A Novel Approach to Cyclic Polysulfides via the Controlled Ring-Expansion Polymerization of Cyclic Thiourethane with Thiiranes

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The development of synthetic process for well-defined cyclic polymers has more attractive attention for advancement of polymer chemistry. There are two well-known strategies for synthesizing cyclic polymers. One is the ring-closure reaction[1] of linear compounds containing two reactive groups at the ends, and the other is the ring-expansion polymerization[2] of cyclic compounds. The former approach generally requires highly diluted conditions, and it is difficult to obtain the cyclic polymers in satisfactory yields, because linear polymers can be also formed at the same time. The latter approach has the advantage that the higher molecular weights cyclic polymers can be synthesized in high yields by adjustment of the monomer feed ratio, but in this case, it is not easy to control the molecular weights and the polydispersity ratios of the resulting cyclic polymers often increase with increasing their molecular weights. In previous reports, we[3] presented a ring-expansion polymerization of cyclic thioesters using quaternary onium salts as catalysts for the synthesis of cyclic polymers. Both intra- and intermolecular reactions proceeded between the thioester moieties to give various sizes of macrocycles.

In this paper, we succeeded the synthesis of new cyclic polymers with controlled molecular weight by the continuous insertion reaction of thiirane into cyclic thiourethane.

As the references, the continuous insertion reaction of thiirane into linear thiourethane was examined in the presence of tetrabutylammonium bromide (TBAB) as a catalyst in NMP for 24 h with the various feed molar ratios of phenoxypropyrenesulfide (PPS) and phenyl benzenethiocarbamate (PBT) (Scheme 1A).

In the case of feed of PBT/PPS = 1/50 in the feed, the corresponding polysulfide PBT-*l*-poly(PPS)$_{50}$ was obtained with number-average molecular weights (M_n) = 6100 and polydispersity ratio (M_w/M_n) = 1.17. The structure of PBT-*l*-poly(PPS)$_{50}$ was confirmed by the ^{1}H NMR and IR spectroscopy.[4] The extent of the continuous insertion reaction (DI) of PPS into the thiourethane moiety was calculated based on the signals of the −NH− protons at 10.42 ppm and methylene protons of $-CH_2O-$ moieties produced by the insertion reaction of PPS at 4.06−4.13 ppm, and it was found that the DI value coincided with the feed ratio of PPS; i.e., it was 50.0. At the other feed ratios of PBT/PPS = 1/1, 1/5, 1/10, and 1/20, the corresponding polysulfides PBT-*l*-poly(PPS)$_n$ were obtained with M_n's = 300, 700, 1400, and 2800, respectively, and M_w/M_n = 1.07−1.17. These results show that the molecular weights of PBT-*l*-poly(PPS)$_n$ can be controlled by varying the feed ratio of PPS and PBT. That is, the continuous insertion reaction of PPS into thiourethane moieties proceeded in a living polymerization-like fashions as found in our previous studies[5] on the reaction of PPS and thioester compounds.

Table 1. Synthesis of Cyclic Polysulfides by the Continuous Insertion Reaction of PPS to TZD[a]

run	feed molar ratio PPS/T	convn[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]	DI[e]
1	1/1	75		400	1.11	2.9
2	5/1	>99	92	1500	1.43	5.1
3	10/1	>99	98	2800	1.32	10.0
4	20/1	>99	>99	4800	1.32	20.7
5	30/1	>99	>99	7000	1.19	30.1
6	40 /1	>99	>99	8500	1.21	40.1
7	50/1	>99	>99	10 000	1.91	50.7

[a] The reaction of TZD was carried out in NMP at 60 °C for 12 h. [b] Calculated by SEC based on polystyrene standards; eluent: a solution of LiBr and phosphoric acid (20 mM) in DMF. [c] Methanol-insoluble part. [d] Estimated by SEC. [e] The degree of insertion of PPS into cyclic dithioester (DI) was calculated from ^{1}H NMR data (see text).

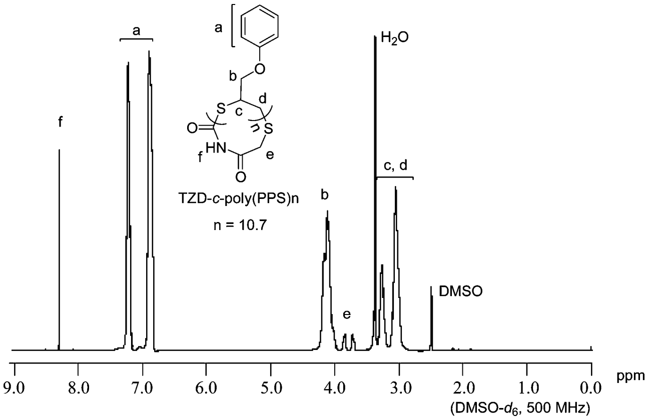

Figure 1. ^{1}H NMR spectrum of TZD-*c*-poly(PPS)$_n$ (M_n = 2800, run 3 in Table 1) obtained by the reaction of TZD and PPS (10 equiv).

From these background data, we examined the insertion reaction of PPS into cyclic thiourethane thiazolidine-2,4-dione (TZD) in a similar way (Scheme 1B). When the reaction of TZD and PPS was carried out with feed ratios in the range of TZD/PPS = 1/1−1/50, the insertion reaction of PPS proceeded to give the corresponding polymers with M_n = 400−10 000 and M_w/M_n = 1.11−1.91 in satisfactory yields.[6] The conversion of PPS was calculated from the results of size exclusion chromatography (SEC) to be from 75 to >99%. These conditions and results are summarized in Table 1. The structures of the resulting polymers were confirmed by IR, ^{1}H NMR, and MALDI−TOF mass spectroscopy.

Figure 1 illustrates the ^{1}H NMR spectrum of the obtained polymer (M_n = 2800, run 3 in Table 1), which shows the signals assignable to the skeletons produced by the insertion reaction of PPS: the methylene protons of the ether moieties at 4.13−4.18 ppm, and methylene and methine protons at 3.06−3.38. This figure also shows the signals assignable to methylene protons at 3.71−3.88 ppm and −NH− protons at 8.53 ppm of the TZD moieties. The value of DI of PPS was calculated from the methylene protons signals of TZD and PPS to be 10.0, in agreement with the feed ratio. Furthermore, no proton signals

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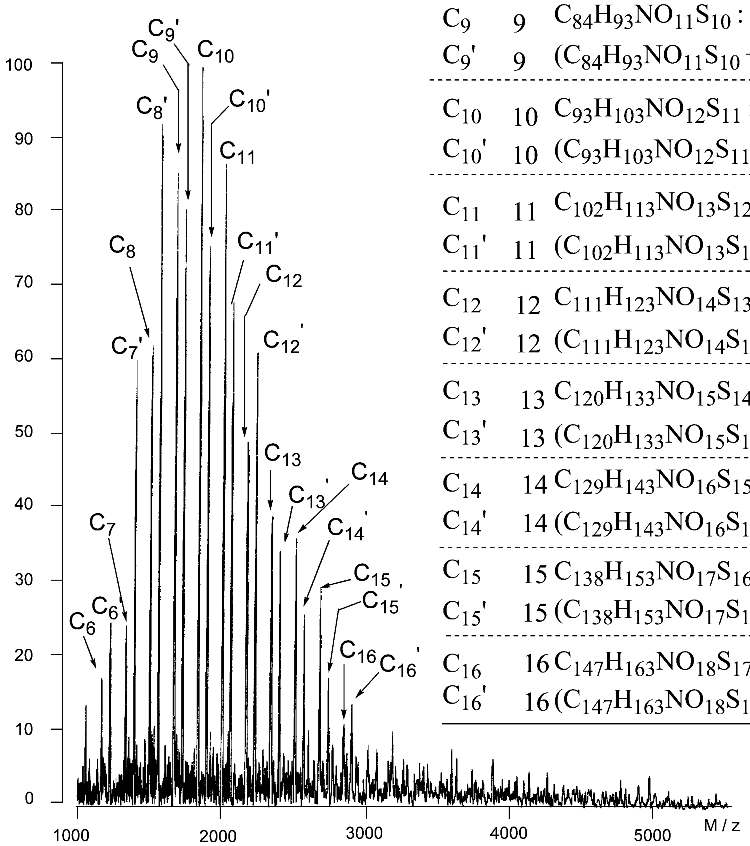
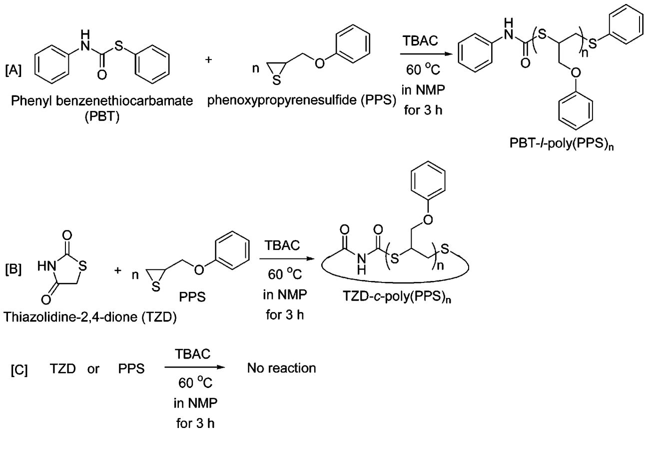


poly[TZD-(PPS)$_n$]	n	m / z (calcd) $C_{3+9n}H_{3+10n}NO_{2+n}S_{1+n}$	m / z (found)
C_6	6	$C_{57}H_{63}NO_8S_7$: 1113.29	1113.21
C_6'	6	($C_{57}H_{63}NO_8S_7$ + Ag): 1220.02	1220.11
C_7	7	$C_{66}H_{73}NO_9S_8$: 1279.34	1279.05
C_7'	7	($C_{66}H_{73}NO_9S_8$ + Ag) : 1386.25	1385.97
C_8	8	$C_{75}H_{83}NO_{10}S_9$: 1445.39	1445.44
C_8'	8	($C_{75}H_{83}NO_{10}S_9$ + Ag) : 1552.30	1552.37
C_9	9	$C_{84}H_{93}NO_{11}S_{10}$: 1611.44	1611.21
C_9'	9	($C_{84}H_{93}NO_{11}S_{10}$ + Ag) : 1718.35	1718.76
C_{10}	10	$C_{93}H_{103}NO_{12}S_{11}$: 1777.49	1777.23
C_{10}'	10	($C_{93}H_{103}NO_{12}S_{11}$ + Ag) : 1884.44	1884.13
C_{11}	11	$C_{102}H_{113}NO_{13}S_{12}$: 1943.54	1943.45
C_{11}'	11	($C_{102}H_{113}NO_{13}S_{12}$+ Ag) : 2050.45	2050.22
C_{12}	12	$C_{111}H_{123}NO_{14}S_{13}$: 2109.59	2109.67
C_{12}'	12	($C_{111}H_{123}NO_{14}S_{13}$ +Ag) : 2216.5	2216.32
C_{13}	13	$C_{120}H_{133}NO_{15}S_{14}$: 2275.64	2275.55
C_{13}'	13	($C_{120}H_{133}NO_{15}S_{14}$ + Ag) : 2382.55	2382.25
C_{14}	14	$C_{129}H_{143}NO_{16}S_{15}$: 2441.69	2441.87
C_{14}'	14	($C_{129}H_{143}NO_{16}S_{15}$ + Ag) : 2548.60	2548.46
C_{15}	15	$C_{138}H_{153}NO_{17}S_{16}$: 2607.74	2607.89
C_{15}'	15	($C_{138}H_{153}NO_{17}S_{16}$ + Ag): 2714.65	2714.68
C_{16}	16	$C_{147}H_{163}NO_{18}S_{17}$: 2773.79	2773.29
C_{16}'	16	($C_{147}H_{163}NO_{18}S_{17}$ + Ag) : 2880.70	2880.34

Figure 2. MALDI−TOF mass spectra of TZD-*c*-poly(PPS)$_n$ (M_n = 2800, run 3 in Table 1) obtained by the reaction of TZD and PPS (10 equiv).

Scheme 1. Reaction of Thiourethanes Using Quaternary Onium Salts as Catalysts



due to end groups of polymers were observed. Figure 2 depicts the MALDI−TOF mass spectrum of this polymer after Ag^+ doping showing mass parent peaks at 1777.23 and 1884.13, which correspond to the mass of a cyclic polymer obtained by the continuous insertion reaction of 10 equiv of PPS into TZD. Furthermore, a mass difference pattern in the peaks corresponded exactly to the molar mass of PPS (M = 166.05). This result shows that any intra- and inter-exchange reaction between the thiourethane moieties did not occur in the insertion reaction of PPS. Furthermore, when the reactions of only TZD or only PPS were carried out, no other reaction occurred (Scheme 1C). These results means that the obtained polymers are cyclic polysulfides TZD-*c*-poly(PPS)$_n$[7] generated by the continuous insertion reaction of PPS into thiourethane moieties of TZD as shown in Scheme 1B.

The SEC curves of the cyclic polysulfides showed unimodal peaks up to the feed ratio of TZD/PPS = 1/20, and the polydispersity ratios were narrow (M_w/M_n = 1.11−1.32) (runs 1−4 in Table 1). However, at feed ratios of TZD/PPS = 1/30, 1/40 and 1/50, the SEC curves did not show completely unimodal peaks and included weak shoulder part (runs 5−7 in Table 1). That is, complete control of the size of TZD-*c*-poly(PPS)$_n$ (n ≥ 30) was found to be difficult, presumably because the concentration of TZD decreases with increase of the feed ratio of PPS.

In summary, the continuous insertion reaction of PPS into the thiourethane moiety of TZD proceeded selectively, affording the corresponding cyclic polysulfides without any inter- or intra-exchange reaction of the thiourethane moieties. Well-defined cyclic polysulfides could be synthesized up to the feed ratio of TZD/PPS = 1/20. This new system seems to have considerable potential for the synthesis of well-defined larger cyclic polymers, and the synthesis of other cyclic thiourethanes as a useful initiators is now under investigation.

Supporting Information Available: Text giving experimental procedure and a table of chacterization data of linear polysulfides PBT-*l*-poly(PPS)$_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Spectroscopic data of *l*-poly[PBT-(PPS)$_{50}$]. ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ (ppm): 3.00−3.30 (m, 150 H, >CH− and −CH$_2$−S), 4.06−4.13 (m, 100 H, −CH$_2$−O−), 6.84−7.50 (m, 260 H, aromatic H), 10.4 (s, 1.0 H, −NH−). IR (film, cm^{-1}): 3060 (ν_{C-H} aromatic), 2925 (ν_{C-H} aliphatic), 1681 ($\nu_{C=O}$ thiourethane), 1599 and 1587 ($\nu_{C=C}$ aromatic), 1300 and 1031 (ν_{C-O-C} ether), 754 (ν_{C-S-C} sulfide).

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(6) Typical procedure for the reaction of PPS and TZD. TZD (0.04 g, 0.3 mmol), PPS (0.50 g, 3.0 mmol), and TBAC (0.005 g, 0.018 mmol) were dissolved in NMP (0.3 mL) in a polymerization tube. The tube was cooled, degassed, and sealed off. The obtained tube was heated at 60 °C for 12 h. The resulting reaction mixture was diluted by the addition of CHCl$_3$ and poured into methanol to precipitate a polymer, which was dried *in vacuo* at 60 °C for 24 h, affording a white solid. The yield was 98% (0.55 g). $M_n = 2800$, $M_w/M_n = 1.32$ (run 3 in Table 1).

(7) Spectroscopic data of *c*-poly[TZD-(PPS)$_{10}$]. IR (film, cm^{-1}): 3038 (ν_{C-H} aromatic), 2925 (ν_{C-H} aliphatic), 1752 ($\nu_{C=O}$ of NH−C(O)−S), 1685 ($\nu_{C=O}$ of NH−C(O)−CH$_2$−), 1599 and 1586 ($\nu_{C=C}$ aromatic), 1301 and 1031 (ν_{C-O-C} ether), 756 (ν_{C-S-C} sulfide). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 3.06−3.38 (broad m, 31.8 H, −CH$_2$−S− and >CH− of PPS), 3.71−3.88 (m, 2H, −CH$_2$−S− of TZD), 4.13−4.18 (broad m, 21.2H, −CH$_2$O−), 6.89−7.06 (m, 53H, aromatic H), 8.53 (s, 1H, −NH−).

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