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Controlled Cationic Ring-Opening Polymerization of 1,3-Oxazolidine-2-thione Derived from L-Serine

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ABSTRACT: The cationic ring-opening polymerization of a 1,3-oxazolidine-2-thione derivative ($\mathbf{S_L}$) from L-serine was examined. $\mathbf{S_L}$ was synthesized by the reaction of L-serine methyl ester hydrochloride with carbon disulfide and hydrogen peroxide in the presence of triethylamine. Cationic polymerizations using methyl trifluoromethanesulfonate (TfOMe), trifluoromethanesulfonic acid (TfOH), and boron trifluoride etherate ($BF_3{\cdot}OEt_2$) as initiators gave polymers with polythiourethane structures in quantitative yields. The obtained polymers showed inverted specific rotations with respect to the monomer, where the large increase of the absolute values suggested the possibility of high-order structures. The molecular weight of the polymer was controlled by the feed ratio of $\mathbf{S_L}$ to TfOMe and its distribution was constantly narrow ($M_w/M_n < 1.14$), supporting the controlled character of the polymerization. The reaction mechanism was examined for TfOMe. According to NMR spectroscopic experiments, the polymerization with TfOMe proceeds via an active chain end mechanism in which the protonated cyclic endo iminothiocarbonate **2** is the active species. The propagation step involves a nucleophilic attack of $\mathbf{S_L}$ to the active species.

Introduction

Sulfur-containing polymers including polythiourethane have been widely considered as optical materials because of their high refractive indexes.[1,2] A possible method for the synthesis of polythiourethanes is reaction of dithiols with diisocyanates, yielding A_2B_2 polymers. However this type of polyaddition system is not appropriate for synthesizing polythiourethanes with highly organized macromolecular architectures with controlled molecular weight and head-to-tail structure. Chain polymerizations, especially living polymerizations, should provide polythiourethanes with controlled architectures. Previously, Mukaiyama et al. have reported that a cationic ring-opening polymerization of 1,3-oxazolidine-2-thiones derived from aminoethanols afforded polythiourethanes.[3] However, the polymers were obtained in lower yields and were not characterized sufficiently. Since we have developed controlled polymerizations of sulfur-containing cyclic monomers such as monothiocarbonate and dithiocarbonate,[4] we assumed that the polymerization of this interesting monomer would also be controlled. One of the most commonly used aminoethanols that can be transformed to 1,3-oxazolidine-2-thiones, should be L-serine which is one of the 20 natural amino acids constructing proteins. Recent remarkable advances in fermentation and chemical synthetic methods have enabled us to obtain amino acids with high optical purity at lower prices.[5] If L-serine is employed as a starting material, we should be able to obtain polythiourethanes with highly organized architectures. Furthermore, the polymers should serve not only as biocompatible materials but also as chemically functional materials, because amino acids are indispensable components for life process and have functional groups with chiral backbone. Amino acids and oligopeptides are now widely used not only for drug, food, and chiral sources in organic synthesis[6] but also for constituents of optically active polymers.[7] For instance, precisely controlled polyadditions of optically active monomers derived from cysteine or tyrosine were carried out to obtain the heterotelecheric polymers, where the main chain of the polymer consisted of chiral amino acid skeletons.[8,9] These results prompted us to examine the ring-opening polymerization of a 1,3-oxazolidine-2-thione derivative from an amino acid L-serine. We herein describe the first well-characterized example of the controlled cationic ring-opening polymerization of 1,3-oxazolidine-2-thione derived from L-serine affording a chiral polythiourethane with controllable molecular weight.

Experimental Section

Measurements. ^1H (270 MHz) and ^{13}C NMR (64.5 MHz) spectra were recorded on JEOL EX-270 spectrometers, using tetramethylsilane (TMS) as an internal standard in $CDCl_3$ and DMSO-d_6. FT-IR spectra were obtained with a JASCO FT/IR-210 spectrometer. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-1000 digital polarimeter equipped a sodium lamp as a light source. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by size-exclusion chromatography (SEC) using a Tosoh HPLC HLC-8020 system equipped with four consecutive polystyrene gel columns [TSK-gels (bead size); αM (13 μm), α4000H (10 μm), α3000H (7 μm) and α2500H (7 μm)] and refractive index and ultraviolet detectors at 40 °C. The system was operated at a flow rate of 1.0 mL/min, using *N*,*N*-dimethylformamide (DMF, 5.0 mM lithium bromide, and 5.0 mM phosphoric acid solution) as an eluent. Polystyrene standards were employed for calibration. X-ray crystallographic analysis was carried out by Rigaku/MSC Mercury CCD diffractometer at −123 °C using the $\theta-2\theta$ scan method. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques. $R = 0.022$, $R_w = 0.024$.

Materials. L-Serine methyl ester hydrochloride was synthesized from L-serine (Kanto Chemical, Co., 99%) according to the reported method.[10] Thionyl chloride (Kanto Chemical, Co., 98%), carbon disulfide (Kanto Chemical, Co., 99%),

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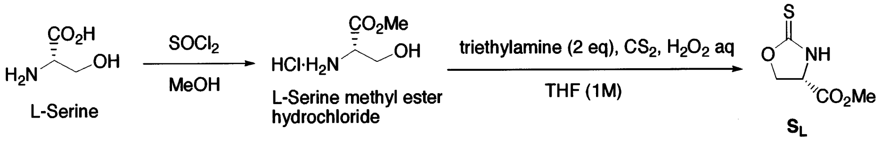
Scheme 1



hydrogen peroxide (30.0−35.5% solution in water) (Kanto Chemical, Co.), triethylamine (Tokyo Kasei Kogyo, Co., >99%), and 2,2,2-trifluoroethanol (TFE) (Aldrich Chemical, Co., >99%) were used as received. Methyl trifluoromethanesulfonate (TfOMe) (Aldrich Chemical, Co., >99%), boron trifluoride etherate (BF_3OEt_2) [Kanto Chemical, Co., 48% (as BF_3)], and dichloromethane were distilled over CaH_2 before use. Trifluoromethanesulfonic acid (TfOH) (Tokyo Kasei Kogyo, Co., 98%) was distilled just before use.

4(S)-(Methoxycarbonyl)-1,3-oxazolidine-2-thione ($\mathbf{S_L}$). Triethylamine (55.4 mL, 400 mmol) was slowly added to a suspension of L-serine methyl ester hydrochloride (31.12 g, 200 mmol) in THF (200 mL) at 0 °C under nitrogen. A solution of carbon disulfide (22.84 g, 300 mmol) in THF (20 mL) at 0 °C was then added. The mixture was stirred at 0 °C for 10 min and then at room temperature for 1 h. After that, hydrogen peroxide (30 %, 40 mL) was slowly added to the resulting mixture at room temperature, and the mixture was concentrated by a rotary evaporator. Ethyl acetate (1000 mL) was added to the residual mass. The organic phase was dried over $MgSO_4$ and volatile products were evaporated. The residue was purified by silica gel column chromatography eluted with chloroform/acetone (95:5 = v/v). Recrystallization from a mixed solvent [*n*-hexane/ethyl acetate/acetone (4:2:1 = v/v/v)] gave a single crystal of $\mathbf{S_L}$. Yield = 26.7 g (165.7 mmol, 83%). Mp = 55−56 °C. $[\alpha]^{25}_{D}$ = 5.39 ° (*c* = 1.0 g/dL, TFE). ^{1}H NMR ($CDCl_3$): $\delta = 3.85$ (s, 3H, $-OCH_3$), 4.82−4.92 (m, 3H, $>CH-$ and $-CH_2-$), 8.56 (broad s, 1H, $-NH-$) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 53.23$ ($-OCH_3$), 57.01 ($-CH<$), 71.99 ($-CH_2-$), 168.97 ($C{=}O$), 189.93 ($C{=}S$) ppm. IR (KBr): 3317, 1743 (−COOMe), 1504 (C=S), 1234, 1187, 1025, 964, 571 cm^{-1}. Anal. Calcd for $C_5H_7NO_3S$: C, 37.26; H, 4.38; N, 8.69; S, 19.89. Found C, 37.17; H, 4.26; N, 8.70; S, 19.85. Crystal data for $\mathbf{S_L}$ $C_5H_7NO_3S$, $M = 161.18$, orthorhombic, space group $P2_12_12_1$, $a = 10.420(5)$ Å, $b = 17.286(8)$ Å, $c = 7.829(4)$ Å, $V = 1410(2)$ Å^3, $Z = 8$, $\rho = 1.518$ g/cm^3, $\mu = 4.03$ cm^{-1}, F (000) = 672.

Cationic Polymerization of $\mathbf{S_L}$. Typical Procedure. Dry CH_2Cl_2 (6.0 mL) and 3.0 mol % of TfOMe introduced to a polymerization tube containing $\mathbf{S_L}$ (0.48 g, 3.0 mmol) subsequently. The resulting mixture was stirred at 30 °C for 18 h under nitrogen. The reaction mixture remained homogeneous. After being quenched with triethylamine (0.2 mL), the resulting mixture was poured into methanol (300 mL) to precipitate a polymer. The polymer was collected by filtration with suction and dried under vacuum. Poly$\mathbf{S_L}$ was obtained as a colorless solid quantitatively. Yield = 0.47 g (2.92 mmol, 97%). ^{1}H NMR ($CDCl_3$): $\delta = 2.34$ (initiating end, $S-CH_3$) 3.03−3.01 (1H, $-CH_2-$), 3.79 (s, 3H, $-OCH_3$), 4.00−4.01 (1H, $-CH_2-$), 5.39−5.42(1H, $>CH-$), 8.29 (1H, $-NH-$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 29.58$ ($-CH_2-$), 52.30 ($-OCH_3$), 54.37 ($>CH-$), 165.87 ($-SCONH-$), 170.38 ($-COOMe$) ppm. IR (KBr): 3301, 1743 (−COOMe), 1658 (−SCONH−), 1512, 1203 cm^{-1}; Anal. Calcd for $(C_5H_7NO_3S)_n$: C, 37.26; H, 4.38; N, 8.69; S, 19.89. Found: C, 37.22; H, 4.40; N, 8.97; S, 19.86.

The Equivalent Reaction of $\mathbf{S_L}$ with TfOMe. A solution of $\mathbf{S_L}$ (0.15 g, 0.77 mmol) in $CDCl_3$ was placed in an NMR tube under nitrogen atmosphere. The tube was sealed after the addition of TfOMe (93 μL, 0.85 mmol), and the mixture was stirred for 1.0 min at room temperature. The adduct of $\mathbf{S_L}$ and TfOMe (**2**) was characterized by ^{1}H NMR and ^{13}C NMR spectra. ^{1}H NMR ($CDCl_3$): $\delta = 2.77$ (s, 3H, $-SCH_3$), 3.85 (s, 3H, $-OCH_3$), 5.20−5.43 (m, 3H, $>CH-$ and $-CH_2-$), 11.76 (broad s, 1H, $=HN^+$) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 13.53$ ($-SCH_3$), 53.37 ($-OCH_3$), 59.14 ($>CH-$), 76.84 ($-CH_2-$), 166.98 ($-COOMe$), 183.01 ($-C{=}HN^+$) ppm.

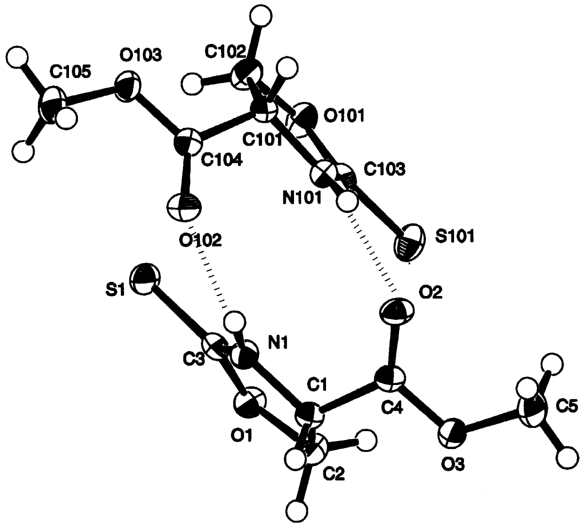
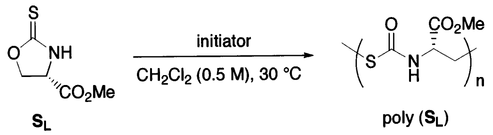


Figure 1. X-ray crystal structure of $\mathbf{S_L}$.

Scheme 2



Results and Discussion

Synthesis of $\mathbf{S_L}$. The L-serine-based monomer, 4(*S*)−(methoxycarbonyl)-1,3-oxazolidine-2-thione ($\mathbf{S_L}$), was synthesized by reaction of L-serine methyl ester hydrochloride with carbon disulfide and hydrogen peroxide in the presence of triethylamine (Scheme 1). $\mathbf{S_L}$ was obtained as a single crystal by recrystallization from the mixed solvent (ethyl acetate, acetone and *n*-hexane). X-ray analysis indicated that $\mathbf{S_L}$ in the crystal form exists as a dimer bridged with the hydrogen bond between amine protons and ester carbonyls. Its absolute configuration was also *S* configuration (Figure 1). The structure of $\mathbf{S_L}$ was also confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies, and by elemental analysis.

Cationic Polymerization of $\mathbf{S_L}$. The cationic polymerization of $\mathbf{S_L}$ with methyl trifluoromethanesulfonate (TfOMe) was carried out in CH_2Cl_2 at 30 °C. The SEC analysis of the crude mixture from a feed ratio of $[\mathbf{S_L}]_0/[\mathrm{TfOMe}]_0 = 65.8$ (Scheme 2, run 3 in Table 1) showed a unimodal peak indicating formation of a polymer (number-average molecular weight (M_n) ≈ 13300). This M_n was a little higher than the theoretical value (10931.3) based on the feed ratio [i.e., M_n (theoretical) = (formula weight of $\mathbf{S_L}$; 161.2) × ($[\mathbf{S_L}]_0/[\mathrm{TfOMe}]_0$; 65.8) + (formula weights of end groups; the initiating methyl group and $\mathbf{S_L}$ at the terminal group). In contrast, the M_n value (11000) determined from the ^{1}H NMR spectrum [based on the integral ratio of the methyl ester protons in the repeating unit (3.79 ppm) to the S−Me protons of the initiating end (2.34 ppm)] was in excellent agreement with the theoretical one. The molecular weight distribution (M_w/M_n = 1.06) was

Table 1. Cationic Ring-Opening Polymerization of S_L[a]

run	initiator	$[S_L]/[I]$	time (h)	convn[b] (%)	yield[c] (%)	$M_{n\ NMR}$[b]	$M_{n\ SEC}$[d]	M_w/M_n	$[M]_D^{30}$ [e]
1	TfOMe	8.9	12	>99	98	1800	3000	1.11	−194.5
2	TfOMe	19.3	15	>99	98	3600	4400	1.14	−210.6
3	TfOMe	65.8	22	>99	>99	11000	13300	1.06	−359.9
4	TfOH	8.9	23	98	88		3500	1.24	−202.8
5	TfOH	19.3	30	97	90		7400	1.26	−225.3
6	$BF_3{\cdot}OEt_2$	19.3	32	94	80	7500	8500	1.21	−223.7

[a] Conditions: S_L (3.0 mmol); CH_2Cl_2 (6.0 mL). [b] Determined by ^1H NMR spectroscopy. [c] Insoluble part in methanol. [d] Estimated by SEC based on polystyrene standards. Eluent: LiBr (5.0 mM) and phosphonic acid (5.0 mM) solution in DMF. [e] $[M]_D = [\alpha]_D \times MW/100$, where MW represents the formula weight of the polymer repeating unit, and $[\alpha]_D$ was measured by a polarimeter at 30 °C ($c = 1.0$ g/dL, DMF).

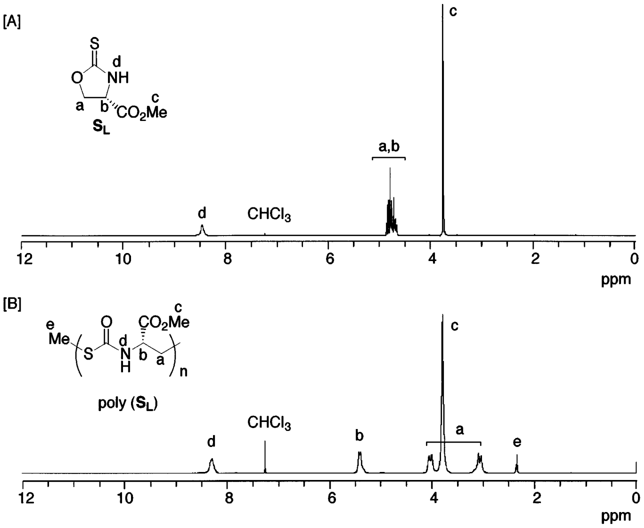


Figure 2. ^1H NMR (270 MHz) spectra of (a) $\mathbf{S_L}$ and (b) poly($\mathbf{S_L}$) obtained by the polymerization of $\mathbf{S_L}$ with TfOMe (11.24 mol %) in CH_2Cl_2 at 30 °C for 12 h (run 1 in Table 1).

relatively narrow, and the yield of the polymer was nearly quantitative after isolation via precipitation of the crude mixture into methanol. Although triflu-omethanesulfonic acid (TfOH) and boron trifluoride etherate ($BF_3{\cdot}OEt_2$) could also polymerize $\mathbf{S_L}$ in high yields, M_w/M_n of the obtained polymers were not narrow enough (run 4−6 in Table 1). As a result, TfOMe was found to be a suitable initiator for polymerization of $\mathbf{S_L}$.

The structure of the resulting polymers was confirmed by the ^1H NMR, ^{13}C NMR, and IR spectroscopy. Figure 2 illustrates the ^1H NMR spectrum of poly$\mathbf{S_L}$ (run 1 in Table 1) along with that of $\mathbf{S_L}$. The methylene and methine protons of $\mathbf{S_L}$ were observed at 4.82−4.92 ppm (Figure 2a). The methylene protons of poly$\mathbf{S_L}$ were observed at 3.03−3.01 and 4.00−4.01 ppm, and the methine protons were at 5.39−5.42 ppm (Figure 2b). In the ^{13}C NMR spectrum of poly$\mathbf{S_L}$, the characteristic signal assignable to carbonyl group was observed at 165.9 ppm and no signal assignable to thiocarbonyl group (186.5 ppm for $\mathbf{S_L}$) was observed at all. In the IR spectra, the characteristic absorption of the thiocarbonyl in $\mathbf{S_L}$ was observed at 1504 cm^{-1}, while that of carbonyl in poly$\mathbf{S_L}$ was at 1658 cm^{-1} instead. These findings indicate that the cationic ring-opening polymerization proceeds through specific isomerization of the thiocarbonyl group into the carbonyl group, which is in same manners with the controlled polymerization of C(=S)O monomers.[4]

Living Character of the Polymerization of $\mathbf{S_L}$. Since the controlled molecular weight suggests that the present polymerization proceeds in a controlled fashion, the cationic polymerization of $\mathbf{S_L}$ with TfOMe was carried out under varied $[\mathbf{S_L}]$/[TfOMe] ratios. Regardless of the $[\mathbf{S_L}]$/[TfOMe] ratios, polymers with narrow molecular weight distributions were obtained in quantitative yields and the SEC profiles exhibited unimodal peaks. The molecular weights of the polymers had a linear relationship with $[\mathbf{S_L}]$/[TfOMe] ratios (Figure 3). Although the number-average molecular weights of these polymers estimated by the SEC analyses were a little higher than those expected from the ratios of $[\mathbf{S_L}]$/[TfOMe], those determined by ^1H NMR spectroscopy agreed well with the expected ones (vide supra). Accordingly, it was suggested that the present system therefore proceeds in a controlled nature and the initiation efficiency is almost quantitative.

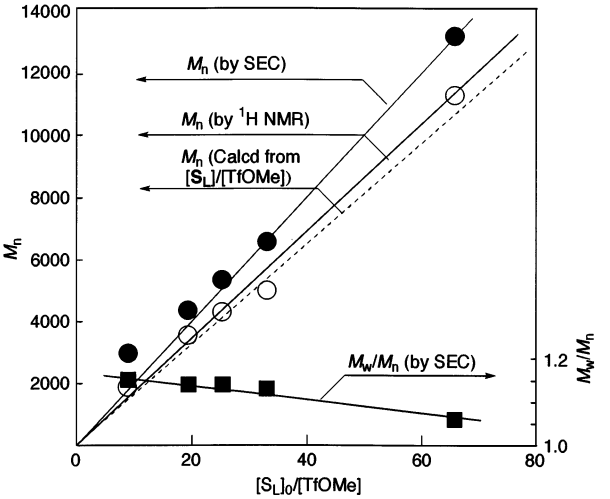


Figure 3. M_n and M_w/M_n vs feed ratio ($[\mathbf{S_L}]$/[TfOMe]).

To confirm whether the cationic polymerization of $\mathbf{S_L}$ proceeds without termination, we examined the relationship between M_n, M_w/M_n, conversion, and reaction time on the polymerization of $\mathbf{S_L}$ at 30 °C. Figure 4a shows the straight line of $\ln([\mathbf{S_L}]_0/[\mathbf{S_L}])$ vs time, supporting the constant concentration of active species during the polymerization until the conversion reached 99%. Both the SEC profiles and the ^1H NMR spectroscopy of each obtained polymer showed that the M_ns increased linearly with the monomer conversion keeping the narrow unimodal peaks (Figure 4b). These data demonstrate that termination and chain transfer reactions are not detectable in the present polymerization.

A post-polymerization experiment was also performed to elucidate the stability of the growing ends. When $\mathbf{S_L}$ was recharged after the complete consumption of the monomer fed at the first stage and the post-polymerization was conducted, the recharged monomer was completely consumed to give a polymer in quantitative yield with respect to the total amounts of $\mathbf{S_L}$. As shown in Figure 5, the elution peak in the SEC profile shifted

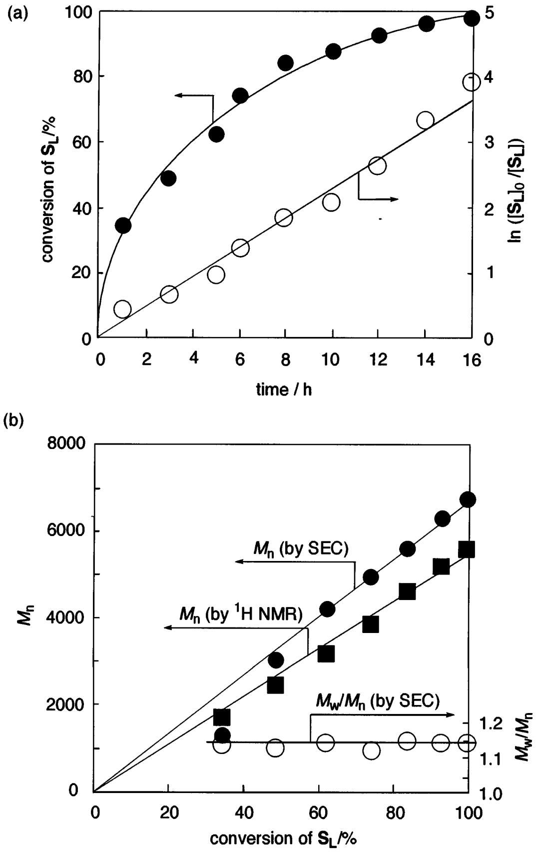


Figure 4. (a) Time–conversion and first-order time–conversion plots for the polymerization of $\mathbf{S_L}$ with TfOMe in CH_2Cl_2 at 30 °C. (b) Conversion–M_n and conversion–M_w/M_n plots in the polymerization of $\mathbf{S_L}$ with TfOMe in CH_2Cl_2 at 30 °C; $[TfOMe]_0 = 0.015$ M, $[\mathbf{S_L}]_0/[TfOMe]_0 = 32.9$.

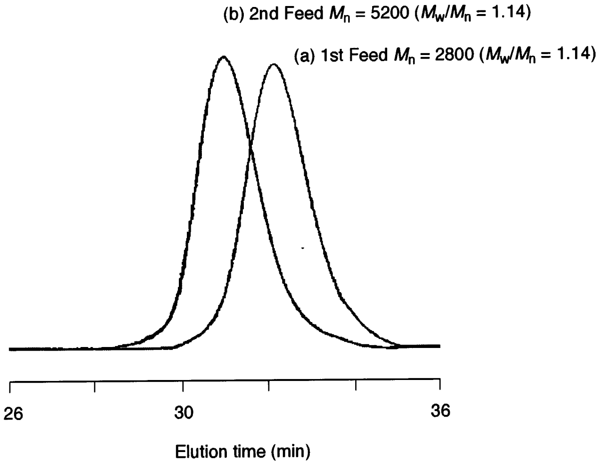
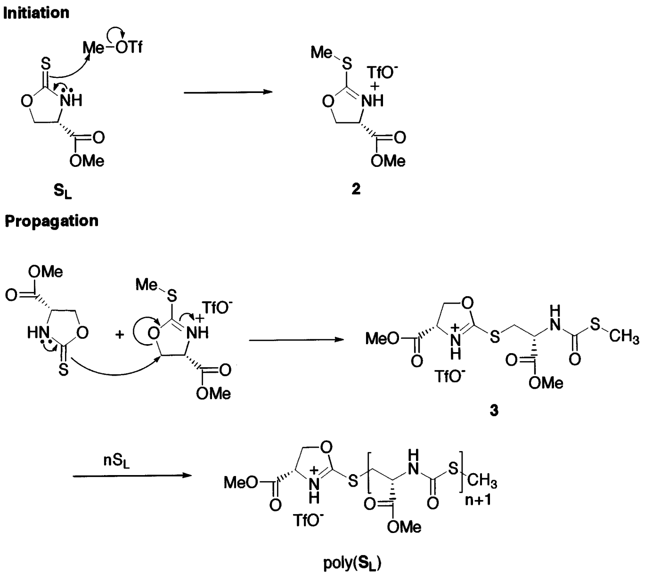


Figure 5. SEC profiles before and after the post-polymerization experiment of $\mathbf{S_L}$. Poly$\mathbf{S_L}$: prepolymer obtained in the first-stage polymerization, $M_n = 2800$, $M_w/M_n = 1.14$. Poly($\mathbf{S_L}$-*p*-$\mathbf{S_L}$): postpolymer obtained in the second stage polymerization, $M_n = 5{,}200$, $M_w/M_n = 1.14$.

toward the higher molecular weight region after the post-polymerization keeping a unimodal distribution, which confirms that a growing end in the cationic polymerization of $\mathbf{S_L}$ is stable enough to reinitiate the further polymerization.

Scheme 3. Plausible Mechanism of the Cationic Polymerization of $\mathbf{S_L}$ Initiated with TfOMe



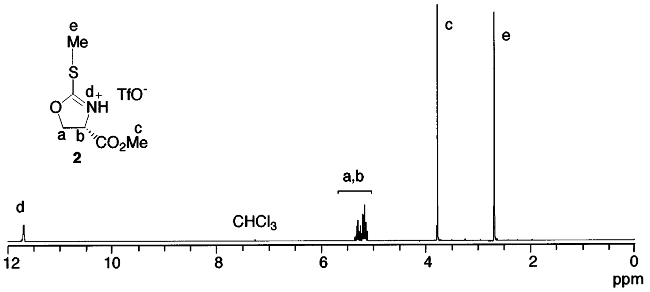


Figure 6. ^{1}H NMR spectrum of the triflate of a cyclic endo iminothiocarbonate **2** in $CDCl_3$.

The initiation reaction was studied by ^{1}H NMR spectroscopy in $CDCl_3$ at room temperature. In the reaction of $\mathbf{S_L}$ with TfOMe, a salt of a cyclic end iminothiocarbonate (**2**) is formed by methylation of carbonyl sulfur of $\mathbf{S_L}$ (Scheme 3). Since no polymerization of $\mathbf{S_L}$ was found, k_i (the rate constant of initiation) must be larger than k_p (the rate constant of propagation). This polymerization system involves fast initiation and slow propagation, which is a necessary condition for controlled polymerization. When a small excess of TfOMe (1.1 equiv) is used, adduct **2** is isolated in quantitative yield as a colorless oil. The structure of which was identified by the ^{1}H NMR and ^{13}C NMR spectroscopies. The ^{1}H NMR spectrum shows the typical signals for five-membered iminothiocarbonate at $\delta = 5.20–5.43$ and 3.85 ppm for methylene, methine, and methyl ester protons, and at $\delta = 11.76$ ppm for the NH$^+$ proton (Figure 6). Furthermore, the ^{13}C NMR spectrum showed the methylene peak at 76.84 ppm, which is shifted 4.85 ppm downfield from $\mathbf{S_L}$, indicating that the methylene carbon is susceptible to nucleophilic attack than that of $\mathbf{S_L}$.

The plausible mechanism of the cationic ring-opening polymerization of $\mathbf{S_L}$ initiated with TfOMe is outlined in Scheme 3. In the first step, a monomer molecule $\mathbf{S_L}$ nucleophilically attacks to the primary adduct **2** formed in the initiation reaction at the methylene carbon by the thiocarbonyl sulfur atom, which has the highest nucleophilicity. Ring-opening takes place via the *S*-alkyl scission and the iminothiocarbonate function is isomerized to form a methyl thiourethane end group while an iminothiocarbonate is regenerated at the active chain end. The active growing end of **3** provides sequential addition of further monomers to afford poly($\mathbf{S_L}$).

In summary, the controlled cationic ring-opening polymerization of an optically active cyclic monomer derived from L-serine $\mathbf{S_L}$ was performed to afford the corresponding polythiourethane with controlled molecular weight. The controlled character of the polymerization of $\mathbf{S_L}$ was supported by the following evidence: constant concentration of propagating species up to 99% conversion, narrow molecular weight distribution (<1.14), and molecular weight controlled by the feed monomer concentration. Because we have found that (a) the obtained polythiourethane showed inverted specific rotations with respective to the monomer and (b) a large increase of the absolute values was observed, detailed investigation on the optical properties of poly($\mathbf{S_L}$) is ongoing.

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