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Communications to the Editor

Novel Anionic Ring-Opening Polymerization of Seven-Membered Monothiocarbonate Depending on Initiators

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Sulfur-containing polymers are important because of excellent properties, such as optical and thermal behavior.[1−5] Many researchers have therefore developed ring-opening polymerization of cyclic monomers bearing sulfur atoms,[6−19] including cyclic thiocarbonates (TCs). Earlier works on the polymerization of TCs were carried out for five-[6] and six-membered[7,8] TCs having no substituent, which give rise to isomerization or polymerization giving poorly soluble polymers, respectively. We accordingly carried out detailed investigation on polymerization of TCs with appropriate substituents to control the polymerization.[11,12] We have recently reported that cationic polymerization of 1,3-dioxepan-2-thione (7TC) gives a poly(thiocarbonate) through specific isomerization of thiocarbonyl to carbonyl moieties.[19] Although the polymerization proceeds via a controlled fashion, slow termination occurred after complete consumption of the monomer. If more precisely controlled polymerization is constructed, wide varieties of molecular designs will be available for poly(thiocarbonate)s. Herein, we describe anionic polymerization of 7TC to control polymer structure and molecular weight.

Anionic polymerization of 7TC was carried out using various initiators in THF (Scheme 1, Table 1). When lithium initiators were used (runs 1−4), THF-insoluble products precipitated within 5 min.[20] The ^{1}H NMR analysis revealed complete consumption of 7TC regardless of initiators. We separated the insoluble products into THF-soluble and -insoluble parts by the Soxhlet extraction procedure.

Scheme 1. Anionic Polymerization of 7TC

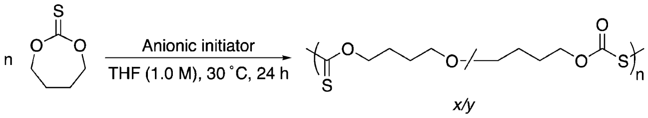

Table 1. Anionic Polymerization of 7TC[a]

run	initiator	conv (%)[b]	yield (%)[c]	M_n[c]	M_w/M_n[c]	unit ratio (x/y)[b]
1	*n*-BuLi	>99	55[d]	2400	1.08	100:0
2	*s*-BuLi	>99	57[d]	1500	1.53	100:0
3	*t*-BuLi	>99	42[d]	n.d.[f]	n.d.[f]	100:0
4	*t*-BuOLi	>99	56[d]	n.d.[f]	n.d.[f]	100:0
5	*t*-BuOK	>99	94[e]	8800	1.07	0:100
6	TEA	>99	91[e]	50400	1.56	0:100
7	pyridine	68	72[e]	38300	1.96	0:100
8	DBU	>99	98[e]	9600	1.10	42:58

[a] Conditions: THF, $[7TC] = 1.0$ mol/L, $[\text{initiator}]/[7TC] = 0.02$ (runs 1−5) or 0.04 (runs 6−8), 30 °C, 24 h. [b] Determined by ^{1}H NMR spectroscopy ($CDCl_3$). [c] Estimated from SEC eluted with THF based on polystyrene standards. [d] Isolated yield after Soxhlet extraction with THF. [e] Isolated yield after precipitation into *n*-hexane. [f] Not determined. Dimer or trimer.

The structure of THF-soluble products was determined by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. The IR and ^{13}C NMR spectra show peaks assignable to thiocarbonyl groups at 1134 cm^{-1} and 196.2 ppm, respectively, but no peak assignable to carbonyl groups (see Supporting Information). Because the identical IR spectrum was observed for the THF-insoluble parts and results of elemental analysis of the two parts agreed well with the theoretical value, the polymerization evidently proceeds without isomerization of the thiocarbonyl to carbonyl groups. It is probable that the poor solubility of the polymer originates from intermolecular stacking of thiocarbonyl moieties.

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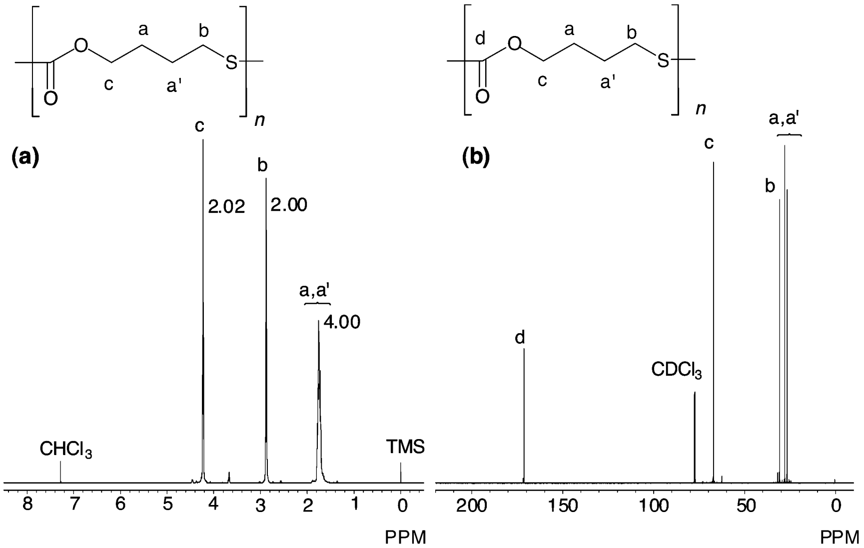

Figure 1. ^{1}H (a) and ^{13}C (b) NMR spectra of poly7TC obtained in run 5 (Table 1).

In contrast, polymerizations initiated by *t*-BuOK, TEA (triethylamine), pyridine, and DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) afforded polymers with good solubility in common organic solvents such as THF, chloroform, and DMF (runs 5−8).[21] The higher molecular weight of polymers from TEA and pyridine may originate from the lower initiation efficiency probably due to the less nucleophilic character of the initiators. Figure 1 shows the ^{1}H and ^{13}C NMR spectra of poly7TC obtained in run 5. The peak at approximately 171.4 ppm in the ^{13}C NMR spectrum clearly indicates the presence of a carbonyl moiety, and no peak assignable to thiocarbonyl moieties was observed. The IR spectrum also shows characteristic absorption assignable to a carbonyl moiety at 1699 cm^{-1}. These spectra are identical to those of poly7TC obtained in the cationic isomerization polymerization,[19] suggesting that the polymerization proceeds via isomerization of thiocarbonyl to carbonyl moieties. The polymers obtained using TEA and pyridine also consisted of the isomerized structure, which was determined by the identical spectra.

When DBU was used as the initiator (run 8), the ^{1}H and ^{13}C NMR spectra show peaks observed in each spectrum of polymers obtained in runs 1 and 5, suggesting the presence of the two units. The unit ratio was determined from the ^{1}H NMR to be 42:58, and the IR spectrum shows the two peaks assignable to the carbonyl (1699 cm^{-1}) and thiocarbonyl (1134 cm^{-1}) moieties.

Lithium initiators add to the thiocarbonyl group, cleaving the C−O bond to form an alkoxide. Sequential addition of the alkoxide affords poly7TC without isomerization. In the case of isomerization polymerization initiated by *t*-BuOK, TEA, or pyridine, two pathways are possible. The first one is polymerization taking place after isomerization of the thiocarbonyl to carbonyl group, and the second one is nucleophilic addition to the α-methylene carbon attached to oxygen atom to form thiocarbonate anion.[22] The polymerization using DBU gives poly7TC consisting of the two units and having unimodal molecular weight distribution, suggesting that the first pathway is more plausible; however, detailed investigation is in progress.[25]

Because poly7TC from *t*-BuOK shows narrow molecular distribution, we investigated the living character of the polymerization. We polymerized 7TC under varied feed ratios of 7TC to *t*-BuOK. Regardless of the feed ratio, 7TC was consumed completely and poly7TC was obtained in quantitative yield. A linear relationship was found between the feed ratio and M_n, indicating the controlled nature of the polymerization (Figure 2). The living character of this polymerization was confirmed by the following evidence: (a) the molecular weight of poly7TC linearly increases with conversion of 7TC keeping a narrow molecular weight distribution, and (b) a postpolymerization experiment can be successfully conducted (see Supporting Information).

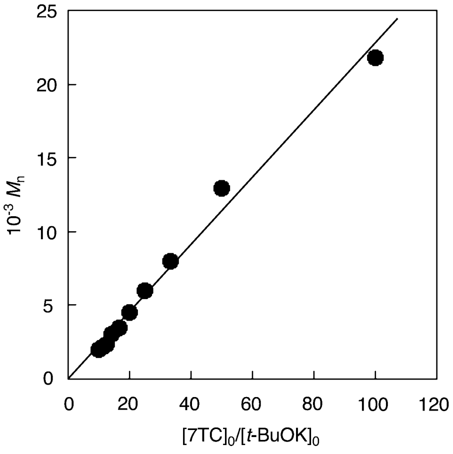

Figure 2. Relationship between M_n and [7TC]/[*t*-BuOK]. Conditions: 7TC, 0.50 mmol; THF, 0.50 mL; 30 °C; conversion of 7TC = 100%.

In conclusion, anionic polymerization of 7TC produces a poly(thiocarbonate) whose structure depends on the initiators used. Polymerization using *t*-BuOK, propagating with thiolate anion, proceeds in a living fashion. We are now investigating the properties of the resulting poly7TC and synthesis of multiarmed poly(thiocarbonate) and block copolymers based on the living character.

Supporting Information Available: Measurement conditions, the ^{1}H and ^{13}C NMR spectra of poly7TC obtained in runs 1 and 8, a figure showing the relationship between M_n and M_w/M_n vs conversion of 7TC, and GPC traces in the postpolymerization experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Imai, Y.; Ueda, M.; Ii, M. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 85.

(2) Podkoscielny, W.; Szubinska, S. *J. Appl. Polym. Sci.* **1988**, *35*, 85.

(3) Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29*, 4811.

(4) Moore, J. A.; Kelley, J. E.; Harpp, D. N.; Back, T. G. *Macromolecules* **1977**, *10*, 718.

(5) Marianucci, E.; Berti, C.; Pilati, F.; Manaresi, P.; Guaita, M.; Chiantore, O. *Polymer* **1994**, *35*, 1564.

(6) Jones, F. N.; Andereades, S. *J. Org. Chem.* **1969**, *34*, 3011.

(7) Kricheldorf, H. R.; Damrau, D.-O. *Macromol. Chem. Phys.* **1998**, *199*, 2589.

(8) Sanda, F.; Kamatani, J.; Endo, T. *Macromolecules* **1999**, *32*, 5715.

(9) Choi, W.; Sanda, F.; Kihara, N.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3853.

(10) Choi, W.; Sanda, F.; Endo, T. *Macromolecules* **1998**, *31*, 9093.

(11) Nemoto, N.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 7229.

(12) Nemoto, N.; Yoshii, K.; Kameshima, H.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 185.

(13) Sanda, F.; Jirakanjana, D.; Hitomi, M.; Endo, T. *Macromolecules* **1999**, *32*, 8010.

(14) Sanda, F.; Jirakanjana, D.; Hitomi, M.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4057.

(15) Nagai, A.; Miyagawa, H.; Kudo, H.; Endo, T. *Macromolecules* **2003**, *36*, 9335.

(16) Nagai, A.; Ochiai, B.; Endo, T. *Chem. Commun.* **2003**, 3018.

(17) Sigwalt, P.; Spassky, S. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: London, 1984; Vol. 2, p 603.

(18) Boileau, S.; Champetier, G.; Sigwalt, P. *Makromol. Chem.* **1963**, *69*, 180.

(19) Ochiai, B.; Yoshii, K.; Nagai, D.; Endo, T. *Macromol. Chem. Phys.*, submitted for publication.

(20) An *n*-hexane solution of *n*-BuLi (21 μL, 54 μmol) was added to a reaction vessel containing 7TC (0.36 g, 2.7 mmol) in purified THF (2.68 mL) at 30 °C under a nitrogen atmosphere. The solution was stirred for 24 h. After a few drops of phosphoric acid in methanol (v/v = 1/9) was added for quenching, the resulting mixture was poured into *n*-hexane. THF-soluble products were obtained by Soxhlet extraction using THF for 8 h. THF-soluble part: ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, δ in ppm): 4.48 ($-\mathrm{C}H_2\mathrm{O}-$, 4H), 1.90 ($-\mathrm{OCH_2}$-$(\mathrm{C}H_2)_2-$, 4H). ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, δ in ppm): 196.2 ($C{=}\mathrm{O}$), 73.2 ($-C\mathrm{H_2O}-$), 28.1, 25.6 ($-\mathrm{OCH_2}(C\mathrm{H_2})_2-$). IR (KBr, cm^{-1}): 1034 (C=S). EA calcd for $\mathrm{C_5H_8O_2S}$: C, 45.43; H, 6.10; S, 24.26. Found: C, 45.61; H, 6.24; S, 24.05. THF-insoluble part: IR (KBr, cm^{-1}): 1035 (C=S). EA calcd for $\mathrm{C_5H_8O_2S}$: C, 45.43; H, 6.10; S, 24.26. Found: C, 45.42; H, 6.28; S, 24.05.

(21) Polymerization was carried out in a similar manner using *t*-BuOK in THF (40 μL, 54 μmol) instead of *n*-BuLi in *n*-hexane. *n*-Hexane-insoluble products were collected as poly7TC (yield 94%). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, δ in ppm): 4.23 ($-\mathrm{C}H_2\mathrm{S}-$, 2H), 2.88 ($-\mathrm{C}H_2\mathrm{O}-$, 2H), 1.75 ($-\mathrm{OCH_2}$-$(\mathrm{C}H_2)_2-$, 4H). ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, δ in ppm): 171.4 ($C{=}\mathrm{S}$), 67.2 ($-C\mathrm{H_2O}-$), 28.1 ($-C\mathrm{H_2S}-$), 26.7, 25.6 ($-\mathrm{OCH_2}$-$(C\mathrm{H_2})_2-$). IR (KBr, cm^{-1}): 1707 (C=O). EA calcd for $\mathrm{C_5H_8O_2S}$: C, 45.43; H, 6.10; S, 24.26. Found: C, 45.61; H, 6.24; S, 24.05.

(22) Isomerization of a five-membered analogue of 7TC, 1,3-dioxoran-2-thione, takes place by treatment with KI. See ref 6. For other catalytic isomerization of thiocarbonyl moieties in thiocarbonates to carbonyl moieties, see refs 23 and 24.

(23) Ko, S. Y. *J. Org. Chem.* **1995**, *60*, 6250.

(24) Tsuda, Y.; Noguchi, S.; Kanemitsu, K.; Sato, Y.; Kakimoto, K. *Chem. Pharm. Bull.* **1997**, *45*, 971.

(25) This kind of difference in the polymerization pathway was also observed in the anionic polymerization of ϵ-thionocaprolactone, in which nucleophilicity of the initiators was discussed. For details see ref 13.

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