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Living Ring-Opening Polymerization Based on Neighboring Group Participation

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SUMMARY: Cationic ring-opening polymerization of a five-membered cyclic dithiocarbonate having benzoxymethyl group; 5-benzoxymethyl-1,3-oxathiolane-2-thione, was carried out with TfOH or TfOMe as an initiator in PhCl at rt – 60 °C. The molecular weight distribution (M_w /M_n) of the polymer obtained with TfOMe was very narrow even at 60 °C (M_w /M_n 1.14), and the Mn value of the polymers estimated by GPC was in good agreement with the molecular weight determined from ^{1}H-NMR. The living nature of the polymerization was confirmed by the conversion dependence of the Mn (M_w /M_n) and the correlation of the experimental and theoretical M_n (M_w /M_n) values.

Introduction

Since the discovery of anionic living polymerization,[1)] the chemistry of living polymerization has been developed in the field of coordination,[2)] metathesis,[3)] 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 counter anion. 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_3Me (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

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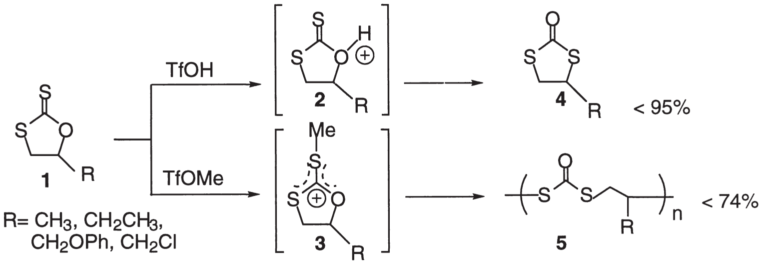
cyclic carbenium cation (**3**) has been confirmed in the reactions of **1** with TfOH and TfOMe, respectively (Scheme 1).[12] The selectivity of the cationic isomerization and polymerization of **1** is attributable to the different intermediates depending on the catalysts.

Scheme 1



Neighboring group participation plays an important role in selective chemical synthesis of oligosaccarides[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. This work deals 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.

Results and Discussion

The five-membered cyclic dithiocarbonate (**1a**) was synthesized 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. 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 Mn values of the polymers estimated by GPC based on polystyrene calibration were in good agreement with the molecular weights determined from the ^{1}H-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 (Fig. 1).

Scheme 2

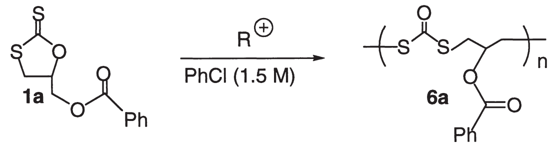


Table 1. Cationic Polymerization of **1a**.

run	init (mol %)	temp (°C)	time (min)	conv [a] (%)	yield (%)	MW$_{\mathrm{NMR}}$ [a]	$M_{\mathrm{n\,GPC}}$ [b]	Mw/Mn [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 ^{1}H-NMR. [b] Estimated by GPC eluted by THF based on polystyrene standards. [c] Isolated by preparative HPLC. [d] *n*-Hexane-insoluble part.

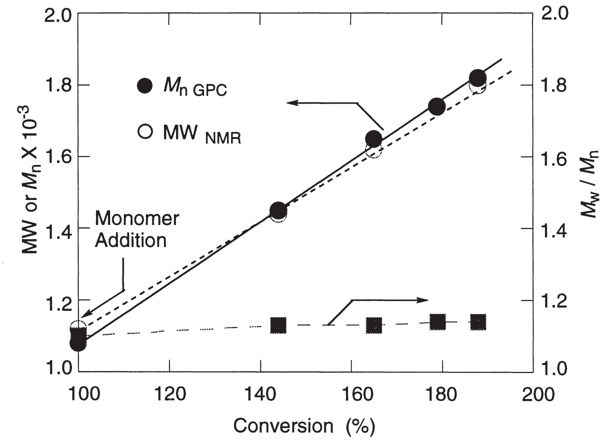


Fig. 1: Conversion dependence of the M_n and M_w /M_n of **6a** obtained by the polymerization of **1a** with TfOMe (2.5 mol %) in PhCl (1.5 M) at 30 °C.

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 32600, M_w /M_n 1.18), as shown Fig. 2. Further, the polymerization was quenched with myristyltrimethylammonium bromide to examine the chain-end functionalization of the polymer. The obtained polymer showed ^{1}H-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.

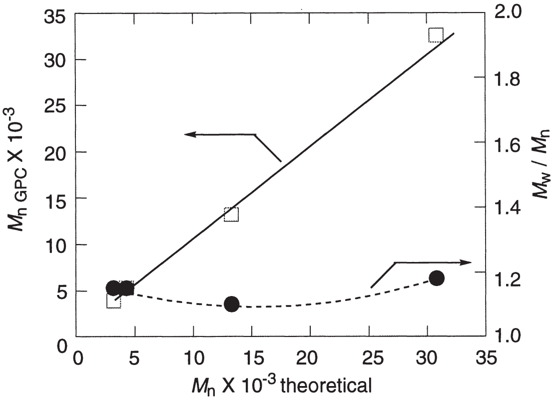


Fig. 2: Correlation of the theoretical and experimental M_n and M_w/M_n of **6a** obtained by the polymerization of **1a** with TfOMe (0.8 - 8 mol %) in PhCl (1.5 M) at room temperature.

The structure of the polymer was confirmed by IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy besides elemental analysis. Fig. 3 shows the ^{1}H-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 ^{1}H-NMR spectrum of the polymer, the signal at 4.7 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.

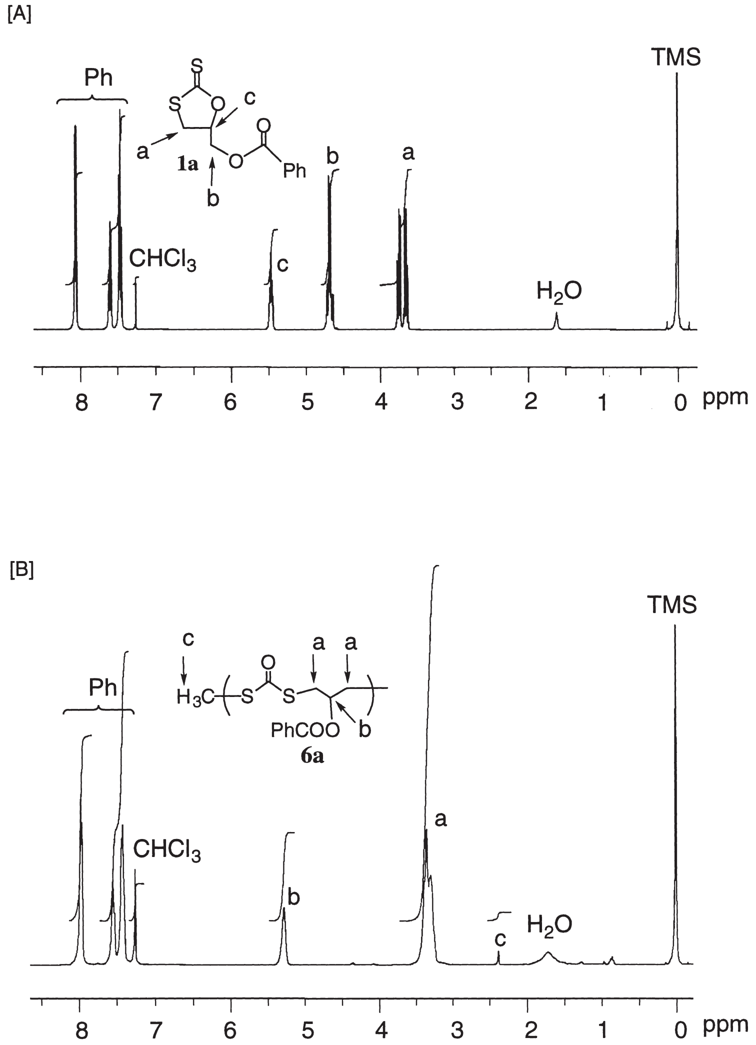


Fig. 3: ^{1}H-NMR (400 MHz) spectra of **1a** [A] and **6a** [B] obtained by the polymerization of **1a** with TfOMe (3 mol %) in PhCl (1.5 M) at 60 °C for 1 h.

The ^{1}H- and ^{13}C-NMR spectra were measured for the mixture of **1a** with TfOMe (1.2 eq) 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 ^{1}H-NMR) was confirmed with a small amount of a carbenium cation (**3a**, 12%) as shown in Fig. 4.

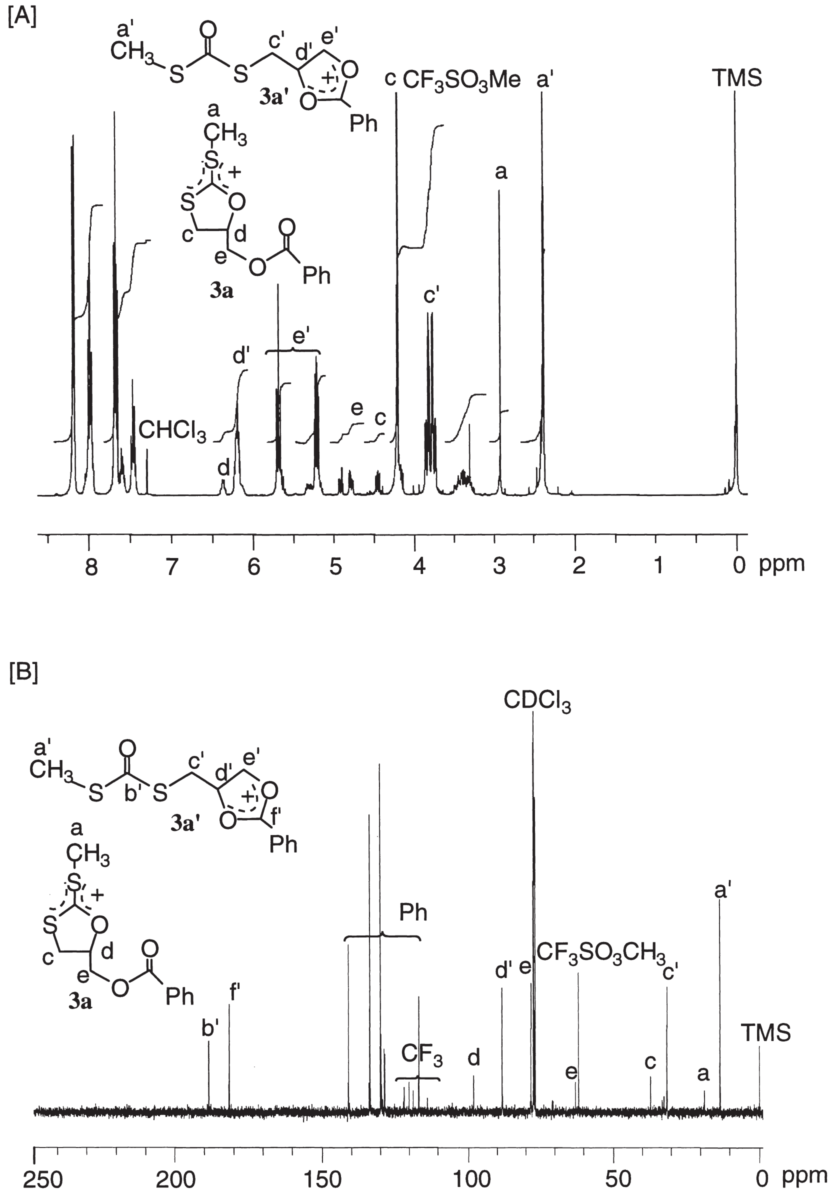
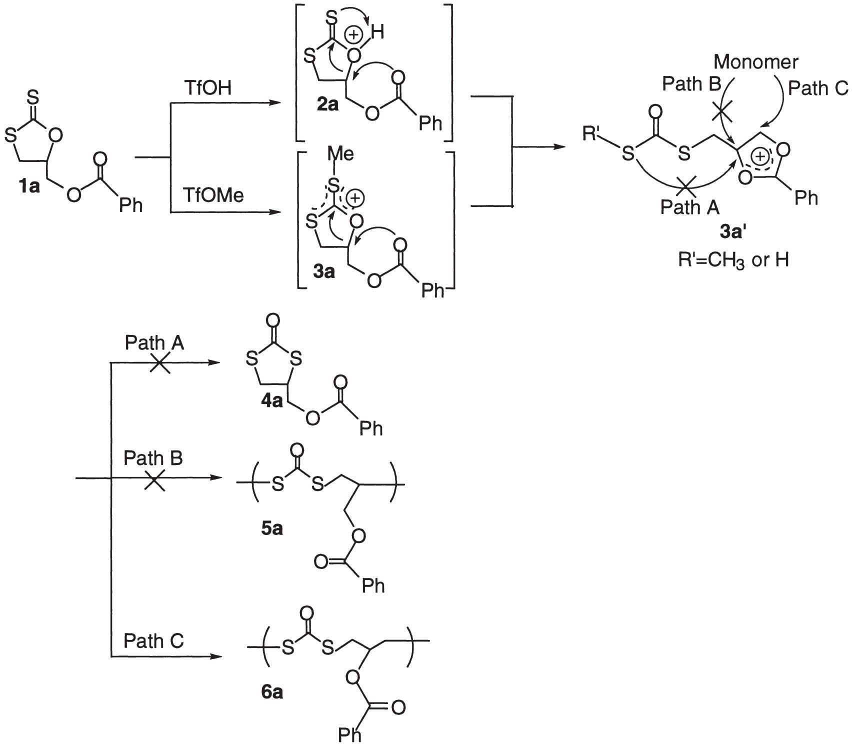


Fig. 4: [A] ^{1}H-NMR (400 MHz) and [B] ^{13}C-NMR (100 MHz) spectra of the mixture of **1a** and TfOMe (1.2 eq) in $CDCl_3$ at room temperature.

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. 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 intramolecular isomerization from **2a** may be suppressed by the formation of the more stable benzoxonium cation (**3a'**) than **2a** and **3a**.

Scheme 3



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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