First Example of Cationic Ring-Opening Polymerization of γ-Thionobutyrolactone

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This paper deals with the cationic ring-opening polymerization of γ-thiobutyrolactone (**2**) and γ-thionobutyrolactone (**3**). The ring-opening polymerization of **3** was carried out in bulk at 100 °C for 2 h by various cationic initiators. Scandium trifuoromethane-sulfonate induced the polymerization of **3**, which did not afford polythionoester but polythioester selectively. On the other hand, the polymerization of **2** did not proceed with various cationic initiators under the similar conditions.

Sulfur-containing polymers such as polythiocarbonates and polythioesters have received much attention because of their excellent optical and thermal properties.[1–7] Ring-opening polymerizations of four-, six-, and seven-membered lactones, and six-, and seven-membered thiolactones are also known to produce the corresponding polyesters and polythioesters, respectively.[8,9] However, among the lactones in various ring sizes, generally, five-membered lactones such as γ-butyrolactone (**1**) (Chart 1) and γ-thiobutyrolactone (**2**) do not polymerize to the corresponding poly(thio)esters at all probably because of lower strain energy.[9,10] Recently, we have reported that anionic and cationic polymerization of ε-thionocaprolactone afforded polythiocarboxylic *O*-ester and *S*-ester whose structure depends on the initiators used.[11,12] In addition, it was found that polythioesters could be synthesized not only by a chemical synthesis based on the ring opening polymerization process, but also a bacterial fermentation process. Steinbüchel et al. have reported that poly-(3-hydroxybutyrate-co-3-mercaptobutyrate) was synthesized by *Ralstonia eutropha* from appropriate carbon sources and the genetically engineered *Escherichia coli* successfully produced poly(3-mercaptoalkanoate) from 3-mercaptoalkanoate.[13] However, they could not succeed in the biosynthesis of poly(4-mercaptobutyrate)-containing poly(3-hydroxybutyrate) (PHB) in spite of successful biosynthesis of poly(4-hydroxybutyrate)-containing PHB.[14] Here, we describe cationic ring-opening polymerization of γ-thionobutyrolactone (**3**: five-membered lactone) to afford poly(4-mercaptobutyrate) (Scheme 1).

The monomer **3** was synthesized from **1** by using Lawesson's reagent.[15] Lanthanide triflates were used in this study as cationic initiators because these catalysts might offer the advantages of their stability toward the hydrolysis and there is no report on ring-opening polymerization of thiolactones and thionolactones by these catalysts.[16] In this study, scandium trifuoromethane-sulfonate: Sc(OTf)$_3$, yttrium trifluoromethane-sulfonate: Y(OTf)$_3$, ytterbium trifluoromethane-sulfonate: Yb(OTf)$_3$, and lanthanum trifluoromethane-sulfonate: La(OTf)$_3$ were also employed as cationic catalysts. Table 1 summarizes the results of cationic ring-opening polymerization of **3**. Monomer conversion was monitored from the ^{1}H NMR analysis of *d*-chloroform solution of the resulting mixture. At first, cationic polymerization of **1** and **2** was carried out in bulk at 100 °C for 24 h. From the ^{1}H NMR analysis, these polymerizations did not take place probably because of thermodynamic reason. Next, the polymerization of **3** was carried out using Sc(OTf)$_3$ in bulk at 100 °C (Run 1 in Table 1) to result in that the conversion of **3** was 78% and the resulting mixture contained a small amount of unknown unit besides the unreacted monomer and the corresponding polymer. The resulting mixture was poured into *n*-hexane to precipitate the polymer. The obtained polymer was also soluble in common organic solvents such as toluene, CH$_2$Cl$_2$, and THF. The number-average molecular weight and polydispersity were determined by SEC to be 3400 and 2.2. SEC analysis of the resulting polymer showed a unimodal distribution. The monomer **3** was completely recovered in the polymerization without Sc(OTf)$_3$ (control experiment).

The structure of poly(**3**) was determined by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Figure 1 shows ^{1}H NMR spectrum of poly(**3**) (Run 1 in Table 1). In the ^{1}H NMR, three main peaks were observed: a triplet peak at δ 2.67 and δ 2.94 were assignable to the α-, γ-methylene protons of the thioester moiety, a multiple peak at δ 1.96 due to β-methylene protons of the thio-

Chart 1.

Scheme 1.

Table 1. Ring-opening polymerization of **3** with various cationic initiators[a]

Run	Initiator	Conv.[b] (%)	Yield.[c] (%)	$M_n(M_w/M_n)$[d]
1	Sc(OTf)$_3$	78	50	3400 (2.2)
2	Y(OTf)$_3$	79	42	4500 (2.7)
3	Yb(OTf)$_3$	84	45	3600 (2.9)
4	La(OTf)$_3$	53	30	6300 (2.2)

[a]Condition: monomer 1.0 mmol, initiator 1.0 mol%, at bulk, at 100 °C, for 2 h. [b]Determined by ^{1}H NMR spectroscopy (CDCl$_3$). [c]Isolated yield after precipitation into *n*-hexane. [d]Determined by SEC based on polystyrene standards eluted by CHCl$_3$ (*n*-hexane-insoluble part).
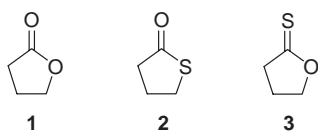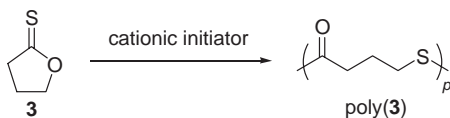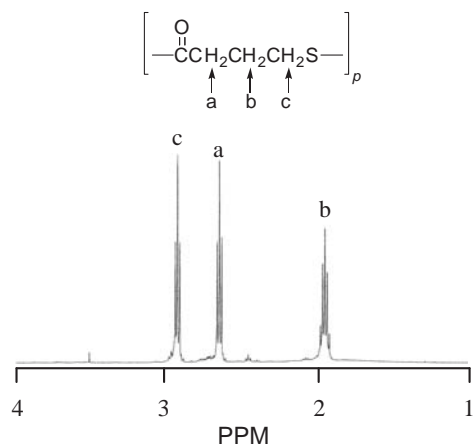
Figure 1. 1H NMR spectrum of poly(**3**) obtained in Run 1 (Table 1).

ester moiety. In the ^{13}C NMR, four characteristic peaks were also observed: the peak at δ 198 assignable to the carbonyl carbon of thioester moiety, the peaks at δ 27.9, δ 25.4, and δ 42.6 were assignable to the α-, β-, and γ-methylene carbon of thioester moiety, respectively (data not shown). The IR spectrum showed peaks assignable to oxocarbonyl groups of thioesters at 1678 cm^{-1} (data not shown). These spectroscopic data completely agreed with those of the polymer obtained by another method.[9,17] These results might support strongly that the polymerization proceeds via isomerization of thionocarbonyl moieties. The others catalysts showed catalytic activity for the polymerization of **3** under similar conditions (Runs 2–4 in Table 1). Among tested catalysts, La(OTf)$_3$ (Run 4 in Table 1) showed less catalytic activity. The structure of resulting polymer was also confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. This isomerizarion was also observed in the polymerization catalyzed by the other cationic initiators.

As mentioned previously, a plausible mechanism for the ring-opening polymerization of **3** was proposed as follows (Scheme 2).[12] At first, a nucleophilic attack of the thionocarbonyl sulfur to the cationic initiator affords carbonium cation species. Then, the thionocarbonyl sulfur nucleophilically attacks to the α-position of the ether oxygene in the cyclic carbonium ion, and the chain reaction of these progress may give the corresponding polythioesters. On the basis of these results, the driving force of ring-opening polymerization of **3** may depend on the structure of thionocarbonyl group. Thought the strain energy in the reaction is not directly related to the polymerizability, the polymerizability of **3** with cationic initiators may reflect the decrease of the activation energy according to the unstableness of the thionocarbonyl group.[18]

The thermal behavior of poly(**3**) obtained in Run 1 (Table 1) was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), where its 5% weight loss temperature (T_{d5}) was 185 °C and melting temperature (T_m)
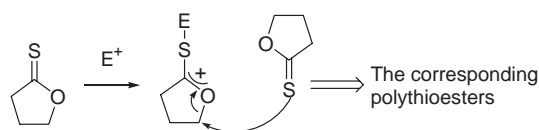
Scheme 2.

was 90 °C, and glass transition temperature (T_g) was not observed. The melting point of poly(**3**) was much higher than that of oxyanalogues: poly(4-hydroxybutyrate).[19]

In summary, cationic ring-opening polymerization of γ-thionobutyrolactone afforded the corresponding polythioester with isomerization from thionocarbonyl to oxocarbonyl. It was observed that the melting temperature is higher than that of the polymer with equivalent oxygene atoms.

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18 The strain energies of **1**, **2**, and **3** were estimated by semiempirical molecular orbital calculations (PM3 method). **1**: 60.4 kcal/mol, **2**: 64.4 kcal/mol, **3**: 91.2 kcal/mol. These strain energies were estimated by taking difference between the formation energy of lactones and the corresponding acyclic repeating units: In the case of **3**, 4-mercaptobutyrate was used. These calculations were made on a personal computer with the use of Chem3D program.
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