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Anionic Ring-Opening Polymerization of ϵ-Thionocaprolactone

Fumio Sanda, Duangjai Jirakanjana, Masakatsu Hitomi, 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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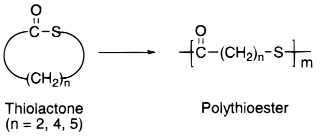
ABSTRACT: Anionic ring-opening polymerization of ϵ-thionocaprolactone was examined. When organolithiums, Grignard reagents, and lithium *tert*-butoxide were used as the initiators, the corresponding polythiocarboxylic-*O*-ester was selectively formed. When potassium *tert*-butoxide and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) were used, the corresponding polythiocarboxylic-*S*-ester was predominantly formed. The monomer conversion and M_n of the obtained polymer increased with the polymerization temperature. Elongation of polymerization time resulted in decrease of the polymer yield and M_n. The polymerization in tetrahydrofuran (THF) proceeded faster compared with the polymerization in toluene. Formation of a cyclic dimer was observed in the polymerization in THF.

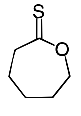
Introduction

Sulfur-containing aromatic polymers draw much attention because of their high thermal stabilities and refractive indexes. They have found important industrial applications, such as polysulfone and polyphenylene sulfide as high-performance engineering plastics.[1] Polythiophene is also gaining importance due to its excellent electron conductivity and optical property.[2] In contrast to these sulfur-containing aromatic polymers, few studies on sulfur-containing aliphatic polythioesters have been reported, probably due to difficult preparation, high cost, and lower stability. Polythioesters have been synthesized by polycondensation of dithiols with diacid chlorides,[3] and ring-opening polymerization of thiolactones.[4] Ring-opening polymerization of thiopropiolactone, δ-thiovalerolactone, and ϵ-thiocaprolactone derivatives can also afford polythioesters (Scheme 1), most of which show higher melting points compared with the corresponding polyesters.

Scheme 1



Meanwhile, five-, six-, and seven-membered thionolactones have been synthesized by several methods;[5] however, no polymerization of thionolactones has been reported so far. This article deals with the first anionic ring-opening polymerization of ϵ-thionocaprolactone.


ε-Thionocaprolactone

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on JEOL EX-400 and Lambda-500 spectrometers using tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. Number- and weight-average molecular weights (M_n and M_w) and polydispersity ratios (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Tosoh HLC-8120 GPC, equipped with two consecutive polystyrene gel columns (G2500H and G4000H), using THF as an eluent with a flow rate of 1.0 mL/min, calibrating with polystyrene standard samples, detected with refractive index (RI) and ultraviolet (UV) at 254 nm. 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), detected with refractive index and ultraviolet at 254 nm using chloroform as an eluent with a flow rate of 3.8 mL/min. Mass spectra were recorded by electron impact mass spectroscopy on Shimadzu GCMS-QP5050A and JEOL JMS-700 GC-MS instruments.

Materials. The monomer, ϵ-thionocaprolactone was synthesized according to the literature.[6] Initiators, *n*-butyllithium (1.54 mol/L solution in *n*-hexane, Kanto Chemical Co., Inc.), *sec*-butyllithium (1.04 mol/L solution in cyclohexane and *n*-hexane, Kanto Chemical Co., Inc.), *tert*-butyllithium (1.54 mol/L solution in *n*-pentane, Kanto Chemical Co., Inc.), methyllithium (1.4 mol/L solution in diethyl ether, Kanto Chemical Co., Inc.), phenyllithium (0.86 mol/L solution in cyclohexane and diethyl ether, Kanto Chemical Co., Inc.), methylmagnesium chloride (3 mol/L solution in THF, Aldrich Co., Ltd.), *tert*-butylmagnesium chloride (2 mol/L in THF, Tokyo Kasei Kogyo Co., Ltd.), lithium *tert*-butoxide (1 mol/L solution in THF, Aldrich Co., Ltd.), and potassium *tert*-butoxide (1 mol/L solution in THF, Aldrich Co., Ltd.) were used as received. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and triethylamine were purified according to the general procedure before use. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was dried under a reduced pressure for 10 h. Acetic acid and *n*-butyl alcohol were used without further purification. THF and toluene were freshly distilled on sodium metal under nitrogen atmosphere before use.

Anionic Polymerization. *Typical Procedure***.** Into a glass tube equipped with a three-way stopcock dried with a heat gun under a reduced pressure before use were fed ϵ-thionocaprolactone (0.22 g, 1.70 mmol) with a syringe under nitrogen atmosphere and then toluene (1.7 mL). The mixture was heated to 100 °C and stirred for 15−20 min to make sure the temperature became a set value. *n*-Butyllithium (1.54 mol/L solution in *n*-hexane, 0.034 mmol, 22 μL) was quickly added to the reaction mixture, and it was stirred for 20 h. The reaction was quenched by the addition of a 10 vol % of acetic acid solution in *n*-butyl alcohol (0.5 mL). Dichloromethane (5 mL) was added to the mixture, and the resulting mixture was poured into *n*-hexane (400 mL) to precipitate a polymer. It was collected as viscous liquid by decantation of the supernatant and dried under vacuum.

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Scheme 2

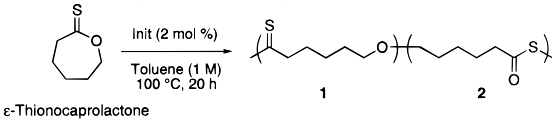


Table 1. Anionic Ring-Opening Polymerization of ε-Thionocaprolactone[a]

entry	initiator	conv.[b]	yield[c]	M_n[d]	M_w/M_n[d]	unit ratio[b] 1:2
1	MeLi	100	77	19,000	2.67	100:0
2	*n*-BuLi	100	65	8,200	1.75	100:0
3	*sec*-BuLi	100	65	8,500	1.55	100:0
4	*tert*-BuLi	100	58	8,300	1.53	100:0
5	PhLi	100	58	10,000	1.81	100:0
6	MeMgCl	100	58	10,500	2.05	100:0
7	*tert*-BuMgCl	100	48	9,200	1.69	100:0
8	*tert*-BuOLi	98	52	9,500	1.78	100:0
9	*tert*-BuOK	30	17	3,800	1.54	37:63
10	DBU	25	10	4,500	1.54	11:89

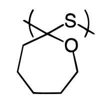
[a] Conditions: initiator, 2 mol %; initial monomer concentration, 1 mol/L in toluene; 100 °C; and 20 h. [b] Determined by ^{1}H NMR (400 MHz). [c] *n*-Hexane-insoluble part. [d] Estimated by GPC on the basis of polystyrene standards eluted by THF.

Ab Initio Calculation. All calculations were done on a Silicon Graphics Indigo2 IMPACT 10000 with use of Gaussian 94. Geometries were fully optimized by the HF/STO-3G basis set, followed by a single point calculation by the HF/6-311G** basis set.

Results and Discussion

Anionic Polymerization. The anionic ring-opening polymerization of ε-thionocaprolactone was carried out with various initiators in toluene (initial monomer concentration, 1 M) at 100 °C for 20 h.[7] The obtained polymers contained two different repeating units, thiocarboxylic *O*-ester (**1**) and thiocarboxylic *S*-ester (**2**), as shown in Scheme 2 and Table 1. The polymerization with organolithium and Grignard reagent initiators selectively afforded the polymer consisting of thiocarboxylic *O*-ester unit **1** irrespective of the initiator substituents with a quantitative monomer conversion (entries 1−7 in Table 1). *tert*-BuOLi also afforded the polymer consisting of unit **1** with a nearly quantitative conversion. Surprisingly, *tert*-BuOK afforded the polymer predominantly consisting of thiocarboxylic *S*-ester unit (63%) **2** with 30% conversion (entry 9 in Table 1). DBU afforded the polymer with 89% unit ratio of unit **2** with 25% conversion (entry 10 in Table 1). Single modal GPC curves of these two polymers suggested that they were not a mixture of two homopolymers (poly-**1** and poly-**2**) but a copolymer. Other amines, triethylamine, and DABCO could not convert the monomer under the conditions in Table 1. The M_n of the polymers ranged from 3800 to 19 000.[8] The polymer obtained with a higher yield tended to show a higher M_n.

Figure 1 depicts the ^{1}H and ^{13}C NMR and IR spectra of the polymer obtained in entries 2 and 9 in Table 1.[9] In Figure 1A, signals based on ε-methylene (*b*) and α-methylene (*f*) protons of a thionoester group are observed at 2.73 and 4.43 ppm, respectively. The ^{13}C NMR signal (*a*) at 224.1 ppm can be assigned to a thiocarbonyl carbon atom of the thionoester group. The presence of small signals at 4.07, 3.65, 3.21, 3.02, and 2.32 ppm suggests that the polymer contains a small amount of unknown units besides thiocarboxylic *O*- and *S*-ester units **1** and **2**. Thioacetal unit **3** may be plausible as this unknown unit, but there is no clear evidence.



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In Figure 1B, signals at 2.73 and 4.43 ppm can be assigned to ε-methylene (*b*) and α-methylene (*f*) protons of thiocarboxylic *O*-ester unit **1** in manner similar to that of Figure 1A. Meanwhile, signals at 2.54 and 2.85 ppm can be assigned to ε-methylene (*k*) and α-methylene (*g*) protons of thiocarboxylic *S*-ester unit **2**, assignments which are supported by the ^{1}H NMR signals of the polymer obtained by the anionic polymerization of ε-thiocaprolactone.[4b] The presence of unit **2** can be also confirmed by the appearance of a signal (*l*) at 199.2 ppm in the ^{13}C NMR spectrum and an IR absorption peak at 1682 cm^{-1}, which are assigned to a carbonyl group of a thiocarboxylic *S*-ester (S−C=O) compound.[4b] ^{1}H NMR signals at 4.07, 3.65, 3.21, 3.02, and 2.32 ppm indicate that the polymer also contains a small amount of unknown unit.

Temperature Effect. Table 2 summarizes the temperature effect on the anionic polymerization of ε-thionocaprolactone with *tert*-BuLi (2 mol %) in toluene (initial monomer concentration, 1 M). The monomer conversion and M_n of the obtained polymer increased with the temperature (entries 1−4 in Table 2). Elongation of time resulted in a decrease of the polymer yield and M_n (entries 4 and 5 in Table 2), probably due to a backbiting reaction. The *n*-hexane-soluble part obtained in the polymerization of entry 5 in Table 2 was characterized after isolation by preparative HPLC to find a cyclic dimer (3% yield), whose structure was determined by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy (Figure 2) besides mass spectrometry. This may be one reason for the polymer yield being lower than that expected from the monomer conversion.

Table 2. Effect of Temperature on the Anionic Polymerization of ε-Thionocaprolactone[a]

entry	temp (°C)	time (h)	conv[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]	cyclic dimer[e] (%)
1	0	2	64	60	8 000	1.26	
2	20	2	94	69	9 000	1.42	
3	50	2	100	73	13 000	1.55	1
4	100	2	100	68	13 000	1.65	3
5	100	20	100	58	8 300	1.53	4
6[f]	20	2	100	35	6 800	1.36	34

[a] Conditions: *tert*-BuLi, 2 mol %, and initial monomer concentration, 1 mol/L in toluene. [b] Determined by ^{1}H NMR (400 MHz). [c] A percent yield obtained as an *n*-hexane-insoluble part. [d] Estimated by GPC on the basis of polystyrene standards eluted by THF. [e] Estimated by ^{1}H NMR (400 MHz, $CDCl_3$) of *n*-hexane-soluble part. [f] Polymerization was carried out in THF (1 mol/L).

Solvent Effect. The time−conversion relationships were monitored to elucidate the solvent effect on the anionic polymerization of ε-thionocaprolactone with *tert*-BuLi (2 mol %) in THF (1 M) and toluene (1 M) at 20 °C as shown in Figure 3. The polymerization in THF proceeded faster than that in toluene. The monomer was converted quantitatively in the both solvents after 2 h.

When THF was used as the solvent, the polymer yield and M_n decreased, and the formation of the cyclic dimer increased as shown in entry 6 in Table 2. Figure 4 depicts the relationships between the monomer conversion, M_n, and the formation of the cyclic dimer. In toluene (Figure 4A), the M_n of the polymer gradually increased throughout the reaction process without form-

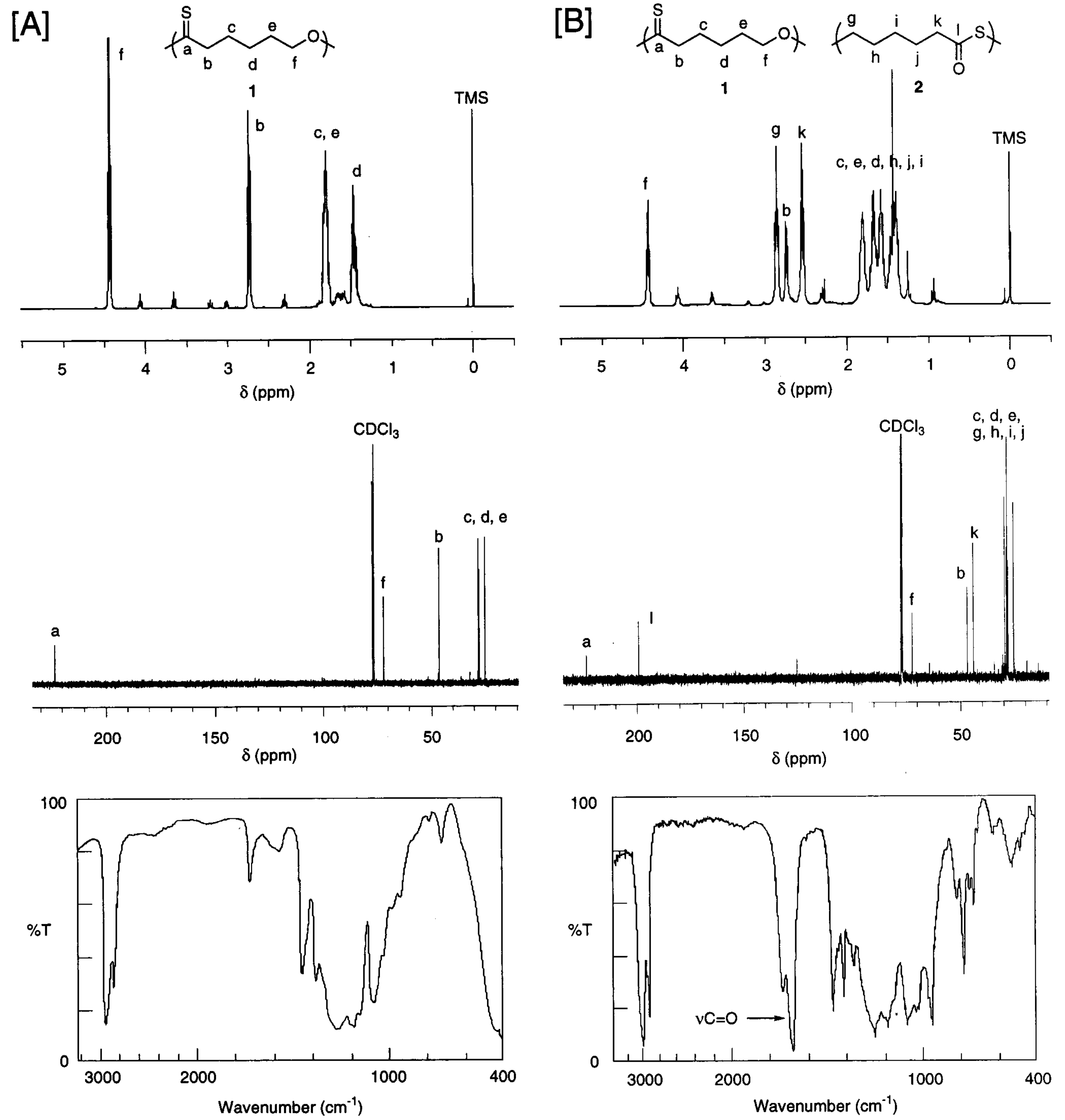


Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz), and IR spectra of the polymer obtained by the polymerization of ϵ-thionocaprolactone at 100 °C for 20 h. (A) Initiator: *n*-BuLi (2 mol %, entry 2 in Table 1). (B) Initiator: *tert*-BuOK (2 mol %, entry 9 in Table 1).

ing the cyclic dimer. In THF (Figure 4B), the M_n increased in the first stage but decreased in the final stage. The cyclic dimer was formed in accordance with decreasing the M_n. A backbiting reaction might proceed slowly together with the polymerization at the first stage to form the cyclic dimer, and it might become predominant as the monomer was consumed. The polymerization in THF formed an amount of the cyclic dimer larger than that in toluene. The former formed the dimer in 8 and 14% yields at 80 and 98% monomer conversions, respectively, whereas the latter did not form the dimer at the similar points. Other byproducts such as low-molecular-weight oligomers might also be formed via the backbiting reaction, although mass spectrometric analysis could not show clear evidence. The backbiting reaction would be a major side reaction that causes the decrease of the polymer yield and molecular weight. THF enhanced the backbiting reaction as well as the polymerization rate.

Polymerization Mechanism. Scheme 3 illustrates a plausible mechanism of the formation of thiocarboxylic *O*- and *S*-ester units **1** and **2** in the anionic polymerization of ϵ-thionocaprolactone. In Path 1, an anionic nucleophile attacks the thiocarbonyl carbon atom of the monomer to form an alcoholate anion as a propagating species. Thiocarboxylic *O*-ester unit **1** is formed by

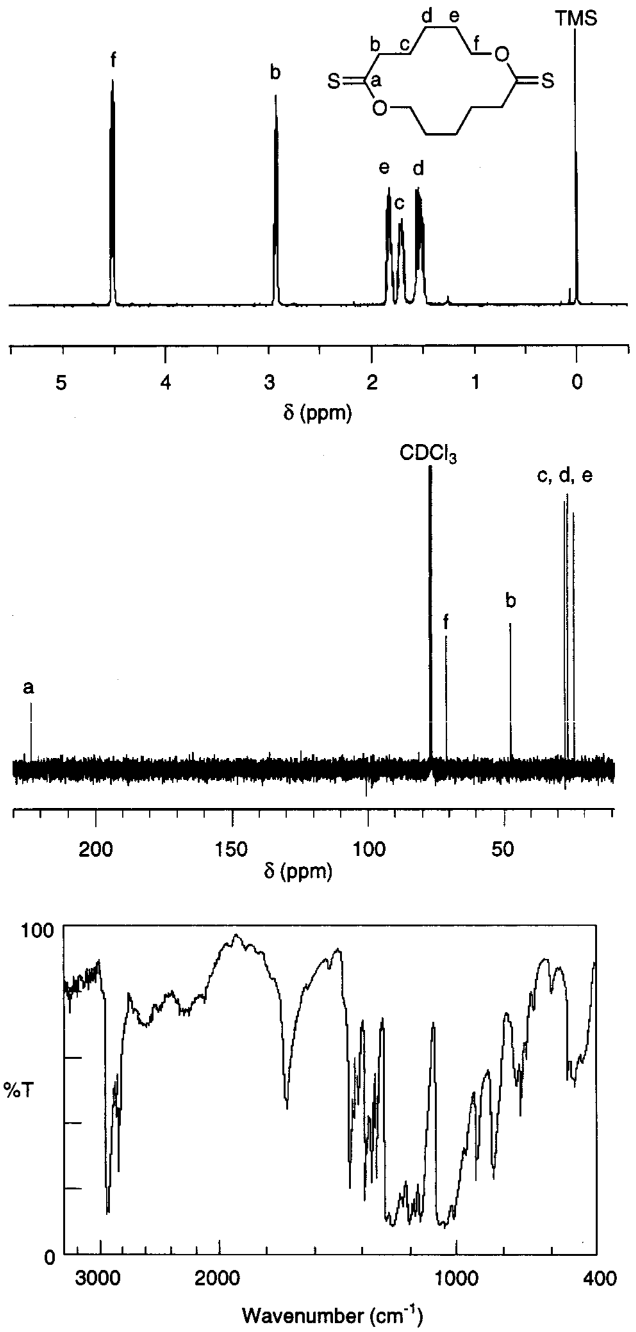


Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz), and IR spectra of a cyclic dimer isolated by preparative HPLC from the *n*-hexane soluble part obtained by the polymerization of ε-thionocaprolactone at 100 °C for 20 h (entry 5 in Table 2).

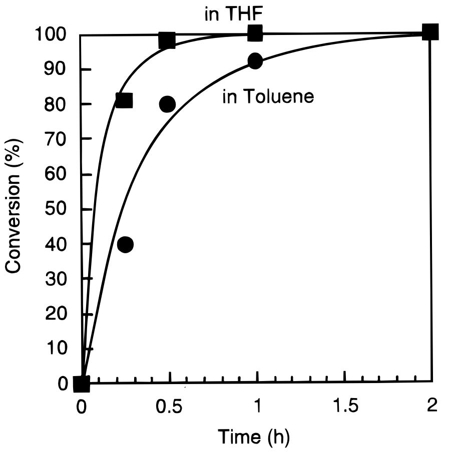


Figure 3. Time–conversion relationships in the anionic ring-opening polymerization of ε-thionocaprolactone with 2 mol % of *tert*-BuLi in toluene and THF. Initial monomer concentration: 1 M.

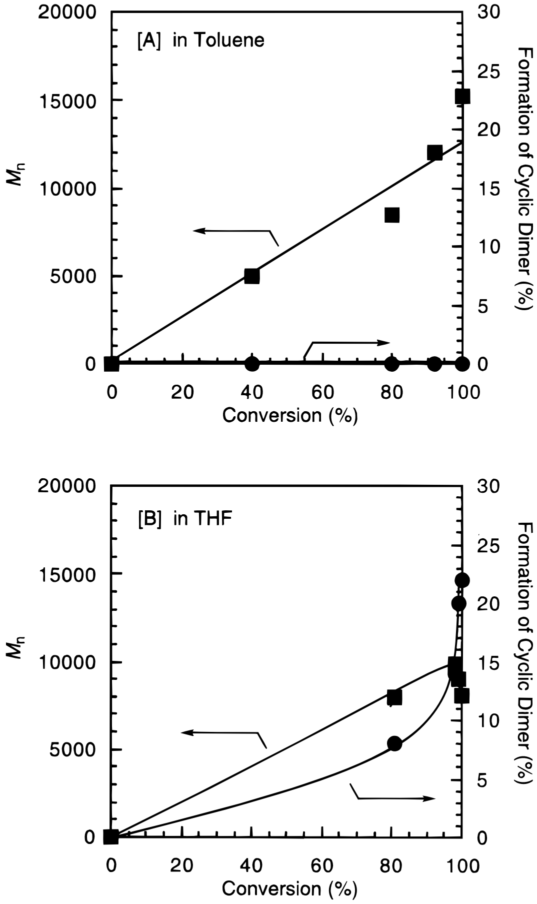
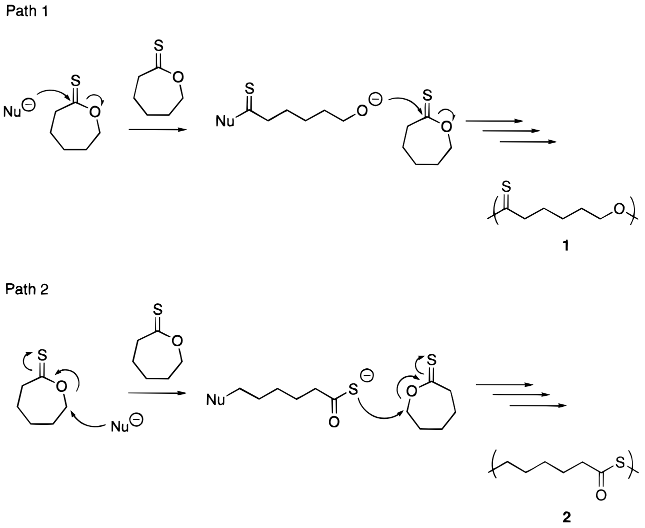


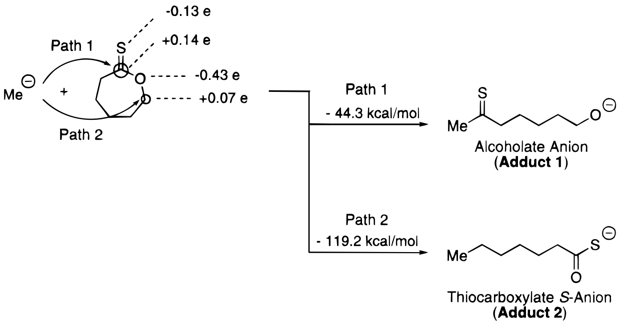
Figure 4. Relationships between the monomer conversion, M_n, and formation of a cyclic dimer in the anionic ring-opening polymerization of ε-thionocaprolactone with 2 mol % of *tert*-BuLi in (A) toluene and (B) THF at 20 °C. Initial monomer concentration: 1 M.

successive nucleophilic attacks of the propagating alcoholate anion to the monomer. In Path 2, an anionic nucleophile attacks the α-methylene carbon of the ether oxygen to form a thiocarboxylate *S*-anion. The successive attacks of thiocarboxylate *S*-anion to the monomer afford thiocarboxylic *S*-ester unit **2**. It should be noted that no unit **2** was formed in the polymerization with organolithiums or Grignard reagents (entries 1–7 in Table 1). These highly nucleophilic anionic initiators may selectively attack the monomer at the thiocarbonyl carbon, followed by a sequential propagation via C–O bond cleavage giving thiocarboxylic *O*-ester unit **1** (Scheme 3, Path 1). It has been reported that less nucleophilic amines initiate the anionic polymerization of β-propiolactones by attacking the monomer at the methylene group adjacent to the internal oxygen atom to give a carboxylate anion as a growing anion.[10] In the similar manner, DBU may predominantly attack the monomer at the α–methylene group adjacent to the oxygen atom in the initiating step to provide a thiocarboxylate anion as a growing species in this work. The nucleophilicity of the formed thiocarboxylate anion would also be lower due to the resonance structure, which might result in the successive attacks on the

Scheme 3



Scheme 4



α-methylene group adjacent to the oxygen of the monomer. The drastic difference between the polymerizations initiated with *tert*-BuOLi and *tert*-BuOK (entries 8 and 9 in Table 1) apparently indicates that counteranions also affect the selectivity of the formation of thiocarboxylic *O*- and *S*-ester units **1** and **2**.[11]

Scheme 4 summarizes the ΔH of the reaction of ϵ-thionocaprolactone with methyl anion and net atomic charges of some atoms of ϵ-thionocaprolactone concerning the reaction, which have been calculated by the ab initio method, *Gaussian 94*, HF/6-311G**// STO-3G. The results indicate that the thiocarbonyl carbon (net atomic charge, +0.14 e) is more electrophilic than the α-methylene carbon (net atomic charge, +0.07 e) of the ether oxygen, whereas **Adduct 1**, an alcoholate anion formed via the thiocarbonyl carbon attack (Path 1), is less stable than **Adduct 2**, a thiocarboxylate *S*-anion, via the attack at the carbon α to the ether oxygen (Path 2).[12] The nucleophilic attack to the thiocarbonyl carbon is kinetically favorable, while the attack on the methylene carbon a to the ether oxygen generates a thermodynamically favorable product. This disagreement between the kinetic and thermodynamic factors of ring opening may be related to the difference of the polymer structure according to the initiator.

In summary, we have demonstrated the first anionic ring-opening polymerization of ϵ-thionocaprolactone and examined the effect of initiator, temperature, and solvent on the polymerization. Organolithiums, Grignard reagents, and lithium *tert*-butoxide afforded polythiocarboxylic *O*-ester selectively and gave potassium *tert*-butoxide and DBU polythiocarboxylic *S*-ester predominantly. The monomer conversion and M_n of the obtained polymer increased with the temperature. THF was effective in enhancing the polymerization rate compared with toluene but resulted in byproduction of a cyclic dimer.

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(7) One of the reviewers has pointed out the possibility of a side reaction of alkyllithium on the methyl group of toluene to give benzyllithium. The authors have no evidence concerning this possibility but guess that the initiation reaction is much faster than the side reaction to afford the polymer satisfactorily in this system.

(8) It may be difficult to discuss the difference between the experimental M_n and theoretical one, because the M_n was estimated by GPC based on polystyrene calibration. The authors tried MALDI-TOF mass spectrometric analysis of the polymers, but they could not observe the molar mass signals. The higher M_n than the theoretical one (6 500) may be due to the low initiator efficiency caused by aggregation of the initiators or some side reactions of the initiators with toluene.

(9) The signals were assigned on the basis of the ^{1}H NMR spectroscopic data of low-molecular-weight analogues: ethyl thioacetate and *S*-methyl thiobutanoate [The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra 1992], and thioic acid esters reported in: Metzner, P.; Rakotonirina, R. *Tetrahedron* **1985**, *41*, 1289.

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(11) This result may be explained by the hard and soft theory. Namely, harder Li$^+$ shows higher affinity with harder alcoholate anions, whereas softer K$^+$ cation shows higher affinity with softer thiocarboxylate anions. In fact, the polymerization with soft countercation DBU$^+$ (entry 10 in Table 1) mainly afforded unit **2**, which would be formed by the propagation with the soft thiocarboxylate anion.

(12) One of the reviewers has pointed out the absolute values of the enthalpies, 44.3 and 119.2 kcal/mol, are rather high. This should be due to the calculation state, i.e., no countercation and solvent.

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