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The First Anionic Ring-Opening Polymerization of Cyclic Monothiocarbonate via Selective Ring-Opening with C−S Bond Cleavage

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Cyclic carbonates undergo ring-opening polymerization with both cationic and anionic initiators. Höcker et al.[1] and Kricheldorf et al.[2] have extensively studied the anionic and cationic ring-opening polymerizations of cyclic carbonates. New polymerization methods of cyclic carbonates have also been developed such as lipase-catalyzed polymerization[3] and living ring-opening polymerization with a cationic zirconocene complex catalyst.[4] Ring-opening polymerization of cyclic oligomeric carbonates has developed the synthesis of high-molecular-weight bisphenol A polycarbonate, which is commercially interesting in that processing (shaping, forming, wetting, etc.) is simultaneous with polymerization.[5] Aliphatic polycarbonates are expected as biocompatible and biodegradable materials for medical applications.[6] We have 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.[7] As described above, cyclic carbonates are an interesting monomer from the viewpoints of both the polymerization behavior and the function of the polymer. Recently, sulfur-containing polymers such as polythioethers[8] and polythioesters[9] 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 an analogue of cyclic carbonate, i.e., cyclic monothiocarbonate. Cyclic monothiocarbonate has been only reported as a byproduct in the synthesis of 2-chloroethyl diazohydroxide.[10] This communication deals with the first anionic ring-opening polymerization of a six-membered cyclic monothiocarbonate, 1,3-oxathian-2-one (6CMTC).

The monomer 6CMTC was synthesized by the reaction of 3-mercapto-1-propanol with $^1/_3$ equiv of triphosgene in the presence of 2 equiv of 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one in $CHCl_3$ at room temperature for 18 h in 22% yield.[11] The anionic polymerization of 6CMTC was carried out with *tert*-BuOK as an initiator at −78 to 30 °C in tetrahydrofuran (THF) and tetrahydrothiophene (THT) for 1 h under a nitrogen atmosphere. The polymers precipitated in less than 10 min after the polymerization had started in all cases. After quenching the polymerization by the addition of 1 N HCl/methanol, the obtained polymer was isolated by precipitation with ether to avoid the loss of lower-molecular-weight parts. The molecular weights of the polymers were estimated by ^{1}H NMR and GPC. Table 1 summarizes the conditions and results of the polymerization. The conversion estimated by ^{1}H NMR spectroscopy was nearly equal to the yield of the polymer. The monomer conversion and the polymer yield in the polymerization at −78 °C (run 3) were lower when compared with those at 0 and 30 °C, while the M_n of the polymer showed no clear tendency, probably due to the precipitation of the polymer during the polymerization. The M_n of the polymer obtained in THT (run 4) was lower than those in THF. The polymer obtained in run 2 showed T_m at 116 °C.

Table 1. Anionic Polymerization of 6CMTC[a]

run	solv (0.5 M)	temp (°C)	conv[b] (%)	yield[c] (%)	M_n NMR[d]	M_n GPC[e]	M_w/M_n
1	THF	30	67	61	3800	14 000	1.38
2	THF	0	75	70	5800	18 000	1.51
3	THF	−78	55	44	4100	13 000	2.03
4	THT	0	65	60	2400	3 500	1.57

[a] Initiator: *tert*-BuOK (1 mol %); time: 1 h. [b] Estimated by ^{1}H NMR. [c] Ether-insoluble part. [d] Determined by the integration ratio of the ^{1}H NMR signals of the *tert*-butyl group of the initiating end at 1.48 ppm and the signal of $CH_2-CH_2-CH_2$ at 2.15−2.21 ppm. [e] Determined by GPC, polystyrene calibration eluted by *o*-dichlorobenzene at 140 °C.

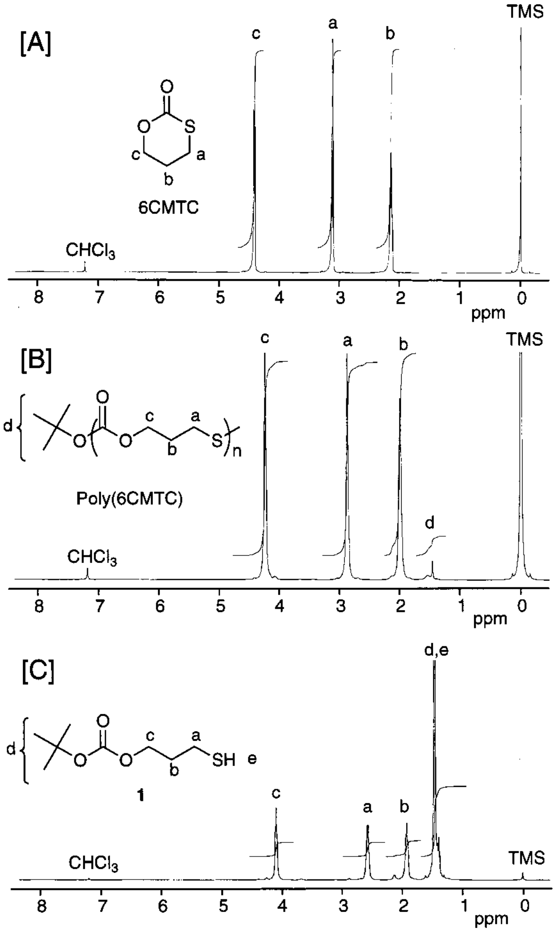

Figure 1. (A) ^{1}H NMR spectra (solvent; $CDCl_3$, 400 MHz) of 6CMTC, (B) the polymer obtained in the polymerization in run 3 in Table 1, and (C) the adduct obtained by the reaction of 6CMTC with an equivalent of *tert*-BuOK in THF (0.2 M) at −78 °C for 15 min.

The structure of the obtained polymer was examined by ^{1}H NMR, ^{13}C, NMR, and IR spectroscopy. Figures 1

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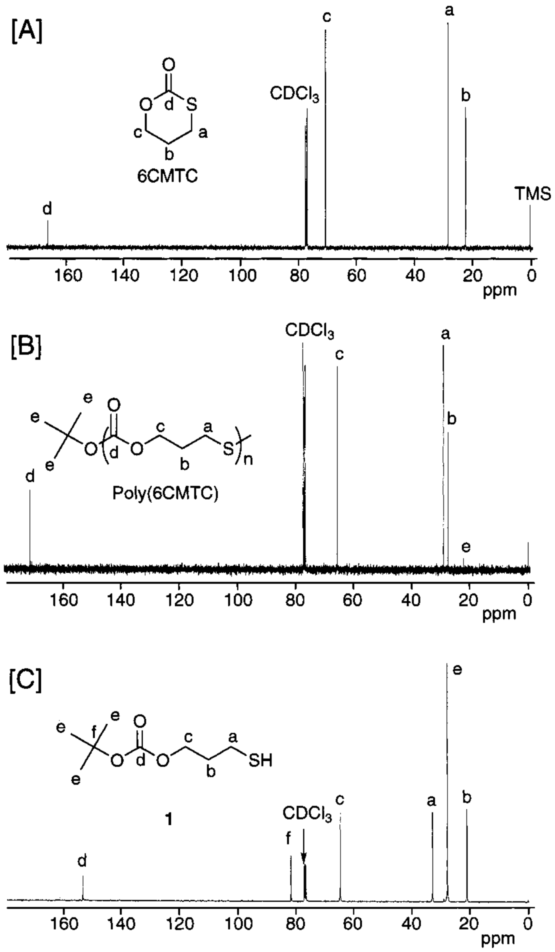
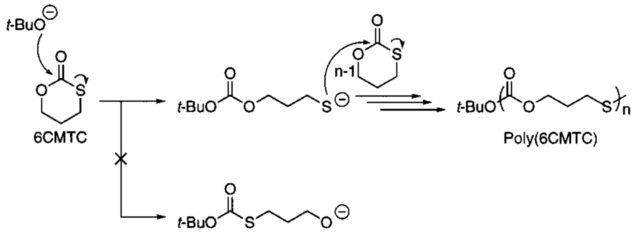


Figure 2. (A) ^{13}C NMR spectra (solvent; CDCl$_3$, 100 MHz) of 6CMTC, (B) the polymer obtained in the polymerization in run 3 in Table 1, and (C) the adduct obtained by the reaction of 6CMTC with an equivalent of *tert*-BuOK in THF (0.2 M) at −78 °C for 15 min.

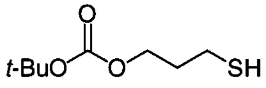
and 2 illustrate the ^{1}H and ^{13}C NMR spectra of 6CMTC and the polymer obtained in the polymerization in run 3 in Table 1, along with a carbonate−thiol (**1**), which was obtained by the reaction of 6CMTC with an equivalent of *tert*-BuOK (see below). The ^{1}H NMR spectrum of the polymer (Figure 1B) showed three broad singlet signals at 2.04, 2.92, and 4.31 ppm, which were assignable to β-, α-, and γ-methylenes of the thiocarbonate sulfur, respectively. All the signals of the monomer (Figure 1A) were shifted 0.13−0.24 ppm to the higher field after the polymerization. No signal assignable to α-methylene protons of a disulfide moiety was observed at 2.4−2.5 ppm, which indicated the absence of a polymer with a disulfide linkage by oxidative coupling of the polymer end thiol groups. The ^{13}C NMR spectrum of the polymer (Figure 2B) showed the corresponding three methylene carbon signals at 27.4, 29.0, and 65.7 ppm but no other signals indicating the presence of a carbonate or a dithiocarbonate group. The IR spectrum of the polymer showed a carbonyl absorption at 1739 cm^{-1}, which was 54 cm^{-1} higher compared with that of 6CMTC.

An equivalent reaction of 6CMTC with *tert*-BuOK was carried out to obtain information about the bond cleavage. It afforded no monothiocarbonate−alcohol (**2**) but a carbonate−thiol (**1**) selectively and quantitatively in THF (0.2 M) at −78 °C for 15 min, which suggested no formation of an alcoholate anion in the polymerization.

Scheme 1



This complete selectivity might be a result of the leaving ability and nucleophilicity of the thiolate anion being larger than those of the alcoholate anion.



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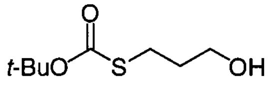

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Consequently, it has been confirmed that the polymer is a polymonothiocarbonate formed by selective ring-opening with the carbonyl−sulfur bond cleavage as illustrated in Scheme 1. In the initiation step, *tert*-BuOK may attack the carbonyl carbon to form a thiolate anion selectively. The propagating step should be the attack of the propagating thiolate end group to the carbonyl carbon of the monomer, which results in the polymonothiocarbonate.

In summary, this article has demonstrated the first anionic ring-opening polymerization of the six-membered cyclic monothiocarbonate, 6CMTC. The anionic ring-opening polymerization of 6CMTC proceeded via selective bond cleavage through a thiolate anion to afford a polymonothiocarbonate.

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(11) Mp 35 °C. ^{1}H NMR δ ($CDCl_3$, 400 MHz): 2.15−2.21 (m, 2 H, $CH_2{-}CH_2{-}CH_2$), 3.17 (t, $J = 6.8$ Hz, 2 H, $S{-}CH_2{-}CH_2$), 4.48 (t, $J = 6.4$ Hz, 2 H, $O{-}CH_2{-}CH_2$) ppm. ^{13}C NMR δ ($CDCl_3$, 100 MHz): 22.1 ($CH_2{-}CH_2{-}CH_2$), 28.1 ($S{-}CH_2{-}CH_2$), 70.5 ($O{-}CH_2{-}CH_2$), 165.6 (S−CO−O) ppm. IR (KBr disk): 3460, 2924, 1685 (C═O), 1219, 1118, 1005, 644 cm^{-1}. EA. Calcd for $C_4H_6O_2S$: C, 40.66; H, 5.12; S, 27.14. Found: C, 40.69; H, 5.14; S, 27.22.

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