Novel Sequence-Ordered Polymers by Transformation of Polymer Backbone: Quantitative and Regioselective Insertion of Thiiranes into Poly(*S*-aryl Thioester)

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ABSTRACT: Novel sequence-ordered poly(*S*-alkyl thioester)s were synthesized on the basis of transformation of a backbone of the poly(*S*-aryl thioester) (**P-1**) using the regioselective insertion of thiiranes. The insertion reaction of 3-butoxypropylene sulfide (BPS) into **P-1** using catalysts such as tetrabutylammonium chloride (TBAC), tetrabutylphosphonium chloride, or 18-crown-6-ether/potassium chloride in DMAc at 70 °C for 6 h proceeded completely and regioselectively to provide an ordered poly(*S*-alkyl thioester) (**P-2a**) with a new sequence. The molecular weight of **P-2a** was reasonably higher than that of the starting polymer **P-1**. The structure of **P-2a** including a head-to-tail sequence of BPS unit was well-characterized by IR, ^{1}H NMR, ^{13}C NMR spectroscopies, GPC, and elemental analysis. Various sequence-ordered poly(*S*-alkyl thioester)s were successfully synthesized by the insertion reaction of 3-phenoxypropylene sulfide, BPS, or cyclohexene sulfide using the TBAC catalyst under the same conditions. It was demonstrated that the transformation of the polymer backbone because of the regioselective insertion of thiiranes using quaternary onium salts was a useful method for achieving the synthesis of sequence-ordered polymers.

Introduction

The synthesis of sequence-ordered polymers is one of the most important subjects in polymer synthesis from the viewpoint of macromolecular design with a well-defined structure, such as with controlled molecular weight and stereotacticities. In addition, polymer properties such as thermal properties might be changed due to sequence ordering along the backbones. The most common sequence-ordered polymers are the alternating copolymers with an A−B sequence. These polymers have been synthesized by alternating copolymerizations of electron-donating olefin monomers with electron-accepting olefin monomers based on the charge-transfer complex,[1] ring-opening copolymerizations of cyclic ethers with cyclic carboxylic anhydrides,[2] carbon dioxide,[3] and ring-opening copolymerizations of oxazolines with lactones.[4] The alternating terpolymerization of three monomers such as tetrahydrofuran, epichlorohydrin, and phthalic anhydride,[5] or ethylene phenylphosphonite, acrylonitrile (or methyl acrylate), and carbon dioxide[6] provided polymers with an A−B−C sequence. Although sequence-ordered copolyamides could be synthesized ordinarily by two-step processes,[7] Ueda et al. recently reported a one-step synthesis[8] of sequence-ordered copolyamides by direct polycondensation of various nonsymmetric monomers using an activating agent. The control of sequences in the above-mentioned copolymers is essentially based on the differences in reactivity between the monomers, and the combinations of monomers applicable for the copolymerizations are restricted within some monomers. In addition, the synthesis of polymers with a multiple sequence is still very difficult.

Meanwhile, some insertion reactions of small molecules into polymer backbones were reported. For instance, the insertion of oxiranes into a poly(aryl ester),[9] the insertion of cyclosiloxanes into polysiloxanes,[10] and the insertion of acetylenes[11] or quinones[12] into polysilanes were investigated. Although these are not complete insertion reactions, the insertion of ϵ-caprolactam into a polycarbonate[13] and that of 9,10-phenanthraquinone into a poly(disilanylene)[14] proceeded quantitatively to produce polymers with an A−B repeating unit.

The authors recently proposed a novel concept for the synthesis of sequence-ordered polymers by the selective transformation of polymer backbones using the insertion reaction of cyclic compounds. Sequence-ordered polymers[15] were successfully synthesized by the insertion reaction of thiiranes into a poly(*S*-aryl thioester) catalyzed by quaternary onium salts under mild conditions. The concept is represented in Figure 1.

To achieve the sequence-ordered polymers, a selective transformation of polymer backbones by quantitative insertion is essential. That is to say, the insertion reaction with low conversion would produce disordered polymers. Furthermore, to obtain a head-to-tail sequence, it is necessary that the cyclic compound is inserted in a totally regioselective manner.

In this paper, we describe a novel method for the synthesis of sequence-ordered polymers by the complete transformation of poly(*S*-aryl thioester) (**P-1**) using the insertion of thiiranes. The characteristics of the transformation of **P-1** and the mechanistic features of the insertion reaction will be discussed.

Experimental Section

Measurements. ^{1}H NMR spectra were obtained on a JEOL FX-200 or α-500 operating in the pulsed Fourier transform (FT) modes, using tetramethylsilane (TMS) as an internal standard in $CDCl_3$. IR spectra were recorded on a JASCO IR-700. The M_n and M_w/M_n of polymers were measured with a TOSOH HLC-8020 GPC unit using TSK−gel columns (eluent, THF; calibration, polystyrene standards).

Materials. Solvents were dried using CaH_2 or Na metal and purified in the usual way before use. 3-Phenoxypropylene

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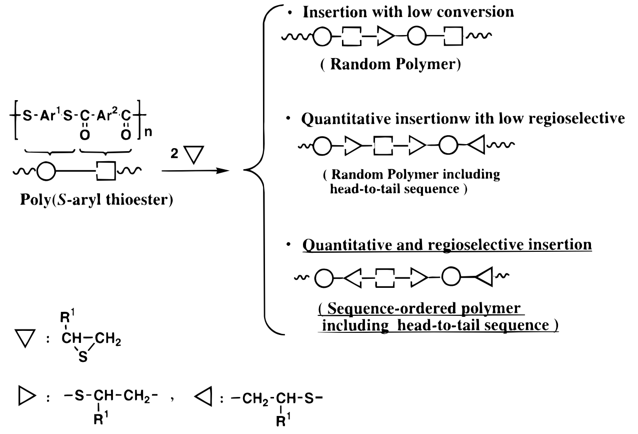


Figure 1. Schematic representation of concept for the synthesis of sequence-ordered polymers by transformation of polymer backbones.

sulfide (PPS) was prepared from phenyl glycidyl ether with thiourea according to the reported procedure.[16] Yield: 81%. Bp: 86.0−87.5 °C/0.9 mmHg. 3-Butoxypropylene sulfide (BPS) was prepared from butyl glycidyl ether. Yield: 46%. Bp: 78.0 °C/13 mmHg. Cyclohexene sulfide (CHS) was also prepared from cyclohexene oxide. Yield: 47%. Bp: 54−55 °C/12 mmHg. *S*-Phenyl thiobenzoate (PTB) (mp, 55.1−55.8 °C) was prepared by the reaction of benzoyl chloride with benzenethiol using equimolar triethylamine and then purified by recrystallization from dried *n*-hexane. Yield: 52%. Phenyl glycidyl ether and butyl glycidyl ether were purified twice by distillation under reduced pressure. Poly(*S*-aryl thioester) (**P-1**) was prepared by interfacial polycondensation of bis(4-mercaptophenyl)sulfide with hexafluoropropanylene−bis(benzoyl chloride). The yield of polymer (**P-1**) was 77%, and the number-average molecular weight (M_n) was 7800. Tetrabutylammonium bromide (TBAB) was purified by recrystallization from dried ethyl acetate. Tetrabutylammonium chloride (TBAC), Tetrabutylphosphonium chloride (TBPC), 18-crown-6 (18-C-6), KCl, and KI were used as received.

Addition reaction of BPS with PTB. The reaction of BPS with PTB was carried out as follows: TBAC (0.027 g, 0.1 mmol) was placed in an ampule tube under dry atmosphere and vacuum-dried at 40 °C for 5 h. BPS (0.293 g, 2 mmol), PTB (0.429 g, 2 mmol), DMAc (5 mL), and 1-chloronaphthalene (0.3 g) as the internal standard for gas chromatography (GLC) were added into the ampule tube, then the tube was sealed and heated to 70 °C for 24 h. An addition product was obtained in 100% GLC yield. The reaction mixture was diluted with chloroform, washed twice with water, then dried with $MgSO_4$. The solvent was evaporated in vacuo. The obtained product was purified by silica gel column chromatography eluent, chloroform/*n*-hexane (1:2, v/v)]. The isolated yield of the resulting *S*-alkyl thioester was 85%. IR (KBr): 1668 ($\nu_{C=O}$), 1122 cm^{-1} (ν_{C-O-C}). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): 0.91 (t, J = 7.1 Hz, 3 H, CH_3), 1.36 (m, 2 H, O−C−CH_2), 1.52 (q, J = 7.1 Hz, 2 H, O−CH_2−C), 3.37 (d, 2 H, S−CH_2−C), 3.41 (t, J = 7.1 Hz, 2 H, O−CH_2−C), 3.61 (dd, J = 10.0 Hz, J = 4.9 Hz, 1 H, O−CH_2−C−S), 3.92 (dd, J = 10.0 Hz, J = 3.70 Hz, 1 H, O−CH_2−C−S), 4.06−4.16 (m, 1 H, C−CH−S), 7.16−7.62 (m, 8 H, aromatic H), 7.97 (dd, J = 1.5 Hz, J = 7.1 Hz, 2 H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS): δ 13.86, 19.19, 31.53, 35.27, 43.91, 70.07, 71.04, 126.09, 135.85, 191.05. Anal. Calcd for $C_{20}H_{24}O_2S_2$: C, 66.63; H, 6.71. Found: C, 66.34; H, 6.64.

Synthesis of a Sequence-Ordered Polymer (P-2a) by Insertion Reaction of BPS into P-1. A typical procedure is as follows: TBAC (0.028 g, 0.1 mmol) was placed in an ampule tube under dry atmosphere and dried under reduced pressure at 40 °C for 5 h. BPS (0.293 g, 2 mmol) and **P-1** (0.607 g, 1 mmol, M_n = 7800, M_w/M_n = 2.16) and DMAc (2 mL) were added into the ampule tube, then the tube was sealed and heated to 70 °C for 5 h. The reaction mixture was diluted with 10 mL of chloroform and washed thrice with minimal amounts of water. The polymer solution was concentrated to about 2 mL, and the solution was poured into 100 mL of methanol to precipitate the polymer. The resulting polymer was reprecipitated once from chloroform into methanol. The yield of polymer **P-2a** was 0.857 g (96%). The number-average molecular weight (M_n) of the polymer determined from GPC was 13 800 (M_w/M_n = 1.80). The degree of insertion (DI) was 100 mol %, calculated from the intensity ratio of ^{1}H NMR spectrum. IR (film): 1663 ($\nu_{C=O}$), 1118 cm^{-1} (ν_{C-O-C}). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 0.91(t, J = 7.3 Hz, 6 H, CH_3), 1.35 (sex, J = 7.3 Hz, 4 H, O−C−CH_2), 1.53 (q, J = 7.3 Hz, 4 H, O−CH_2−C), 3.33 (dd, J = 14.0 Hz, J = 6.1 Hz, 2 H, S−CH_2−C), 3.36 (dd, J = 14.0 Hz, J = 7.9 Hz, 2 H, S−CH_2−C), 3.41 (t, J = 6.7 Hz, 2 H, O−CH_2−C), 3.60 (dd, J = 9.8 Hz, J = 4.9 Hz, 1 H, O−CH_2−C−S), 3.91 (dd, J = 9.80 Hz, J = 3.70 Hz, 2 H, O−CH_2−C−S), 4.06−4.11 (m, 2 H, C−CH−S), 7.27 (d, J = 8.5 Hz, 4 H, aromatic H), 7.39 (d, J = 8.5 Hz, 4 H, aromatic H), 7.95 (d, J = 8.5 Hz, 4 H, aromatic H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 13.91, 19.27, 31.59, 35.25, 44.34, 70.06, 71.24, 123.63, 127.16, 129.82, 130.45, 131.54, 133.51, 135.15, 137.39, 137.92, 190.30. Anal. Calcd for $C_{43}H_{44}F_6O_4S_5$: C, 57.44; H, 4.93. Found: C, 57.68; H, 4.97.

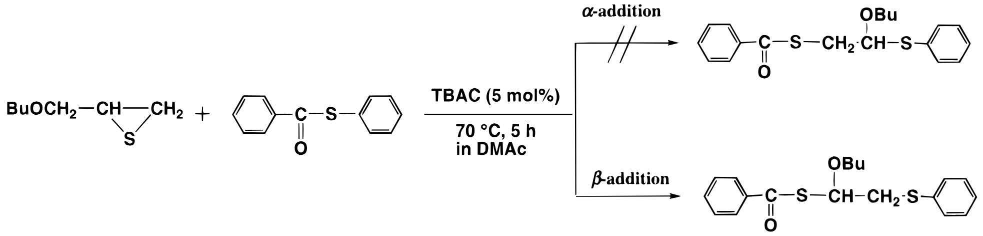
Synthesis of a Sequence-Ordered Polymer (P-2b) by Insertion Reaction of PPS into P-1. The insertion of PPS (0.333 g, 2 mmol) into **P-1** (0.607 g, 1 mmol) in DMAc (5 mL) was carried out in the presence of TBAC (0.028 g, 0.1 mmol) in a sealed tube, and the solution was stirred for 24 h at 70 °C. The reaction mixture was diluted with chloroform and washed with water. The contents were poured into methanol, and the polymer obtained was purified by one reprecipitation with chloroform−methanol. The yield of polymer P-2b was 0.924 g (98%), and the DI was 100%, calculated from the ^{1}H NMR spectrum. The M_n of the polymer determined from GPC was 12 500 (M_w/M_n = 1.79). IR (film): 1664 ($\nu_{C=O}$), 1240 cm^{-1} (ν_{C-O-C}). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 3.40−3.50 (m, 4 H, S−CH_2−C), 4.15 (dd, J = 9.8 Hz, J = 4.9 Hz, 2 H, O−CH_2−C), 4.20−4.38 (m, 2 H, C−CH−S), 4.49 (dd, J = 9.8 Hz, J = 3.4 Hz, 2 H, O−CH_2−C), 6.80−8.08 (m, 26 H, aromatic H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 35.14, 43.66, 67.43, 123.60, 111.62, 121.43, 127.25, 129.54, 130.03, 130.52, 131.56, 133.75, 134.52, 137.15, 138.07, 158.15, 189.95. Anal. Calcd for $C_{47}H_{36}F_6O_4S_5$: C, 60.11; H, 3.86. Found: C, 59.83; H, 4.17.

Synthesis of a Sequence-Ordered Polymer (P-2c) by Insertion Reaction of CHS into P-1. CHS (0.228 g, 2 mmol), **P-1** (0.607 g, 1 mmol), and TBAC (0.028 g, 0.1 mmol) were dissolved into DMAc (5 mL) in a sealed ampule tube. After 24 h at 70 °C, the ampule was opened, the contents were washed with water, and the product was purified by the same procedure as described above. The final yield of polymer P-2c was 0.814 g (98%). The resulting polymer had a DI of 100%, and the M_n of the polymer was 15 000. IR (film): 1662 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 1.20−2.42 (m, 16 H, −$(CH_2)_4$−), 3.20−3.42 (m, 2 H, S−CH_2−C), 3.80−4.00 (m, 2 H, S−C−CH), 7.06−8.10 (m, 16 H, aromatic H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 23.95, 24.65, 31.53, 32.02, 46.81, 50.45, 123.63, 131.47, 127.09, 130.38, 131.29, 132.89, 133.63, 134.45, 137.59, 137.72, 189.89. Anal. Calcd for $C_{41}H_{36}F_6O_4S_5$: C, 58.97; H, 4.35. Found: C, 58.66; H, 4.63.

Results and Discussion

Model Reaction. The reaction of a thiirane BPS with PTB was examined as a model reaction for the reaction of poly(*S*-aryl thioester) to obtain information concerning reactivity and regioselectivity. The reaction of BPS with PTB using 5 mol % of TBAC was carried out in DMAc at 70 °C for 5 h. The conversions of BPS and PTB were 100%, and a product was obtained in 85% yield. In the IR spectrum of the product, a characteristic peak at 1668 cm^{-1} due to the C=O stretching of *S*-alkyl thioester was observed. The ^{1}H NMR spectrum showed the signals of aliphatic and aromatic protons with reasonable intensity ratios, which supports the struc-

Scheme 1



ture as shown in Scheme 1. In particular, the methine proton from the ring-opened structure of BPS was observed at 4.04−4.16 ppm with the expected intensity ratio assuming selective β-addition of BPS to PTB. In the ^{13}C NMR spectrum, the signals due to methine and methylene carbons of the ring-opened structure of BPS were observed at 43.91 and 71.04 ppm, respectively. In addition, the signal due to the carbonyl carbon was identified at 191.05 ppm. Moreover, elemental analysis of the product agreed with the calculated values. These proved that the reaction of BPS with PTB using TBAC proceeded completely and regioselectively to obtain only the β-addition product.

Synthesis of a Sequence-Ordered Polymer by the Transformation of P-1 with BPS. On the basis of the results of the model reaction, the synthesis of a sequence-ordered polymer by the transformation of a poly(*S*-aryl thioester) with thiiranes was investigated. The reaction of poly(*S*-aryl thioester) **P-1** ($M_n = 7800$) with BPS was conducted using 5 mol % of TBAC (for the thiirane) in DMAc at 70 °C for 6 h to provide a polymer in 96% yield. The degree of insertion of BPS into **P-1** was 100%, which was estimated by the intensity ratio of aromatic protons and methyl protons of butyl group from BPS in the ^{1}H NMR of the resulting polymer.

Characterization of P-2a. The obtained polymer was well-characterized by the IR, ^{1}H NMR, ^{13}C NMR spectra, and GPC analysis. The IR spectrum of **P-2a** showed the characteristic peak due to C═O stretching of the *S*-aryl thioester group at 1679 cm^{-1}. On the contrary, the spectrum of **P-2a** showed the peaks due to C−H stretching around 2800 cm^{-1} and C═O stretching of *S*-alkyl thioester group at 1662 cm^{-1}, and the peak of 1679 cm^{-1} was not observed at all.

The ^{1}H NMR spectra of **P-2a** (Figure 2B) showed the aliphatic signals based on BPS and aromatic protons with reasonable intensity ratios. The methine proton due to the ring-opened structure of BPS was observed as multiple signals at 4.06−4.11 ppm with the expected intensity ratio of 2 H, assuming the selective β-addition of BPS. Moreover, the signals due to the methylene protons were observed at 3.33 and 3.36 ppm.

The ^{13}C NMR spectra of **P-1** and **P-2a** are presented in Figure 3A, B, respectively. Each signal was assigned

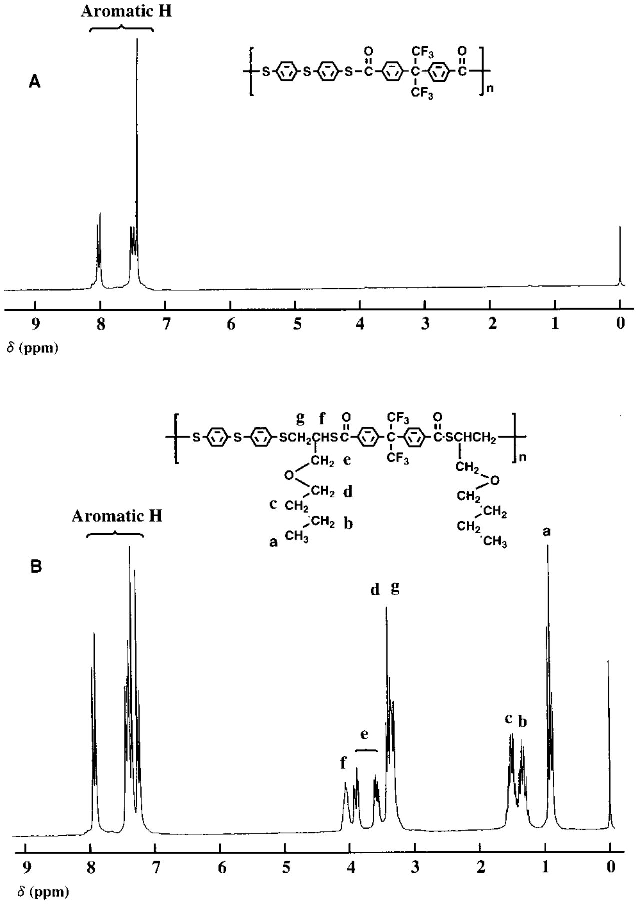


Figure 2. ^{1}H NMR spectra of **P-1** (A) and **P-2a** (B).

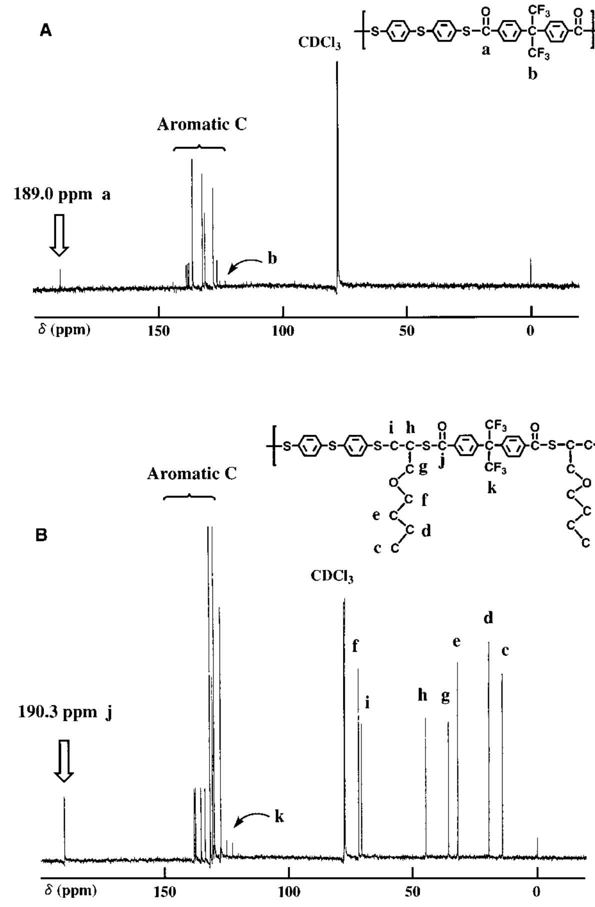
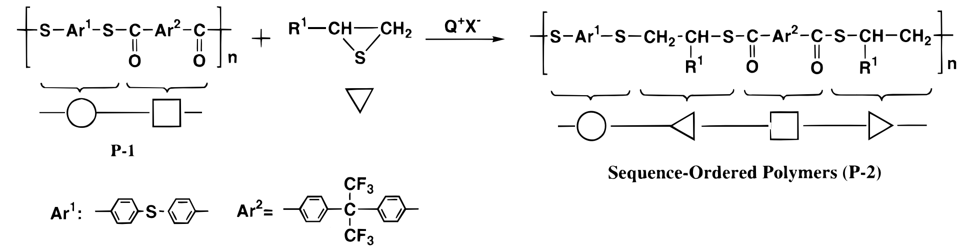


Figure 3. ^{13}C NMR spectra of **P-1** (A) and **P-2a** (B)

Scheme 2



R^1 : $BuOCH_2$- (BPS)(P-2a), $PhOCH_2$- (PPS)(P-2b), $MeOCH_2$- (MPS)(P-2c), -$(CH_2)_4$- (CHS)(P-2d)

to each carbon of the structure **P-2a** in Scheme 2. In particular, the signals due to methine and methylene carbons corresponding to the ring-opened structure of BPS were observed at 44.34 and 70.06 ppm, respectively, which was supported by the identification of the product from the model reaction. The signal of C=O carbon of *S*-alkyl thioester group was exhibited at 190.3 ppm, and the signal due to the C=O carbon of **P-1** at 189.0 ppm was not observed at all in Figure 3B.

In Figure 4, the unimodal GPC profile of **P-2a** was demonstrated in the higher molecular region compared to that of starting **P-1**. The M_n of **P-2a** was 13 800, which was nearly identical to the calculated molecular weight of 12 000. These suggest the insertion of BPS proceeded without any side reactions such as hydrolysis which would have induced cleavage of the polymer backbone of the poly(*S*-aryl thioester) **P-1**.

Furthermore, elemental analysis of **P-2a** agreed reasonably well with the calculated values. Therefore, it was proved that polymer **P-1** was transformed to **P-2a** with a new sequence (Scheme 2) by the quantitative and regioselective insertion reaction of BPS into the *S*-aryl thioester group of **P-1** under mild conditions using the TBAC catalyst.

A difference in properties between **P-1** and **P-2a** was observed in their solubility. Although **P-1** was not soluble in acetone and DMSO, **P-2a** with a new sequence was soluble in those solvents. This would be because of the alkylene chain of the ring-opened structure of BPS.

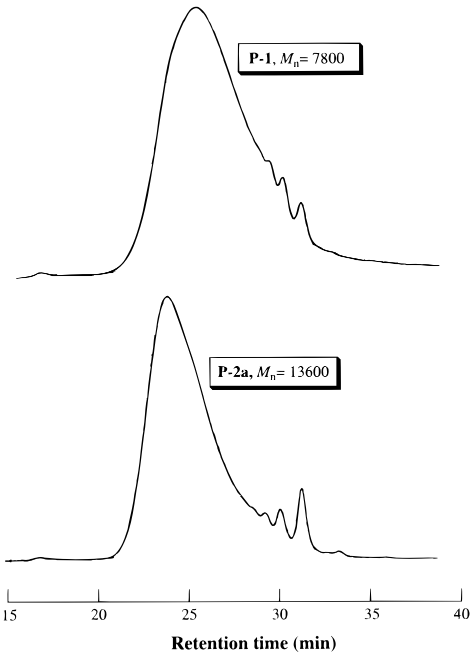


Figure 4. GPC profiles of **P-1** and **P-2a**.

Table 1. Catalytic Effect on the Insertion of BPS into P-1[a]

no.	catalyst	yield (%)[b]	DI (%)[c]	$M_n \times 10^{-4}$ [d]	M_w/M_n[d]
1	TBAB	89	67	1.30	2.07
2	TBAC	98	100	1.38	1.80
3	TBPC	95	100	1.35	1.78
4	18-C-6/KCl	96	100	1.39	1.79
5	18-C-6/KI	75	24	1.18	2.18

[a] The reaction was carried out with **P-1** (1 mmol, $M_n = 0.78 \times 10^4$, $M_w/M_n = 2.16$) and BPS (2 mmol) using catalyst (0.1 mmol) in DMAc (5 mL) at 70 °C for 6 h. [b] Insoluble parts in methanol. [c] Degree of insertion calculated from ^{1}H-NMR. [d] Estimated by GPC on the basis of polystyrene standards in THF.

Table 2. Solvent Effect on the Insertion of BPS into P-1[a]

no.	solvent	yield (%)[b]	DI (%)[c]	$M_n \times 10^{-4}$ [d]	M_w/M_n[d]
1	toluene	71	15	1.62	1.86
2	anisole	71	20	1.53	2.02
3	chlorobenzene	73	18	1.56	2.19
4	DMAc	96	100	2.06	1.68
5	NMP	97	100	1.85	1.88

[a] The reaction was carried out with **P-1** (1 mmol, $M_n = 1.08 \times 10^4$, $M_w/M_n = 2.00$) and BPS (2 mmol) using TBAC (0.1 mmol) in solvent (5 mL) at 70 °C for 6 h. [b] Insoluble parts in methanol. [c] Degree of insertion calculated from ^{1}H NMR. [d] Estimated by GPC on the basis of polystyrene standards in THF.

Reaction Behavior of Insertion of BPS into P-1. The transformation of the backbone of **P-1** by the insertion reaction of BPS was investigated to demonstrate the reaction behavior. The reaction was conducted using 5 mol % of catalysts such as quaternary onium salts or crown ether complexes in DMAc at 70 °C for 6 h (Table 1). The reaction using TBPC or 18-C-6/KCl also proceeded with 100% DI and regioselectively to provide the sequence-ordered **P-2a**, as did the reaction using TBAC. When the reaction was conducted using TBAB or 18-C-6/KI, the DIs were 67% and 24%, respectively. This means that the targeted polymers with ordered sequences were not obtained from these reactions. Thus, it was found that quaternary ammonium, phosphonium salts, or crown ether complexes with chloride as the counteranion have higher catalytic activities in the reaction of **P-1** with BPS.

Table 2 shows the solvent effect on the insertion of BPS into **P-1**. The polymer with a DI of 100% was obtained in quantitative yields from the reaction in DMAc or NMP. On the other hand, when the reaction was conducted in chlorobenzene, toluene, or anisole, the DIs were about 20%. This suggests that aprotic polar solvents are good reaction media for the quantitative insertion of BPS into **P-1** under these conditions. This difference of DIs in the solvents seems to be caused by the polarity of the solvents used.

Figure 5 shows the time course of the insertion of BPS into **P-1** using the TBAC catalyst in DMAc at 70 °C.

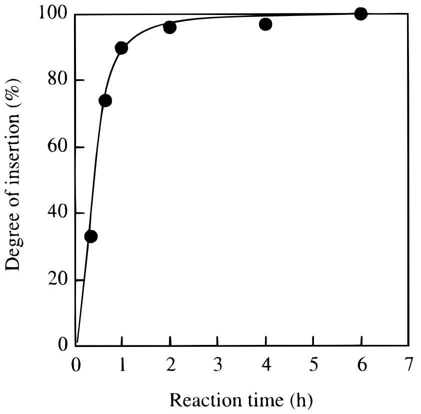


Figure 5. Time course of the insertion reaction of BPS into **P-1** using 5 mol % of TBAC in DMAc at 70 °C.

Table 3. Insertion Reaction of Various Cyclic Compounds into P-1[a]

no.	cyclic compd	yield[b] (%)	DI[c] (%)	Sβ[d]	$M_n \times 10^{-4}$ [c]	M_w/M_n[e]
1	PPS	98	100	100	1.25	1.79
2	BPS	88	100	100	1.36	1.83
3	MPS[f]	95	92		1.55	2.95
4	CHS[f]	99	100		1.50	1.77
5	PGE	92	90		0.43	1.61
6	BGE	91	91		0.31	1.79

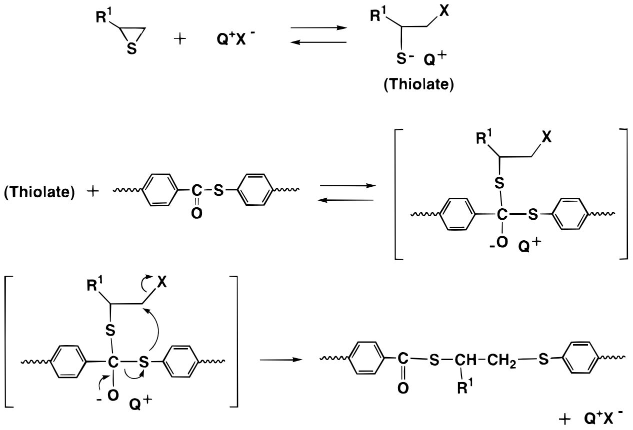
[a] The reaction was carried out with **P-1** (1 mmol, $M_n = 0.78 \times 10^4$, $M_w/M_n = 2.16$) and cyclic compd (2 mmol) using TBAC (0.1 mmol) in DMAc (5 mmol) at 70 °C for 24 h. [b] Insoluble parts in methanol. [c] Degree of insertion calculated from ^{1}H NMR. [d] Selectivity of β-cleavage determined by ^{1}H NMR. [e] Estimated by GPC on the basis of polystyrene standards using THF. [f] Using **P-1** ($M_n = 1.08 \times 10^4$, $M_w/M_n = 2.00$).

The reaction proceeded very smoothly with a DI of 90% for 1 h, and the reaction was completed in 6 h. It should be noted that the transformation of polymer backbones proceeds quite smoothly under mild conditions, because it is known that the achievement of quantitative polymer reactions is not easy even in the reaction of the polymer side chains.

Synthesis of Various Sequence-Ordered Polymers by the Insertion of Thiiranes or Oxiranes into P-1. The synthesis of various sequence-ordered polymers by the insertions of thiiranes and oxiranes into **P-1** was carried out using TBAC in DMAc at 70 °C for 24 h. The results are summarized in Table 3. The insertion reaction of PPS proceeded with a DI of 100% to produce a sequence-ordered polymer (**P-2b**) as did the reaction with BPS. The selectivity of the β-addition (Sβ) of PPS was 100%; this means the reaction proceeded regioselectively. Cyclic thiirane CHS was also inserted into **P-1** to produce a corresponding polymer with an ordered sequence. On the other hand, the reaction of **P-1** with MPS proceeded with a DI of 92%, because of lower reactivity. The insertion reaction of oxirane PGE or BGE into **P-1** was also carried out under the same conditions, and the DI of the reaction was about 90%. The molecular weight of the resulting polymer was less than that of **P-1**. The IR spectra of the resulting polymers showed a weak absorption peak at about 3500 cm^{-1} due to O−H stretching. This suggests that hydrolysis of the backbone occurred during the reaction because of a trace amount of water in the reaction system.

Mechanistic Feature. The authors previously proposed a mechanism[17] for the reaction of thiiranes with carboxylic acid derivatives such as *S*-aryl thioesters and *S*-alkyl thioesters catalyzed by quaternary onium salts. The insertion reaction of thiiranes into **P-1** would be considered similar to this reaction. As shown in Scheme 3, halides of the quaternary onium salts or crown ether complexes used here activate thiiranes in nucleophilic interaction with their β-carbon to produce a thiolate. The thiolates attack the carbonyl carbon of carboxylic *S*-thioesters to form tetrahedral intermediates. Then, aryl thiolate would be released to replace the halides (X$^-$), recovering the used catalyst Q$^+$X$^-$. For the reaction of BPS with **P-1**, catalysts with chlorides showed high catalytic activity because of the good balance of the nucleophilicity toward thiiranes and the leaving ability of the intermediate. The effect of catalysts suggested that key species in the reaction were anions such as thiolates and alcholates. Thus, the reaction would proceed effectively in basic solvents such as NMP and DMAc; an anionic reaction generally proceeds smoothly in basic solvents. The regioselectivity of the reaction would be achieved by the steric effect of the substituent at the α-carbon of the used thiiranes.

Scheme 3



Conclusion

It was demonstrated that the quantitative and selective transformation of the polymer backbone with insertion reaction of thiiranes using quaternary onium salts was a useful method to achieve the synthesis of sequence-ordered polymers.

The insertion reaction of BPS, PPS, and CHS into **P-1** using TBAC provided the poly(*S*-alkyl thioester)s with the new ordered sequence, which were characterized well by IR, ^{1}H NMR, and ^{13}C NMR. The behavior of the insertion reaction was found to occur effectively with the quaternary onium salts or crown ether complexes containing chlorides as the counteranions in basic solvents such as NMP or DMAc. The novel synthetic method would make it possible to synthesize functional polymers with ordered sequences.

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