Synthesis of Cyclic Polysulfides: Controlled Ring-Expansion Polymerization of Cyclic Tetrathioester with Thiirane

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ABSTRACT: We synthesized cyclic tetrathioesters containing thioester moieties at the *o*-position (*o*-CTE) and *m*-position (*m*-CTE) of an aromatic skeleton. The reaction of phenoxy propylenesulfide (PPS) with *o*-CTE and *m*-CTE was examined using tetrabutylammonium chloride as a catalyst in 1-methyl-2-pyrrolidinone, yielding the corresponding cyclic polysulfides poly[*o*-CTE(PPS)$_n$] with M_n's = 37,000–54,000 at 34–61% yields and poly[*m*-CTE(PPS)$_n$] with M_n's = 46,600–107,200 at 63–>99% yields. Although the molecular weights of poly[*o*-CTE(PPS)$_n$] could not be controlled, those of poly[*m*-CTE(PPS)$_n$] could be controlled by the feed ratios of PPS and reaction temperature. Furthermore, the glass transition temperature (T_g) and thermal decomposition temperature (T_d^i) of poly[*m*-CTE(PPS)$_n$] increased with decreasing molecular weights. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 857–866

KEYWORDS: cyclic polymer; cyclopolymerization; insertion reaction; macrocycles; polysulfides; ring-expansion polymerization; synthesis

INTRODUCTION The synthetic strategies of polymers are usually classified into two categories: chain-growth and step-growth polymerization. However, the synthetic strategies of cyclic polymers cannot belong to either of these categories, because cyclic polymers have no end group. Although the physical properties, such as thermal stability, glass transition temperature, and viscoelastic behavior of cyclic polymers have attractive much attention compared to linear polymers,[1] their detailed examinations have been restricted by the synthetic limitations. Three strategies for the synthesis of cyclic polymers are well known:[2] (1) ring-closure reaction of linear polymers, (2) ring-expansion polymerization of cyclic monomers, and (3) ring-crossover polymerization (ring–ring equilibration) of cyclic monomers. Hocker and Geiser[3] and Toporowski and Roovers[4] independently reported the first synthesis of cyclic polystyrenes by the ring-closure reaction using living polystyrenes containing two reactive end groups. Barner-Kowollik and coworker[5] reported the synthesis of cyclic poly(alkyl acrylates) by the Diels–Alder coupling reaction of two end groups of linear polymers. Recently, Tillman and coworker[6] also reported that cyclic polystyrenes were synthesized by an intramolecular radical coupling reaction using a nitroso radical trap at a high yield. Grayson[7] succeeded in the synthesis of narrow polydispersity cyclic poly(caprolactone) by the cyclic coupling reaction of α-akynyl-ω-azido heterodifunctional polymers. Kricheldorf and coworker[8,9] reported ring-expansion polymerization by the insertion of lactones into cyclic compounds, yielding cyclic polyesters. Waymouth and coworkers[10] reported the synthesis of cyclic polyesters by the ring-expansion polymerization of β-lactone. Shea et al.[11] also examined the synthesis of cyclic polymers using the ring-expansion polymerization of cyclic borane by the insertion of a methylene unit. Grubbs and coworkers[12,13] reported the synthesis of ring-expanded cyclic polymers by a ring-closing metathesis reaction and the physical properties of the cyclic polymers were compared with those of linear polymers. Furthermore, Sanders and coworkers and Otto et al.[14–17] showed that a dynamic covalent chemistry (DCC) system is a very useful approach for the synthesis of well-defined macrocycles at excellent yields. Otsuka and coworkers[18] reported the synthesis of cyclic polyesters by the reversible radical ring-crossover polymerization of a cyclic monomer containing an alkoxyamine bond as a dynamic covalent bond.

Additional Supporting Information may be found in the online version of this article.

Endo and Yamanaka[19] also reported the synthesis of interlocking cyclic polymers by the thermal ring-crossover polymerization of cyclic disulfide.

Meanwhile, Nishikubo and coworkers reported that the insertion of thiirane into thiocarbamate or thioester proceeded in a living-like fashion, yielding well-defined linear polysulfides, respectively.[20–22] Furthermore, these insertion reaction systems were applicable to ring-expansion polymerization for the synthesis of cyclic polymers. The insertion of thiirane into cyclic dithioester[23] or monothiocarbamate[24] was performed, selectively yielding cyclic polysulfides. In the case of cyclic monothiocarbamate,[24] well-defined cyclic polysulfides could be obtained with a narrow polydispersity ratio and a number average molecular weight (M_n) = 8000. However, Vana and Schuetz[25,26] reported that the ratios of polydispersities increased with increasing M_n's by the continuous insertion of thiirane. In the case of cyclic dithioester, various sizes of cyclic polysulfide were obtained due to both the insertion reaction and ring-crossover polymerization. Ring-crossover polymerization is due to the thioester bond as a dynamic covalent bond; that is, the ring size of the cyclic polysulfides is related to the DCC system.[27]

In this article, we focused on the ring-expansion polymerization behavior of thiirane using cyclic tetrathioester compounds for the synthesis of cyclic polysulfides.

EXPERIMENTAL

Materials

1-Methyl-2-pyrrolidinone (NMP) was dried with CaH_2 and purified by distillation before use. Tetrabutylammonium chloride (TBAC), tetraphenylphosphonium chloride (TPPC), magnesium sulfoxide ($MgSO_4$), phthaloyl dichloride, chloroform ($CHCl_3$), methanol, benzene thiol (BT), and triethyl amine were used without further purification.

Measurements

Infrared (IR) ray spectra were taken with a Nicolet 380 FTIR (Thermo Fisher Scientific). The ^{1}H NMR spectra were recorded on JEOL Model JNM α-500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) instruments in $CDCl_3$ using Me_4Si (TMS) as an internal standard reagent for ^{1}H NMR. Matrix-assisted laser desorption ionization time-of flight mass (MALDI-TOF-MS) experiments were performed with AXIMA-CFRplus (Shimazu/Kratos) using dihydroxy benzoic acid as a matrix and $CHCl_3$ as a solvent. The number-average molecular weight (M_n) and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of the polymers were estimated by size exclusion chromatography (SEC) with a Tosoh HLC-8220 SEC instrument equipped with refractive-index and ultraviolet detectors with TSK gel columns (Tskgel SuperHzM-M × 3) in THF as an eluent and calibrated with narrow molecular weight polystyrene standards. The reaction products were separated by preparative HPLC (Nihon Bunseki Kogyo) equipped with two polystyrene gel columns (JAIGEL 1H-40 and 2H-40) using $CHCl_3$ as an eluent. The melting point (mp) was determined by a YANAKO micromelting point apparatus.

Synthesis of Cyclic Tetrathioester (o-CTE)

A mixture of hexadecyl trimethylammonium bromide (HTAB) (0.0240 g, 0.0659 mmol) in water (50 mL) and $CHCl_3$ (300 mL) was prepared. Two solutions of *o*-phthaloyl dichloride (2.01 g, 9.90 mmol) in $CHCl_3$ (66 mL) and 4,4′-thiobisbenzenedithiol (TBBT) (2.48 g, 9.90 mmol) in NaOH (0.810 g, 20.25 mmol) alkaline aqueous solution water (66 mL) were added to the resulting mixture slowly and stirred at 25 °C for 12 h. The organic layer was dried over $MgSO_4$, and concentrated in a rotary evaporator to obtain a solid. The obtained solid was purified by recrystallization from the mixture of $CHCl_3$ and *n*-hexane to obtain a colorless solid (cyclic tetrathioester at *o*-poistion, *o*-CTE).

Yield = 1.25 g (38%). Mp = 289.4–291.3 °C. IR (film, cm^{-1}): 3018 (ν C—H aromatic), 1680 (ν C=O thioester), 1572 and 1475 (ν C=C aromatic), 700 and 659 (ν C—S—C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 7.44 (d, $J = 8.5$ Hz, 8.0 H, aromatic protons of —S-Ar-S—), 7.49 (d, $J_{ab} = 8.5$ Hz, 8.0 H, aromatic protons of —S-Ar-S—), 7.65–7.67 (m, 4.0 H, aromatic protons of —(O)C-Ar-C(O)—), 7.84–7.87 (m, 4.0 H, aromatic protons of —(O)C-Ar-C(O)—). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm): 126.3, 128.4, 131.3, 131.8, 135.2, and 137.0 (aromatic C). MALDI-TOF mass: calcd. for [*o*-CTE ($C_{40}H_{24}O_4S_6$) + Na]$^+$: 782.99, found: 783.10.

Reaction on Insertion of PPS into o*-CTE*

A Typical Procedure

o-CTE (0.0761 g, 0.1 mmol), TBAC (0.0013 g, 0.0046 mmol), and PPS (0.0673 g, 0.405 mmol) were dissolved in NMP (1.0 mL) in a polymerization tube. The tube was cooled, degassed, and sealed, and then the reaction was carried out at 50 °C for 24 h. The reaction mixture was diluted by the addition of $CHCl_3$, poured into methanol to precipitate the solid, and dried *in vacuo* at 25 °C for 24 h. The polymer poly[*o*-CTE(PPS)$_n$] and oligomer *o*-CTE(PPS)$_4$ were separated by HPLC and their structures were confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies, beside MALDI-TOF mass spectroscopy.

Poly[o-CTE(PPS)$_n$]

$M_n = 52{,}000$, $M_w/M_n = 1.71$. IR (film, cm^{-1}): 3062 (ν C—H aromatic), 2928 and 2871 (ν C—H aliphatic), 1783 (ν C=O lactone), 1684 (ν C=O thioester), 1598 and 1495 (ν C=C aromatic), 1241 and 1214 (ν C—O—C), 1097 (ν C—O—Ph), 754 (ν C—S—C sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 3.13–3.44 (broad m, —CH_2—O—), 4.08–4.20 (broad m, —CH_2—S—), 4.44 (broad s, =CH—), 6.70–7.73 (m, aromatic protons).

o-CTE(PPS)$_4$

IR (film, cm^{-1}): 3062 (ν C—H aromatic), 2924 and 2866 (ν C—H aliphatic), 1663 (ν C=O thioester), 1598 and 1496 (ν C=C aromatic), 1239 and 1215 (ν C—O—C), 1098 (ν C—O—Ph), 754 (ν C—S—C sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 3.38–3.51 (m, 8.0H, —CH_2—O—), 4.09–

4.22 (m, 8.0H, —CH_2—S—), 4.52 (d, $J = 10.0$ Hz, 4.0 H, ═CH—), 6.85–6.88 (m, 4.0H, aromatic H), 6.95 (t, $J = 7.5$ Hz, 8.0H, aromatic H), 7.13–7.16 (m, 8.0 H, aromatic H), 7.24–7.26 (m, 8.0H, aromatic H), 7.33 (t, $J = 3.5$ Hz, 8.0H, aromatic H), 7.55 and 7.57 (dd, $J = 5.0$ Hz, 4.0H, aromatic H), 7.71 (d, $J = 4.5$ Hz, 4.0H, aromatic H). MALDI-TOF mass: calcd for [Oligomer ($C_{76}H_{64}O_8S_{10}$) + Na]$^+$: 1447.17, found: 1447.66.

Ring-Crossover Polymerization of *o*-CTE

A Typical Procedure

o-CTE (0.0761 g, 0.1 mmol) and TPPC (0.0018 g, 0.005 mmol) were dissolved in NMP (1.0 mL) in a polymerization tube. The tube was cooled, degassed, and sealed, and then the reaction was carried out at 180 °C for 24 h. The reaction mixture was diluted by the addition of $CHCl_3$, poured into methanol to precipitate a polymer, and dried *in vacuo* at 25 °C for 24 h. The polymer yield was 68%. M_n and M_w/M_n of the obtained polymer were 7400 and 1.06, respectively (Run 5 in Table 2). The structure of the obtained polymer was confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 6.72–7.90 (m, aromatic H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm): 14.2–30.9 (m, quaternary carbon), 126.3–137.1 (m, aromatic carbon), 171.1 (carbonyl of lactone), and 190.4 (carbonyl thioester). IR (film, cm^{-1}): 3013 (ν C—H aromatic), 1772 (ν C═O lactone), 1683 (ν C═O thioester), 1473 (ν C═C aromatic), 741 (ν C—S—C sulfide).

Synthesis of 1,2-Bis(phenyl thioester)benzene

A mixture of BT (2.21 g, 20.1 mmol) and triethylamine (2.02 g, 20.0 mmol) in $CHCl_3$ (40 mL) was prepared. The solution of *o*-phthaloyl dichloride (2.07 g, 10.2 mmol) in $CHCl_3$ (20 mL) was added to the resulting mixture slowly and stirred at 25 °C for 12 h. Then, the mixture was washed with citric acid aqueous solution (0.1 mol/L), saturated $NaHCO_3$ aqueous solution, and water twice, respectively. The separated organic layer was dried over $MgSO_4$, and concentrated in a rotary evaporator to obtain a colorless solid. The obtained solid was purified by recrystallization from the mixture of $CHCl_3$ and *n*-hexane to obtain a colorless solid (1,2-bis(phenyl thioester)benzene, *o*-PTB).

Yield = 2.74 g (77%). IR (film, cm^{-1}): 3052 (ν C—H aromatic), 1692 and 1675 (ν C═O thioester), 1475 (ν C═C aromatic), and 745 (ν C—S—C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 7.42–7.44 (m, 6.0 H, aromatic protons of —S-Ar), 7.51–7.55 (m, 4.0 H, aromatic protons of —S-Ar), 7.60 and 7.64 (dd, $J = 7.5$ Hz, 2.0 H, aromatic protons of —(O)C-Ar-C(O) —), 7.82 and 7.86 (dd, $J = 7.5$ Hz, aromatic protons of —(O)C-Ar-C(O) —). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm): 127.4, 128.4, 129.3, 129.6, 131.6, 134.7, 137.2, and 191.1 (aromatic C).

Synthesis of 1,3-Bis(phenyl thioester)benzene

The reaction of isophthaloyl chloride and BT was carried out in the same way as the synthesis of *o*-PTB. Yield = 27.6%. IR (film, cm^{-1}): 3064 (ν C—H aromatic), 1673 (ν C═O thioester), 1478 (ν C═C aromatic) and 750 (ν C—S—C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 7.47–7.54 (m, 10.0 H, aromatic protons of —S-Ar), 7.62 and 7.65 (dd, $J = 7.5$ Hz, 1.0 H, aromatic protons of —S-Ar), 8.23 and 8.27 (dd, $J = 1.5$ Hz, 2.0 H, aromatic protons of —(O)C-Ar-C(O)—), 8.67 and 8.68 (dd, $J = 1.5$ Hz, aromatic protons of —(O)C-Ar-C(O) —). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm): 126.4, 126.7, 129.4, 129.8, 132.0, 135.0, 137.2, and 189.4 (aromatic C).

Model Reaction of 1,2-Bis(phenyl thioester)benzene and 1,3-Bis(phenyl thioester)benzene

A Typical Procedure

The reaction of *o*-PTB (0.0349 g, 0.202 mmol) was carried out at 120 °C using TPPC as a catalyst for 24 h in the same way as the ring-crossover polymerization of *o*-CTE.

Yield = 0.022 g (64%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 7.13–7.80 (m, aromatic protons). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm): 10.9, 22.8, 23.6, 29.5, 30.2, 38.5, 68.0, 99.1 (aliphtatich carbon), 123.3–148.6 (aromatic C), 167.1 (C═O of lactone moiety), 190.9 (C═O of thioester moiety).

*Synthesis of (5-*tert*-Buthyl)isophythaloyl Dichloride (TID)*

The mixture of (5-*tert*-buthyl)isophthalic (2.22 g, 10.0 mmol) acid, $SOCl_2$ (4.77 g, 40.1 mmol), and DMF (0.0156 g, 0.216 mmol) was stirred at 60 °C for 2 h, and then refluxed for 3 h. The resulting mixture was concentrated by a rotary evaporator to obtain a viscous yellow liquid. The obtained residue was purified by recrystallization from *n*-hexane to obtain a colorless solid (TID).

IR (film, cm^{-1}): 2969 (ν C—H aromatic), 2874 (ν C—H aliphatic), 1765 (ν C═O), 1587 (ν C═C aromatic), 689 (ν C—Cl). ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ (ppm): 1.42 (s, 9.0 H, —CH_3), 8.41 (s, 2.0 H, aromatic protons), 8.70 (s, 1.0 H, aromatic proton). ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ (ppm): 31.0 (—CH_3), 35.3 (═C═), 131.7, 134.1, 134.2, and 153.9 (aromatic carbon), 167.6 (C═O).

Synthesis of Cyclic Tetrathioester m-*CTE*

A mixture of triethyl amine (0.608 g, 6.01 mmol) in CH_2Cl_2 (2.9 L) was prepared. Two solutions of TID (0.779 g, 3.01 mmol) in CH_2Cl_2 (40 mL) and TBBT (0.753 g, 3.01 mmol) in CH_2Cl_2 (40 mL) were added to the resulting mixture slowly and stirred at 25 °C for 40 h. The mixture was then concentrated in a rotary evaporator and washed with water. The organic layer was dried over $MgSO_4$, and then concentrated in a rotary evaporator to obtain a white solid.

Yield = 0.25 g (25%). IR (film, cm^{-1}): 2955 (ν C—H aliphatic), 1696 and 1673 (ν C═O thioester), 1476 (ν C═C aromatic), 731 (ν C—S—C). ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ (ppm): 1.56 (s, 18.0H, —CH_3), 7.26–7.44 (m, 16.0 H, aromatic protons), 8.13 (s, 4.0 H, aromatic proton), 8.27 (s, 2.0 H, aromatic proton). MALDI-TOF mass: calcd. for [*m*-CTE ($C_{48}H_{40}O_4S_6$) + Na]$^+$: 895.13, found: 894.67.

Ring-Crossover Polymerization of *m*-CTE

A Typical Procedure

m-CTE (0.0342 g, 0.0392 mmol) and TBAC (0.0013 g, 0.0046 mmol), were dissolved in NMP (0.5 mL) in a polymerization tube. The tube was cooled, degassed, and sealed, and then the reaction was carried out at 50 °C for 24 h. The reaction mixture was diluted by the addition of $CHCl_3$, poured into methanol to precipitate a polymer, and dried *in vacuo* at 25 °C for 24 h. The polymer yield was 93%. M_n and M_w/M_n of the obtained polymer were 6990 and 1.93, respectively. The structure of the obtained polymer was confirmed by ^1H NMR and IR spectroscopies.

^1H NMR (600 MHz, $CDCl_3$, TMS) δ (ppm): 1.40–1.52 (m, —CH_3), 7.39–7.57 and 8.13–8.51 (m, aromatic H). IR (film, cm^{-1}): 3077 (ν C—H aromatic), 2956 and 2904 (ν C—H aliphatic), 1695 and 1672 (ν C=O thioester), 1475 (ν C=C aromatic), 731 (ν C—S—C sulfide).

Reaction of PPS on Insertion into *m*-CTE

A Typical Procedure

m-CTE (0.0349 g, 0.0399 mmol), TBAC (0.0013 g, 0.0046 mmol), and PPS (0.0265 g, 0.159 mmol) were dissolved in NMP (0.2 mL) in a polymerization tube. The tube was cooled, degassed, and sealed, and then the reaction was carried out at 50 °°C for 24 h. The reaction mixture was diluted by the addition of $CHCl_3$ and poured into methanol to precipitate a polymer and dried *in vacuo* at 25 °C for 24 h. The structure of the obtained polymer was confirmed by ^1H NMR, ^{13}C NMR, and IR spectroscopies. Yield = 0.0436 g (71%). $M_n = 46{,}700$, $M_w/M_n = 1.78$. IR (film, cm^{-1}): 3063 (ν C—H aromatic), 2964 and 2871 (ν C—H aliphatic), 1661 (ν C=C thioester), 1496 (ν C=C aromatic), 1239 (ν C—O—C), 752 (ν C—S-C). ^1H NMR (600 MHz, $CDCl_3$, TMS) δ(ppm): 1.36 (s, -CH_3), 3.45–3.48 (m, methylene proton of -CH_2-OPh), 4.16–4.28 (m, methylene proton of -CH_2-S), 4.50–4.51 (m, methine proton of >CH-), 6.88–7.37 (m, aromatic proton), 8.15 (s, aromatic proton), 8.35 (aromatic proton).

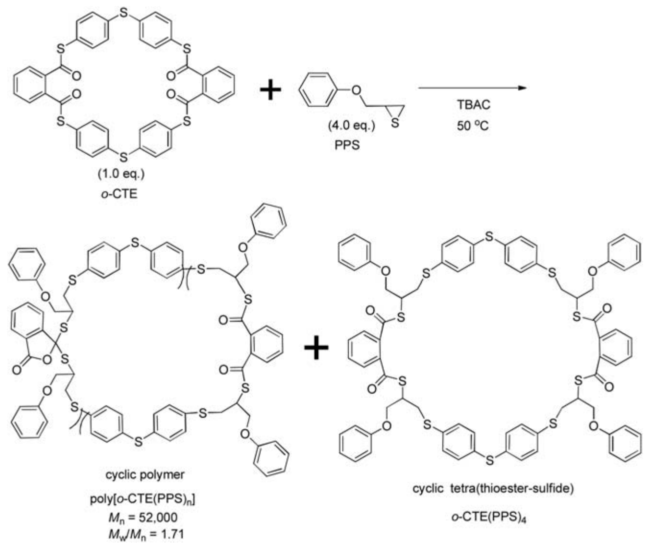
RESULT AND DISCUSSION

Reaction of Thiirane on Insertion into Cyclic Tetrathioester *o*-CTE

Equivalent Reaction of PPS and o-CTE

A cyclic tetrathioester (*o*-CTE) was synthesized by the condensation reaction of phthaloyl dichloride and 4,4'-thiobisbenzenedithiol, and its structure was confirmed by ^1H NMR, ^{13}C NMR, IR, and MALDI-TOF mass spectroscopies. *o*-CTE has a cyclic skeleton and four thioester moieties in a molecule. If the continuous insertion of PPS into *o*-CTE can proceed in a living-like fashion, well-defined cyclic polysulfides can be synthesized.

At first, we examined the reaction on the insertion of PPS (4 mmol) into *o*-CTE (1 mmol) with an equivalent feed ratio in the presence of TBAC as a catalyst for 24 h in NMP at 50 °C (Scheme 1). SEC profiles of the obtained products showed multimodal peaks, and a corresponding polymer at a retention time = 7–9 min with $M_n = 52{,}000$ ($M_w/M_n = 1.71$) and an oligomer with $M_n = 910$ ($M_w/M_n = 1.07$) at a retention time = 10.5 min as shown in Figure 1. The conversion of PPS was calculated by ^1H NMR spectroscopy to be 53%.



SCHEME 1 Reaction of *o*-CTE and PPS.

The synthesized polymer and oligomer were separated by HPLC and each structure was confirmed by IR, ^1H NMR, and MALDI-TOF mass spectroscopies. From ^1H NMR spectra of the separated polymer, the peaks at 3.13–3.44 and 4.08–4.20 ppm assignable to methylene protons of —O—CH_2— and —S—CH_2— moieties were seen, indicating these are produced by the insertion of PPS into thioester moieties [Supporting Information Fig. S1(a,b)]. The degree of insertion of PPS into cyclic *o*-CTE could be calculated by the integration ratios of aromatic protons and methylene protons to be 95% (DI = 95). In IR spectra of this polymer, a new peak was seen at 1783 cm^{-1}. Except for this peak, the other peaks of the separated polymer were almost the same as those of *o*-CTE [Supporting Information Fig. S2(a,b)]. The peak at 1783 cm^{-1} might be assignable to the ester moiety. This means that an intracyclization reaction might proceed during the insertion of PPS into *o*-CTE to produce cyclic lactone moieties in the corresponding polymer poly[*o*-CTE$(PPS)_n$], as shown in Scheme 1.

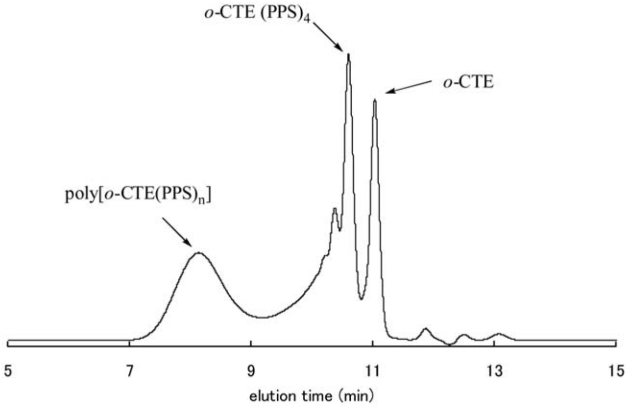


FIGURE 1 SEC profiles (elution; THF) of the products by the insertion of 4 equiv of PPS into *o*-CTE.

TABLE 1 Insertion Reaction of PPS with Cyclic *o*-CTE[a]

	Feed Ratio		Polymer[c]		
Run	PPS/*o*-CTE	Conv. (%)[b]	Yield (%)	M_n (M_w/M_n)[d]	DI (%)[e]
1	4	53	34	54,000 (1.67)	95
2	8	>99	51	37,000 (1.63)	>99
3	12	83	52	33,000 (1.64)	>99
4	24	34	51	38,000 (1.60)	>99
5	32	35	61	47,000 (1.72)	>99

[a] The reaction of PPS and *o*-CTE was carried out using TBAC as a catalyst in NMP at 50 °C for 24 h.
[b] Calculated by ^{1}H NMR.
[c] Methanol insoluble part.
[d] Estimated by SEC based on polystyrene standards; eluent: a solution of LiBr and phosphoric acid (20 mM) in DMF.
[e] The degree of insertion of PPS into *o*-CTE (DI) was calculated from ^{1}H NMR data (see text).

Furthermore, in the case of a separated oligomer, the ^{1}H NMR spectrum showed peaks at 3.38–3.51, 4.09–4.22, and 4.52 ppm assignable to methylene protons of $—CH_2O—$, methylene protons of $—CH_2—S—$, and methine protons of $=CH—$, respectively [Supporting Information Fig. S1(c)]. In IR analysis, no peak assignable to cyclic lactone moieties was seen [Supporting Information Fig. S2(c)]. The MALDI-TOF mass spectrum of this oligomer after Na^+ doping showed a mass parent peak at 1447.66 which correspond to the mass of a cyclic tetra(thioester-sulfide) *o*-CTE(PPS)$_4$, as shown in Scheme 1 (Supporting Information Fig. S3). These indicate that, although *o*-CTE(PPS)$_4$ was synthesized by the insertion of 4 equiv of PPS into 1 equiv of *o*-CTE, another reaction occurred to produce cyclic polysulfide poly[*o*-CTE(PPS)$_n$] containing cyclic lactone moieties in the main chain.

Insertion Reaction of PPS and *o*-CTE in the Certain Feeds Ratios

Based on the aforementioned results, another reaction might proceed in the equivalent insertion of PPS with *o*-CTE to give cyclic polysulfides. We examined the effects of feeds ratios in the insertion reaction of PPS with *o*-CTE. These conditions and results are summarized in Table 1.

The corresponding polymers with M_ns = 33,000–47,000 were obtained at 51–61% yields (Runs 2–5 in Table 1). Although almost all thioester moieties in *o*-CTE converted in all cases (>99%), the conversions of PPS decreased with an increase in the feed-ratios of PPS. ^{1}H NMR and IR spectroscopies of the corresponding polymers also indicated that cyclic polymers poly[*o*-CTE(PPS)$_n$] contained cyclic lactone moieties in the main chain. This might be because intracyclization occurred during the insertion reaction of PPS to produce the cyclic lactone moieties, and then the insertion reaction with PPS could not proceed. As a result, the values of M_n's of the obtained cyclic polysulfides were independent of the feeds ratios of PPS and could not be controlled.

Ring-Crossover Polymerization of *o*-CTE

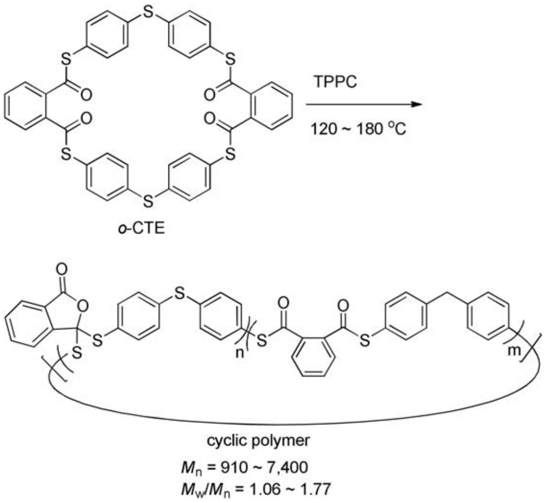
To confirm the intracyclization of thioester moieties in *o*-CTE, the ring-crossover polymerization of *o*-CTE was examined (Scheme 2). When the reaction of PPS was carried out in the presence of quaternary onium salts as catalysts in NMP at temperatures in the range between 50 and 180 °C, the corresponding oligomers and polymers with M_n's = 910–7,400 were obtained at 64–78% yields more than at 120 °C (Runs 3–5 in Table 2). However, no reaction proceeded at lower reaction temperatures (Runs 1–2 in Table 2). These results are summarized in Table 2.

The structures of the obtained products were confirmed by IR and ^{1}H NMR spectroscopies. Although their ^{1}H NMR spectra mostly coincided with that of *o*-CTE, their IR spectra showed peaks around 1780 cm^{-1} [Supporting Information Figs. S1(d) and S2(d)] assignable to cyclic lactone moieties. These indicate that the intracyclization of thioester moieties

TABLE 2 Ring-Crossover Polymerization of *o*-CTE[a]

Run	Temperature (°C)	Catalyst	Yield (%)[b]	M_n (M_w/M_n)[c]
1	50	TBAC	–[d]	–[d]
2	70	TBAC	–[d]	–[d]
3	120	TPPC	64	1,220 (1.58)
4	150	TPPC	78	910 (1.77)
5	180	TPPC	68	7,400 (1.06)

[a] The reaction of *o*-CTE was carried out in NMP for 24 h.
[b] Methanol-insoluble part.
[c] Estimated by SEC based on polystyrene standards; eluent: a solution of LiBr and phosphoric acid (20 mM) in DMF.
[d] Not determined.

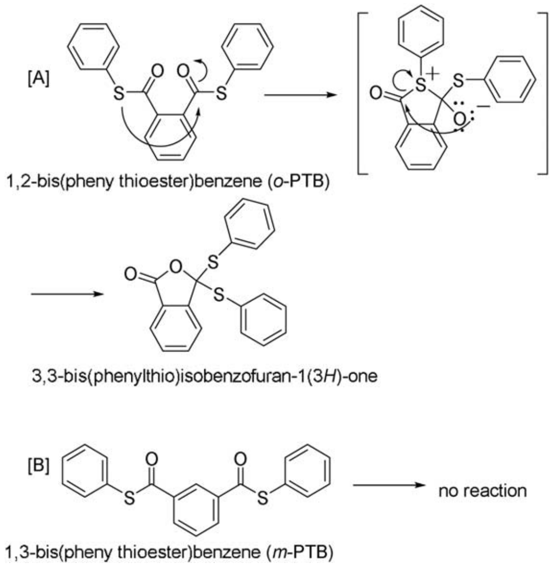


SCHEME 2 Ring-crossover polymerization of *o*-CTE.

proceeded to yield cyclic lactone moieties during ring-crossover polymerization as shown in Scheme 2. After the cyclic lactone moieties were produced, ring-crossover polymerization could not proceed. In our previous report, the ring-crossover polymerization of cyclic-dithioester afforded the corresponding cyclic polythioester and their molecular weights were consistent with the reaction temperatures.[24] However, in the case of *o*-CTE, M_n could not be controlled due to intracyclization occurring during ring-crossover polymerization.

Model Reaction of 1,2-Bis(phenyl thioester)benzene and 1,3-bis(phenyl thioester)benzene

Next, we examined the model reaction using *o*-PTB and 1,3-bis(phenyl thioester)benzene (*m*-PTB) under the same reaction conditions for the insertion reaction of PPS with *o*-CTE (Scheme 3). In the case of *o*-diphenyl dithioester *o*-PTB, intracyclization proceeded to produce a cyclic lactone moiety. However, in the case of *m*-diphenyl thioester *m*-PTB, no reaction proceeded. These mean that the cyclic lactone moiety was produced by the intracyclization of neighboring thioester groups as shown in Scheme 3.



SCHEME 3 Model reaction of *o*-PTB and *m*-PTB.

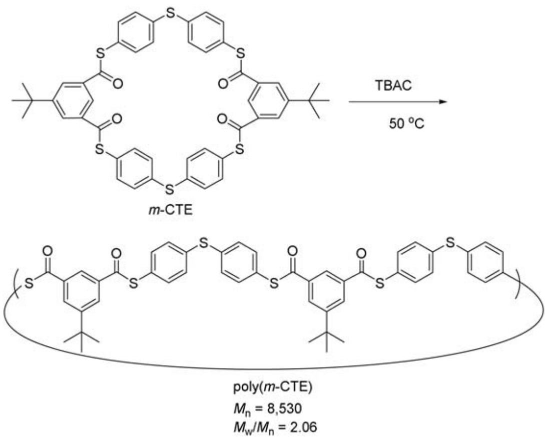
Ring-Crossover Polymerization of *m*-CTE

To avoid the intracyclization of thioester groups, we designed and synthesized a new cyclic tetrathioester (*m*-CTE) containing thioester moieties at the *m*-position of the aromatic moiety. The ring-crossover polymerization of *m*-CTE was carried out in the presence of TBAC as a catalyst in NMP at 50 °C for 24 h, yielding the corresponding polymer poly(*m*-CTE) with $M_n = 6990$ ($M_w/M_n = 1.93$) at 51% yield. The structure of poly(*m*-CTE) was confirmed by ^{1}H NMR and IR spectroscopies. The ^{1}H NMR spectrum of poly(*m*-CTE) showed that poly(*m*-CTE) had the same repeating unit of *m*-CTE. In the IR spectra, no peak at about 1780 cm^{-1} was seen, indicating that the product had no cyclic lactone moiety. This means that intracyclization between thioester moieties did not occur and only thioester-exchanging reactions proceeded, yielding corresponding cyclic polythioester poly(*m*-CTE), as shown in Scheme 4.

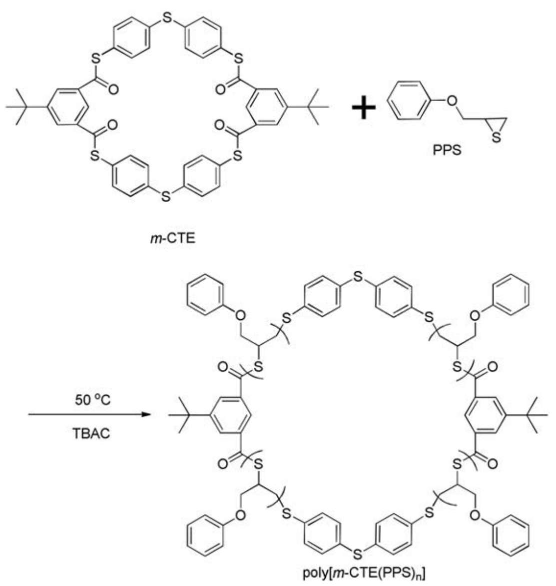
Insertion Reaction of PPS and *m*-CTE

Furthermore, the insertion reaction of PPS with *m*-CTE was examined at the various feed ratios in the range of *m*-CTE / PPS = 1/4–1/34, yielding polymers with M_n = 46,700–100,500 and M_w/M_n = 1.78–2.48 (Scheme 5). These conditions and results are summarized in Table 3. The SEC profiles of these polymers showed unimodal peaks, as presented in Figure 2.

Their structures were also confirmed by IR and ^{1}H NMR spectroscopies. Figures 3 and 4 depict the ^{1}H NMR and IR spectra of the obtained polymer with M_n = 46,700 (Run 1 in Table 3) along with *m*-CTE. ^{1}H NMR spectra showed the peaks at 3.45–3.48 and 4.16–4.28 ppm assignable to methylene protons of —O—CH_2— and —S—CH_2— moieties, and the peaks at 4.51 ppm assignable to methine protons of ═CH— (Fig. 3). Furthermore, its IR spectrum showed no peak at about 1780 cm^{-1} assignable to the cyclic lactone moiety



SCHEME 4 Ring-crossover polymerization of *m*-CTE.



SCHEME 5 Reaction of *m*-CTE and PPS.

(Fig. 4). These indicate that the intraexchange reaction of thioester moieties to produce cyclic lactone moieties did not occur on the insertion of PPS into *m*-CTE. Thus, cyclic polysulfide poly[*m*-CTE(PPS)$_n$] with a unimodal peak, as shown in SEC, could be obtained by the ring crossover polymerization and insertion reaction of PPS.

Figure 5 also depicts the relationships among M_n, DI, and feed ratios on the continuous insertion of PPS into *m*-CTE. Although DI values were consistent with the feed ratios of PPS, the values of M_n's were almost the same, at 50,000 in the feed ratios of PPS/*m*-CTE = 1/1–16/1 (Runs 1–3 in Table 3), and then increased with increasing feed ratios of PPS (Runs 3–5 in Table 3). When the feed ratios of PPS were lower, ring-crossover polymerization occurred frequently under thermodynamic control. After that, its molecular weight increased with increasing feed ratios of PPS, indicating that the cyclic polymers could be synthesized under kinetic control. These mean that the ring-expansion polymerization of *m*-CTE with PPS could be controlled by the feed ratios.

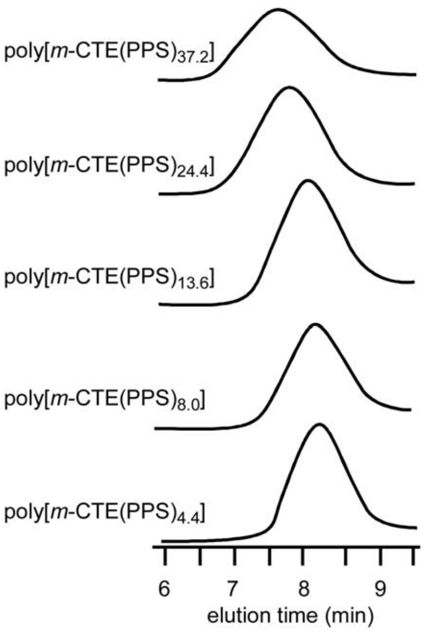


FIGURE 2 SEC profiles (elution; THF) of the products by the insertion of PPS into *m*-CTE.

Furthermore, the effect of reaction times and temperatures on the ring-expansion polymerization of PPS into *m*-CTE in the feed ratios of *m*-CTE/PPS = 1/4 and 1/32. These conditions and results are summarized in Table 4.

When its ring-expansion polymerization was performed at temperatures in the range between 50 and 90 °C, the molecular weights of poly[(*m*-CTE(PPS)$_n$] decreased with increasing reaction temperatures (Runs 1–6 in Table 4). This suggests that ring-crossover polymerization proceeded under thermodynamic control to give more stable cyclic polysulfides. Furthermore, this ring expansion polymerization was examined at 50 °C for a longer reaction time. As the result, the corresponding poly[*m*-CTE(PPS)$_n$] ($n = 5.2$) could be obtained with $M_n = 48{,}700$ at 75% yield (Run 7 in Table 4), that is, M_n could not be markedly increased by the longer reaction time. Consequently, higher molecular weight poly[*m*-CTE(PPS)$_n$] could be obtained at lower reaction temperatures.

TABLE 3 Insertion Reaction of PPS with *m*-CTE at 50 °C for 24 h at Various Feeds Ratios[a]

Run	PPS/*m*-CTE	Conv.[b] (%)	Yield[c] (%)	M_n (M_w/M_n)[d]	DP$_n$[e]
1	4	98	71	46,700 (1.78)	4.4
2	8	73	63	46,600 (1.91)	8.0
3	16	72	67	50,400 (2.17)	13.6
4	24	88	85	85,100 (2.24)	24.4
5	34	91	91	100,500 (2.48)	37.2

[a] The reaction of PPS and *m*-CTE was carried out using TBAC as a catalyst in NMP.
[b] Calculated by SEC.
[c] Methanol-insoluble part.
[d] Estimated by SEC based on polystyrene standards; eluent: a solution of LiBr and phosphoric acid (20 mM) in DMF.
[e] The degree of insertion of PPS into *m*-CTE (DI) was calculated from ^{1}H NMR data (see text).

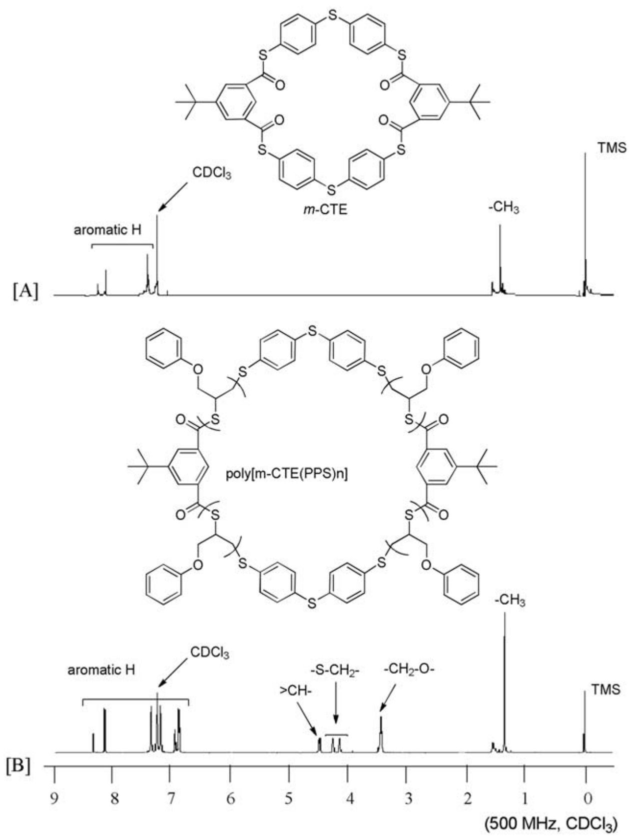


FIGURE 3 ^{1}H NMR spectra of *m*-CTE and poly[*m*-CTE(PPS)$_n$].

Physical Properties of Cyclic and Linear Polysulfides

Cyclic polymers have no end group and are expected to show some characteristic physical properties in comparison with linear polymers.[28] A linear polysulfide containing similar units of poly[*m*-CTE(PPS)$_n$] can be synthesized easily by the anionic polymerization of PPS. We examined the reaction of PPS in the presence of TBAC in NMP at 90 °C for 24 h, yielding corresponding polysulfide polyPPS with $M_n = 102{,}600$ and $M_w/M_n = 2.66$ at 70% yield. The weight average molecular weights [$M_{w(MALLS)}$] of polyPPS, poly[*m*-CTE(PPS)$_{4.4}$], and poly[*m*-CTE(PPS)$_{30.8}$] were also measured by MALLS. Table 5 summarizes the results regarding the molecular weights of these polymers and their thermal properties. The $M_{w(MALLS)}$ was in the range between 173,100 and 380,700. The ratios of $M_{w(SEC)}/M_{w(MALLS)}$ of poly[*m*-CTE (PPS)$_{4.4}$], poly[*m*-CTE(PPS)$_{30.8}$], and polyPPS were 0.48, 0.68, and 0.83, respectively. These values depended on the excluded volume effect in the synthesized polymers, that is, a lower molecular weight cyclic polymer has a larger excluded volume effect due to its cyclic structure. Furthermore, the glass transition temperature (T_g) and initial decomposition temperature ($T_d{}^i$) were also determined. The values of T_g and $T_d{}^i$ of poly[*m*-CTE(PPS)$_{4.4}$] were larger than those of poly[*m*-CTE(PPS)$_{30.8}$] and polyPPS (Table 5). These results might be because the degree of PPS in poly[*m*-CTE(PPS)$_{30.8}$] is too long, and its morphological properties might be similar to those of linear polysulfide polyPPS. This means that the characteristic physical properties based on cyclic structures might be consistent with the molecular weight.

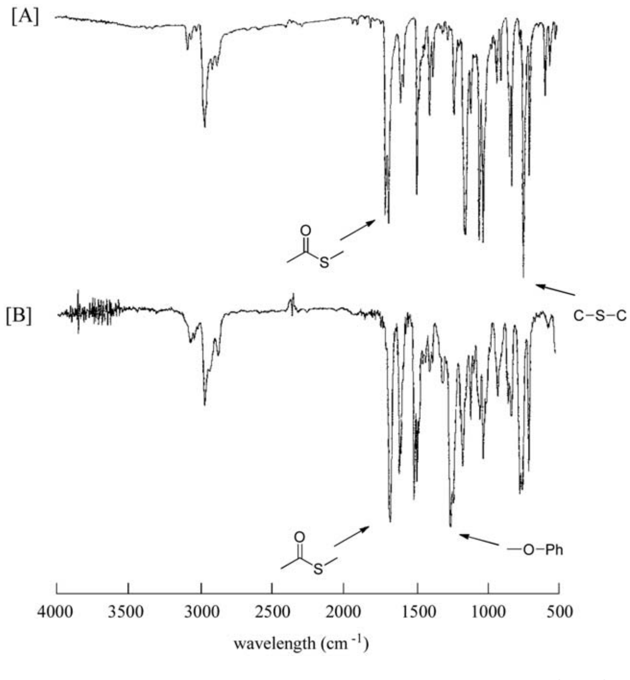


FIGURE 4 IR spectra of [A] *m*-CTE and [B] poly[*m*-CTE(PPS)$_n$].

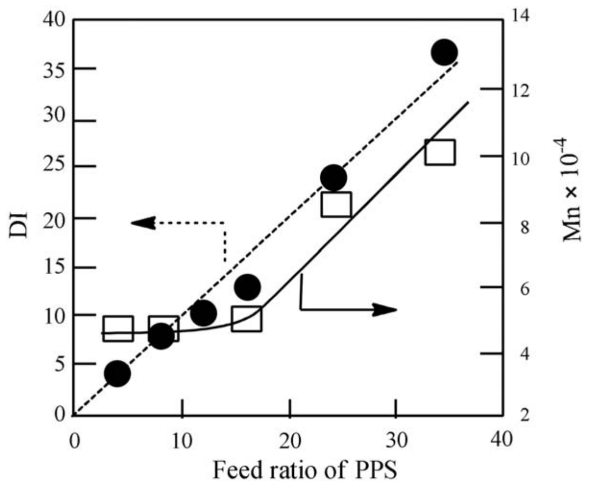


FIGURE 5 Relationships of DI (degree of insertion of PPS), M_n, and feed ratios of PPS on ring-expansion polymerization of PPS with *m*-CTE.

CONCLUSIONS

We examined the reaction on the insertion of PPS into the cyclic tetrathioesters *o*-CTE and *m*-CTE. When the insertion of PPS into *o*-CTE was performed using TBAC as a catalyst in NMP at 50 °C for 24 h, both the intracyclization of thioester groups and ring-crossover polymerization proceeded, and cyclic polysulfides poly[*o*-CTE(PPS)$_n$] containing cyclic lactone moieties with M_n's = 37,000–54,000 were synthesized

TABLE 4 Effect of the Reaction Time and Temperature on Insertion Reaction of PPS with *m*-CTE[a]

Run	Reaction Time (h)	Reaction Temperature (°C)	Feed ratio	Conv.[b] (%)	Yield[c] (%)[a)]	M_n (M_w/M_n)[d]	DP$_n$[e]
			m-CTE/PPS				
1	24	50	1/4	98	71	46,700 (1.78)	4.4
2		70		>99	72	45,700 (1.76)	5.2
3		90		>99	78	36,200 (2.18)	4.8
4	24	50	1/32	91	91	100,500 (2.48)	37.2
5		70		90	90	107,200 (2.44)	30.8
6		90		>99	91	61100 (5.00)	38.0
7	192	50	1/4	>99	75	48,700 (1.81)	5.2

[a] The reaction of PPS and *m*-CTE was carried out using TBAC as a catalyst in NMP.
[b] Calculated by SEC.
[c] Methanol-insoluble part.
[d] Estimated by SEC based on polystyrene standards; eluent: a solution of LiBr and phosphoric acid (20 mM) in DMF.
[e] The degree of insertion of PPS into *m*-CTE (DI) was calculated from ^{1}H NMR data (see text).

TABLE 5 Molecular Weight and Thermal Properties of Poly[*m*-CTE(PPS)$_n$] and PolyPPS

Run	Polymers	Morphology	$M_{w\ (SEC)}$[c]	$M_{w\ (MALLS)}$[d]	$M_{w(SEC)}/M_{w\ (MALLS)}$	T_g[e] (°C)	T_d[if] (°C)
1	Poly[*m*-CTE(PPS)$_{4.4}$][a]	Cyclic	82,830	173,100	0.48	81	231
2	Poly[*m*-CTE(PPS)$_{30.8}$][b]	Cyclic	257,910	380,700	0.68	28	199
3	PolyPPS	Linear	272,770	328,100	0.83	20	208

[a] Poly[*m*-CTE(PPS)$_{4.4}$] was obtained in run 1 in Table 3.
[b] Poly[*m*-CTE(PPS)$_{30.8}$] was obtained in run 5 in Table 4.
[c] Estimated by SEC based on polystyrene standards; eluent: a solution of LiBr and phosphoric acid (20 mM) in DMF.
[d] Determined by MALLS.
[e] Measured by DSC.
[f] Measured by TGA.

at 34–61% yields, and their molecular weights could not be controlled. In the case of the reaction of PPS and *m*-CTE, insertion reaction of PPS into *m*-CTE proceeded smoothly without intracyclization of thioester groups. With the supply of PPS and *m*-CTE, the molecular weight of the corresponding polysulfides could be controlled, yielding poly[*m*-CTE(PPS)$_n$] with M_n's = 46,600–107,200 in 63–>99% yields. The absolute molecular weights ($M_{w(MALLS)}$) of the cyclic polysulfides (poly[*m*-CTE(PPS)$_{4.4}$], $M_n = 46{,}700$, poly[*m*-CTE(PPS)$_{30.8}$], $M_n = 107{,}200$) and linear polysulfide (polyPPS, $M_n = 102{,}600$) were also determined by MALLS, and the ratio of $M_{w(SEC)}/M_{w(MALLS)}$ of poly[*m*-CTE(PPS)$_{4.4}$] was larger than for any other polymer. The glass transition temperature (T_g) and initial decomposition temperature (T_d^i) of poly[*m*-CTE(PPS)$_{4.4}$] were largest in all synthesized polymers, that is, a lower molecular weight cyclic polymer could show a characteristic physical property due to its cyclic skeleton.

REFERENCES AND NOTES

1 K. Endo, In New Frontiers in Polymer Synthesis; S. Kobayashi, Ed.; Springer: Berline/Heidelberg, **2008**; Vol. *217*, p 121.

2 H. R. Kricheldorf, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 251–284.

3 D. Geiser, H. Hocker, *Macromolecules* **1980**, *13*, 653–656.

4 J. Roovers, P. M. Toporowski, *Macromolecules* **1983**, *16*, 843–849.

5 M. Glassner, J. P. Blinco, C. Barner-Kowollik, *Macromol. Rapid Commun.* **2011**, *32*, 724–728.

6 A. F. Voter, E. S. Tillman, P. M. Findeis, S. C. Radzinski, *ACS Macro Lett.* **2012**, *1*, 1066–1070.

7 J. N. Hoskins, S. M. Grayson, *Macromolecules* **2009**, *42*, 6406–6413.

8 H. R. Kricheldorf, S. R. Lee, N. Schittenhelm, *Macromol. Chem. Phys.* **1998**, *199*, 273–282.

9 H. R. Kricheldorf, S. Eggerstedt, *Macromol. Chem. Phys.* **1998**, *199*, 283–290.

10 W. Jeong, J. L. Hedrick, R. M. Waymouth, *J. Am. Chem. Soc.* **2007**, *129*, 8414–8415.

11 K. J. Shea, H. D. Zhu, J. Walker, M. Paz, J. Greaves, *J. Am. Chem. Soc.* **1997**, *119*, 9049–9050.

12 C. W. Lee, T. L. Choi, R. H. Grubbs, *J. Am. Chem. Soc.* **2002**, *124*, 3224–3225.

13 C. W. Bielawski, D. Benitez, R. H. Grubbs, *Science* **2002**, *297*, 2041–2044.

14 P. T. Corbett, L. H. Tong, J. K. M. Sanders, S. Otto, *J. Am. Chem. Soc.* **2005**, *127*, 8902–8903.

15 S. Otto, R. L. E. Furlan, J. K. M. Sanders, *Science* **2002**, *297*, 590–593.

16 R. T. S. Lam, A. Belenguer, S. L. Roberts, C. Naumann, T. Jarrosson, S. Otto, J. K. M. Sanders, *Science* **2005**, *308*, 667–669.

17 S. Otto, S. Kubik, *J. Am. Chem. Soc.* **2003**, *125*, 7804–7805.

18 G. Yamaguchio, Y. Higaki, H. Otsuka, A. Takahara, *Macromolecules* **2005**, *38*, 6316–6320.

19 K. Endo, T. Yamanaka, *Macromolecules* **2006**, *39*, 4038–4043.

20 A. Kameyama, M. Kiyota, T. Nishikubo, *Tetrahedron Lett.* **1994**, *35*, 4571–4574.

21 A. Kameyama, K. Shimotsuma, T. Nishikubo, *Macromol. Rapid. Commun.* **1994**, *15*, 335–342.

22 H. Kudo, K. Sato, T. Nishikubo, *Macromolecules* **2010**, *43*, 9655–9659.

23 H. Kudo, M. Sato, R. Wakai, T. Iwamoto, T. Nishikubo, *Macromolecules* **2010**, *41*,521–523.

24 H. Kudo, S. Makino, A. Kameyama, T. Nishikubo, *Macromolecules* **2005**, *38*, 5964–5969.

25 J. H. Schuetz, P. Vana, *Macromol. Chem. Phys.* **2011**, *212*, 1263–1275.

26 J. H. Schuetz, P. Vana, *Macromol. Chem. Phys.* **2013**, *214*, 1484–1495.

27 H. Kudo, S. Makino, A. Kameyama, T. Nishikubo, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 680–687.

28 T. E. Hogen-Esch, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 2139–2155.