Synthesis and Radical Polymerization of a Novel Macromonomer Obtained by Living Cationic Ring-Opening Polymerization of an Optically Active Cyclic Thiourethane by a New Initiator Carrying Styryl Group

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ABSTRACT: A new cationic initiator, 4-vinylbenzoic acid 2-methylsulfanyl-4,5-dihydrooxazolinium-4-ylmethyl ester trifluoromethanesulfonate (**1**), carrying both vinyl and triflate groups, was synthesized in quantitative yield by reaction of 1,3-oxazolidine-2-thione derivative with methyl trifluoromethanesulfonate. Living cationic ring-opening polymerization of an optically active cyclic thiourethane ($\mathbf{S_L}$) derived from L-serine was carried out by with **1** as an initiator in dichloromethane to give the corresponding macromonomers ($\mathbf{MS_L}$; $M_n > 10^4$, $M_w/M_n < 1.18$), and the molecular weight of $\mathbf{MS_L}$ could be controlled by [$\mathbf{S_L}$]/[**1**]. $\mathbf{MS_L}$ consists of the optically active thiourethane main chain and styryl group in the initiating end quantitatively. The radical homopolymerization of $\mathbf{MS_L}$ and the copolymerization with styrene were carried out to obtain the corresponding polymers in higher yields. The obtained polymer from $\mathbf{MS_L}$ showed higher specific rotation ($[\alpha]^{25}_D$), melting point (T_m), and Cotton effect than $\mathbf{MS_L}$, supporting the stabilized secondary structure of grafted poly($\mathbf{S_L}$) side chain.

Introduction

Polythiourethanes have a high refractive index and may be applicable to optical devices.[1,2] Although a general method for the synthesis of polythiourethanes, polyaddition of dithiols with diisocyanates, is not adequate to synthesize polythiourethanes with highly organized macromolecular architectures (i.e., controlled molecular weight, head-to-tail structure),[3] we have recently reported an alternative method for the synthesis of polythiourethanes with controlled architecture by living cationic ring-opening polymerization of a cyclic thiourethane ($\mathbf{S_L}$).[4] The highly stable propagating species are also the advantage of this polymerization system. That is, this living polymerization can be conducted under air and moisture by employing a water-stable initiator synthesized by reaction of cyclic thiourethane derivative and methyl trifluoromethanesulfonate (TfOMe).[5] This ensures the high chemoselectivity in this polymerization and prompted us to explore polythiourethanes with functional end groups. An attractive candidate is macromonomer synthesis. Polymerization of a macromonomer with controlled chirality is expected to produce comb polymers with grafted macromolecular side chains. The densely organized side chain will result in giving new functionality. Although a variety of macromonomers have already been prepared, most have been based on the modification of terminal groups.[6−13] These techniques are sometimes accompanied by insufficient transformation, which produce polymers contaminated with nonfunctionalized polymers. Another method to afford a macromonomer has used an initiator with two polymerizable groups in which one group remains unreacted during the macromonomer synthesis.[14] The polymerization must have high chemoselectivity. Hence, this living polymerization of $\mathbf{S_L}$ will be adequate to prepare a graft copolymer based on macromonomer, although typical cationic polymerization is less suitable because of the wide range of polymerizable monomers.[15] Herein, this paper describes (a) synthesis of a new cationic initiator comprising both vinyl and triflate group, (b) living polymerization using this initiator to obtain the macromonomer, and (c) radical polymerization of the macromonomer to obtain optically active graft copolymers.

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Experimental Part

Materials. 4(*S*)-(Methoxycarbonyl)-1,3-oxazolidine-2-thione ($\mathbf{S_L}$)[4] and 4-hydroxymethyl-1,3-oxazolidine-2-thione[5] were synthesized according to the previously reported method. TfOMe (Aldrich Chemical, Co., >99%), chlorobenzene (PhCl), acetonitrile, DMF, DMSO, and CH_2Cl_2 were distilled over CaH_2 before use. Styrene (St) (Kanto Chemical, Co., >99%) was purified by distillation under reduced pressure. 4-Vinylbenzoyl chloride was synthesized according to the literature.[16] Other reagents were used as received.

Measurement. ^{1}H (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were recorded on a JEOL JNH EX-270 spectrometer, using tetramethylsilane (TMS) as an internal standard in $CDCl_3$, CD_2Cl_2, or 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 polydispersity (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. Differential scanning calorimetry (DSC) measure-

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Table 1. Solubility of MS_Ls[a]

run	$M_{n,NMR}$	benzene	MeOH	acetone	PhCl	CH_2Cl_2	$CHCl_3$	DMF	DMSO
1	1600	+ −	+ +	+ +	+ +	+ +	+ +	+ +	+ +
2	5700	−	−	+ −	+ −	+ −	+ −	+ +	+ +
3	11600	−	−	−	−	−	−	+ +	+ +

[a] + +: soluble at room temperature; + −: partially soluble or swelling; −: insoluble.

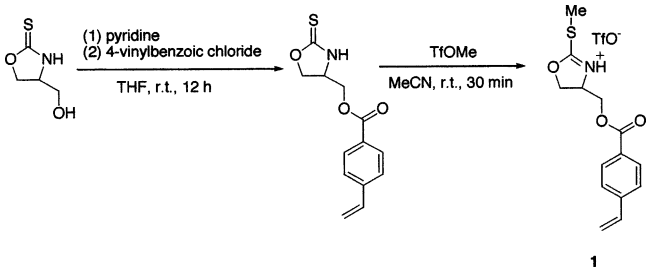
ments were carried out using an SII DSC-6200 instrument at a heating rate of 10 °C/min under a nitrogen atmosphere.

Synthesis of 4-Vinylbenzoic Acid 2-Thioxo-oxazolidin-4-ylmethyl Ester. A solution of 4-vinylbenzoyl chloride (21.0 g, 126 mmol) in dry THF (50 mL) was added to a solution of 4-hydroxymethyl-1,3-oxazolidine-2-thione (14.0 g, 105 mmol) in dry THF (250 mL) and pyridine (10.2 mL, 126 mmol) at 0 °C. After 12 h of stirring at room temperature, pyridine hydrochloride was filtered off, and the solvent was evaporated out in vacuo. The residue was purified by silica gel column chromatography eluted with ethyl acetate/acetone (1/1 = v/v), followed by recrystallization from a mixed solvent [*n*-hexane/ethyl acetate (3/1 = v/v)] to afford 4-vinylbenzoic acid 2-thioxo-oxazolidin-4-ylmethyl ester as a colorless solid. Yield 73% (24.1 g, 91.5 mmol). ^{1}H NMR (DMSO-d_6): δ = 4.25−4.77 (5H, ⟩C*H*−, −C*H*$_2$−O(CO)−, and −(SC)O−C*H*$_2$−), 5.45 (d, J = 10.8 Hz, 1H, −CH=C*H*$_2$), 6.03 (d, J = 17.8 Hz, 1H, −CH=C*H*$_2$), 6.84 (dd, J = 11.3 and 17.7 Hz, 1H, −C*H*=CH$_2$), 7.64 (d, J = 8.1 Hz, 2H, −C$_6$*H*$_4$−), 8.01 (d. J = 8.1 Hz, 2H, −C$_6$*H*$_4$−), 10.3 ppm (broad s, 1H, −N*H*−). ^{13}C NMR (DMSO-d_6): δ = 55.0 (CO−*C*H$_2$−CH⟨), 65.1 (⟩C*H*−), 71.8 (−C*H*$_2$−O(CO)−), 117.7 (−CH=*C*H$_2$), 126.5, 128.6, 130.1 (−*C*$_6$H$_4$−), 136.0 (−*C*H=CH$_2$), 142.2 (−*C*$_6$H$_4$−), 165.6 (−O(*C*O)−C$_6$H$_4$−), 189.3 ppm (⟩*C*=S). IR (KBr): 3185, 1712 (−O*C*OPh), 1504 (C=S), 1280, 1180, 1110, 971 cm^{-1}.

Synthesis of 4-Vinylbenzoic Acid 2-Methylsulfanyl-4,5-dihydro-oxazolinium-4-ylmethyl Ester Trifluoromethanesulfonate (1). Methyl trifluoromethanesulfonate (0.89 mL, 7.00 mmol) was added to a solution of 4-vinylbenzoic acid 2-thioxooxazolidine-4-ylmethyl ester (1.58 g, 6.00 mmol) in dry acetonitrile (10 mL) at room temperature under a dry nitrogen atmosphere. After the mixture was stirred for 3 h, the solution was poured into dry diethyl ether, and the precipitate was isolated by filtration followed by recrystallization from dichloromethane/*n*-hexane to obtain **1** as a white powder. Yield 98% (3.01 g, 7.01 mmol). ^{1}H NMR (CD_2Cl_2): δ = 2.77 (s, 3H, −S−C*H*$_3$), 4.52−4.61 (dd, J = 3.0 and 12.6 Hz, 1H, −C*H*$_2$−O(CO)−), 4.62−4.72 (dd, J = 3.0 and 12.4 Hz, 1H, −C*H*$_2$−O(CO)−), 4.67−5.07 (m, 2H, CO−C*H*$_2$−CH⟨), 5.11−5.20 (m, 1H, ⟩C*H*−), 5.38−5.48 (dd, J = 0.8 and 10.8 Hz, 1H, −CH=C*H*$_2$), 5.85−5.99 (dd, J = 0.8 and 17.4 Hz, 1H, −CH=C*H*$_2$), 6.79 (dd, J = 11.1 and 17.8 Hz, 1H, −C*H*=CH$_2$), 7.52 (d, J = 8.4 Hz, 2H, −C$_6$*H*$_4$−), 7.97 (d, J = 8.4 Hz, 2H, −C$_6$*H*$_4$−), 12.41 ppm (broad s, 1H, ⟩C=N*H*$^+$−). ^{13}C NMR (CD_2Cl_2): δ = 14.6 (−S−*C*H$_3$), 59.3 (CO−*C*H$_2$−CH⟨), 63.6 (⟩*C*H−), 77.4 (−C*H*$_2$−O(CO)−), 117.6 (−CH=*C*H$_2$), 127.0, 128.5, 130.7 (−*C*$_6$H$_4$−), 136.5 (−*C*H=CH$_2$), 143.5 (−*C*$_6$H$_4$−), 166.2 (−O(*C*O)−C$_6$H$_4$−), 183.2 ppm (−*C*=NH$^+$−). IR (KBr): 2992, 1720 (−O*C*OPh), 1589 (−*C*=NH$^+$−), 1288, 1241, 1164, 1241, 1118, 1025, 640 cm^{-1}. $C_{15}H_{16}F_3NO_6S_2$: Calcd: C, 42.15; H, 3.77; N, 32.8; S, 15.00. Found: C, 42.16; H, 3.81; N, 32.4; S, 15.16.

Synthesis of Macromonomer (MS_L). A solution of 4(*S*)-(methoxycarbonyl)-1,3-oxazolidine-2-thione (**S_L**) (2.0 g, 12 mmol) and **1** (0.8 g, 1.9 mg) in dry CH_2Cl_2 (25 mL) was placed in a round-bottom flask (50 mL) under a nitrogen atmosphere. The resulting mixture was subjected to polymerization at 30 °C for 24 h under nitrogen. The reaction mixture remained homogeneous during the reaction. After adding methanol for quenching, the resulting mixture was poured into ethyl ether to precipitate a polymer. The polymer was collected by filtration with suction and dried under vacuum. A macromonomer (**MS_L**) was obtained as a colorless solid in quantitative yield. $[\alpha]^{30}_D$ = 46.4° (c = 1.0 g/dL, CH_2Cl_2). $F_w \approx$ 1600 (calculated from ^{1}H NMR spectra). ^{1}H NMR (DMSO-d_6): δ = 2.21 (initiating end, −S−C*H*$_3$), 2.97−3.05 (1H, −C*H*$_2$−), 3.25−3.38 (1H, −C*H*$_2$−), 3.64 (3H, −OC*H*$_3$), 4.19−4.40 (1H, ⟩C*H*−), 5.49−5.46 (initiating end, −CH=C*H*$_2$), 5.99−6.05 (initiating end, −CH=C*H*$_2$), 6.78−6.88 (initiating end, −C*H*=CH$_2$), 7.61−7.65 (initiating end, −C$_6$*H*$_4$−), 7.95−7.98 (initiating end, −C$_6$*H*$_4$−), 8.40−8.42 (initiating end, −N*H*−), 8.76−8.79 (terminal group, −N*H*−), 8.86−8.89 ppm (1H, −N*H*−). ^{13}C NMR (DMSO-d_6): δ = 9.16 (initiating end, −S−*C*H$_3$), 27.58 (−*C*H$_2$−), 49.72 (−OCH$_3$), 54.09 (⟩*C*H−), 114.70 (initiating end, −CH=*C*H$_2$), 123.87, 126.55, 127.41 (−*C*$_6$H$_4$−), 133.01 (initiating end, −*C*H=CH$_2$), 139.30 (initiating end, −*C*$_6$H$_4$−), 162.57 (initiating end, −S(*C*O)NH−), 163.32 (−S(*C*O)NH−), 167.82 (initiating end, −O(*C*O)−C$_6$H$_4$−) 167.89 ppm (−*C*OOMe). IR (KBr): 3309 (−NH−), 1743 (−O*C*OPh), 1658 (−S*C*ONH−), 1512, 1211, 856 cm^{-1}.

Scheme 1



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Polymerization of MS_L. A typical procedure for the polymerization of **MS_L** is shown as follows. A mixture of **MS_L** (0.100 g, 0.058 mmol) and AIBN (1.00 mg, 0.00610 mmol) was heated at 60 °C in PhCl for 20 h in a degassed sealed tube. After the reaction, the resulting mixture was dissolved in DMSO and poured into methanol to precipitate a white powdery polymer. To precipitate copolymers with styrene, acetone was employed as poor solvent instead. The precipitated product was collected by filtration and dried under vacuum. Yield = 89% (90 mg, 0.0520 mmol). ^{1}H NMR (DMSO-d_6): δ = 2.18 (initiating end, −S−C*H*$_3$), 2.93−3.12 (1H, −C*H*$_2$−), 3.23−3.40 (1H, −C*H*$_2$−), 3.64 (3H, −OC*H*$_3$), 4.10−4.40 (1H, ⟩C*H*−), 7.65−7.97 (initiating end, −C$_6$*H*$_4$−), 8.04−8.15 (initiating end, −C$_6$*H*$_4$−), 8.39−8.40 (initiating end, −N*H*−), 8.85−8.92 ppm (1H, −N*H*−). M_n = 10 700 (M_w/M_n = 1.75) (run 3 in Table 1).

Results and Discussion

Synthesis of Cationic Initiator 1. A bifunctional initiator **1** was synthesized in quantitative yield by reaction of 4-vinylbenzoic acid 2-thioxo-oxazolidin-4-ylmethyl ester and TfOMe in dry acetonitrile (Scheme 1). The structure of **1** was confirmed by ^{1}H NMR, ^{13}C NMR, IR spectroscopies, and elemental analysis. Although a styryl group is relatively susceptible toward cationic species, the iminum salt could be selectively formed, owing to the stability of the resulting salt and the electron-accepting ester group on the benzene ring that decreases the nucleophilicity of the vinyl group.

Synthesis of Macromonomer. Cationic ring-opening polymerization of **S_L** was carried out at 30 °C in dry CH_2Cl_2 by **1** as an initiator under dry nitrogen (Scheme 2). When the feed ratio $[\mathbf{S_L}]_0/[\mathbf{1}]_0$ was 6.6, the reaction was complete within 24 h, and the corresponding polymer was obtained almost quantitatively. The M_n and M_w/M_n are estimated to be 1700 and 1.18, respectively, from SEC analysis. The structure of the resulting polymer was confirmed by the ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. The IR spectra showed the character-

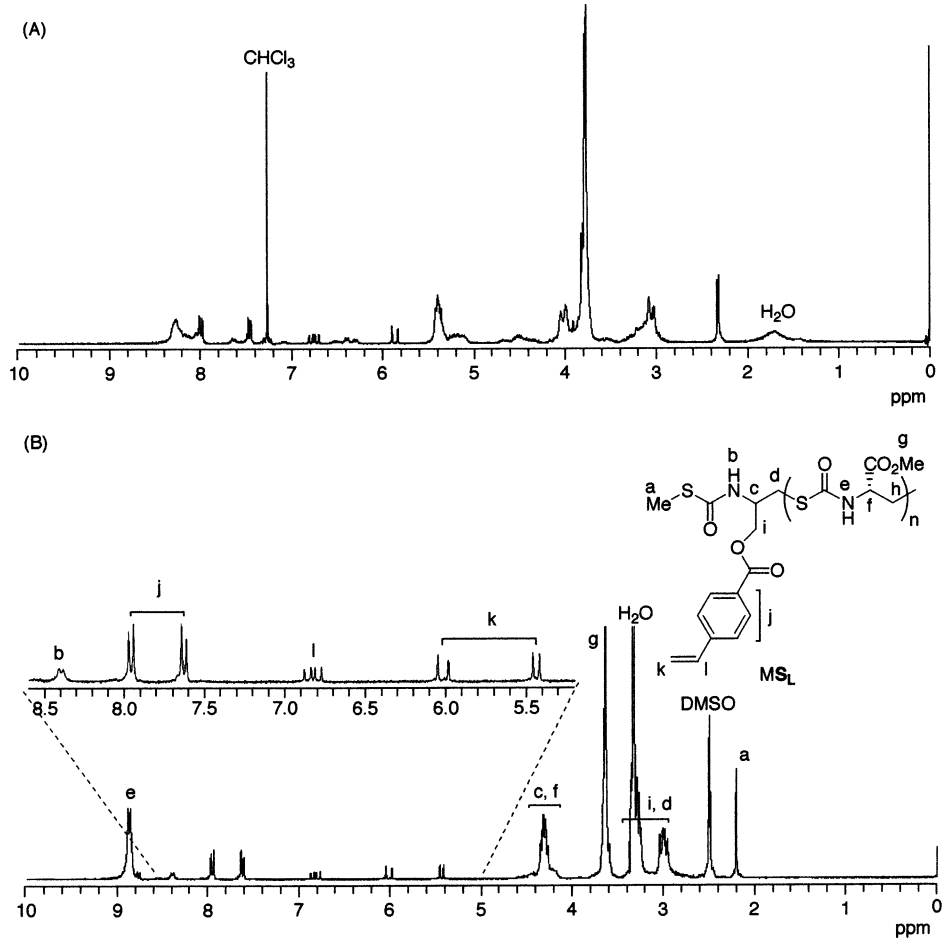
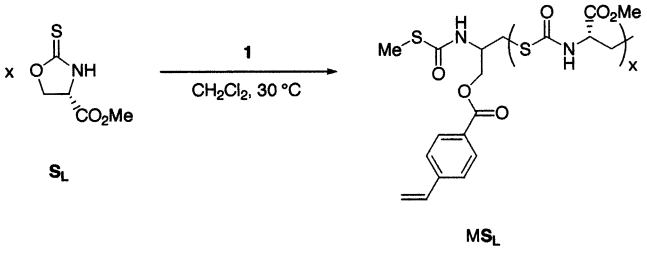


Figure 1. ^{1}H NMR (270 MHz) spectra of **MS$_L$** (A) in $CDCl_3$ and (B) in DMSO-d_6 obtained by cationic polymerization of **S$_L$** with **1** (15 mol %) in CH_2Cl_2 for 24 h.

Scheme 2



istic absorption of the carbonyl group in the thiourethane moiety at 1658 cm^{-1}. These data indicate that the obtained polymer consists of a thiourethane main chain.[3,4] Figure 1 illustrates the ^{1}H NMR spectrum of the polymer in $CDCl_3$ with that in DMSO-d_6. Although the ^{1}H NMR spectrum of the polymer in $CDCl_3$ seems to suggest complicated structure (Figure 1A), that of the polymer in DMSO-d_6 showed clear peaks (Figure 1B). These data should indicate that the protons of **MS$_L$** in $CDCl_3$ are under a diverse environment because of secondary structure depending on the hydrogen bond; however, in DMSO the protons are under a similar circumstance due to independence from the hydrogen bond. We observed the signals assignable to the S−Me group at 2.21 ppm, the vinyl group at 5.42−5.46, 5.99−6.05, and 6.78−6.88 ppm, and the aromatic group at 7.61−7.65 and 8.40−8.42 ppm. The M_n estimated from the integral ratios of the initiating end and repeating units (M_n from vinyl group = 1654, M_n from aromatic group = 1568) agree well with the theoretical value (1465).

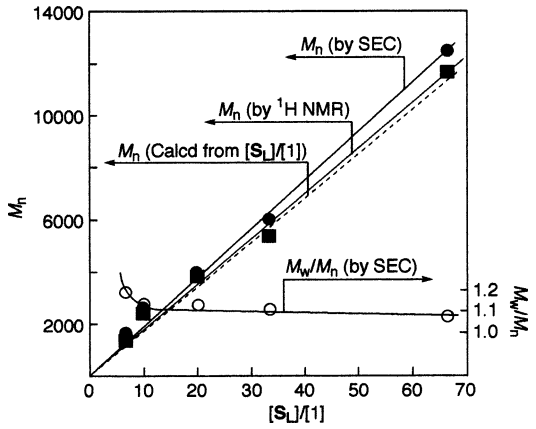


Figure 2. M_n and M_w/M_n vs feed ratio ([**S$_L$**]/[**1**]). Conditions: solvent CH_2Cl_2 (0.5 M), temperature 30 °C, [**S$_L$**]/[**1**] = 6.6−67, conversion of **S$_L$** = 100%.

AU: Does the above sentence beginning with "These data should indicate..." convey the intended meaning? If not, please rephrase.

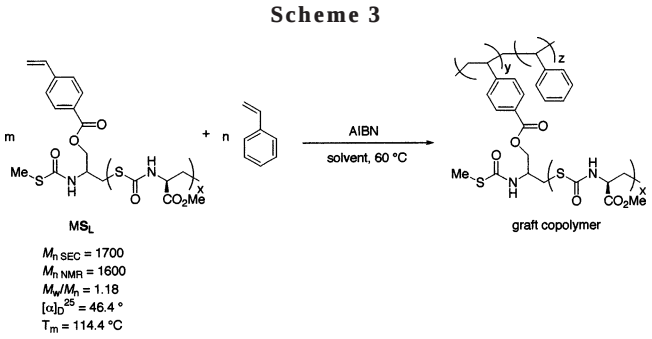
When polymerization reactions were carried out at 30 °C with varying the feed ratio [**S$_L$**]/[**1**], the relationship between feed ratio and M_n estimated by both from SEC and ^{1}H NMR was linear (Figure 2). Although the M_n estimated by the SEC analysis were a little higher than those expected from the ratios of [**S$_L$**]/[**1**], those determined by ^{1}H NMR spectroscopy agree well with

Table 2. Radical Polymerization of MS_L[a]

run	feed ratio (molar) **MS**$_L$:St	solvent	yield[b] (%)	*y*:*z*[d]	M_n[e]	M_w/M_n[e]	$[\alpha]_D^{25}$[f] (deg)	T_m[g] (°C)
1	100:0	DMF	0		*h*	*h*	*h*	*h*
2	100:0	DMSO	10	100:0	1 050	2.50	15.5	58.8
3	100:0	PhCl	89	100:0	10 700	1.75	60.0	122.9
4	75:25	PhCl	79[c]	92:8	19 800	2.77	50.2	109.5
5	50:50	PhCl	69[c]	82:18	16 000	3.39	24.8	101.4

[a] Conditions: total monomer (0.058 mmol) in solvent (1.0 mL), initiator AIBN (10 mol %), 60 °C, 20 h. [b] Methanol-insoluble part. [c] Acetone-insoluble part. [d] Determined by ^{1}H NMR spectra. [e] Estimated by SEC (polystyrene standard, eluent; DMF containing 5.0 mM lithium bromide and 5.0 mM phosphoric acid). [f] Measured by a polarimeter at 25 °C (c = 0.1 g/dL, CH_2Cl_2). [g] Determined by DSC under N_2. [h] Not determined.

Scheme 3



the expected ones as the case of the polymerization initiated with TfOMe.[3,4] Furthermore, a postpolymerization could be conducted successfully. Accordingly, the present polymerization system proceeded through a living process despite the existence of the styryl groups, which remained unreacted during the macromonomer synthesis. The solubility of obtained **MS**$_L$ (M_n = 1600, 5700, and 11 600) toward various organic solvents was examined to determine appropriate solvents for the polymerization of **MS**$_L$. About 5% (w/v) solution was taken as a criterion for the solubility test. As shown in Table 1, **MS**$_L$ was soluble in highly polar solvents such as DMF and DMSO regardless of the M_n. As the M_n of the obtained macromonomers increased, they became insoluble in less polar solvents. From these results, we selected **MS**$_L$ (M_n = 1600) with lower molecular weight that was soluble in a wide range of solvents to obtain graft copolymers.

Radical Polymerization of Macromonomer. Radical polymerization of **MS**$_L$ ($M_n \approx$ 1600) was carried out at 60 °C for 20 h in several solvents using AIBN (10 mol %) as an initiator to afford the corresponding copolymers (Scheme 3 and Table 2). Polymerization in either DMF or DMSO as polar solvents gave the corresponding graft copolymers, and especially that in DMF led to decrease of the molecular weight due to decomposition of **MS**$_L$ (runs 1 and 2 in Table 2). To examine why **MS**$_L$ decomposed under these conditions, a DMF solution of **MS**$_L$ was stirred at 60 °C for 20 h without radical initiator, which resulted in the decomposition of **MS**$_L$. Namely, **MS**$_L$ proved to be very heat sensitive in polar solvents. In contrast, the radical polymerization of **MS**$_L$ in PhCl, a less polar solvent than DMF or DMSO, provided the corresponding graft copolymer in good yield, although the reaction mixture became heterogeneous within 12 h. No residual vinyl proton signal of the obtained polymer was observed in the ^{1}H NMR spectrum (run 3 in Table 2). The M_n of side chain in the graft copolymer was calculated from S−Me protons by the ^{1}H NMR spectrum. The M_n showed almost same value with the M_n of **MS**$_L$ before the polymerization (1651 and 1658, respectively). This

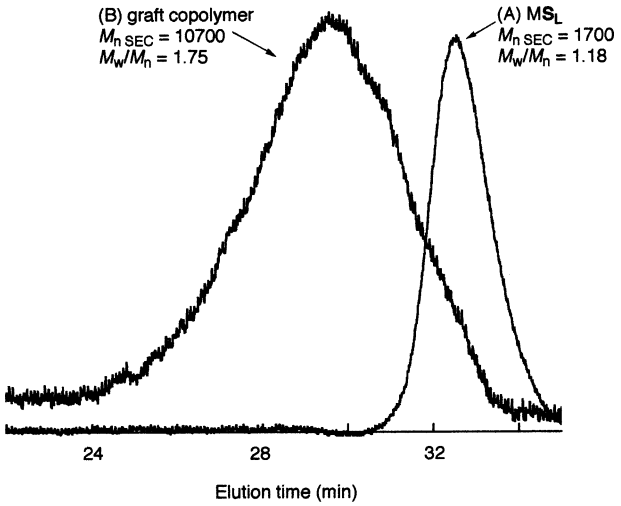


Figure 3. SEC profiles (UV detector) of (A) **MS**$_L$ and (B) graft copolymer obtained by radical polymerization (run 3 in Table 2).

result should indicate that the decomposition of thiourethane moieties did not take place in the present polymerization because of the stable secondary structure in PhCl that may protect the thiourethane moieties. Although the polymerization proceeded quantitatively, graft copolymers from **MS**$_L$ having high molecular weight (M_n > 5700) were poorly soluble in common organic solvents, and the detailed characterization could not be performed. However, we could not observe a negligible difference between the wavenumbers of NH and C═O absorptions in IR spectra of the graft copolymers obtained from **MS**$_L$ with M_n = 5700 and 1600. These data might indicate that the insolubility of the graft polymers originates from the stable hydrogen bond through the grafted side chain polymers that will be strengthened with increase of M_n.

As shown in Figure 3, the elution peak in the SEC profile shifted toward the higher molecular weight region after the polymerization keeping a unimodal distribution. The specific rotation and melting point of the graft copolymer increased from the macromonomer. The Cotton effects [both thiourethane (228 nm) and ester (195 nm)] in the CD spectra also increased (Figure 4). These data support that the secondary structure of the grafted **MS**$_L$ is more stable than that of **MS**$_L$. Radical copolymerization of **MS**$_L$ with St was examined under feed molar ratios of 75:25 and 50:50 (runs 4 and 5 in Table 2). In these cases, the reaction mixtures also became heterogeneous within 10 h. The copolymers with St were separated from oligoSt by precipitation with acetone after the copolymerization. The unit ratio of the copolymers was estimated by comparing the integral ratio of peaks attributable to the S−Me and the aromatic group to be **MS**$_L$: St = 92:8 and 82:18, respec-

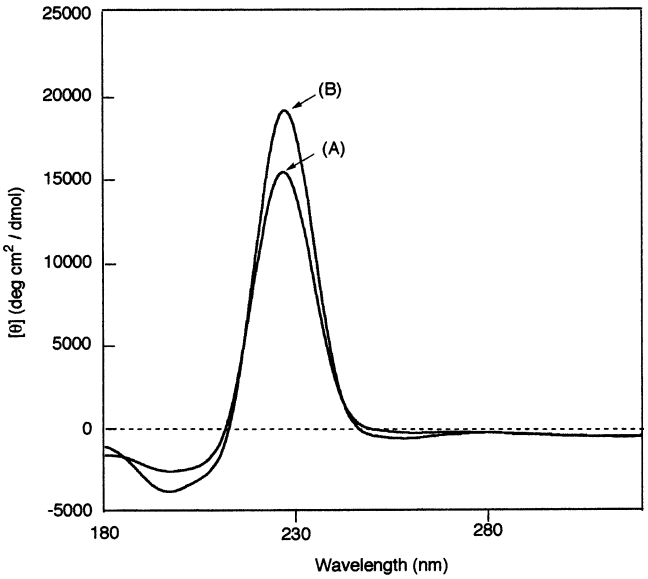


Figure 4. CD spectra (c = 0.1 g/dL, CH_2Cl_2) of (A) $\mathbf{MS_L}$ and (B) graft copolymer (run 3 in Table 2).

tively. This finding may indicate that the reaction rates of $\mathbf{MS_L}$ were higher than that of St. A plausible reason for this phenomenon is the gel effect owing to the poor solubility of $\mathbf{MS_L}$ growing end in PhCl. The specific rotation and melting point decreased with increase of the styrene component, probably because polystyrene structure was intercalated in grafted $\mathbf{MS_L}$ to impair the secondary structure.

Summary

A new cationic initiator (**1**) comprising both vinyl and triflate groups was synthesized in quantitative yield by a reaction of 1,3-oxazolidine-2-thione derivative with TfOMe and was employed to polymerization of a cyclic thiourethane ($\mathbf{S_L}$) to obtain a macromonomer. The cationic ring-opening polymerization of $\mathbf{S_L}$ derived from L-serine using **1** proceeded in living fashion to give the corresponding macromonomers ($\mathbf{MS_L}$). $\mathbf{MS_L}$, which consists of the thiourethane main chain and styryl group in the initiating end quantitatively, had a high molecular weight ($>10^4$) and a narrow polydispersity (<1.18). The molecular weight of $\mathbf{MS_L}$ could be controlled by [$\mathbf{S_L}$]/[**1**]. Graft copolymers from $\mathbf{MS_L}$ were obtained by the radical polymerization and copolymerization with styrene using PhCl as a solvent in high yields. In contrast, polar solvents such as DMF and DMSO led to the decomposition of the $\mathbf{MS_L}$, which may originate from the disordered secondary structure that became unable to protect the thiourethane moieties. The obtained graft copolymer showed the higher specific rotation, melting point, and the Cotton effect than the $\mathbf{MS_L}$, supporting the more stable secondary structure than that of the macromonomer.

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