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Dependence of Ring-Opening Reaction of Five-Membered Dithiocarbonates on Cationic Catalyst: Control of Isomerization and Polymerization

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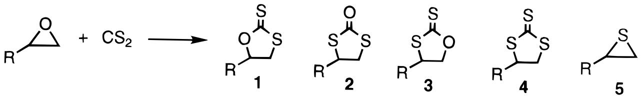
ABSTRACT: The selective cationic isomerizations and ring-opening polymerizations of cyclic five-membered dithiocarbonates (**1a**, 5-phenoxymethyl-1,3-oxathiolane-2-thione; **1b**, 5-methyl-1,3-oxathiolane-2-thione; **1c**, 5-ethyl-1,3-oxathiolane-2-thione; **1d**, 5-chloromethyl-1,3-oxathiolane-2-thione) have been achieved by the selection of the catalysts, which have enabled the first facile preparations of 1,3-dithiolan-2-one derivatives (**2a**−**d**) and polydithiocarbonates (**P1a**−**d**). The mechanism of the selectivity was elucidated by the ^{1}H and ^{13}C NMR spectroscopic analyses for their reaction intermediates. The initiation steps of the reactions of **1a** with TfOEt or TfOH were different, wherein the formation of the cyclic carbenium ion (**6**) *via* the ethylation of TfOEt on the thiocarbonyl sulfur and the oxonium cation (**7**) *via* the protonation of TfOH on the ether oxygen were observed, respectively. The cation **7** might not be electrophilic enough to be attacked by the monomer (**1**), which could explain the fact that the results in the reaction of **1** selectively gave the isomer with TfOH. The polymerization and isomerization should proceed predominantly *via* **6** and **7**, respectively. The reactivities of **1a**−**d** decreased in the order of **1b** $\cong$ **1c** > **1a** > **1d**, which showed good agreement with the ^{1}H NMR chemical shifts of the methine protons of **6a**−**d**.

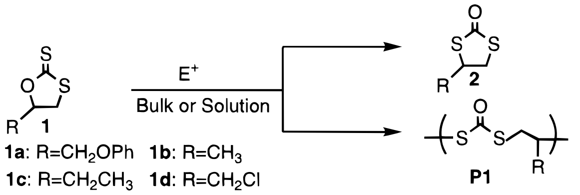
Introduction

In polymer chemistry, precise control of polymer structure, molecular weight, molecular weight distribution, tacticity, and unit sequence have been achieved by the development of precisely designed catalysts and monomers. However, no successful work has been reported on catalytic control of isomerization and polymerization so far. There have been many reports on the reactions of oxiranes with CS2, but most cases give a mixture of many products such as **1**−**5** (Scheme 1).[1] Recently, we have succeeded in the selective synthesis of five-membered dithiocarbonates (**1**)[2a] and their application to polymer synthesis by the polyaddition of bifunctional cyclic dithiocarbonates with diamines.[2b] The other cyclic dithiocarbonate, 1,3-dithiolan-2-one (**2**) is also useful because of its biological activity.[3] Although the cationic rearrangements of thionic esters (RO−CS−SR′) to thiolic esters (RS−CO−SR′) have been reported,[4] the selective synthesis of **2** has not been successful as yet. The efficient synthesis of **2** may be possible by the application of this catalytic rearrangement from **1**. Recently, much attention has been paid to sulfur-containing polymers such as poly(thiocarbonate)s and poly(dithiocarbonate)s obtained by the reactions of dithiols with phosgene or chloroformates, and they can be expected to be useful as optical lenses and fibers because of their superior optical and thermal properties.[5] Ring-opening polymerization of **1** may be also possible for preparation of sulfur-containing polymers. However, previous studies on the ring-opening polymerizations of five-membered dithiocarbonates[6] and trithiocarbonates[7] have been unsatisfactory because of their lower polymerizabilities, which are similar to those of five-membered carbonates.[8] Recently, we have reported the first successful cationic ring-opening polymerization of **1a** to afford the corresponding polydithiocarbonate (**P1a**) and the facile and quantitative preparation of **2a** in a preliminary communication, as shown in Scheme 2.[9] Namely, we have succeeded in the control of the selectivity on the cationic isomerization and ring-opening polymerization of **1a** by the selection of the catalysts. In this paper, we describe the syntheses, selective cationic isomerization, and ring-opening polymerization of several five-membered dithiocarbonates and the mechanistic aspects on the selectivity of the isomerization and polymerization of **1** in detail.

Scheme 1



Scheme 2



Results and Discussion

Isomerization and Ring-Opening Polymerization of a Five-Membered Dithiocarbonate (1a) with Cationic Catalysts. The monomer **1a** was synthesized by the reaction of glycidyl phenyl ether and CS$_2$ in the presence of LiBr as a catalyst according to the previously reported method.[2a] The reaction of **1a** was carried out under various cationic conditions to give the isomer, 5-phenoxymethyl-1,3-dithiolan-2-one (**2a**), and the polymer (**P1a**), as shown in Table 1. The

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Table 1. Cationic Isomerization and Polymerization of 1a[g]

run	catal	solv	temp (°C)	time (h)	conv[a] (%)	yield (%)	product[a] ratio (%) **P1a**:**2a**	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[b] of **P1a**
1	$ZnCl_2$	PhCl	60	3	0			
2	$ZnCl_2$	PhCl	80	2	43	*c*	0:100	
3	$ZnCl_2$	PhCl	80	12	100	87[d]	0:100	
4	$SnCl_4$[e]	none	60	5	100	*c*	6:94	
5	TfOH	$CDCl_3$	60	1	55	*c*	1:99	
6	TfOH	$CDCl_3$	60	2	100	86[d]	2:98	
7	TfOH	none	60	12	100	*c*	0:100	
8	CH_3SO_3H[e]	none	60	5	46	*c*	0:100	
9	TfOMe	PhCl	rt	15	0			
10	TfOMe	none	60	3	100	92[f]	96:4	11000 (1.25)
11	TfOEt	none	60	2	73	68[f]	98:2	9000 (1.23)
12	TfOEt	none	60	3	100	98[f]	98:2	10500 (1.25)
13	TfOEt	PhCl	60	1	49	48[f]	97:3	6700 (1.25)
14	TfOEt	PhCl	60	2	100	94[f]	96:4	8700 (1.46)
15	MeI[e]	none	80	44	0			
16	$PhCH_2Br$[e]	none	120	72	0			

[a] Estimated by ^1H NMR. [b] Estimated by GPC (eluent, THF, based on polystyrene standards). [c] Not determined. [d] Yield of **2a**, isolated by preparative HPLC. [e] Catalyst: 5 mol % vs **1a**. [f] Yield of **P1a**, *n*-hexane-insoluble part. [g] Catalyst: 2 mol % vs **1a**. Concentration of **1a** in solution polymerization: 3 M.

Table 2. Cationic Isomerization and Polymerization of 1a with BF_3OEt_2 in Bulk

run	BF_3OEt_2 (mol %)	temp (°C)	time (h)	product[a] ratio (%) **P1a**:**2a**	yield[b] of **P1a** (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c] of **P1a**
1	2	60	2	38:62	-[d]	11 300 (1.38)
2	10	60	12	72:28	68	14 300 (1.39)
3	20	60	5	82:18	77	10 100 (1.51)
4	2	80	12	40:60	39	16 700 (2.45)
5	2	100	12	42:58	-[d]	14 800 (2.00)

[a] Estimated by ^1H NMR. [b] *n*-Hexane-insoluble part. [c] Estimated by GPC (eluent, THF, based on polystyrene standards). [d] Not determined.

reaction of **1a** selectively gave **2a** in the presence of Lewis acids ($ZnCl_2$, $SnCl_4$) or protonic acids (TfOH, CH_3SO_3H) as catalysts in the bulk or in solution at 60–80 °C (runs 1–8). Monomer **1a** did not react at 60 °C for 3 h with $ZnCl_2$ (run 1), and the conversion of **1a** was low with CH_3SO_3H (run 8), probably due to their low acidities. On the contrary, the cationic polymerization of **1a** selectively proceeded in the presence of TfOMe (run 10) or TfOEt (runs 11–14) at 60 °C to obtain the corresponding poly(dithiocarbonate) (**P1a**) predominantly. The ratios of the reaction products in the bulk reactions (runs 10–12) were similar to those in chlorobenzene (runs 13 and 14). At room temperature, **1a** did not react with TfOMe (run 9). Neither MeI nor $PhCH_2Br$ catalyzed the reaction even at 80–120 °C (runs 15 and 16). The structures of **2a** and **P1a** were confirmed by IR, ^1H NMR, ^{13}C NMR, and mass spectroscopy as well as elemental analyses. The product ratio of the reaction mixture was estimated by the integration ratio of the methylene proton signals at 3.75 and 3.45 ppm for **2a** and **P1a** in their ^1H NMR spectra, respectively. In the IR spectra, the characteristic absorption peak of C=S of **1a** at 1190 cm^{-1} changed to the characteristic absorptions peaks of C=O of **2a** and **P1a** at 1651 and 1645 cm^{-1}, respectively.

Cationic Isomerization and Ring-Opening Polymerization of 1a with BF_3OEt_2. The reactions of **1a** were carried out with BF_3OEt_2 under various conditions, and the results are summarized in Table 2. Although the selective cationic isomerization will be expected in the reaction of **1a** with BF_3OEt_2 as a Lewis acid, the reaction of **1a** with 2 mol % of BF_3OEt_2 at 60 °C for 2 h gave a mixture of **P1a** (38%) and **2a** (62%) (Table 2, run 1). The ratio of **P1a** slightly increased as the reaction temperature increased (Table 2, runs 1, 4, and 5). The selectivity of **P1a** increased as the amount of BF_3OEt_2 increased at 60 °C (Table 2, runs 1–3). The concentration effect of BF_3OEt_2 on the reaction of **1a** was also examined at 80 °C in the bulk to observe that the selectivity of the polymerization increased from 29 to 87% with an increase in the amount of BF_3OEt_2 from 1 to 20 mol % similar to that at 60 °C, as shown in Figure 1, which includes the $\bar{M}_n$ of **P1a** obtained.

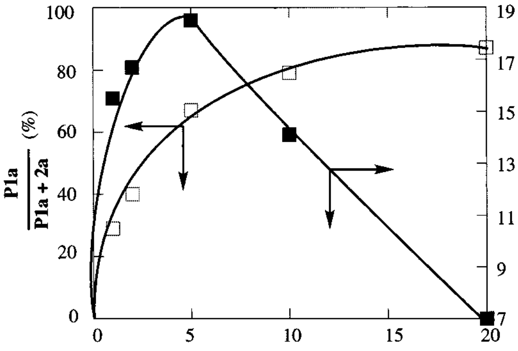


Figure 1. Concentration effect of BF_3OEt_2 on the cationic reaction of **1a** in bulk at 80 °C. Key: (□) content of **P1a**; (■) $\bar{M}_n$ of **P1a**.

It is known that BF_3OEt_2 acts a strong alkylating agent and as a strong protonic acid in the presence of H_2O. When a small amount of BF_3OEt_2 was employed, the selectivity of polymerization might be low because of the low concentration of alkyl cationic species due to the presence of a trace amount of H_2O in the reaction mixture. The selectivity of the polymerization increased as the amount of BF_3OEt_2 increased, wherein the amount of alkyl cationic species increased. $\bar{M}_n$ of **P1a** increased in accordance with the amount of BF_3OEt_2 up to 5 mol %, while $\bar{M}_n$ of **P1a** decreased gradually with further increase of the amount of BF_3OEt_2, similar to common cationic polymerizations. The signals assignable to the ethyl group as the polymer end group were observed in the ^1H NMR spectrum of **P1a** obtained by the reaction of **1a** with 10 mol % of BF_3OEt_2 (run 2 in Table 2), indicating that the polymerization was initiated by transfer of an ethyl group as a cation (Figure 2).

Cationic Isomerizations and Ring-Opening Polymerizations of Five-Membered Dithiocarbonates (1b–1d). New five-membered dithiocarbonates

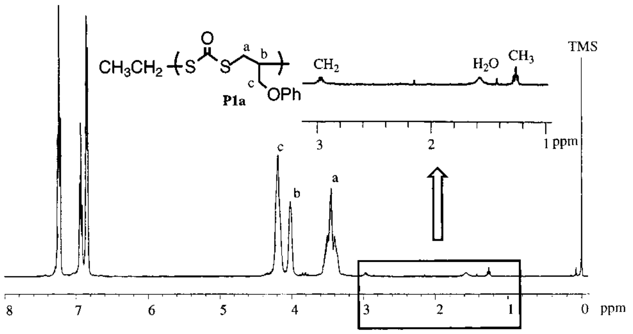


Figure 2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **P1a** obtained by the reaction of **1a** with BF_3OEt_2 (10 mol %) in bulk at 60 °C for 12 h (run 2 in Table 2).

(**1b**, R = CH_3; **1c**, R = CH_2CH_3; and **1d**, R = CH_2Cl) were synthesized to examine the generality of the cationic isomerization and ring-opening polymerization. Although the reactions of **1b** selectively afforded the isomer 5-methyl-1,3-dithiolan-2-one (**2b**) in the presence of $ZnCl_2$ or TfOH (runs 1–4 in Table 3), **1b** afforded the corresponding poly(dithiocabonate) (**P1b**) accompanied by partial isomerization in the presence of TfOMe or TfOEt (runs 5–9 in Table 3). The reactions of **1b** with TfOMe or TfOEt proceeded at room temperature (runs 5 and 8 in Table 3), but the selectivity of polymerization was lower than that at 60 °C (runs 6, 7, and 9 in Table 3). Similar selectivities of the polymerization and isomerization could be observed in the reactions of **1c** and **1d**. The cationic isomerization of **1d** with TfOH was accompanied by partial polymerization at 60 °C (run 18 in Table 3), and the selectivity of isomerization of **1d** with TfOH increased at 80 °C (run 19 in Table 3). The reactivities of **1a**–**d** decreased in the order **1b** ≅ **1c** > **1a** > **1d**, which might reflect the order of the electron-donating characters of the substituents.

Mechanistic Aspects on the Selectivity of Isomerization and Polymerization. The mechanisms of cationic ring-opening polymerizations of lactones, cyclic carbonates, and urethanes have been discussed on the basis of the detailed ^{1}H NMR studies. It has been indicated that the initiation and propagation steps involve the alkylation of the exocyclic carbonyl oxygen along with the cleavage of the alkyl–oxygen bond.[10] The mixtures of **1a** and the catalysts were analyzed by ^{1}H and ^{13}C NMR spectroscopy in $CDCl_3$ at room temperature and 60 °C to obtain information on the mechanism of the cationic isomerization and polymerization. The formation of a cyclic carbenium ion (**6a**) was confirmed in the mixture of **1a** and TfOEt (1.2 equiv) both at room temperature and at 60 °C as shown in Figure 3. The methine proton signal (c′) of **6a** appeared at 1 ppm downfield than that of **1a**, and both the methylene proton signals (a′ and b′) showed slight downfield shifts at room temperature (Figure 3A). At 60 °C, the methine proton signal (c) of **1a** completely disappeared and the corresponding signal (c′) of **6a** and small signals (c″, x″, and y″) assignable to a noncyclic dithiocarbonate appeared (Figure 3B). The thiocarbonyl (d′) and methine carbon signals (c′) of **6a** appeared at 10.1 and 10.7 ppm downfield of those of **1a**, and slightly downfield shifts of the methylene carbon signals (a′ and b′) were observed in ^{13}C NMR (Figures 3C,D). The carbenium ion **6a** existed stably even at 60 °C. Thus, these results strongly suggest that the initiation step in the reaction of **1a** with TfOEt is the formation of **6a**.

Figure 4 illustrates the ^{1}H and ^{13}C NMR spectra of the reaction mixture of **1a** and TfOH (1.2 equiv) in $CDCl_3$ at room temperature. In this case, protonation on the thiocarbonyl sulfur of **1a** is expected from the results of the NMR analyses of the mixture of **1a** and TfOEt described above. However, the methine proton signal (c′) showed a 0.5 ppm downfield shift, and the thiocarbonyl carbon (d′) and the methine carbon signals (c′) showed 5.2 and 5.4 ppm downfield shifts, all of which were smaller compared to the chemical shift changes of **1a** with TfOEt. It has been reported that a thiol proton signal formed by the protonation of dithiocarbonic acid appears at 7.19 ppm and an oxonium proton signal appears at 12.0 ppm.[11] Therefore, it is suggested that the protonation of **1a** occurs not on the thiocarbonyl sulfur but on the ether oxygen by the weaker downfield shifts of ^{1}H and ^{13}C NMR signals, the absence of the thiol proton signal, and the presence of the oxonium proton signal at 12.0 ppm. These different results of ethylation (Figure 3) and protonation (Figure 4) of **1a** may be explained by the hard and soft theory. Namely, the ethyl cation (soft acid) may predominantly attack the thiocarbonyl sulfur (soft base), while the proton (hard acid) may predominantly attack the ether oxygen (hard base). The initiation with TfOEt should proceed rapidly compared with the propagation in the polymerization of **1a**, because the presence of **6a** was confirmed at room temperature, although **1a** did not polymerize at room temperature. The mixtures of **1b**–**d** and the catalysts were similarly analyzed by NMR spectroscopy. In the mixtures of **1b**, **1c**, and TfOEt, the signals of the corresponding isomers (**2b** and **2c**) appeared besides the cyclic carbenium ions (**6b** and **6c**) even at room temperature in the ^{1}H and ^{13}C NMR spectra. In the mixture of **1d** and TfOEt, the cyclic carbenium cation (**6d**) was confirmed at 60 °C, and not at room temperature, indicating the lower reactivity of **1d** compared with those of **1a**–**c**.

Table 4 summarizes the change of the ^{1}H and ^{13}C NMR chemical shifts of **1a**–**d** by the additions of TfOEt or TfOH (1.2 equiv), together with the ^{1}H and ^{13}C NMR shifts of **1a**–**d** and Taft's polar substituent constant values of aliphatic compounds (σ^*).[12] The order of cationic reactivities of dithiocarbonates showed good agreement with that of σ^*, that is, the dithiocarbonate having a stronger electron-donating group showed a higher reactivity. The ^{1}H NMR chemical shifts of the methine protons of **6** well reflected their reactivities, whereas the ^{13}C NMR chemical shifts could not show the tendency. Furthermore, ^{1}H and ^{13}C NMR spectra of the mixtures of **2a** and TfOH (1.2 equiv) were measured in $CDCl_3$. The protonation of **2a** resulted in only slight downfield shifts both in ^{1}H and ^{13}C NMR, which might support the much lower reactivity of **2a** compared with that of **1a**.[13]

The propagating end was directly analyzed by ^{1}H and ^{13}C NMR spectroscopy for the reaction of **1a** with 0.5 eq of TfOEt, which clearly demonstrated that the active species is cyclic carbenium (**9a**) as shown in Figure 5. The ring-methine proton signal (c″) appeared at the same position as that (c′) of **6a**, and the *S*-ethyl proton signals (x′, y′) of **6a** appeared at higher fields of 2.97 and 1.28 ppm than those of **6a**. The propagation should proceed *via* the attack of the thiocarbonyl sulfur of the monomer on the methine carbon (c′ or c″) to give the corresponding polymer.

Table 3. Cationic Isomerization and Polymerization of 1b–1d[g]

run	compd	catal	temp (°C)	time (min.)	conv[a] (%)	yield (%)	product[a] ratio (%) **P1**:**2**	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[b] of **P1**
1	**1b**	$ZnCl_2$	60	30	27	*c*	0:100	
2	**1b**	$ZnCl_2$	60	720	100	87[d]	0:100	
3	**1b**	TfOH	60	10	100	*c*	0:100	
4	**1b**	TfOH	60	60	100	89[d]	0:100	
5	**1b**	TfOMe	rt	720	100	*c*	63:37	*c*
6	**1b**	TfOMe	60	20	88	64[e]	74:26	10400 (1.45)
7	**1b**	TfOMe	60	60	100	68[e]	73:27	8500 (1.34)
8	**1b**	TfOEt	rt	480	96	66[e]	67:33	7600 (1.37)
9	**1b**	TfOEt	60	60	100	74[e]	74:26	12800 (1.45)
10	**1c**	TfOH	rt	300	100	*c*	0:100	
11	**1c**	TfOH	60	20	100	93[d]	0:100	
12[f]	**1c**	TfOMe	rt	300	74	24[d]	43:57	*c*
13	**1c**	TfOMe	60	10	77	53[e]	69:31	*c*
14[f]	**1c**	TfOMe	60	10	71	55[e]	77:23	5700 (1.31)
15[f]	**1c**	TfOMe	60	20	100	66[e]	71:29	6700 (1.38)
16[f]	**1c**	TfOMe	60	60	100	60[e]	63:37	5200 (1.34)
17	**1d**	TfOH	60	120	16	*c*	*c*	
18	**1d**	TfOH	60	720	92	*c*	13:87	
19	**1d**	TfOH	80	720	100	86[e]	5:95	
20	**1d**	TfOEt	60	120	83	82[e]	98:2	8700 (1.24)
21	**1d**	TfOEt	60	300	100	97[e]	96:4	10000 (1.29)

[a] Estimated by ^{1}H NMR. [b] Estimated by GPC (eluent, THF, based on polystyrene standards). [c] Not determined. [d] Yield of **2**, isolated by preparative HPLC. [e] Yield of **P1**, *n*-hexane-insoluble part. [f] In the presence of molecular sieve 3A. [g] Catalyst: 2 mol % vs **1b**–**1d**.

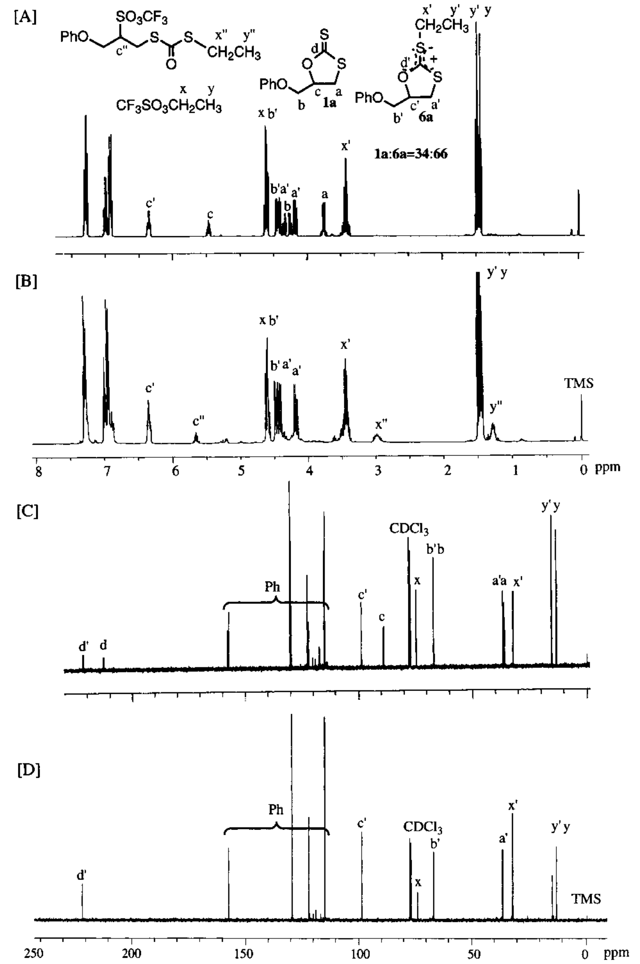


Figure 3. (A) ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of a mixture of **1a** and TfOEt (1.2 equiv) at room temperature. (B) ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of a mixture of **1a** and TfOEt (1.2 equiv) at 60 °C. (C) ^{13}C NMR spectrrum (100 MHz, $CDCl_3$) of a mixture of **1a** and TfOEt (1.2 equiv) at room temperature. (D) ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of a mixture of **1a** and TfOEt (1.2 equiv) at 60 °C.

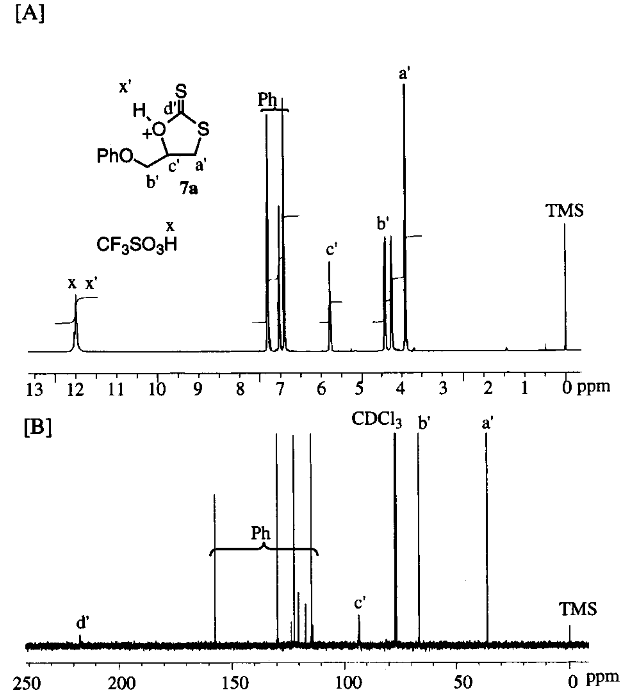


Figure 4. (A) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of a mixture of **1a** and TfOH (1.2 equiv) at room temperature. (B) ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of a mixture of **1a** and TfOH (1.2 equiv) at room temperature.

Scheme 3 illustrates a plausible mechanism for the cationic isomerization and polymerization of **1**. When TfOMe or TfOEt is used as the catalyst, a carbenium cation (**6**) is formed by the alkylation of the thiocarbonyl sulfur. The intramolecular isomerization *via* the attack of exocyclic sulfur of **6** to the methine carbon (path A) may be impossible, because the ring of **6** is flat. The isomerization is expected to proceed *via* path A′. Therefore, the polymerizations of dithiocabonates **1b** and **1c** having electron-donating substituents might be accompanied by partial isomerizations because **6b′** and **6c′** are more favorable than **6a′** due to the stabilizing effect of the substituents. On the contrary, the isomerization of the dithiocabonate **1d** might be suppressed by the electron-withdrawing substituent, which is unfavorable for **6d′** to cause isomerization. When TfOH

Table 4. ^{1}H and ^{13}C NMR Chemical Shifts δ Found by the Reaction of Dithiocarbonates (1a–1d) with TfOEt, TfOMe, or TfOH (1.2 equiv) at 60 °C

		chem shift (ppm)			
		^{13}C NMR		^{1}H NMR	
compound	σ* of R[a]	C=S	C–O	C–S	H–C–O
1a (R = CH_2OPh)	+0.85	211.4	87.9	36.3	5.3
1a-TfOEt		221.6	98.6	36.8	6.4
1a-TfOMe		222.6	98.9	36.6	6.3
1a-TfOH		216.7	93.2	36.4	5.8
1b (R = CH_2CH_3)	−0.10	212.6	93.2	39.0	5.1
1b-TfOEt[b]		221.3	103.8	39.3	5.9
1c (R = CH_3)	0.00	211.4	88.3	40.9	5.3
1c-TfOEt[b]		221.3	99.4	41.4	6.1
1d (R = CH_2Cl)	+1.05	210.7	88.2	42.7	5.3
1d-TfOEt		221.9	98.7	43.7	6.4

[a] σ*; Taft's polar substituent constants for aliphatic compounds. [b] At room temperature.

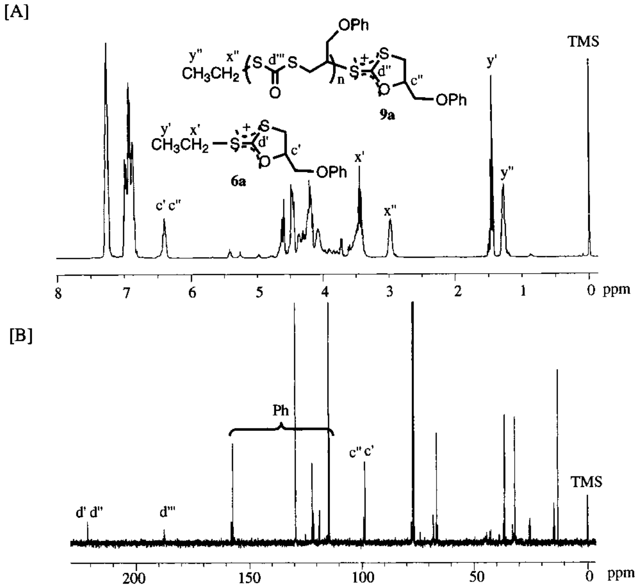


Figure 5. (A) ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of a mixture of **1a** and TfOEt (0.5 equiv) at 60 °C. (B) ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of a mixture of **1a** and TfOEt (0.5 equiv) at 60 °C.

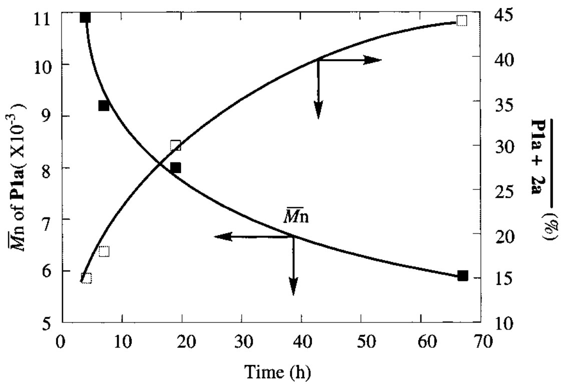
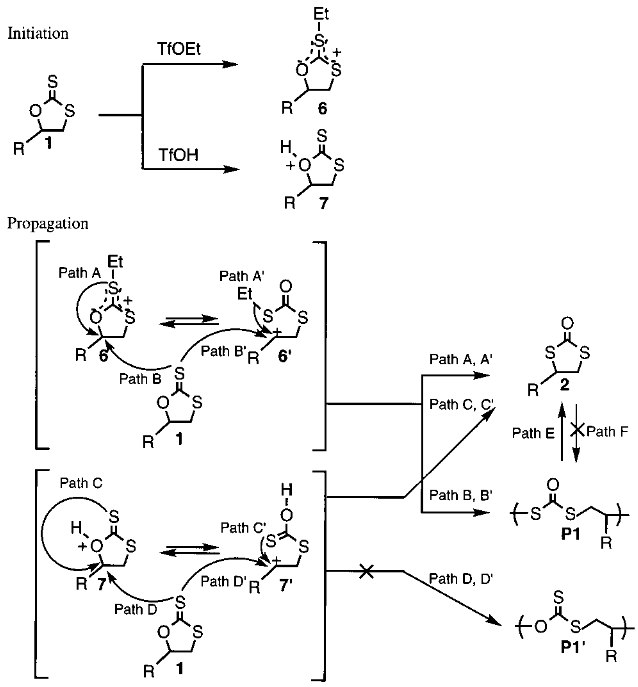


Figure 6. Relationships between the reaction time and the $\bar{M}_n$ of **P1a** and the content of **2a**. Conditions: TfOEt; 2 mol % vs **1a**, in PhCl (3 M), at 60 °C. Key (□) content of **2a**; (■) $\bar{M}_n$ of **P1a**.

Scheme 3



is used as the catalyst, the protonation of **1** occur on the ether oxygen to give a cyclic oxonium ion (**7**) or carbenium ion (**7′**) as the intermediate. The isomerization may mainly proceed *via* **7′**, because **7** may not be electrophilic enough to be attacked by **1**, which can be understood by the downfield shifts of the NMR signals being weaker than those of **6**. The flat structure of **7** may be also the reason for the unfavorable isomerization *via* **7**. Paths D and D′ are negligible, because the unit **P1′** is not contained in the polymer. The isomerization of the dithiocabonate **1d** having an electron-withdrawing substituent might be accompanied by the polymerization with TfOH, because of the low electron density of the ether oxygen causing protonation on the thiocarbonyl sulfur. Depolymerization of **P1** to **2** (path E) and polymerization of **2** to **P1** (path F) may be possible during these reactions. To examine these possibilities, the reaction of **1a** in the presence of $ZnCl_2$ (run 2 in Table 1) or TfOH (run 5 in Table 1) was stopped at 43 or 55% conversion, in both of which cases only **2a** could be detected. The elongation of the reaction time of **1a** with TfOH only gave **2a** (run 7 in Table 1). Therefore, the isomerization of **1a** may selectively proceed to afford **2a**, and path E in the conditions should be absent. Figure 6 illustrates the change of the $\bar{M}_n$ of **P1a** and the content of **2a** as the time progress by the reaction of **1a** in the presence of TfOEt. Elongation of the reaction time from 4 to 67 h increased the ratio of **2a** from 15 to 44% and decreased the $\bar{M}_n$ of **P1a** after the conversion of **1a** reached 100% at 2 h. These results indicate the occurrence of a back-biting reaction of **P1** to afford **2** (path E) in the reaction with TfOEt. Polymerization of **2** (path F) did not take place under any conditions.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on JEOL EX-90 (^{1}H, 90 MHz) and JEOL EX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometers, using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$). IR spectra were obtained with a JASCO FT/IR-5300 spectrometer. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$, number and weight-average molecular weights) and the distributions ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCP & 8000 system with a data processor, equipped with a polystyrene gel column (G3000H), using THF as an eluent (flow rate 1.0 mL/min, polystyrene calibration, and refractive index and ultraviolet (254 nm) detectors). Preparative high pressure liquid chromatography (HPLC) was performed with a Japan Analytical Industry LC-908 equipped with two consecutive gel columns, JAIGELs 1H and 2H (eluent, $CHCl_3$; flow rate, 3.8 mL/min), and refractive index and ultraviolet (254 nm) detectors.

Materials. Initiators methyl trifluormethanesulfonate (TfOMe), ethyl trifluormethanesulfonate (TfOEt), methanesulfonic acid, trifluormethanesulfonic acid (TfOH), methyl iodide (MeI), benzyl bromide ($PhCH_2Br$), and zinc chloride ($ZnCl_2$) were purified by distillation or recrystallization. Chlorobenzene (PhCl) was distilled from P_2O_5 under a nitrogen atmosphere. $CDCl_3$ was dried over molecular sieves 4A.

Syntheses of Five-Membered Carbonates. To a solution of 0.43 g (0.005 mol) of LiBr and oxirane (0.1 mol) in 80 mL of THF was added 7.2 mL (0.12 mol) of carbon disulfide, and the reaction mixture was stirred at room temperature for 12−24 h. After the reaction mixture was concentrated by rotary evaporation, a five-membered carbonate (**1b**−**1d**) was obtained by distillation from the residue. 5-Methyl-1,3-oxathiolane-2-thione (**1b**): bp 111 °C/2 mmHg; yield 65%; IR 1195 cm^{-1} ($\nu_{C=S}$); ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.64 (d, J = 6.4 Hz, 3H, CH_3), 3.40−3.45 (m, 1H, one proton of CH_2), 3.71−3.75 (m, 1H, one proton of CH_2), 5.3 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), δ 19.2, 40.9, 88.3, 212.5 ppm. Anal. Calcd (found) for $C_4H_6OS_2$: C, 35.80 (35.95); H, 4.51 (4.45). 5-Ethyl-1,3-oxathiolane-2-thione (**1c**): bp 131 °C/5 mmHg; yield 38%; IR 1190 cm-1 ($\nu_{C=S}$); ^{1}H NMR (400 MHz, CDCl3) δ 1.08−1.13 (m, 3H, CH_3), 1.89−1.94, 2.01−2.07 (m, 2H, CH_3CH_2), 3.41−3.67 (m, 2H, SCH_2), 5.07−5.11 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), δ 9.71, 26.9, 39.0, 93.2, 212.6 ppm. Anal. Calcd (found) for $C_5H_8OS_2$: C, 40.51 (40.49); H, 5.44 (5.18). 5-Chloromethyl-1,3-oxathiolane-2-thione (**1d**): bp 112−116 °C/0.5 mmHg; yield 75%; IR 1186 cm-1 ($\nu_{C=S}$); ^{1}H NMR (400 MHz, $CDCl_3$), δ 3.69−3.80 (m, 2H, SCH_2), 3.84−3.92 (m, 2H, $ClCH_2$), 5.31−5.38 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), δ 36.8, 42.7, 88.17, 210.7 ppm. Anal. Calcd (found) for $C_4H_5ClOS_2$: C, 28.58 (28.58); H, 3.00 (3.09).

Cationic Isomerization and Ring-Opening Polymerization of 1. Typical Procedure. To a glass tube containing **1a** in bulk or solution, an initiator was added at a set temperature under a nitrogen atmosphere. After the reaction mixture was stirred for a set time, it was quenched by the addition of pyridine or triethylamine. The isomer (**2a**) was isolated from the reaction mixture by preparative HPLC eluted by $CHCl_3$, and the polymer (**P1a**) was obtained by precipitation with *n*-hexane. 5-Phenoxymethyl-1,3-dithiolan-2-one (**2a**): MS 226 (M^+); IR (neat) 1651 cm^{-1} ($\nu_{C=O}$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (dd, J = 4.4 and 12.4 Hz, 1H, one proton of S−CH_2), 3.83 (dd, J = 5.2 and 12.4 Hz, 1H, one proton of S−CH_2), 4.07−4.09 (m, 1H, CH) ppm, 4.22−4.26 (m, 1H, one proton of PhO-CH_2), 4.29−4.35 (m, 1H, one proton of PhO-CH_2), 6.89−6.91 (m, 2H, two protons of Ph), 6.96−7.00 (m, 1H, one proton of Ph), 7.29−7.31 (m, 2H, two protons of Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.80, 49.23, 66.9, 114.1, 121.2, 129.2, 157.3, 196.3 ppm. Anal. Calcd (found) for $C_{10}H_{10}O_2S_2$: C, 53.07 (53.10); H, 4.45 (4.37). **P1a:** IR (film) 1645 cm^{-1} ($\nu_{C=O}$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 (br, 2H, S−CH_2), 4.02 (br, 1H, CH), 4.19 (br, 2H, PhO−CH_2), 6.85 (m, 2H, two protons of Ph), 6.91−6.95 (m, 1H, one proton of Ph), 7.22−7.25 (m, 2H, two protons of Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 45.0, 67.9, 114.6, 121.5, 129.5, 157.9, 187.3 ppm. Anal. Calcd (found) for $C_{10}H_{10}O_2S_2$: C, 53.07 (52.87); H, 4.45 (4.07). 5-Methyl-1,3-dithiolan-2-one (**2b**): IR 1643 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.60 (d, J = 6.8 Hz, 3H, CH_3), 3.36−3.39 (m, 1H, one proton of CH_2), 3.71−3.75 (m, 1H, one proton of CH_2), 4.18−4.24 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), δ 20.0, 43.0, 47.9, 191.7 ppm. Anal. Calcd (found) for $C_4H_6OS_2$: C, 35.80 (35.44); H, 4.51 (4.49). **P1b:** IR 1643 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.37 (d, J = 7.2 Hz, 3H, CH_3), 3.25−3.34 (m, 2H, CH_2), 3.87 (br, 1H, CH) ppm; ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 18.8, 36.0, 40.9, 187.3 ppm. Anal. Calcd (found) for $C_4H_6OS_2$: C, 35.80 (35.67); H, 4.51 (4.53). 5-Ethyl-1,3-dithiolan-2-one (**2c**): IR 1651 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (400 MHz, CDCl3) δ 1.04−1.09 (m, 3H, CH_3), 1.92−1.94 (m, 2H, CH_3CH_2), 3.39−3.46, 3.69−3.74 (m, 2H, SCH_2), 4.01−4.04 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 27.8, 40.8, 55.1, 197.6 ppm. Anal. Calcd (found) for $C_5H_8OS_2$: C, 40.51 (40.29); H, 5.44 (5.47). **P1c:** IR 1641 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR δ 0.98−1.02 (m, 3H, CH_3), 1.60−1.64, 1.79−1.83 (m, 2H, CH_3CH_2), 3.33 (broad s, 2H, SCH_2), 3.75 (broad s, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), δ 12.5, 27.8, 40.8, 55.1, 197.6 ppm. Anal. Calcd (found) for $C_5H_8OS_2$: C, 40.51 (40.39); H, 5.44 (5.44). 5-Chloromethyl-1,3-dithiolan-2-one (**2d**): IR 1647 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74−3.94 (m, 4H, S−CH_2 and CH_2Cl), 4.18−4.24 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.7, 43.8, 51.7, 195.7 ppm. Anal. Calcd (found) for $C_4H_5ClOS_2$: C, 28.58 (28.36); H, 3.00 (3.01). **P1d:** IR 1641 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35−3.45 (m, 2H, SCH_2), δ = 3.69−3.72, 3.85−3.88 (m, 2H, CH_2Cl), 4.12 (broad s, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.3, 45.9, 47.1, 186.9 ppm. Anal. Calcd (found) for $C_4H_5ClOS_2$: C, 28.58 (29.21); H, 3.00 (3.23).

Supporting Information Available: Figure S1, showing the [A] ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of a mixture of **1b** and TfOEt (1.2 equiv) at room temperature, [B] the ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of a mixture of **1c** and TfOEt (1.2 equiv) at room temperature, and [C] the ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of a mixture of **1d** and TfOEt (1.2 equiv) at 60 °C, and **Figure S2**, showing [A] the ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of a mixture of **2a** and TfOH (1.2 equiv), at room temperature and [B] the ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of a mixture of **2a** and TfOH (1.2 equiv) at room temperature (2 pages). See any current masthead page for ordering information and Internet access instructions.

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