A Novel Construction of Living Polymerization by Neighboring Group Participation: Living Cationic Ring-Opening Polymerization of a Five-Membered Cyclic Dithiocarbonate

Wonmun Choi, Fumio Sanda, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

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Since the discovery of anionic living polymerization,[1] the chemistry of living polymerization has been developed in the field of coordination,[2] metathesis,[3] and radical[4] and cationic polymerizations in addition to anionic polymerization. Considerable advances have been achieved in living cationic polymerization for a variety of vinyl monomers such as vinyl ethers,[5] isobutene,[6] styrene,[7] and *N*-vinylcarbazole.[8] Living cationic polymerization is based on the stabilization of a growing carbocation by an added base or a counteranion. Meanwhile, some cyclic monomers such as tetrahydrofuran[9] and oxazoline[10] can undergo cationic living ring-opening polymerization with a stabilized propagating polymer end, because the chain transfer reaction of these cyclic monomers is unfavorable. Recently, we have reported the first example of selective cationic isomerization and ring-opening polymerization of five-membered cyclic dithiocarbonates (**1**). The monomer **1** selectively isomerizes to **4** in the presence of Lewis acids such as $ZnCl_2$ and $SnCl_4$, and protonic acids such as CF_3SO_3H (TfOH) and CH_3SO_3H as the catalysts, whereas **1** selectively polymerizes with CF_3SO_3-Me (TfOMe) and CF_3SO_3Et (TfOEt) as the initiators to afford the corresponding polydithiocarbonates (**5**) (Scheme 1).[11] The formation of a cyclic oxonium cation (**2**) and a cyclic carbenium cation (**3**) has been confirmed in the reactions of **1** with TfOH and TfOMe, respectively (Scheme 1).[12] The selectivity of the cationic isomerization and polymerization of **1** is attributable to the different intermediates depending on the catalysts.

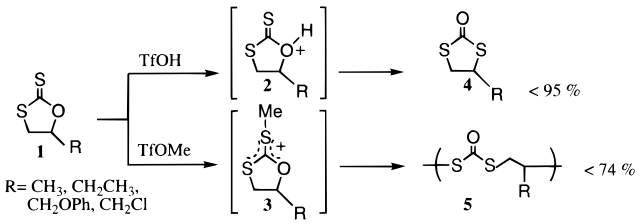
Neighboring group participation plays an important role in selective chemical synthesis of oligosaccharides[13] and regiochemical control on the ring-opening of oxirane by nucleophiles.[14] If this neighboring group participation is employed to stabilize a propagating polymer end, a new class of living polymerization will be constructed. In this communication, we wish to report the first example of a controlled living cationic ring-opening polymerization of a five-membered cyclic dithiocarbonate having a benzoxymethyl group (**1a**) based on the stabilization of the growing carbocation by neighboring group participation.

The five-membered cyclic dithiocarbonate (**1a**) was prepared by the reaction of the corresponding oxirane and CS_2 in the presence of LiBr catalyst according to the previously reported method.[15] The cationic polymerization of **1a** was carried out under various conditions to give the corresponding polymers as summarized in Scheme 2 and Table 1.[16] TfOH as well as TfOMe selectively gave the polymer, which was completely different from the other cyclic dithiocarbonates (**1**). It is noteworthy that the molecular weight distributions (M_w/M_n) of the polymers obtained with TfOMe are very narrow even at 60 °C (M_w/M_n 1.14). The M_n values of the polymers estimated by GPC based on polystyrene calibration were in good agreement with the molecular weights determined from the ^1H NMR peak integration ratio of the S−Me group at the initiating end. After the complete consumption of **1a**, the polymerization took place again when the same amount of **1a** was introduced in the reaction mixture. The M_n of the polymer increased in direct proportion to the monomer conversion and showed a good agreement with the molecular weight calculated by NMR (Figure 1).

The polymerization of **1a** was carried out with various amounts of TfOMe (0.8−8 mol %) at room temperature to confirm the living nature of the polymerization. The M_n of the polymer agreed well with the theoretical value, although the molecular weight distribution was slightly broad with 0.8 mol % of TfOMe (M_n 32 600; M_w/M_n 1.18), as shown in Figure 2. Further, the polymerization was quenched with myristyltrimethylammonium bromide to examine the chain-end functionalization of the polymer. The obtained polymer showed ^1H NMR signals assignable to initiating S−Me and terminating bromomethyl end group protons, where the functionality of the terminating end group was 92%, supporting the living nature of the polymerization.[17]

The structure of the polymer was confirmed by IR, ^1H NMR, and ^{13}C NMR spectroscopy besides elemental analysis. Figure 3 shows the ^1H NMR spectrum of the polymer obtained by the polymerization of **1a** with TfOMe (3 mol %) at 60 °C for 1 h (run 6 in Table 1). In the ^1H NMR spectrum of the polymer, the signal at 4.7

Scheme 1



Scheme 2

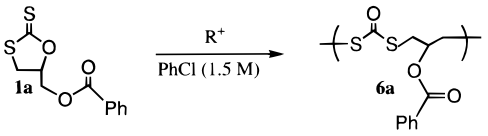


Table 1. Cationic Polymerization of 1a

run	init (mol %)	temp (°C)	time (min)	conv[a] (%)	yield (%)	MW_{NMR}[a]	$M_{n\ GPC}$[b]	M_w/M_n[b]
1	TfOH (2)	rt	240	60	55[c]		24600	1.31
2	TfOH (2)	60	60	100	98[d]		16700	1.22
3	TfOMe (2)	rt	480	93	94[d]	12900	13200	1.10
4	TfOMe (2)	45	30	73	73[d]	9100	9300	1.09
5	TfOMe (2)	45	90	100	100[d]	12300	12700	1.10
6	TfOMe (3)	60	60	100	100[d]	8500	9900	1.14

[a] Estimated by ^1H NMR. [b] Estimated by GPC eluted by THF based on polystyrene standards. [c] Isolated by preparative HPLC. [d] *n*-Hexane-insoluble part.

* To whom all correspondence should be addressed.

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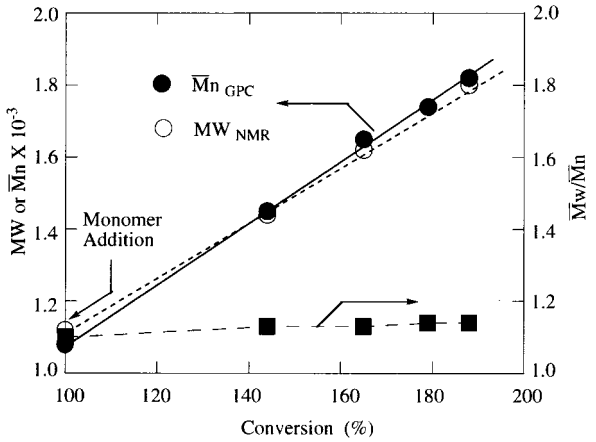


Figure 1. Conversion dependence of the M_n and M_w/M_n of **6a** obtained by the polymerization of **1a** with TfOMe (2.5 mol %) in PhCl (1.5 M) at 30 °C.

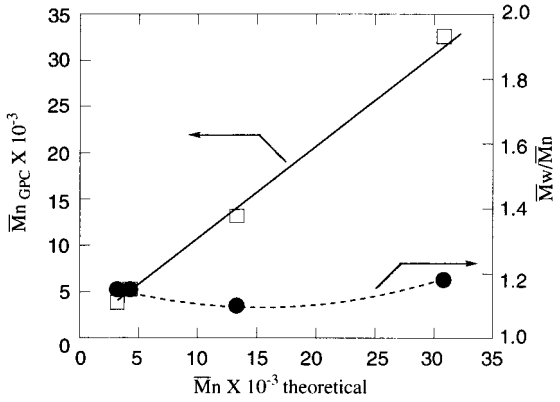


Figure 2. Correlation of the theoretical and experimental M_n and M_w/M_n of **6a** obtained by the polymerization of **1a** with TfOMe (0.8−8 mol %) in PhCl (1.5 M) at room temperature.

ppm of the α-methylene protons of benzoxy group completely disappeared, and signal b assignable to α-methine proton of the benzoxy group appeared at 5.2 ppm. No signal was observed at 4.5−5 ppm, which was expected for the α-methylene protons of the benzoxy group in **5a**. Consequently, it can be concluded that the structure of the polymer is not **5a** but **6a**, which is supported by IR and ^{13}C NMR spectroscopy. It is quite surprising that the polymer structure is different depending on the substituent on the monomer.

The ^1H and ^{13}C NMR spectra were measured for a mixture of **1a** with TfOMe (1.2 equiv) in $CDCl_3$ at room temperature to examine the possibility of neighboring group participation in the polymerization. The formation of a carbenium cation (**3a′**, 88%, calculated from ^1H NMR) was confirmed with a small amount of another carbenium cation (**3a**, 12%) as shown in Figure 4.

Scheme 3 illustrates a plausible mechanism of the polymerization of **1a**. The monomer **1a** forms an oxonium cation (**2a**) and a carbenium cation (**3a**) by protonation or methylation, followed by isomerization to yield a more stable carbenium cation (**3a′**) stabilized by two oxygen atoms and phenyl group.[18] The results suggest that path C selectively proceeds from **3a′** to afford the polymer (**6a**) among the three possible paths; path A to afford the isomer (**4a**), path B to afford the polymer (**5a**) and path C. Path C may be more favorable than paths A and B probably due to steric factors. The stability of **3a′** plays an important role on the selectivity of the polymerization and isomerization; namely, the

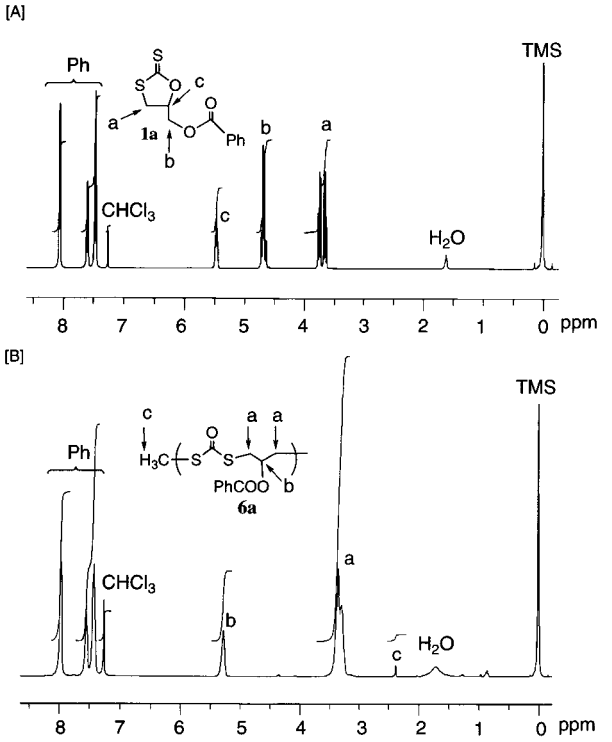


Figure 3. ^1H NMR (400 MHz) spectra of **1a** (A) and **6a** (B) obtained by the polymerization of **1a** with TfOMe (3 mol %) in PhCl (1.5 M) at 60 °C for 1 h.

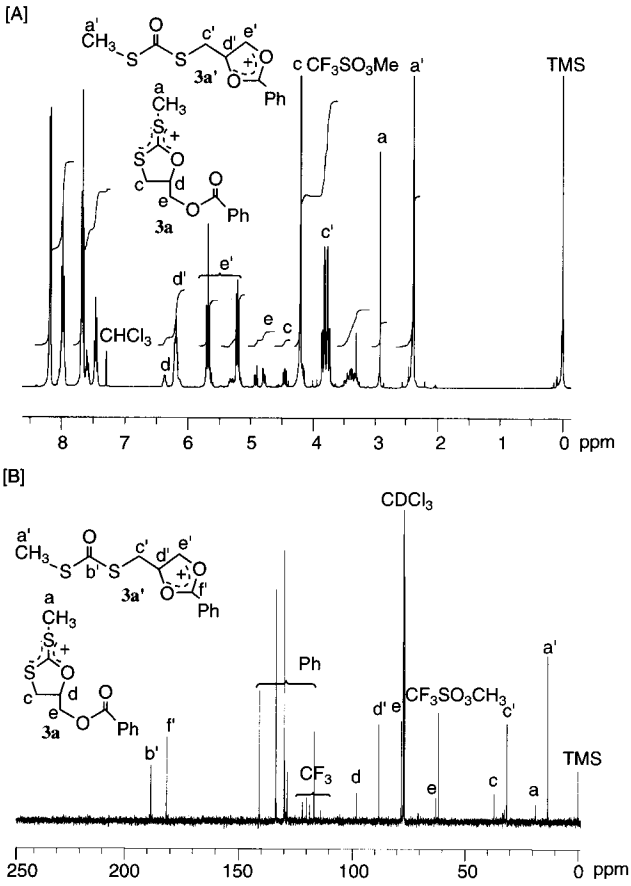
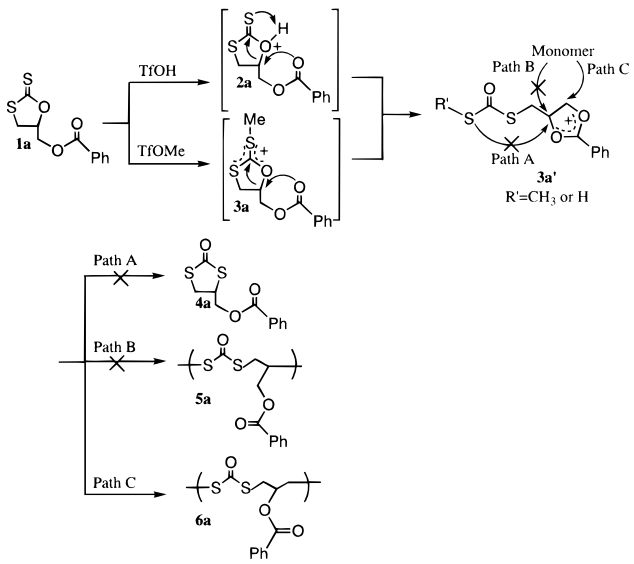


Figure 4. (A) ^1H NMR (400 MHz) and (B) ^{13}C NMR (100 MHz) spectra of the mixture of **1a** and TfOMe (1.2 equiv) in $CDCl_3$ at room temperature.

intramolecular isomerization from **2a** may be suppressed by the formation of the more stable benzoxo-

Scheme 3



nium cation (**3a′**) than **2a** and **3a**.

In conclusion, we have demonstrated the first example of a controlled living cationic ring-opening polymerization of the five-membered cyclic dithiocarbonate based on the neighboring group participation. This new concept of living polymerization may be applied to the design of well-defined novel functional polymers.

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(15) Kihara, N.; Nakawaki, Y.; Endo, T. *J. Org. Chem.* **1995**, *60*, 473. **1a**: Mp 71.0−72.0 °C (lit. 69.0−70.5 °C). IR (neat on NaCl disk) 1186 ($\nu_{C=S}$, dithiocarbonate), 1722 ($\nu_{C=O}$, ester) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.62−3.78 (m, 2H, S-CH_2), 4.62−4.72 (m, 2H, $COOCH_2$), 5.43−5.50 (m, 1H, CH), 7.27−8.07 (m, 5H, Ph) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.03 (S−CH_2), 63.56 (O−CH), 87.81 (CH) 128.54 (Ph), 128.85 (Ph), 129.70 (Ph), 133.59 (Ph), 165.79 (C═O, ester), 211.45 (C═S, dithiocarbonate) ppm; MS 254 (M^+).

(16) Cationic ring-opening polymerization of **1a**. Typical procedure: To a glass tube containing **1a** in PhCl (1.5 M) was added an initiator 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. A white powdery polymer (**6a**) was obtained by precipitation with *n*-hexane. (**6a**): IR (KBr) 1649 ($\nu_{C=O}$, dithiocarbonate), 1722 cm^{-1} ($\nu_{C=O}$, ester); ^1H NMR (400 MHz, $CDCl_3$) δ 3.22−3.32 (m, 4H, S−CH_2), 5.20 (m, 1H, CH), 7.42−7.98 (m, 5H, Ph) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.7 (S−CH_2), 70.9 (O−CH), 128.4 (Ph), 129.3 (Ph), 129.8 (Ph), 133.4 (Ph), 165.3 (C═O, ester), 187.7 (C═O, dithiocarbonate) ppm. Anal. Calcd. for ($C_{11}H_{10}O_3S_2$): C, 51.95; H, 3.96; S, 25.21. Found: C, 51.37; H.; 4.23; S, 25.36.

(17) Experimental procedure: To a solution of **1a** (123 mg, 0.5 mmol) in PhCl (0.33 mL) was added TfOMe (10 mol % vs **1a**), and the mixture was stirred at 45 °C for 1.5 h. After that, a solution of myristyltrimethylammonium bromide (30 mol % vs **1a**) in CH_2Cl_2 (1 mL) was added to the polymerization mixture, and it was stirred at room temperature for 1 h. The polymerization mixture was diluted with CH_2Cl_2 and washed with water two times. The organic layer was dried over anhydrous magnesium sulfate. The polymer **6a** (M_n 2300, M_w/M_n 1.06) was isolated in 96% yield by preparative HPLC eluted with $CHCl_3$. In the ^1H NMR spectrum of the polymer, signals assignable to CH_3S− and −CH_2Br groups were observed at 2.38 and 3.62 ppm with contents of 10.7 and 9.8 mol %, respectively.

(18) The carbenium cation (**3a′**, R′ = H) was formed in the mixture of **1a** with TfOH (1.2 equiv) in $CDCl_3$ at room temperature, but the carbonyl carbon signal of the dithiocarbonic acid moiety slowly disappeared. The dithiocarbonic acid moiety of **3a′** (R′ = H) may be unstable to be transformed to thiol with releasing COS, which may affect the propagating end. This should be one reason for the broader molecular weight distribution of the polymer obtained with TfOH than that with TfOMe.

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