Controlled Cationic Ring-Opening Polymerization of a Six-Membered Cyclic Thiourethane

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Tremendous effort has been devoted to the development of sulfur-containing polymers because these polymers are potentially applicable to optical and biocompatible materials.[1] However, the high reactivity of sulfur-containing monomers and the poor solubility of the resulting polymers frequently limit versatility in designing sulfur-containing polymers. We have developed controlled polymerization of a variety of sulfur-containing cyclic monomers such as monothiocarbonate[2] and dithiocarbonate.[3] Cyclic thiourethanes giving polythiourethanes are also attractive candidates for synthesis of sulfur-containing polymers. Although cationic polymerization of a five-membered cyclic thiourethane without substituents has been examined, the resulting polymer was poorly soluble in common organic solvents, and hence the polymerization system would not be effective for preparing well-defined polythiourethanes.[4] In contrast, we have found that controlled cationic polymerization of five-membered thiourethanes can be conducted when the monomer is substituted.[5] This prompted us to expand the scope of this polymerization system by designing appropriate monomer structures. Herein, we describe the cationic polymerization of six-membered cyclic thiourethane (3-benzyltetrahydro-1,3-oxazolidine-2-thione) to obtain the corresponding well-defined polythiourethane (Scheme 1).

Cationic polymerization of tetrahydron-1,3-oxazolidine-2-thione (TOT)[6] was carried out using boron trifluoride etherate (BF_3OEt_2) as an initiator in CH_2Cl_2 at 30 °C for 24 h and was quenched with MeOH. The resulting polymer was poorly soluble in common organic solvents probably due to intermolecular hydrogen bonding between the polymer chain. To obtain a soluble polymer, we synthesized an *N*-benzyl-substituted thiourethane, 3-benzyltetrahydro-1,3-oxazolidine-2-thione (BTOT).[7] Polymerization of BTOT under the above-described conditions afforded a soluble polymer in common organic solvents such as CH_2Cl_2, $CHCl_3$, and THF. However, SEC analysis of the resulting polymer showed a bimodal distribution even if Et_3N was used as a quencher (see Supporting Information). Since the peak in the high molecular weight region exhibits doubled molecular weight from that of the major peak in low molecular weight region, we assumed that intermolecular interaction involving a coupling reaction and/or a strong coordination between two propagating species might occur during termination.[8] Thus, to quench the propagating species more efficiently, a more nucleophilic dithiocarbamate ($Et_2NCS_2Na\cdot 3H_2O$) was used as a terminator, which gave a unimodal SEC peak, indicating efficient termination.[9] Table 1 summarizes the results of polymerization using $Et_2NCS_2\cdot 3H_2O$ as a terminator.[10] Polymerization of BTOT with BF_3OEt_2 afforded the corresponding polymer with lower M_n than that obtained by TfOMe and BF_4OEt_3 because of its higher initiation efficiency (entries 1−3).[11] Nitrobenzene was found to be a better solvent than CH_2Cl_2, which may originate from the increase in free ionic nature of the propagating species in polar solvent. Polymerization in nitrobenzene at 50 °C afforded the corresponding polythiourethane with narrow molecular weight distribution (M_w/M_n) in excellent yield (entry 5).[12] The M_n of the polymer obtained in entry 5 was determined by viscometer light scattering analysis to be 12 200. In a comparison of it and the feed ratio, the initiation efficiency of this polymerization was estimated to be 0.51.

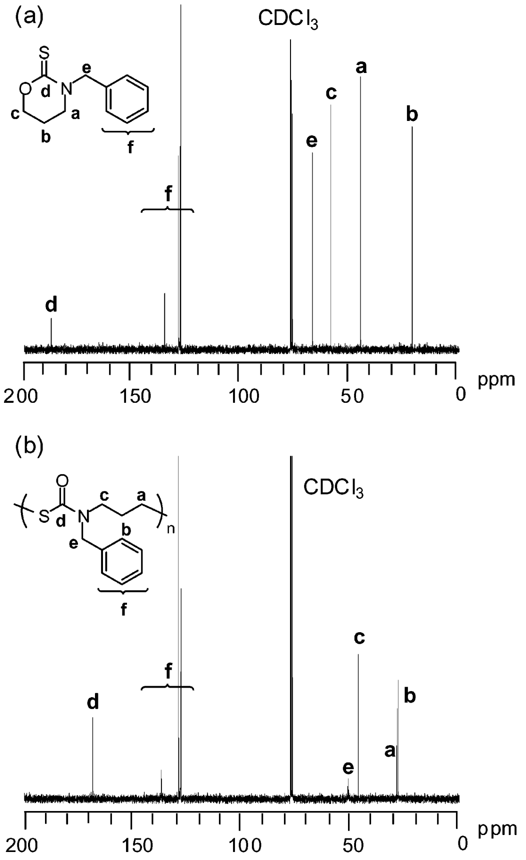

Figure 1. ^{13}C NMR spectra (solvent $CDCl_3$, 270 MHz): (a) BTOT (at room temperature) and (b) polyBTOT (at 60 °C).

Scheme 1

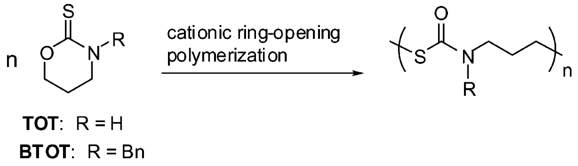

Figure 1 presents the ^{13}C NMR spectra of BTOT (a) and polyBTOT (b), which clearly demonstrate the complete transformation of the thiocarbonyl group in BTOT (188 ppm) into the carbonyl group (169 ppm)

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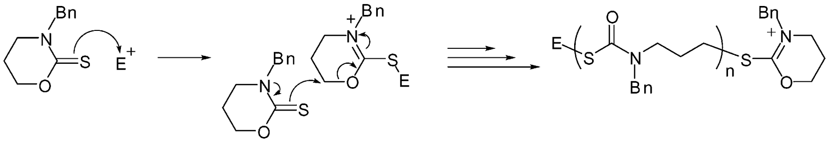
Table 1. Cationic Polymerizations of BTOT under Various Conditions[a]

entry	initiator	temp (°C)	solvent	$[M]_0$ (mol/L)	conv (%)[b]	yield (%)[c]	M_n (M_w/M_n)[d]
1	TfOMe	30	CH_2Cl_2	1.0	20	14	53 100 (1.31)
2	BF_4OEt_3	30	CH_2Cl_2	1.0	69	61	43 900 (1.16)
3	BF_3OEt_2	30	CH_2Cl_2	1.0	74	70	33 400 (1.26)
4	BF_3OEt_2	30	nitrobenzene	0.7	51	47	31 500 (1.11)
5	BF_3OEt_2	50	nitrobenzene	0.7	>99	96	20 400 (1.04)

[a] Polymerization conditions: $[\text{initiator}]_0 = 0.02$ M; $[\text{BTOT}]_0/[\text{initiator}]_0 = 30$; reaction time = 24 h. [b] Determined by ^{1}H NMR analysis. [c] Isolated yield of MeOH-insoluble parts. [d] Estimated by SEC analysis (eluent THF, polystyrene standards) of the crude products.

Scheme 2



upon polymerization. Other peaks in both the ^{1}H and ^{13}C NMR spectra are also consistent with the expected polymer structure. The isomerization was supported by the C=O absorption peak at 1643 cm^{-1} in the IR spectrum of polyBTOT (see Supporting Information). Scheme 2 illustrates a plausible mechanism for the ring-opening polymerization. A nucleophilic attack of the thiocarbonyl sulfur to the cationic initiator affords carbenium cation species. Then, the thiocarbonyl sulfur nucleophilically attacks to the α-position of the ether oxygen in the cyclic carbenium ion, and the chain reaction of these processes gives polyBTOT.

The relationship between the M_n of the obtained polymer and the feed ratio of $[\text{BTOT}]_0/[BF_3OEt_2]_0$ was linear, and M_w/M_n was less than 1.1, as shown in Figure 2. Further, a two-stage polymerization experiment was performed to elucidate the stability of the growing ends. After the first stage polymerization of BTOT (30 equiv to BF_3OEt_2) for 10 h at 50 °C ($M_n = 20\,400$, $M_w/M_n = 1.04$), BTOT (30 equiv to BF_3OEt_2) was fed to react continuously for an additional 10 h at 50 °C. As a result, the second monomer was consumed completely to provide a polymer with higher molecular weight ($M_n = 40\,400$, $M_w/M_n = 1.03$), while maintaining a narrow M_w/M_n. These results indicate that the present polymerization would proceed through a controlled fashion.

The thermal behavior of polyBTOT obtained in entry 5 was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), where its 5% weight loss temperature (T_{d5}) was 353 °C and glass transition temperature (T_g) was 23 °C. The T_{d5}'s of polythiourethanes derived from diisocyanates and dithiols are 76−108 °C,[13] indicating that polyBTOT is more heat-resistant than common polythiourethanes presumably due to the absence of active proton (−NHCOS−) that may accelerate thermal degradation through hydrogen bonding to the carbonyl oxygen in the main chain. Further, polyBTOT has a high refractive index ($n_d = 1.642$), indicating the potential applicability to optical materials.

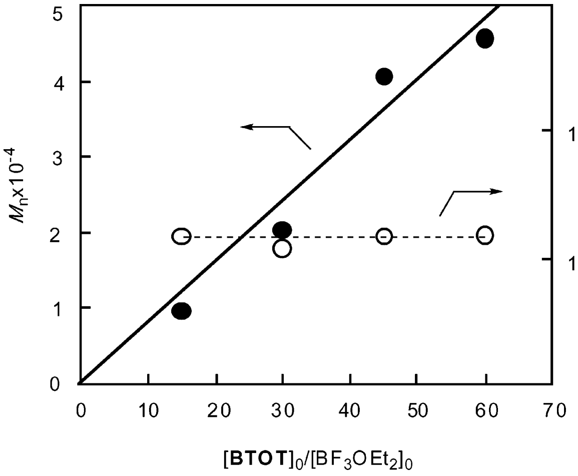


Figure 2. M_n and M_w/M_n vs $[\text{BTOT}]_0/[BF_3OEt_2]_0$ ratio in the polymerization of BTOT in nitrobenzene at 50 °C; $BF_3OEt_2 = 0.033$ mmol, $[\text{BTOT}]_0 = 0.7$ M. Conversion of BTOT = 100%.

In summary, we demonstrated a well-defined synthesis of a polythiourethane by the controlled cationic ring-opening polymerization of 3-benzyltetrahydro-1,3-oxazolidine-2-thione (BTOT). Control of molecular weight was also achieved by using dithiocarbamate as a terminator. PolyBTOT showed high reflactive index and thermal stability, which may be applicable to optical materials.

Supporting Information Available: SEC profiles of the polymers, IR spectra of BTOT and polyBTOT, plot of M_n vs $[H_2O]_0/BF_3OEt_2]_0$ in polymerization of BTOT, ^{1}H NMR spectrum of polymer, scheme showing termination by $Et_2NCS_2Na{\cdot}3H_2O$, and Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(6) For the synthesis of **TOT**, see: Li, G.; Ohtani, T. *Heterocycles* **1997**, *45*, 2471.

(7) Experimental details are given in the Supporting Information.

(8) Because SEC analysis of the resulting polymer without quenching showed a unimodal profile, the bimodal distribution would originate from the termination process using MeOH. To clarify the reaction mechanism for the bimodal distribution, the reaction of BTOT and initiator and MeOH (1:1:1) is now under investigation, and the results will be reported elsewhere.

(9) A plausible mechanism for the termination by $Et_2NCS_2Na{\cdot}3H_2O$ is given in the Supporting Information.

(10) Representative procedure for the polymerization: BTOT (207 mg, 1.0 mmol) and nitrobenzene (1.5 mL) were added to a test tube containing a magnetic stir bar under a nitrogen atmosphere. Then, BF_3OEt_2 (4.0 μL, 0.033 mmol) was added to the solution, and the mixture was stirred for 24 h at 50 °C. An acetonitrile solution (1.5 mL) containing $Et_2NCS_2Na{\cdot}3H_2O$ (37.5 mg, 0.2 mmol) was added for quenching. The mixture was poured into MeOH (100 mL), and the resulting precipitate was collected by filtration with suction and dried under vacuum to obtain polyBTOT (197 mg, 96%) as a white powder. IR (KBr): 1643 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm, at room temperature): 1.88 (2H, br, s, $-NCH_2C\mathit{H}_2CH_2-$), 2.89 (2H, t, $J = 7.2$, $-NCH_2CH_2C\mathit{H}_2-$), 3.36 (2H, br, s, $-NC\mathit{H}_2CH_2CH_2-$), 4.57 (2H, s, $-C\mathit{H}_2Ph$), 7.25–7.31 (5H, m, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm, at 60 °C): 28.01, 28.53, 46.40, 51.01, 127.91, 137.04, 168.45. Anal. Calcd for $C_{11}H_{13}NOS$: C, 63.73; H, 6.32; N, 6.76; S, 15.47. Found: C, 63.49; H, 6.38; N, 6.75; S, 15.61.

(11) The mechanism of the initiation by BF_3OEt_2 was examined. The molecular weights of the resulting polymers decreased as the amount of water in the system increases. In every case, conversion of monomer is quantitative. This indicates that water or HF, etc., contained in BF_3OEt_2 would act as a co-initiator, which was also supported by the absence of the signal attributable to the ethyl group dissociated from BF_3OEt_2 in the ^{1}H NMR spectrum of the polymer ($M_n = 3000$, $M_{w.}/M_n = 1.02$) obtained by BF_3OEt_2 in nitrobenzene at 50 °C followed by termination with MeOH (see Supporting Information).

(12) In every case, monomer was recovered unchanged except for the polymers.

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