Synthesis of Cyclic Polymers: Ring-Expansion Reaction of Cyclic *S*-Dithioester with Thiiranes

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ABSTRACT: The ring-expansion reaction of equimolar cyclic dithioester **1** with 3-phenoxypropyrene sulfide (PPS) (cyclic dithioester **1**/PPS = 1/2) was examined in the presence of TBAC as a catalyst in NMP for 24 h. It was found that intermolecular ester-exchange reaction occurred during the insertion reaction of PPS into cyclic dithioesters, and cyclic polymers with M_ns = 3600−8900 were obtained in 80−96% yields. The structures of the obtained cyclic polymers were confirmed by the ^{1}H NMR, ^{13}C NMR IR, and MALDI TOF-MS spectroscopy. The continuous insertion reaction of excess PPS into cyclic dithioester (cyclic dithioester **1**/PPS = 1 /50) was also examined, and it was found that the insertion reaction proceeded quantitatively to afford the corresponding cyclic polysulfide with M_n = 42 000 and M_w/M_n = 4.50 in a 96% yield.

Introduction

Nonlinear compounds, such as cyclic polymers, star polymers, hyperbranched polymers, dendrimers, catenanes, and rotaxanes, have attracted much attention. This is because their unique structures often result in unusual physical behavior such as extreme thermal or viscoelastic behavior, high densities, and unique solubility characteristics. As a result, new applications are expected to arise from these materials. Furthermore, a variety of synthetic methods for these materials have been reported. In the case of cyclic polymers, two strategies for their syntheses are well-known. One is the ring-closure reaction of linear compounds with difunctional groups at the ends. Hocker[1] and Toporowski et al.[2] reported independently the first synthesis of the cyclic polystyrenes by the ring-closure reaction of a living α,ω-dicarbanionic polystyrene with dibromo-*p*-xylene and dimethyldichlorosilane, respectively, under highly diluted conditions. Recently, Tezuka et al.[3−5] reported the highly selective synthesis of multicyclic polymers by the reliant on electrostatic self-assembly. The another method for the synthesis of cyclic polymers is the ring-expansion polymerization of cyclic compounds. Kricheldorf et al.[6,7] succeeded the synthesis of the cyclic polyesters by the insertion reaction of lactones with cyclic compounds containing stannum. Shea et al.[8,9] also examined the synthesis of cyclic polymers by the polyhomologation reaction of cyclic compounds containing borane atoms. More recently, Grubbs et al.[10,11] reported the synthesis of the ring-expanded cyclic polymers by the ring-closing metathesis reaction. Furthermore, comparison of the physical properties of the cyclic and linear polymers was examined.[11]

Meanwhile, Nishikubo et al.[12] have developed the ring-opening reaction of thiiranes with esters. These reactions proceeded smoothly and regioselectively in the presence of quaternary onium salts as catalysts to afford the corresponding thioesters in high yields.[12] Furthermore, they achieved the synthesis of the linear polysulfides by the acyl transfer polymerization of thiiranes with thioesters (Scheme 1).[13]

In this system, the continuous insertion reaction of thiiranes into thioester moieties proceeded in living like fashion, affording the corresponding polysulfides with narrow molecular weight distribution.

Therefore, in this time, we designed and examined a new approach for the synthesis of cyclic polymers with controlled the ring size by the ring-expansion reaction of the cyclic dithioester **1** with 3-phenoxypropyrene sulfide (PPS) as shown in Scheme 2. Through this ring-expansion reaction, we provided a foundation for synthesizing cyclic polymers.

Experimental Section

Materials. 1-Methyl-2-pyrrolidone (NMP) was dried with CaH_2 and was purified by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized from dried ethyl acetate. Tetrabutylammonium chloride (TBAC) and tetraphenylphosphonium chloride (TPPC) were used without further purification. Cesium carbonate (Cs_2CO_3), tetrahydrofuran (THF), ethyl acetate, chloroform ($CHCl_3$), and *n*-hexane were used without further purification.

Measurements. Infrared (IR) spectra were measured on a Jasco model IR-420 spectrometer. 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 $CDCl_3$ and DMSO-d_6 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 on a Shimazu/Kratos MALDI−TOF-MS using dihydroxybenzoic acid as matrix and chloroform as solvent. The number-average molecular weight (M_{nSEC}) 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 Toso HLC-8220 SEC instrument equipped with refractive index and ultraviolet detectors with TSK gel columns [with a solution of LiBr and phosphoric acid (20 mM) in DMF as an eluent] and calibrated with narrow molecular weight polystyrene standards.

The Equivalent Reaction of Cyclic Dithioester 1 with PPS. *A Typical Procedure*: Cyclic dithioester (0.073 g, 0.2 mmol as dithioester groups), PPS (0.033 g, 0.2 mmol), and TBAC (0.003 g, 0.002 mmol) were dissolved in NMP (0.25 mL) in a polymerization tube. The tube was cooled, degassed, and

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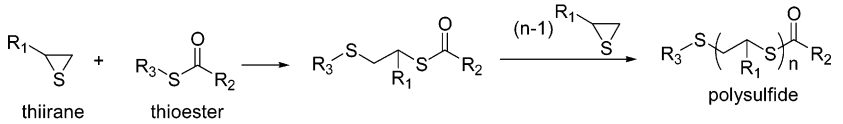
Scheme 1



Scheme 2

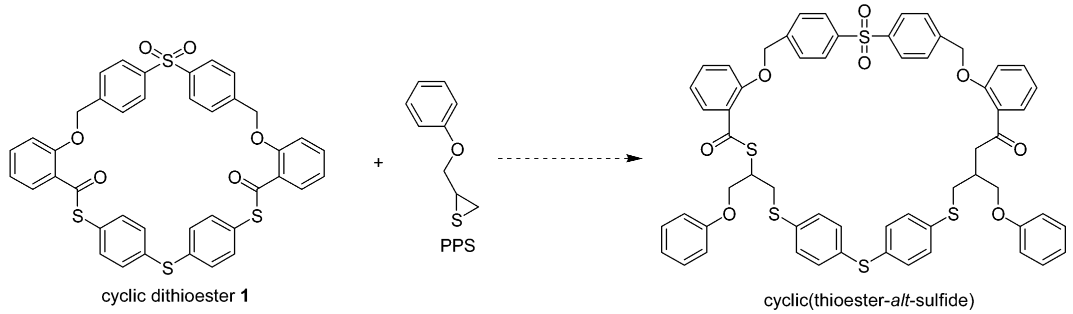


Table 1. Reaction of Cyclic Dithioester 1 with PPS[a]

run	temp (°C)	concn (M)	catalyst	DI (%)[b]	yield (%)[c]	$M_{n,SEC} \times 10^{-3}$ [d]	M_w/M_n[d]
1	30	0.1	TBAC	0	[e]	[e]	[e]
2	50	0.1	TBAC	32	[e]	[e]	[e]
3	70	0.1	TBAC	>99	80	5	3.1
4	50	1.0	TBAC	>99	92	6.1	4.2
5	70	1.0	TBAC	>99	90	6.5	4.1
6	90	1.0	TBAC	>99	96	5.7	4.6
7	120	1.0	TBAC	>99	90	8.9	9.8
8	150	bulk	TPPC	>99	91	3.6	2.3

[a] The reaction of dithioester **1** (0.1 mmol) with PPS (0.2 mmol) in the solvent (0.25 mL) in the presense of catalyst (5 mol %) for 24 h. [b] The degree of insertion of PPS into cyclic dithioester (DI) was calculated by ^{1}H NMR. [c] Methanol-insoluble parts. [d] Estimated by SEC based on polystyrene standards; eluent: solution of LiBr and phosphoric acid (20 mM) in DMF. [e] Not observed.

sealed off, and then the reaction was carried out at 90 °C for 24 h. The reaction mixture was diluted by the addition of $CHCl_3$ and poured into methanol to precipitate a polymer; it was reprecipitated twice from $CHCl_3$ into methanol and dried in vacuo at 60 °C for 24 h. The yield was 96% (0.102 g). M_n = 6500; M_w/M_n = 4.10 (run 5 in Table 1). IR (film, cm^{-1}): 3068 (ν C−H aromatic), 2927 (ν C−H aliphatic), 1671 (ν C=O thioester), 1597 (ν C−C aromatic), 1298 (ν C−O−C ether), 756 (ν C−S−C sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 3.31−3.40 (m, 4.0 H, $-CH_2-S$), 4.12−4.23 (m, 4.0 H, $-CH_2-O-$, side chain), 4.44 (s, 2.0 H, $\rangle$CH−), 5.17 (s, 4.0 H, $-CH_2-O-$, main chain), 6.83−7.93 (m, 34.0 H, aromatic H).

The Equivalent Reaction of Linear Dithioester with PPS. Linear dithioester (0.05 g, 0.2 mmol as thioester groups), PPS (0.033 g, 0.2 mmol), and TBAC (0.003 g, 0.002 mmol) were dissolved in NMP (0.25 mL) in a polymerization tube. The tube was cooled, degassed, and sealed off, and then the reaction was carried out at 70 °C for 24 h. The reaction mixture was diluted by the addition of $CHCl_3$ and poured into methanol to precipitate a reaction product; it was reprecipitated twice from $CHCl_3$ into methanol and dried in vacuo at 60 °C for 24 h. The yield was 90% (0.071 g). IR (film, cm^{-1}): 3068 (ν C−H aromatic), 2927 (ν C−H aliphatic), 1671 (ν C=O thioester), 1597 (ν C−C aromatic), 1298 (ν C−O−C ether), 756 (ν C−S−C sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 3.31−3.40 (m, 4.0 H, $-CH_2-S$), 4.12−4.23 (m, 4.0 H, $-CH_2-O-$, side chain), 4.44 (s, 2.0 H, $\rangle$CH−), 5.17 (s, 4.0 H, $-CH_2-O-$, main chain), 6.83−7.93 (m, 34.0 H, aromatic H).

The Continuous Insertion Reaction of Excess PPS into Cyclic Dithioester 1. The reaction of cyclic dithioester (0.073 g, 0.2 mmol as thioester groups), PPS (1.65 g, 10.0 mmol), and TBAC (0.003 g, 0.002 mmol) was carried out in NMP (5.2 mL) at 90 °C for 24 h by the similar method for the reaction of cyclic dithioester **1** with PPS. The yield was 96% (1.65 g). M_n = 42 000; M_w/M_n = 4.50. IR (film, cm^{-1}): 3019 (ν C−H aromatic), 2923 (ν C−H aliphatic), 1681 (ν C=O thioester), 1595 and 1576 (ν C=C aromatic), 1285 (ν C−O−C ether), 756 (ν C−S−C sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 2.97−3.15 (m, 4.0 H, $-CH_2-S-$), 4.16−4.22 (m, 100.0 H, $\rangle$-CH_2-O-Ph), 5.16 (s, 4.0 H, $Ph-CH_2-O-Ph$), 6.83−7.93 (m, 274.0 H, aromatic H).

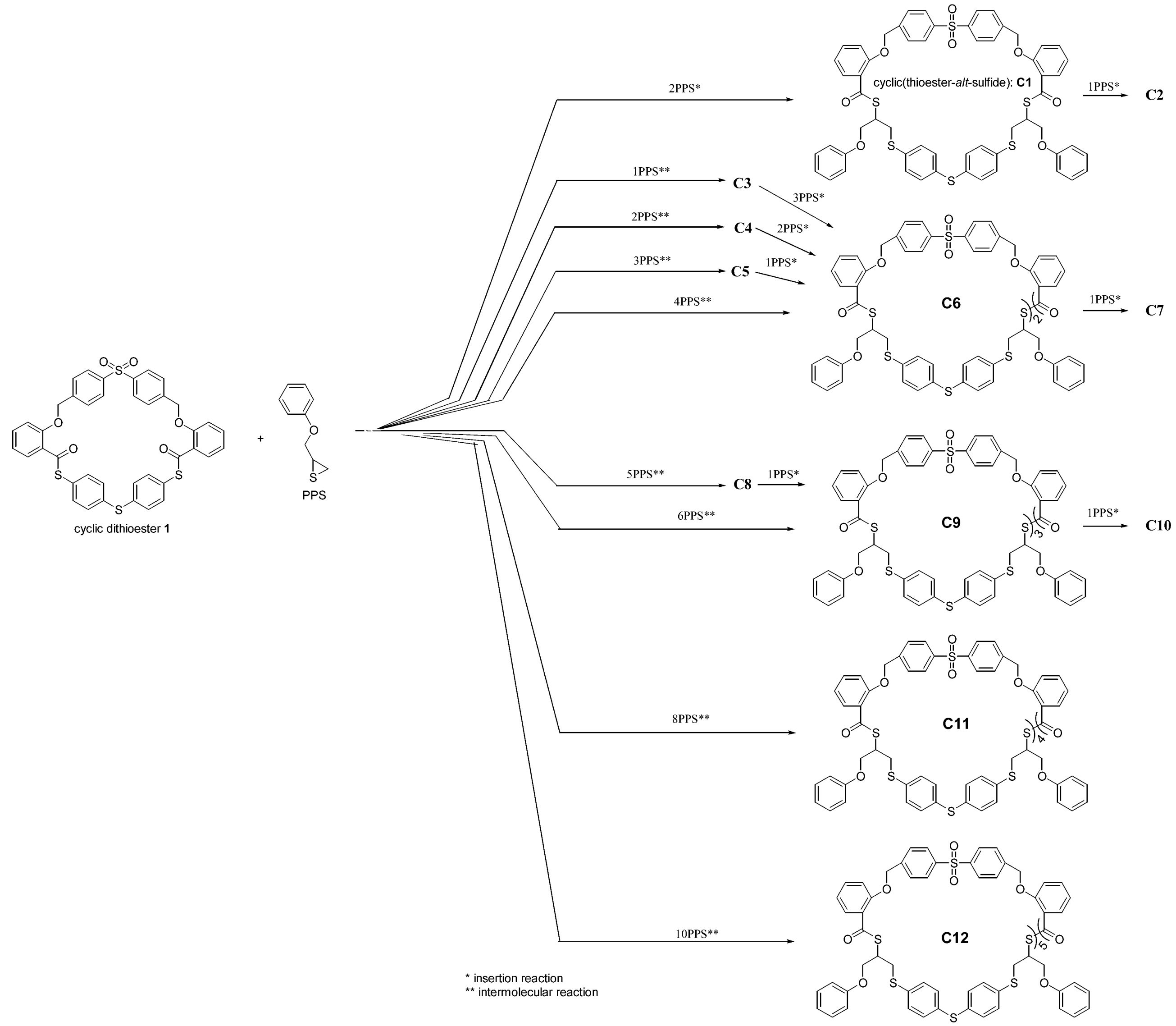
Results and Discussion

The Equivalent Reaction of Cyclic Dithioester 1 with PPS. We examined the reaction of cyclic dithioester **1** (1 mmol) with PPS (2 mmol) in the presence of quaternary onium salts tetrabutylammonium chloride (TBAC) or tetraphenylphosphonium bromide (TPPC) as catalysts for 24 h in NMP (Scheme 3). The reaction conditions and results are summarized in Table 1.

When the reaction was performed at 30 °C under highly diluted conditions (0.1 M), no product was obtained (run 1 in Table 1). The degree of insertion (DI) of PPS into cyclic dithioester was only 32% on the reaction at 50 °C (run 2 in Table 1). However, the insertion reaction proceeded smoothly and completely at 70 °C, and a polymer with M_n = 5000 was obtained in a 80% yield (run 3 in Table 1). Furthermore, we examined the reaction under 1.0 M concentration at the temperatures in the range between 50 and 120 °C, and it was found that the corresponding polymers with M_ns = 5700−8900 were obtained in 90−96% yields. These results show that the M_ns of the resulting polymers increased with the reaction temperature in most cases. It was also observed that the molecular weight distribution (M_w/M_n) of the resulting polymers was broader with increasing the reaction temperatures (runs 4−7 in Table 1). The polymer with M_n = 3600 (M_w/M_n = 2.3) was also obtained in a 90% yield in bulk (run 8 in Table 1). The SEC curves of these polymers showed unimodal peaks. The structures of the resulting polymers were confirmed by IR, ^{1}H NMR, ^{13}C NMR, and MALDI−TOF mass spectroscopy.

Figure 1 illustrates the ^{1}H NMR spectrum of the obtained polymer ($M_{n,SEC}$ = 6500, run 5 in Table 1), which shows the signals assignable to the methylene protons of the sulfide moieties, methylene protons of the ether moieties, and methine protons produced by the insertion reaction of PPS at 3.31−3.42, 4.12−4.23, and 4.44 ppm, respectively. However, any proton signals of end groups of the polymers were not observed.

Scheme 3. Cyclic Products Obtained by the Reaction of Cyclic Dithioester 1 (1 mmol) with PPS (2 mmol)



* insertion reaction
** intermolecular reaction

Figure 2 depicts the MALDI−TOF mass spectra of the obtained polymer with $M_n = 6500$ (run 5 in Table 1) with Na^+ doping.

In this figure, two mass differences patterns in peaks were observed to be exactly the molar mass of PPS ($M = 166.24$) and cyclic(thioester-*alt*-sulfide) **C1** ($M = 1065.39$). **C1** was the cyclic compound obtained by the insertion reaction of two equivalent PPS into cyclic thioester **1**. Therefore, the cyclic size (n) and the degree of polymerization of PPS ($DP_{(PPS)}$) of **C1** were 1 and 2, respectively, as shown in Scheme 3. **C2** was formed by the insertion reaction of PPS into synthesized **C1**, and its n and $DP_{(PPS)}$ were 1 and 3, respectively. Furthermore, **C3**−**C7** ($n = 3$) with $DP_{(PPS)} = 1-5$, **C8**−**C10** ($n = 3$) with $DP_{(PPS)} = 5-7$, **C11** ($n = 4$) with $DP_{(PPS)} = 8$, and **C12** ($n = 5$) with $DP_{(PPS)} = 10$ were also observed. This means that the obtained polymer contained many cycles **C1**−**C12** with different M_ns; the values of *m/z* are listed in Table 2. In addition M_{nSEC} was not same to that of M_n measured by MALDI−TOF mass spectroscopy. This result might be caused by the structures of the obtained cyclic polymers.

Table 2. Data of the MALDI−TOF Mass Spectra

cyclic products	*m/z* (calcd)	*m/z* (found)
C1 ($n = 1$, $DP_{(PPS)} = 2$)	($C_{58}H_{48}O_6S_6$ + Na): 1088.39	1088.11
C2 ($n = 1$, $DP_{(PPS)} = 3$)	($C_{67}H_{58}O_7S_7$ + Na): 1254.63	1254.35
C3 ($n = 2$, $DP_{(PPS)} = 1$)	($C_{89}H_{66}O_9S_9$ + Na): 1655.06	1654.44
C4 ($n = 2$, $DP_{(PPS)} = 2$)	($C_{98}H_{76}O_{10}S_{10}$ + Na): 1821.30	1820.68
C5 ($n = 2$, $DP_{(PPS)} = 3$)	($C_{107}H_{86}O_{11}S_{11}$ + Na): 1987.54	1986.92
C6 ($n = 2$, $DP_{(PPS)} = 4$)	($C_{116}H_{96}O_{12}S_{12}$ + Na): 2153.78	2153.16
C7 ($n = 2$, $DP_{(PPS)} = 5$)	($C_{125}H_{106}O_{13}S_{13}$ + Na): 2320.02	2319.50
C8 ($n = 3$, $DP_{(PPS)} = 5$)	($C_{165}H_{134}O_{17}S_{17}$ + Na): 3052.93	3052.43
C9 ($n = 3$, $DP_{(PPS)} = 6$)	($C_{174}H_{144}O_{18}S_{18}$ + Na): 3219.17	3218.67
C10 ($n = 3$, $DP_{(PPS)} = 7$)	($C_{183}H_{154}O_{19}S_{19}$ + Na): 3385.41	3384.91
C11 ($n = 4DP_{(PPS)} = 8$)	($C_{232}H_{192}O_{24}S_{24}$ + Na): 4284.56	4284.09
C12 ($n = 5$, $DP_{(PPS)} = 10$)	($C_{290}H_{240}O_{30}S_{30}$ + Na): 5349.95	5349.38

MALDI−TOF mass spectra also revealed the existence of the cyclic polymers but did not show any evidence of linear polymers in all samples (runs 3−8 in Table 1).

If controlled insertion reaction of PPS into thioester moieties of cyclic compounds could be achieved, well-defined low-molecular-weight cyclic compound 1:1 adduct **C1** could be only obtained. However, in this reaction system, cyclic polymers with different M_ns were obtained. These results mean that intermolecular ester-exchange reaction occurred between the thioester moieties of the cyclic compounds during the insertion reaction of PPS into cyclic dithioesters (Scheme 3).

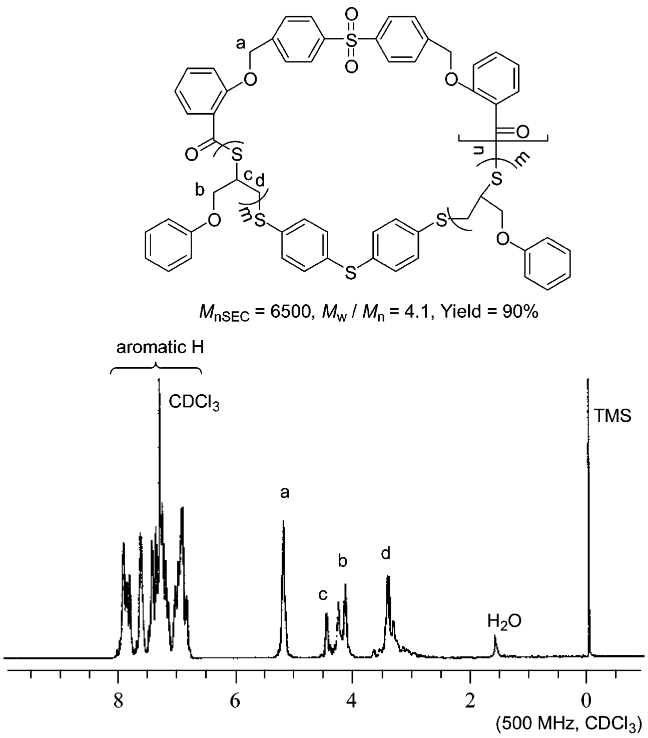


Figure 1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the cyclic polymer ($M_{n,SEC}$ = 6500, M_w/M_n = 4.10, run 5 in Table 1) obtained by the insertion reaction of PPS into cyclic dithioester **1**.

Furthermore, we examined the insertion reaction of linear dithioester **2** with PPS to confirm the intermolecular reaction in this reaction system and discuss the polymerization mechanism (Scheme 4). This reaction was carried out under the same condition as the reaction of cyclic dithioester **1** with PPS, and it was found that only the corresponding 1:1 adduct, linear thioester−sulfide, was obtained in a 90% yield, and any evidence of the polymerization was not observed.

Furthermore, Scheme 5 shows the reaction mechanism of the insertion reaction of cyclic dithioester with PPS. In the first step, thiirane is activated by quaternary onium halide (Q^+X^-) to form a complex **1**, and then **1** reacts with cyclic thioester to form an intermediate **2**. After that, the intramolecular and intermolecular ester-exchange reactions of **2** proceed to afford the ring-expanded cyclic compounds.

Although the intermolecular ester-exchange reaction occurred during the insertion reaction of thiirane into thioester moieties of both linear and cyclic thioester with thiirane in the presence of the quaternary onium salt as the catalyst, the ring-expansion reaction could be only confirmed on the intermolecular ester-exchange reaction of the cyclic thioester, affording the cyclic polymers with high molecular weights in high yields. It is noteworthy that the insertion reaction and intermolecular ester-exchange reaction occurred successively at the same time; that is, this reaction system might be a novel ring-expansion reaction to give larger cyclic polymer.

Therefore, the insertion reaction of excess PPS into cyclic dithioester (PPS/cyclic dithioester = 50 /1) was examined in the presence of TBAC as a catalyst at 90 °C for 24 h in NMP, and it was observed that the insertion reaction proceeded quantitatively (96% yield) to afford the corresponding cyclic polymer, in which the main structure was composed from polysulfide units as shown in Scheme 6. The degree of the insertion reaction of PPS into thioester was calculated by ^{1}H NMR integration of the signal for methylene protons ($-CH_2-O-$) of cyclic dithioesters at 5.16 ppm and methylene protons ($\rangle CH_2-O-$) of PPS at 4.16−4.22 ppm. As the result, the molecular weight calculated from ^{1}H NMR was to be 9000. However, the molecular weight ($M_{n,SEC}$) and polydispersity ratios (M_w/M_n) of resulting polymer estimated by SEC were 42 000 and 4.50, respectively. This means that the intermolecular ester-exchange reaction proceeded during continuous insertion reaction of PPS into thioester moieties to afford the larger cyclic polymer cyclic poly(sulfide) in high yield.

In summary, we examined the insertion reaction of PPS into cyclic dithioester **1** in the presence of TBAC as the catalyst. As a result, it was found that the intermolecular reaction occurred between thioester moieties during the insertion reaction of PPS to produce the cyclic polymers in high yields. That is, the ring-

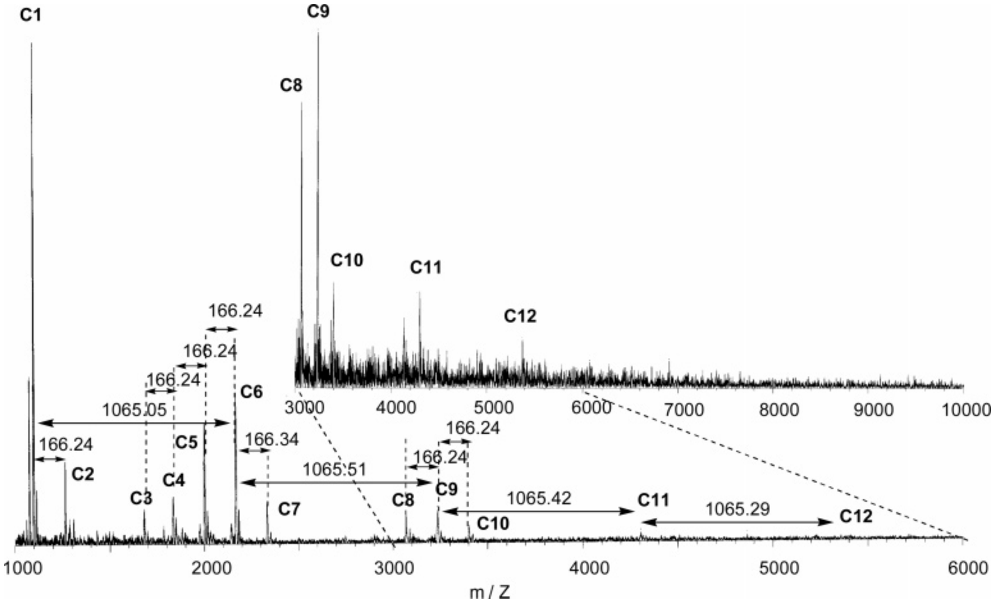
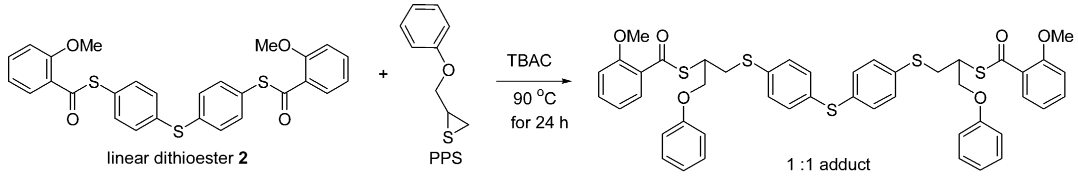
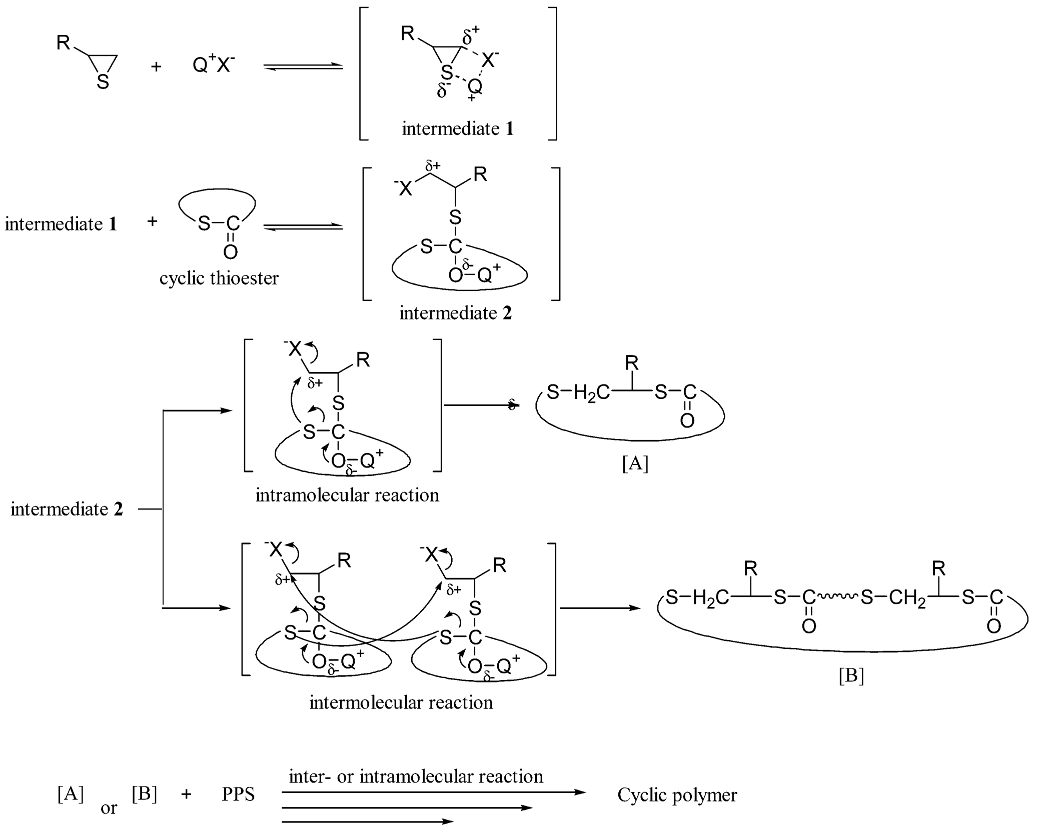


Figure 2. MALDI−TOF MS spectrum of cyclic polymer ($M_{n,SEC}$ = 6500, M_w/M_n = 4.10, run 5 in Table 1) obtained by the insertion reaction of PPS into cyclic dithioester **1**.

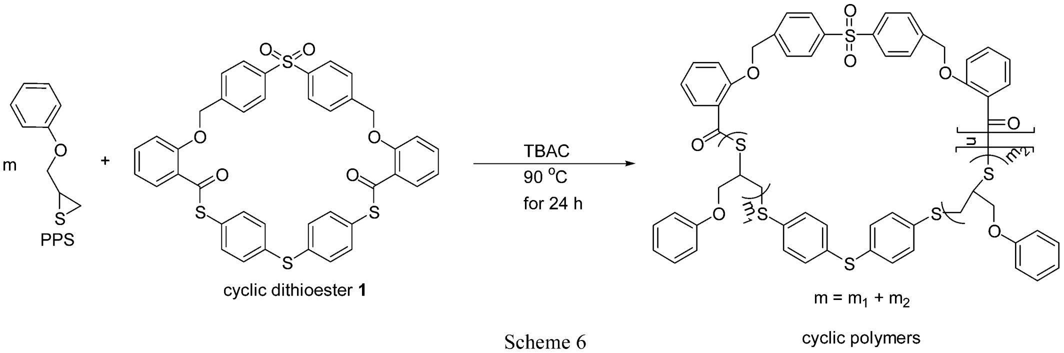
Scheme 4



Scheme 5. Reaction Mechanism of the Insertion Reaction of Cyclic Dithioester with PPS



Scheme 6



Scheme 6

expansition reaction of excess PPS with cyclic dithioester is useful synthetic strategy to obtain large cyclic macromolecules. Furthermore, the synthesis and the properties such as glass transition temperature (T_g), thermal stability, solubility, film-forming ability, and refractive index value of the cyclic macromolecules are also particularly interesting due to their structures and are now under investigation.

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Supporting Information Available: Experimental procedure, ^{1}H NMR, ^{13}C NMR, IR, and MAS data of cyclic dithioester and linear dithioester. This material is available free of charge via the Internet at http://pubs.acs.org.

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