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Cationic Ring-Opening Polymerization of Optically Active N-Substituted Cyclic Thiourethanes

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ABSTRACT: N-substituted cyclic thiourethanes [4(*S*)-(methoxycarbonyl)-*N*-benzyl-1,3-oxazolidine-2-thione (**BnS$_L$**), 4(*S*)-(methoxycarbonyl)-*N*-benzoyl-1,3-oxazolidine-2-thione (**BzS$_L$**), and 4(*S*)-(methoxycarbonyl)-*N*-acetyl-1,3-oxazolidine-2-thione (**AcS$_L$**)] were synthesized from L-serine methyl ester hydrochloride and were polymerized by using methyl trifluoromethanesulfonate to obtain the corresponding well-defined polythiourethanes. The molecular weight of the polymers can be controlled by the ratio of the monomers to the initiator and the molecular weight distributions are narrow ($M_w/M_n < 1.15$) similar to the previously reported polymerization of a cyclic thiourethane [4(*S*)-(methoxycarbonyl)-1,3-oxazolidine-2-thione (**S$_L$**)]. The polymerization rates are on the order of **S$_L$** > **BnS$_L$** > **BzS$_L$** > **AcS$_L$**, which agrees well with the nucleophilicity of the thiocarbonyl moieties of the monomers (**S$_L$**, **BnS$_L$** **BzS$_L$**, and **AcS$_L$**). The Cotton effects in the CD spectra of the polymers from the N-substituted monomers exhibit almost inverse shape with that of poly(**S$_L$**) and the specific rotations' signs also inversed, suggesting the idea that poly(**S$_L$**) and N-substituted polymers take different high order structures.

Introduction

Sulfur-containing polymers have been given attention due to their optical and thermal properties.[1] Although most of these polymers such as polythioester, polysulfide, polysulfone, and polythiocarbonate have been synthesized by polyaddition or polycondensation of bifunctional monomers,[2] several recent works have demonstrated successful ring-opening polymerizations of cyclic sulfur compounds giving these polymers.[3−7] For example, we have reported cationic ring-opening polymerization of dithiocarbonates and six- or seven-membered monothiocarbonates affording polydithiocarbonates and polythiocarbonates[8] and found that living polymerization can be accomplished by aid from a stable carbenium cation or neighboring group participation.[9] This technique provided us versatility in designing polymer architecture and solution to overcome an obvious limitation of traditional methods, which are insufficient to give polymers with controlled molecular weight and complete head-to-tail structure. Further polythiourethane with head-to-tail structure has been also achieved by cationic ring-opening polymerization of cyclic thiourethane.[10] More recently, we have reported that living cationic ring-opening polymerization of an optically active cyclic thiourethane (**S$_L$**) derived from L-serine by methyl trifluoromethanesulfonate (TfOMe) affords a chiral polythiourethane with narrow molecular weight distribution ($M_w/M_n < 1.14$) in quantitative yield[11] and that the living nature is not spoiled under air and moisture by using a water-resistant cationic initiator.[12] Furthermore, the obtained chiral polythiourethane is supposed to take a secondary structure based on intramolecular hydrogen bonds.[13] If the hydrogen atoms in poly(**S$_L$**) are replaced by substituents without electron-accepting moieties, the resulting polymers are expected to take a different secondary structure, and the substituent will affect the polymerization behavior. Herein, this paper reports the cationic ring-opening polymerization behavior of N-substituted cyclic thiourethanes in detail and the chiroptical properties of the obtained polymers.

Experimental Part

Measurement. ^{1}H (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were recorded on a JEOL JNM-LA-270 spectrometer, 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. Circular dichroism (CD) spectra were measured on a JASCO J-720 spectropolarimeter. 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, exclusion limited molecular weight); αM (13 μm, $>1 \times 10^7$), α4000H (10 μm, $>1 \times 10^6$), α3000H (7 μm, $>1 \times 10^5$), and α2500H (7 μm, $>1 \times 10^4$)]; 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) solution (5.0 mM lithium bromide and 5.0 mM phosphoric acid) as an eluent. Polystyrene standards were employed for calibration. All monomer conversion was determined from the ^{1}H NMR spectroscopy.

Materials. 4(*S*)-(Methoxycarbonyl)-1,3-oxazolidine-2-thione (**S$_L$**)[11] and (S)-*N*-benzylserine methyl ester[14] were synthesized according to the previously reported method. Methyl trifluoromethanesulfonate (TfOMe) (Aldrich Chemical, Co., >99%), triethylamine (Tokyo Kasei Kogyo, Co., >99%), and dichloromethane (CH$_2$Cl$_2$) were distilled over CaH$_2$ before use. Tetrahydrofuran (THF) was distilled over sodium. Other reagents were used as received.

4(*S*)-(Methoxycarbonyl)-*N*-benzyl-1,3-oxazolidine-2-thione (BnS$_L$). Thiophosgene (23.8 g, 207 mmol) in dry THF (200 mL) was slowly added to a solution of *N*-benzyl-L-serine (43.4 g, 207 mmol) and triethylamine (41.9 g, 414 mmol) in dry THF (600 mL) at 60 °C under nitrogen. The mixture was stirred for 3 h and was stirred at room temperature for 12 h. Triethylamine hydrochloride was removed by filtration and

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the solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography eluted with ethyl acetate/*n*-hexane (1/1 = v/v). Recrystallization from a mixed solvent [THF/*n*-hexane (2/1 = v/v)] gave $\mathbf{BnS_L}$ (40.1 g, 77%) as a white powder. $[\alpha]^{25}_{D} = 35.0$ ° ($c = 0.1$ g/dL, in CH_2Cl_2). Mp = 101.3−101.8 °C. ^1H NMR (CD_2Cl_2): $\delta = 3.70$ (s, 3H, $-OCH_3$), 4.32−4.37 (m, 1H, $-CH_2-$), 4.54−4.59 (3H, $-CH<$, $-CH_2-$, and $-CH_2-C_6H_5$), 5.31−5.42 (m, 1H, $-CH_2-C_6H_5$), 7.33−7.38 (5H, $-C_6H_5$) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 51.47$ ($-CH_2-C_6H_5$), 53.06 ($-OCH_3$), 59.90 ($-CH<$), 65.55 ($-CH_2-$), 128.98, 129.04, 129.48, 135.09 ($-C_6H_5$), 169.55 ($-COOCH_3$), 189.39 ($-OCSNH-$) ppm. IR (KBr): 1743 ($-COOCH_3$), 1481 ($C{=}S$), 1450, 1357, 1304, 1211, 971, 701 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_3S$: C, 57.35; H, 5.21; N, 5.57; S, 12.76. Found: C, 57.54; H, 5.19; N, 5.64; S, 12.72.

4(*S*)-(Methoxycarbonyl)-*N*-benzoyl-1,3-oxazolidine-2-thione ($\mathbf{BzS_L}$). Benzoyl chloride (14.2 g, 112 mmol) in dry CH_2Cl_2 was slowly added to a solution of $\mathbf{S_L}$ (15.0 g, 93.0 mmol) and pyridine (9.6 g, 121 mmol) at 0 °C under nitrogen. The mixture was allowed to reach room temperature, and then water was added with stirring. The organic phase was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography eluted with ethyl acetate/*n*-hexane (1/1 = v/v). Recrystallization from a mixed solvent [ethyl acetate/*n*-hexane (2/1 = v/v)] gave $\mathbf{BzS_L}$ (23.4 g, 95%) as a colorless solid. $[\alpha]^{25}_{D} = -28.9$ ° ($c = 0.1$ g/dL, in CH_2Cl_2). Mp = 87.2−88.0 °C. ^1H NMR (CD_2Cl_2): $\delta = 3.76$ (s, 3H, $-OCH_3$), 4.56−4.60 (m, 1H, $-CH_2-$), 4.77−4.81 (m, 1H, $-CH<$), 5.21−5.26 (m, 1H, $-CH_2-$), 7.40−7.74 (5H, $-C_6H_5$) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 53.98$ ($-OCH_3$), 60.81 ($-CH<$), 70.05 ($-CH_2-$), 128.72, 130.13, 133.45, 133.59 ($-C_6H_5$), 168.97 ($-COOCH_3$), 170.98 ($-NHCO-C_6H_5$), 186.51 ($-OCSNH-$) ppm. IR (KBr): 1751 ($-COOCH_3$), 1682 ($-NHCO-C_6H_5$), 1442 ($-OCSNH-$), 1373, 1311, 1250, 1219, 1188, 964, 910, 733, 694 cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_4S$: C, 54.26; H, 4.18; N, 5.28; S, 12.09. Found: C, 54.21; H, 4.11; N, 5.28; S, 11.90.

4(*S*)-(Methoxycarbonyl)-*N*-acetyl-1,3-oxazolidine-2-thione ($\mathbf{AcS_L}$). The same procedure was followed as described for $\mathbf{BzS_L}$ using acetyl chloride (8.71 g, 111 mmol). Recrystallization from a mixed solvent [ethyl acetate/*n*-hexane (2/1 = v/v) gave $\mathbf{AcS_L}$ (17.3 g, 92%) as a colorless solid. $[\alpha]^{25}_{D} = -29.0$ ° ($c = 0.1$ g/dL, in CH_2Cl_2). Mp = 68.0−68.4 °C. ^1H NMR (CH_2Cl_2): $\delta = 2.81$ (s, 3H, $-COCH_3$), 3.79 (s, 3H, $-OCH_3$), 4.53 (dd, $J = 4.05$ and 5.97 Hz, 1H, $-CH_2-$), 4.64 (m, 1H, $-CH<$), 5.15 (dd, $J = 4.05$ and 5.40 Hz, 1H, $-CH_2-$) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 25.97$ ($-COCH_3$), 53.64 ($-OCH_3$), 60.00 ($-CH<$), 69.61 ($-CH_2-$), 169.26 ($-COOCH_3$), 171.68 ($-NHCOCH_3$), 186.26 ($-OCSNH-$) ppm. IR (KBr): 1758 ($-COOCH_3$), 1712 ($-NHCOCH_3$), 1419 ($-OCSNH-$), 1373, 1311, 1227, 1180, 1041, 980, 957 cm^{-1}. Anal. Calcd for $C_7H_9NO_4S$: C, 41.37; H, 4.46; N, 6.89; S, 15.78. Found: C, 41.24; H, 4.46; N, 6.88; S, 15.78.

Cationic Polymerization of $\mathbf{S_L}$ Derivatives. A typical procedure is shown as follows. Dry CH_2Cl_2 (6.0 mL) and 3.04 mol % of TfOMe were 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 8 h under nitrogen. The reaction proceeded homogeneously. After being quenched with triethylamine (0.2 mL), the resulting mixture was poured into ethyl ether (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. $M_n = 6100$, $M_w/M_n = 1.13$. ^1H NMR (DMSO-d_6): $\delta = 2.21$ (initiating end, $S-CH_3$), 2.89−3.11 (1H, $-CH_2-$), 3.17−3.37 (1H, $-CH_2-$), 3.55−3.76 (3H, $-OCH_3$), 4.21−4.41 (1H, $>CH-$), 8.79−9.00 (1H, $-NH-$) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 29.5$ ($-CH_2-$), 53.0 ($-OCH_3$), 54.37($>CH-$), 163.89 ($-SCONH-$), 167.38 ($-COOCH_3$) ppm. IR (KBr): 3301, 1743 ($-COOCH_3$), 1658 ($-SCONH-$), 1512, 1203 cm^{-1}.

Poly($\mathbf{BnS_L}$). Yield: quantitative, colorless solid. $M_n = 8200$, $M_w/M_n = 1.04$. ^1H NMR (DMSO-d_6): $\delta = 2.22$ (initiating end, $S-CH_3$), 3.36−3.67 (3H, $-OCH_3$), 4.05−4.92 (3H, $-CH<$ and $-CH_2-$), 7.05−7.28 (5H, $-C_6H_5$) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 29.4$ ($-CH_2-$), 52.3 ($-OCH_3$), 53.18 ($>CH-$), 60.67 ($-CH_2-C_5H_6$), 127.87, 128.13, 128.45, 135.86 ($-C_6H_5$), 168.08 ($-SCONH-$), 169.12 ($-COOCH_3$) ppm. IR (KBr): 3456, 1743-($-COOCH_3$), 1651 ($-SCONH-$), 1404, 1311, 1180, 1072, 987, 710 cm^{-1}.

Poly($\mathbf{BzS_L}$). Yield: quantitative, light green solid. $M_n = 8500$, $M_w/M_n = 1.11$. ^1H NMR (DMSO-d_6): $\delta = 2.21$ (initiating end, $S-CH_3$), 2.88−3.79 (5H, $-CH_2-$ and $-OCH_3$), 4.73−5.06 (1H, $-CH<$), 7.16−8.04 (5H, $-C_6H_5$) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 30.7$ ($-CH_2-$), 52.9 ($-OCH_3$), 59.6 ($-CH<$), 128.60, 129.02, 132.95, 133.88 ($-C_6H_5$), 168.42 ($-SCONH-$), 171.28 ($-NHCO-C_6H_5$), 172.12 ($-COOCH_3$) ppm. IR (KBr): 3394, 1751 ($-COOCH_3$), 1702 ($-NHCO-C_6H_5$), 1658 ($-SCONH-$), 1296, 1203, 1126, 694 cm^{-1}.

Poly($\mathbf{AcS_L}$). Yield: quantitative, colorless solid. $M_n = 6600$, $M_w/M_n = 1.09$. ^1H NMR (DMSO-d_6): $\delta = 2.21$ (initiating end, $S-CH_3$), 2.18−2.44 (3H, $-CH_3$), 2.74−3.81 (5H, $-CH_2-$ and $-OCH_3$), 4.72−5.10 (1H, $-CH<$) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 24.5$ ($-COCH_3$), 29.90 ($-CH_2-$), 52.76 ($-OCH_3$), 59.46 ($-CH<$), 170.00 ($-SCONH-$), 171.50 ($-NHCO-CH_3$), 173.34 ($-COOCH_3$) ppm. IR (KBr): 3370, 1751 ($-COOCH_3$), 1703($-NHCO-CH_3$), 1658 ($-SCONH-$), 1373, 1250, 1203, 1003 cm^{-1}.

Methylation of $\mathbf{S_L}$ derivatives with TfOMe. A typical procedure is shown as follows. A solution of $\mathbf{S_L}$ (0.15 g, 0.77 mmol) in CD_2Cl_2 (0.8 mL) 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 iminothiocarbonate triflate salt (Me-$\mathbf{S_L}$) from $\mathbf{S_L}$ and TfOMe was characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy. ^1H NMR (CD_2Cl_2): $\delta = 2.76$ (s, 3H, $-SCH_3$), 3.85 (s, 3H, $-OCH_3$), 5.20−5.39 (3H, $>CH-$ and $-CH_2-$), 11.92 (broad s, 1H, $=HN^+$) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 14.53$ ($-SCH_3$), 54.23 ($-OCH_3$), 60.07 ($>CH-$), 77.75 ($-CH_2-$), 167.82 ($-COOCH_3$), 183.96 ($-C{=}HN^+$) ppm. IR (CD_2Cl_2): 2962, 1751 ($-COOCH_3$), 1581 ($-C{=}HN^+$), 1481, 1442, 1357, 1281, 1241, 1165, 1034, 957, 918, 640 cm^{-1}.

Me-$\mathbf{BnS_L}$. ^1H NMR (CD_2Cl_2): $\delta = 2.79$ (s, 3H, $-SCH_3$), 3.67 (s, 3H, $-OCH_3$), 4.89 (s, 2H, $-CH_2-C_6H_5$), 5.00−5.45 (3H, $-CH<$ and $-CH_2-$), 7.41 (5H, $-C_6H_5$) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 15.09$ ($-SCH_3$), 52.51 ($-CH_2-C_6H_5$), 54.07 ($-OCH_3$), 63.32 ($>CH-$), 77.29 ($-CH_2-$), 129.96, 130.08, 130.39, 130.73 ($-C_6H_5$), 167.35 ($-COOCH_3$), 183.03 ($-C{=}HN^+$) ppm. IR (CD_2Cl_2): 3502, 3039, 2963, 1751 ($-COOCH_3$), 1566 ($-C{=}HN^+$), 1435, 1412, 1265, 1157, 1034, 964, 926, 710, 640, 517 cm^{-1}.

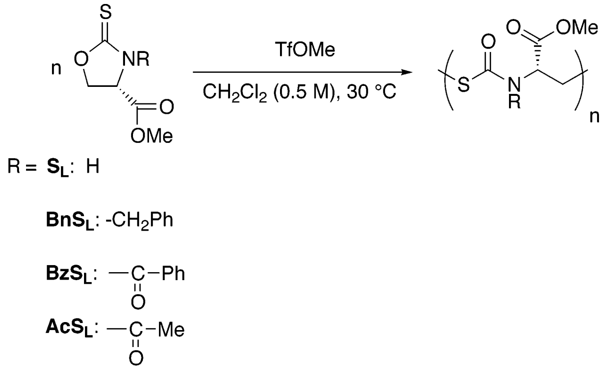
Me-$\mathbf{BzS_L}$. ^1H NMR (CD_2Cl_2): $\delta = 2.74$ (s, 3H, $-SCH_3$), 3.67 (s, 3H, $-OCH_3$), 5.43−5.46 (m, 1H, $-CH_2-$), 5.73−5.87 (3H, $-CH<$ and $-CH_2-$), 7.53−7.90 (5H, $-C_6H_5$) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 16.17$ ($-SCH_3$), 54.05 ($-OCH_3$), 62.94 ($>CH-$), 79.40 ($-CH_2-$), 129.52, 130.07, 130.68, 135.16 ($-C_6H_5$), 167.10 ($-COOCH_3$), 167.52 ($-NHCO-C_6H_5$), 189.79 ($-C{=}HN^+$) ppm. IR (CD_2Cl_2): 3070, 1751 ($-COOCH_3$), 1658 ($-NHCO-C_6H_5$), 1604 ($-C{=}HN^+$), 1543, 1473, 1442, 1381, 1288, 1234, 1165, 1026, 972, 895, 717, 640, 517 cm^{-1}.

Me-$\mathbf{AcS_L}$. ^1H NMR (CD_2Cl_2): $\delta = 2.49$ (s, 3H, $-SCH_3$), 2.73 ($-CH_3$), 3.91 (s, 3H, $-OCH_3$), 5.50 (dd, $J = 3.78$ and 5.13 Hz, 1H, $-CH_2-$), 5.63 (m, 1H, $-CH<$), 5.84 (dd, $J = 4.05$ and 6.21 Hz, 1H, $-CH_2-$) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 15.89$ ($-SCH_3$), 23.67 ($-CH_3$), 54.87 ($-OCH_3$), 61.64 ($>CH-$), 80.14 ($-CH_2-$), 167.66 ($-COOCH_3$), 170.11 ($-NHCO-CH_3$), 188.98 ($-C{=}HN^+$) ppm. IR (CD_2Cl_2): 3032, 2962, 1751 ($-COOCH_3$), 1713 ($-C{=}HN^+$), 1442 ($-NHCO-CH_3$), 1389, 1281, 1234, 1165, 1034, 980, 640 cm^{-1}.

Results and Discussion

Controlled Cationic Ring-Opening Polymerization of *N*-Substituted Cyclic Thiourethanes ($\mathbf{R^nS_L}$). The cationic ring-opening polymerization of N-substituted cyclic thiourethanes ($\mathbf{BnS_L}$, $\mathbf{BzS_L}$, and $\mathbf{AcS_L}$) was carried out using TfOMe (3.04 mol %) as an initiator at 30 °C in CH_2Cl_2 under nitrogen to give polymers (poly($\mathbf{BnS_L}$), poly($\mathbf{BzS_L}$), and poly($\mathbf{AcS_L}$)) in quantitative yields (Scheme 1). In all cases, the polymerization proceeded smoothly accompanying selective isomerization of the thiocarbonyl groups into the carbonyl groups.

Scheme 1. Cationic Ring-Opening Polymerization of RS_L



The molecular weight distributions (M_w/M_n) of the obtained polymers were narrow ($M_w/M_n < 1.15$) and the number-average molecular weight (M_n) (poly(**Bn**$\mathbf{S_L}$) = 8200, poly(**Bz**$\mathbf{S_L}$) = 8500, and poly(**Ac**$\mathbf{S_L}$) = 6600) agreed well with that expected from the feed ratios of [$\mathbf{R^nS_L}$]/[TfOMe] (M_{ncalcd} = 8300, 8700, and 6700, respectively).

We expected that this polymerization of the N-substituted monomers would proceeds through controlled fashion as well as the previously reported polymerization of $\mathbf{S_L}$, and therefore, the controlled nature of the polymerization of these monomers with TfOMe was examined by polymerization under various [$\mathbf{RS_L}$]/[TfOMe] ratios. Regardless of the ratios, the polymers with narrow molecular weight distributions were obtained in quantitative yields and the SEC profiles showed unimodal peaks. The relationship between [$\mathbf{RS_L}$]/[TfOMe] ratios and the molecular weight estimated by both from SEC and ^{1}H NMR was linear, and the M_n of the polymers agreed well with the expected one (Figure 1). To be convinced whether the polymerization of N-substituted monomers proceeds without termination, we examined the relationship between M_n, M_w/M_n, conversion, and reaction time on the polymerizations of their monomers at 30 °C. M_n of the polymers obtained increased with the monomer conversion, maintaining the linear relationship and the narrow unimodal peaks, as shown in Figure 2. These data would seem to indicate that termination and chain transfer reactions are negligible in the present polymerizations.

The Kinetic Studies on Cationic Polymerization of $\mathbf{S_L}$ and N-Substituted Cyclic Thiourethanes. The polymerization rates of $\mathbf{S_L}$ and N-substituted thiourethanes in CH_2Cl_2 (0.5 M) were examined at 30 °C using TfOMe (3.04 mol %). Figure 3 shows the time–conversion (a) and first-order time–conversion (b) plots. The monomer conversions obey the first-order kinetic equation (i.e., $-d[\mathrm{monomer}]/dt = k_{\mathrm{obs}}[\mathrm{monomer}][\mathrm{propagating\ species}]$), indicating that the polymerization proceeded without termination. For the polymerization of $\mathbf{S_L}$, the observed rate coefficient k_{obs} was estimated to be 8.44×10^{-3} L·mol^{-1}·s^{-1} under the assumption that initiation occurred quantitatively and the concentration of the propagating end was constantly equal to the initial concentration of TfOMe (0.015 mol·L^{-1}). This k_{obs} value is 1.8 times larger than that for the polymerization of **Bn**$\mathbf{S_L}$ ($k_{\mathrm{obs}} = 4.58 \times 10^{-3}$ L·mol^{-1}·s^{-1}). As well, the k_{obs} of **Bn**$\mathbf{S_L}$ is 1.5 times larger than that of **Bz**$\mathbf{S_L}$ ($k_{\mathrm{obs}} = 3.12 \times 10^{-3}$ L·mol^{-1}·s^{-1}), and k_{obs} of **Bz**$\mathbf{S_L}$ is 3.3 times larger than that of **Ac**$\mathbf{S_L}$ ($k_{\mathrm{obs}} = 0.93 \times 10^{-3}$ L·mol^{-1}·s^{-1}) (Figure 3b).[15]

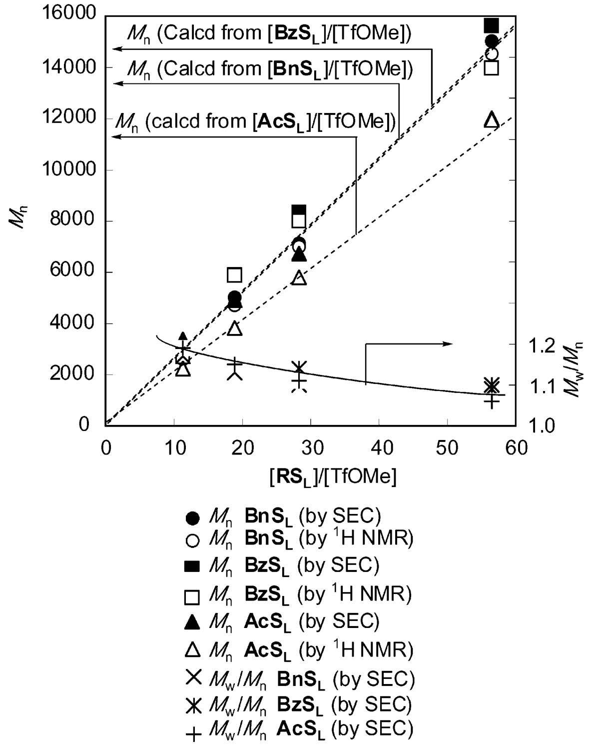


Figure 1. M_n and M_w/M_n vs feed ratio ([$\mathbf{RS_L}$]/[TfOMe]) [conditions: solvent, CH_2Cl_2 (0.5 M); temperature, 30 °C; [$\mathbf{RS_L}$]/[1] = 11.5–56.5; conversion of $\mathbf{RS_L}$ = 100%].

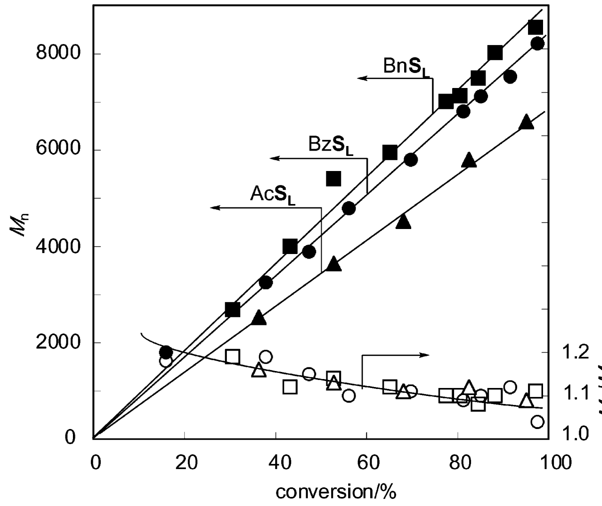


Figure 2. Conversion–M_n and conversion–M_w/M_n in the polymerization of $\mathbf{RS_L}$ with TfOMe in CH_2Cl_2 at 30 °C. $[\mathrm{TfOMe}]_0 = 0.015$ M; $[\mathbf{RS_L}]_0/[\mathrm{TfOMe}]_0 = 32.9$.

Keeping in mind that cyclic endo-iminothiocarbonate triflate salts obtained by initiating reactions are highly stable,[12] we prepared the iminothiocarbonate triflate salts from the monomers with TfOMe and elucidated the electronic character by ^{13}C NMR and IR spectroscopy to discuss the kinetic results (Scheme 2 and Table 1). Both the ^{13}C NMR and IR spectra indicate that the electron densities of the thiocarbonyl groups in the cyclic thiourethanes are in the order of the rates of polymerization. Namely, the nucleophilicities of sulfur atoms will also be on the order of $\mathbf{S_L}$ > **Bn**$\mathbf{S_L}$ > **Bz**$\mathbf{S_L}$ > **Ac**$\mathbf{S_L}$. For cyclic endo-iminothiocarbonate triflate salts, the ^{13}C NMR spectra revealed that the electrophilicites of the methylene groups, which are attacked by sulfur atoms of monomers, are on the order of **Ac**$\mathbf{S_L}$ < **Bz**$\mathbf{S_L}$ < **Bn**$\mathbf{S_L}$

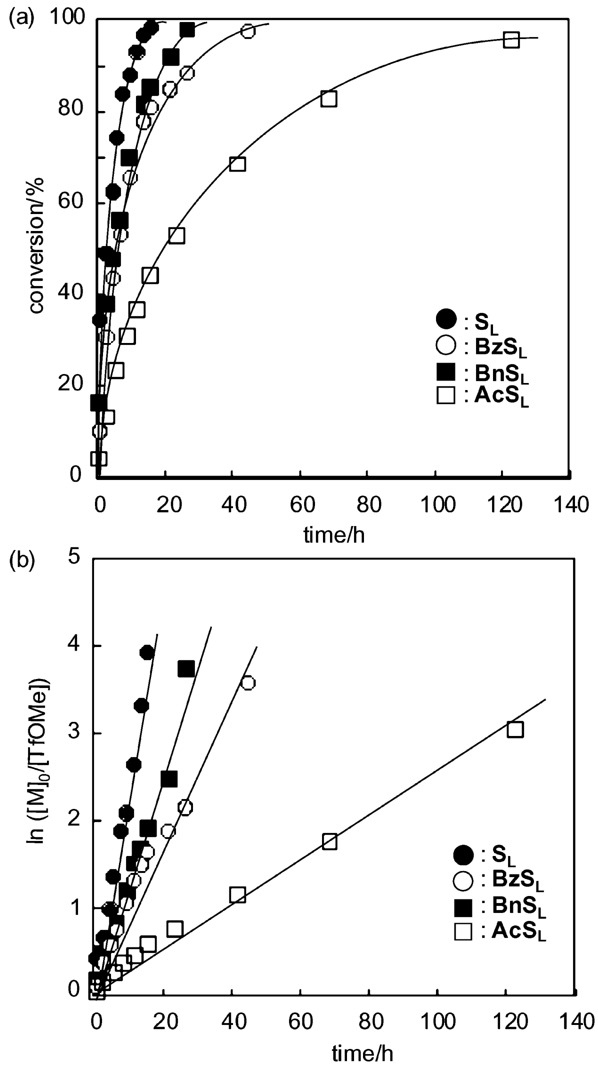
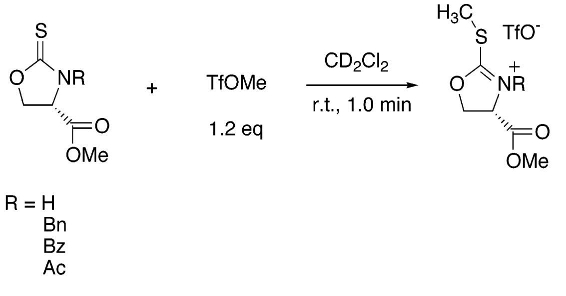


Figure 3. Time–conversion (a) and first-order time–conversion (b) plots for the polymerization of $\mathbf{RS_L}$ with TfOMe in CH_2Cl_2 at 30 °C. $[TfOMe]_0 = 0.015$ M; $[\mathbf{RS_L}]_0/[TfOMe]_0 = 32.9$.

Scheme 2. Addition of TfOMe to $\mathbf{RS_L}$



≈ $\mathbf{S_L}$. Although the electron densities of iminothiocarbonate triflate salts from $\mathbf{BnS_L}$ and $\mathbf{S_L}$ are identical, the nucleophilicty of the thiocarbonyl group of $\mathbf{S_L}$ is higher than that of $\mathbf{BnS_L}$. The electronic character of the propagating species and the monomers described here would have reflected in the actual rates of polymerization ($\mathbf{S_L}$ > $\mathbf{BnS_L}$ > $\mathbf{BzS_L}$ > $\mathbf{AcS_L}$).

Table 1. Spectroscopic Data of Monomers ($\mathbf{RS_L}$) and Iminium Salts from $\mathbf{RS_L}$ and TfOMe

	monomer ($\mathbf{RS_L}$) C=S			iminothiocarbonate triflate salts[a]
run	R	δ/ppm [b]	cm^{-1} [c]	O–CH$_2$–C< δ/ppm [b]
1	H	190.73	1504	77.75
2	Bn	189.34	1481	77.29
3	Bz	186.51	1442	79.40
4	Ac	186.26	1419	80.14

[a] Conditions: Reactions of monomers (0.5 mmol) and TfOMe (0.6 mmol, 68 μL) were carried out in CD_2Cl_2 (0.7 mL) at room temperature for 1.0 min. [b] Observed in ^{13}C NMR spectra (CD_2Cl_2). [c] Observed in IR spectra (KBr).

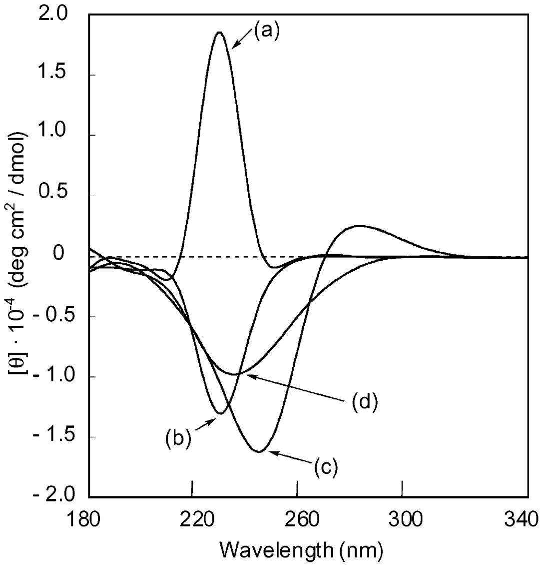


Figure 4. CD spectra of polythiourethane (*c* = 0.1 g/dL, in CH_2Cl_2): (a) poly($\mathbf{S_L}$), (b) poly($\mathbf{BnS_L}$), (c) poly($\mathbf{BzS_L}$), and poly($\mathbf{AcS_L}$).

CD Spectra of The Obtained Polymers. To characterize the chiroptical properties of the obtained polymers, we evaluated the CD spectra and specific rotations ($[\alpha]^{25}_D$) of the polymers. Figure 4 illustrates the CD spectra of poly($\mathbf{S_L}$) ($M_n = 3000$, $M_w/M_n = 1.13$, $[\alpha]^{25}_D = 62.4$ °), poly($\mathbf{BnS_L}$) ($M_n = 3600$, $M_w/M_n = 1.14$, $[\alpha]^{25}_D = -99.6$ °), poly($\mathbf{BzS_L}$) ($M_n = 3500$, $M_w/M_n = 1.15$, $[\alpha]^{25}_D = -127.0$ °), and poly($\mathbf{AcS_L}$) ($M_n = 3400$, $M_w/M_n = 1.15$, $[\alpha]^{25}_D = -213.2$ °). The specific rotation of poly($\mathbf{S_L}$) showed positive value in contrast to those of poly($\mathbf{BnS_L}$), poly($\mathbf{BzS_L}$), and poly($\mathbf{AcS_L}$). The Cotton effect of the thiourethane moiety in poly($\mathbf{S_L}$) at 227 nm is positive, whereas the Cotton effects of the thiourethane moieties in poly($\mathbf{BnS_L}$), poly($\mathbf{BzS_L}$), and poly($\mathbf{AcS_L}$) are negative as are the specific rotations as well. This difference may be attributed to the presence of substituents at the nitrogen atoms that leads to construction of secondary structure based on steric factors, compared to that of poly($\mathbf{S_L}$), which is based on hydrogen bonds between the carbonyl and NH moieties. We speculated that the polythiourethanes from the N-substituted monomers take different secondary structures from that of poly($\mathbf{S_L}$) regulated by hydrogen bonds (e.g., these polymers have inversed helix sense).[17]

Conclusions

In this study, we synthesized N-substituted cyclic thiourethanes ($\mathbf{BnS_L}$, $\mathbf{BzS_L}$, and $\mathbf{AcS_L}$) and conducted the cationic ring-opening polymerizations to obtain the corresponding polythiourethanes. The molecular weight of the obtained polymers can be controlled by the ratio of the monomers to the initiator ([$\mathbf{RS_L}$]/[TfOMe]) and the molecular weight distributions are narrow (M_w/M_n < 1.15). These polymerization rates are on the order of $\mathbf{S_L}$ > $\mathbf{BnS_L}$ > $\mathbf{BzS_L}$ > $\mathbf{AcS_L}$, which depends on the nucleophilicity of the thiocarbonyl moieties of the monomers. The studies on the specific rotations and the CD spectra suggest that secondary structure of poly(**S$_L$**) is different from that of the N-substituted polymers, e.g., inverse helix sense.

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(15) Although the polymerization rate of **BnS$_L$** might be higher than that of **S$_L$** by considering Hammet's σ value (see ref 16), the polymerization rates were in the order **S$_L$** > **BnS$_L$** > **BzS$_L$** > **AcS$_L$**. Less conjugation in **S$_L$** than **BnS$_L$** is a possible reason for the higher nucleophilicity of **S$_L$**.

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(17) A plausible reason for these inversed chiroptical properties is as follows. Although the NH and carbonyl groups in poly(**S$_L$**) are involved in higher-order structure (see ref 13), N-substituted polythiourethanes cannot take a similar structure due to steric hindrance.

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