanesulfonic acid (TfOH) (Tokyo Kasei Kogyo Co., Inc., 98%) was distilled just before use.

Measurements. Melting points (mp) were measured by a Yanaco micro melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR), using tetramethylsilane (TMS) as an internal standard in chloroform-*d*

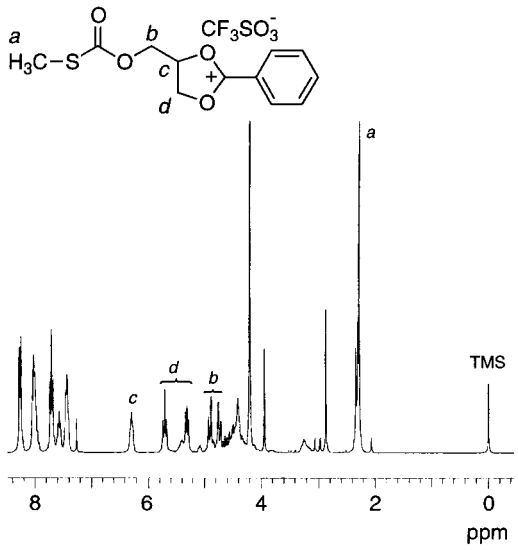


Figure 2. ^{1}H NMR (400 MHz) spectrum of the mixture of **TC1** and TfOMe (1.2 equiv) in $CDCl_3$ at room temperature.

($CDCl_3$). IR spectra were obtained with a JASCO FT/IR-5300 spectrometer. Molecular weights (M_n and M_w: number- and weight-average molecular weights) and the polydispersity (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Tosoh HLC 8120 system, equipped with a refractive index detector and two consecutive polystyrene gel columns (Tosoh TSK gels G2500H and G3000H, whose limitations of size exclusion are 20000 and 60000, respectively) using THF as an eluent, with a flow rate of 1.0 mL/min by polystyrene calibration at 30 °C.

3-Benzoyloxypropane-1,2-diol. A solution of benzoyl chloride (0.070 mol, 9.84 g) in THF (50 mL) was added dropwise to a solution of glycerol (0.21 mol, 19.34 g), dimethyltin dichloride[9] (1.0 mmol, 0.22 g) and potassium carbonate (0.10 mol, 13.82 g) in THF (250 mL). After the solution was stirred at ambient temperature for 20 h, the reaction mixture was poured into water. The crude product was extracted with ethyl acetate, and the organic layer was collected and dried over anhydrous magnesium sulfate. The desired product was separated by silica gel column chromatography eluted with ethyl acetate. Finally, recrystallization from ethyl acetate afforded 3-benzoyloxypropane-1,2-diol in 77% yield. ^{1}H NMR: δ = 3.06 (s, 1H, CH−O*H*), 3.45 (s, 1H, −CH_2−O*H*), 3.66−3.79

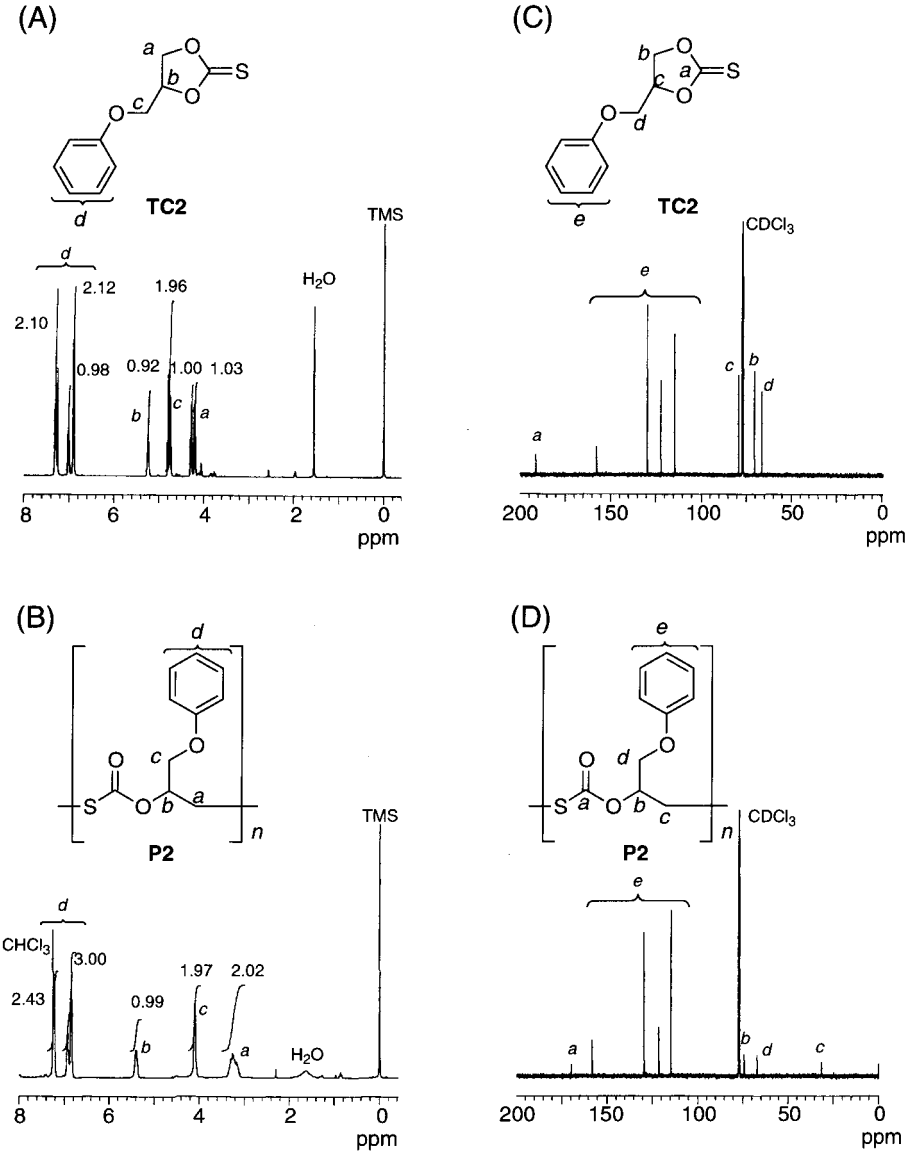
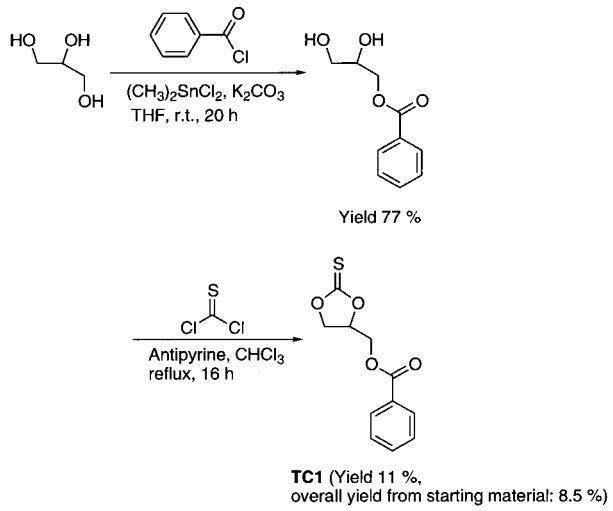


Figure 3. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of (A) **TC2**, and (B) **P2** obtained from the polymerization in run 7 in Table 1. The numbers at the resonance lines represent the integration ratios of the signals. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of (C)**TC2**, and (D) **P2** obtained by the polymerization in run 7 in Table 1.

Scheme 2



(m, 2H, −CH_2−OH), 4.06−4.12 (m, H, −CH-), 4.36−4.42 (m, 2H, −O−CH_2−), 7.27−8.04 (m, 5H, C_6H_5) ppm.

4-Benzoyloxymethyl-1,3-dioxolane-2-thione (TC1). A solution of thiophosgene (0.08 mol, 6.08 mL) in chloroform (100 mL) and a solution of 3-benzoyloxypropane-1,2-diol (0.06 mol, 11.76 g) in chloroform were added simultaneously to a solution of antipyrine (0.1 mol, 18.82 g) in anhydrous chloroform (150 mL) at 65 °C. The reaction mixture was stirred for 16 h. After the reaction solution was washed with 0.1 mol/L HCl, the organic layer was collected and concentrated under reduced pressure. The product was purified by silica gel column chromatography and eluted with ethyl acetate, followed by recrystallization from methanol to afford **TC1** as colorless crystals in 11% yield (Overall yield from the starting material was 8.5%). Mp: 72.5−73.5 °C. ^{1}H NMR: δ = 4.55−4.83 (m, 4H, −O−CH_2), 5.25−5.31 (m, 1H, −CH−O−), 7.45−8.06 (m, 5H, −C_6H_5) ppm. ^{13}C NMR: δ = 63.16 (*C*H_2−O−(C=O)−C_6H_5), 70.31 (−*C*H_2−O−(C=S)), 78.92 (−*C*H−), 128.65, 129.85, 133.80 (−C_6H_5), 165.92 (−*C*=O), 191.12 (−*C*=S) ppm. IR (KBr): 1203 (−C=S), 1728 (−C=O) cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_4S$: C, 55.45; H, 4.23; S, 13.46. Found: C, 55.51; H, 4.19; S, 13.51.

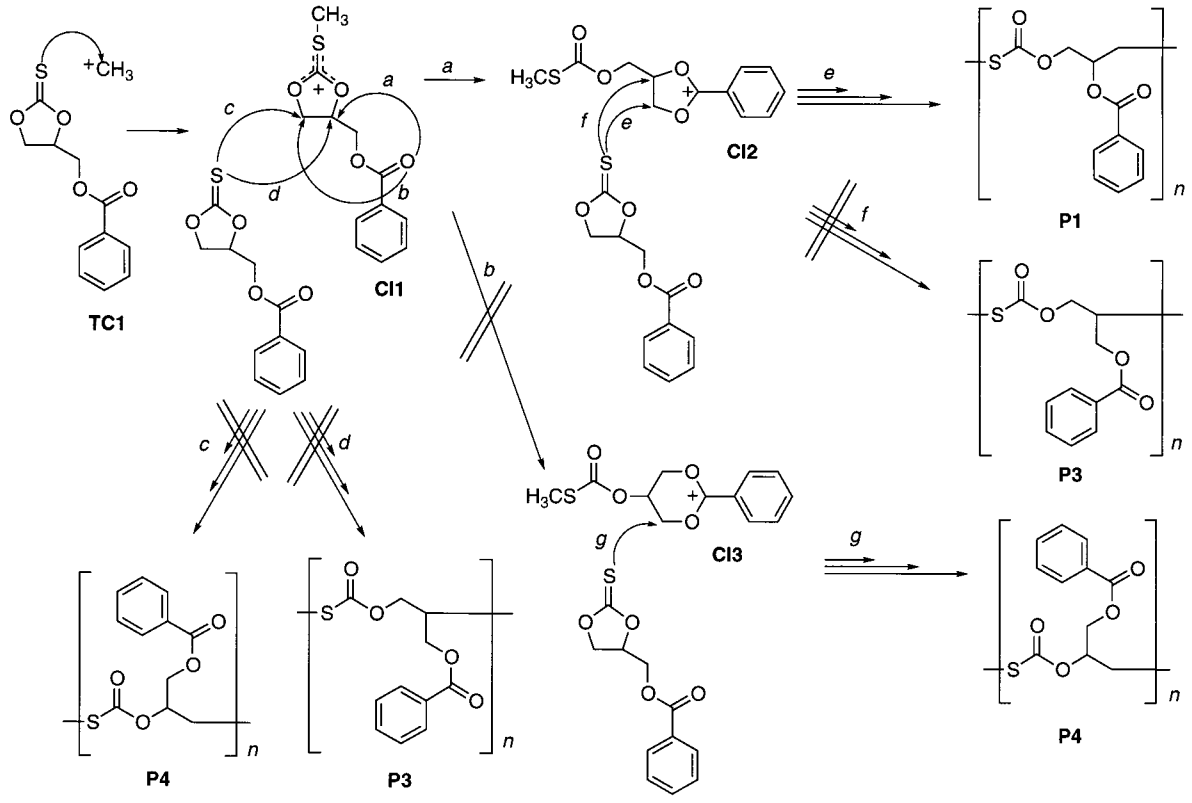
4-Phenoxymethyl-1,3-dioxolane-2-thione (TC2). TC2 was prepared using 3-phenoxypropane-1,2-diol instead of 3-benzoyloxypropane-1,2-diol by the same method as in the preparation of **TC1**. Yield: 15%. Mp: 99.5−100 °C. ^{1}H NMR: δ = 4.06−4.30 (m, 2H, −CH_2−O−C_6H_5), 4.72−4.81 (m, 2H, −CH_2−O−(C=S)−), 5.21−5.26 (m, 1H, −CH−O−), 6.89−7.33 (m, 5H, −C_6H_5). ^{13}C NMR: δ = 66.36 (−*C*H_2−O−(C=O)), 70.49 (−*C*H_2−O−(C=S)), 79.20 (−*C*H−), 114.67, 122.12, 129.69, 157.60 (−C_6H_5), 191.41 (*C*=S). IR (KBr): 1171 (−C=S) cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79; S, 15.25. Found: C, 57.53; H, 4.77; S, 15.16.

Typical Procedure of Polymerization (Run 2 in Table 1). TfOMe (3.3 mg, 0.020 mmol) was added to a glass tube containing **TC1** (0.238 g, 1.0 mmol) in chlorobenzene (1.0 mL) at 80 °C under a nitrogen atmosphere. The reaction mixture was stirred for 8 h. After the polymerization was quenched by the addition of 0.05 mL of triethylamine, the reaction mixture was evaporated and dried under reduced pressure. The conversion ratio was determined by ^{1}H NMR spectroscopy. The polymer was isolated by reprecipitation with hexane. Yield: 92%, M_n: 9600. M_w/M_n: 1.16.

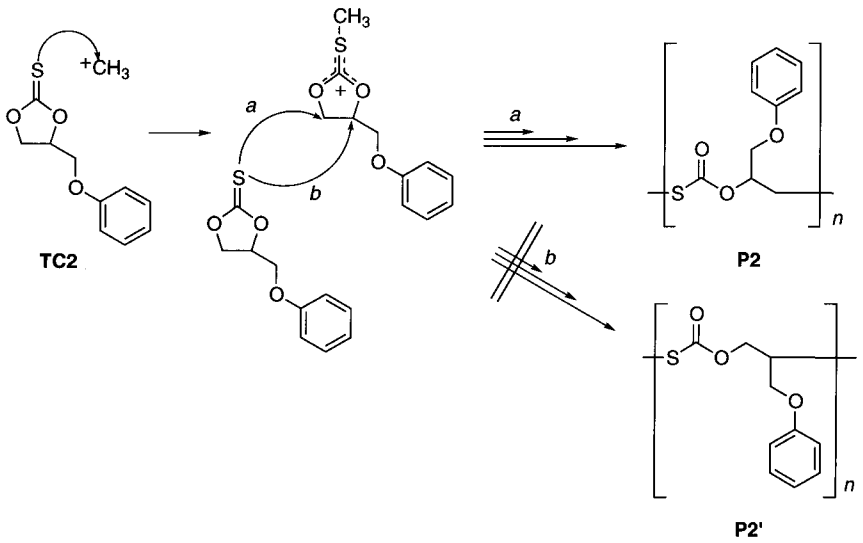
P1. ^{1}H NMR: δ = 3.16−3.23 (m, 2H, −S−CH_2), 4.43−4.67 (m, 2H, −O−CH_2−), 5.40 (m, 1H, −CH−), 7.26−8.07 (m, 5H, −C_6H_5). ^{13}C NMR: δ = 31.37 (−S−*C*H_2−), 66.39 (−*C*H−), 70.18 (−O−*C*H_2−), 128.44, 129.34, 129.80, 133.36 (−C_6H_5), 165.40 (−(*C*=O)−C_6H_5), 169.94 (−*C*=O, on the main chain). IR (KBr): 1721 (−C=O) cm^{-1}

P2. ^{1}H NMR: δ = 3.11−3.30 (m, 2H, −S−CH_2−), 4.10 (s, 2H, −CH_2−O−), 5.39−5.40 (m, 1H, −CH−), 6.84−7.31 (m, 5H, −C_6H_5). ^{13}C NMR: δ = 31.36 (−S−*C*H_2−), 67.15 (−*C*H_2−O−), 74.16−74.43 (−*C*H−O−), 114.76, 121.47, 129.55, 158.16 (−C_6H_5), 169.71 (−*C*=O). IR (KBr): 1716 (−C=O) cm^{-1}.

Scheme 3



Scheme 4



Results and Discussion

The monomer **TC1** was synthesized by the reaction of 3-benzoyloxypropane-1,2-diol with an equivalent amount of thiophosgene in the presence of 2 equiv of antipyrine in chloroform at reflux (Scheme 2). 3-Benzoyloxypropane-1,2-diol was prepared by monobenzoylation of glycerol with benzoyl chloride catalyzed by dimethyltin dichloride in THF. At first, the reaction was carried out according to a reported method of monobenzoylization of diols,[9] using 1 equiv of the triol. However, no desired product was obtained. Use of 3 equiv of triol relative to benzoyl chloride afforded the desired product in good yield.

The cationic polymerization of **TC1** was carried out with 2 mol % of trifluoromethanesulfonic acid (TfOH), methyl trifluoromethanesulfonate (TfOMe), or boron trifluoride etherate (BF_3·OEt_2) as initiator at ambient temperature or 80 °C under a dry nitrogen atmosphere as summarized in Table 1. The monomer was consumed within 8 h at ambient temperature and within 1 h at 80 °C independent of the initiator. There was no significant difference between the M_n's at 1 and 8 h (runs 2 and 3 in Table 1), suggesting the absence of backbiting. The resulting polythiocarbonates were soluble in common organic solvents such as THF, chloroform, dichloromethane, and acetone. BF_3·OEt_2 afforded the polymers with the M_n's higher than TfOMe and TfOH did, presumably due to the low initiation efficiency. The resulting polymers were isolated by precipitation with hexane, and the structure was examined by ^{1}H and ^{13}C NMR spectroscopy. Figure 1 shows the ^{1}H and ^{13}C NMR spectra of **TC1** and the polymer obtained in the run 3 polymerization in Table 1. The assignments of the observed signals are also presented in Figure 1. The ^{13}C NMR spectrum of **TC1** (Figure 1C) has an ester−carbonyl and a thiocarbonyl carbon signal at 165.9 and 191.1 ppm, respectively. The ^{13}C NMR spectrum of **P1** (Figure 1D) has carbonyl carbon signals at 165.4 and 169.9 ppm, which are assignable to ester and thiocarbonate carbonyl carbon atoms, respectively, indicating that cationic ring-opening polymerization involves isomerization of the thiocarbonyl group into a carbonyl group. Scheme 3 illustrates the plausible reaction pathways and products for the cationic ring-opening polymerization of **TC1**. Initiation should involve nucleophilic attack of a thiocarbonyl sulfur at the cationic initiator (CH_3^+) to afford a carbenium ion **CI1**. **CI1** may form **CI2** via path *a* and **CI3** via path *b* by the neighboring ester group participation. **P4** or **P3** may be formed by nucleophilic attack of a thiocarbonyl sulfur at the α-position of an ether oxygen in a cyclic carbenium ion **CI1** through path *c* or path *d*, respectively. **P1** or **P3** may be formed by nucleophilic attack of a thiocarbonyl sulfur at the α-position of an ether oxygen in a cyclic carbenium ion **CI2** through path *e* or path *f*, respectively. **P4** could be formed from a cyclic carbenium ion **CI3**. **TC1** was reacted with 1.2 equiv of TfOMe at ambient temperature to obtain information on the polymerization mechanism. Figure 2 shows the ^{1}H NMR spectrum of this reaction mixture. The signals were assigned based on those of the similar five-membered dithiocarbonate derivative in the previous report,[5] which supported the formation of the carbenium intermediate **CI2**. It is possible for **CI2** to form **P1** or **P3** as mentioned above. The integration ratio of a signal around 5.5 ppm was ca. 1, which was assignable to a methine proton linked to ether oxygen. If **P3** was formed, a methine proton should be linked to thioether and the signal should appear around 3.3 ppm. Thus, we concluded that the cationic ring-opening polymerization of **TC1** proceeded via path *a* followed by path *e* to afford **P1** according to ^{1}H and ^{13}C NMR spectroscopy. The five-membered cyclic monothiocarbonate having a phenoxy group (**TC2**) was polymerized by cationic ring-opening polymerization to clarify the effect of the ester group. The reactivity of **TC2** was almost equal to that of **TC1** based on the conversion and polymer yield. The polydispersity of polythiocarbonate obtained from **TC2** was larger than that from **TC1** (see run 3 and runs 7, 5, and 9 in Table 1). Figure 3 shows the ^{1}H and ^{13}C NMR spectra of **TC2** and the polymer obtained in the polymerization in run 7 in Table 1. The assignments of the observed signals are also presented in Figure 3. The ^{13}C NMR spectrum of **TC2** (Figure 3C) has a thiocarbonyl carbon signal at 191.4 ppm. The ^{13}C NMR spectrum of **P2** (Figure 3D) has a thiocarbonate carbonyl carbon signal at 169.9 ppm, indicating that the cationic ring-opening polymerization involves isomerization of thiocarbonyl group into carbonyl group. In the ^{1}H NMR spectrum of **P2** (Figure 3B), a broad signal assignable to the methylene protons next to the sulfur atom was

observed around 3.1−3.3 ppm. The formation of **P2′** is evidently negligible since the methine and methylene protons at around 3.0−3.2 and 5.5 ppm, respectively, are absent. The main chain of **P2** is different from that of **P1**. These results strongly indicate that **P2** was formed from **TC2** as shown in Scheme 4. The cationic ring-opening polymerization of **TC2** proceeds via nucleophilic attack of a thiocarbonyl sulfur at a cationic initiator, followed by selective nucleophilic attack of a thiocarbonyl sulfur at the α-position of an ether oxygen in a cyclic carbenium ion through path *a* probably due to less steric hindrance.

In summary, we disclosed the polymerization of 4-benzoyloxymethyl-1,3-dioxolane-2-thione (**TC1**) and 4-phenoxymethyl-1,3-dioxolane-2-thione (**TC2**) using several cationic initiators to afford polythiocarbonates with good solubility in common organic solvents. The polymerization of **TC1** proceeded with neighboring ester group participation. The substituent on the thiocarbonate ring can affect the structure of the main chain of the forming polymer by neighboring group participation.

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