Communications to the Editor

Transformation of Poly(*S*-aryl thioester) by Insertion of Thiiranes: A Novel Approach To Achieve the Synthesis of Sequence-Ordered Polymers

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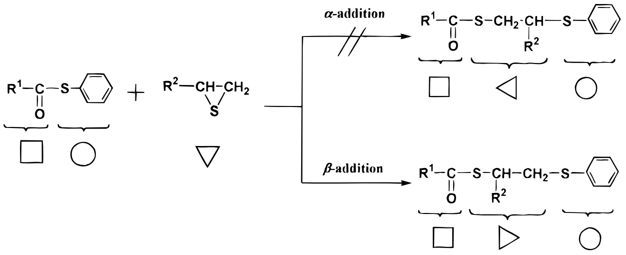
The synthesis of sequence-ordered polymers is a challenging subject from the viewpoint of molecular design of macromolecules with well-defined structures as to the molecular weights and stereotacticities. Some A−B type alternating copolymers have been synthesized successfully by an alternating copolymerization[1] of electron-accepting olefins with electron-donating olefins or copolymerizations of cyclic ethers with cyclic carboxylic anhydrides[2] or carbon dioxide.[3] The alternating terpolymerization[4] of tetrahydrofuran, epichlorohydrin, and phthalic anhydride provided a polymer with an A−B−C sequence. Sequence-ordered copolyamides[5] were also synthesized by two-step processes. However, the combination of the monomers applicable for the synthesis of sequence-ordered polymers is restricted in some monomers, and the synthesis of polymers with multisequences is still very difficult.

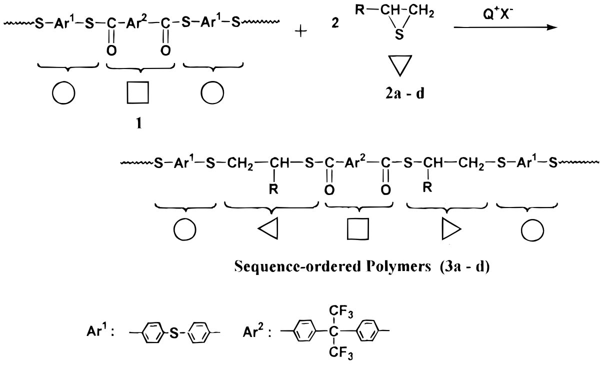
Recently, it was reported that the insertion of ϵ-caprolactam[6] into a polycarbonate and that of 9,10-phenanthraquinone[7] into a poly(disilanylene) provided polymers with an A−B type repeating unit in the polymer main chain. Meanwhile, the authors have investigated the new addition reaction of cyclic ethers[8] and with carboxylic acid derivatives such as active esters catalyzed by quaternary onium salts or crown ether complexes. The chemical modification of polymers by insertion of oxirane compounds[9] into *O*-phenyl ester groups in the polymer side chain and the main chains was also reported. It must be noted that quantitative and selective insertion reactions of small molecules into polymer main chains are few.

More recently, we found the addition reaction of thiiranes[10] with carboxylic acid derivatives such as *S*-phenyl thioacetate using the aforementioned catalysts. An interesting feature of the reaction is that it proceeds regioselectively under neutral conditions to give β-addition products in quantitative yields. The reaction is regarded as a constructing method for the sequence of (carboxylic acid residue)−(thiirane)−(leaving group) as □−▷−○ (Scheme 1). Based on this concept, we have designed a novel synthesis of polymer with an ordered sequence as shown in Scheme 2 by the transformation of the polymer main chain. Selective and quantitative reactions are required to achieve the synthesis of sequence-ordered polymers with molecular weights higher than those of the starting polymers.

Scheme 1



Scheme 2



R : BuOCH$_2$ (2a), PhOCH$_2$ (2b), -(CH$_2$)$_4$- (2c), MeOCH$_2$ (2d)

In this paper, we report a novel synthesis of sequence-ordered polymers by the selective transformation of poly(*S*-aryl thioester) with thiiranes using a quaternary onium salt.

The starting poly(*S*-aryl thioester) (**1**)[11] was prepared by interfacial polycondensation of bis(4-mercaptophenyl) sulfide with (hexafluoropropanylene)bis(benzoyl chloride). The number-average molecular weight (M_n) estimated by GPC was 7800. When the reaction[12] of **1** with 3-butoxypropylene sulfide (**2a**) was carried out using tetrabutylammonium chloride (TBAC) as a catalyst in *N*,*N*′-dimetylacetamide (DMAc) at 70 °C for 6 h, a polymer (**3a**)[13] was obtained in 98% yield. It was found that the molecular weight of the resulting polymer was 13 800, which was markedly higher than that of **1**. The IR spectrum of the resulting polymer showed a new characteristic peak at 1662 cm^{-1} due to C=O stretching of the *S*-alkyl thioester group and C=O stretching at 1679 cm^{-1} due to complete disappearance of the *S*-aryl thioester of **1**. Parts a and b of Figure 1 are the ^{1}H NMR spectra of **1** and **3a**, respectively. Figure 1a shows signals due only to the aromatic protons corresponding to the structure of **1**. In addition to the aromatic signals, aliphatic signals (a−f) based on the ring-opened structure of **2a** were observed in Figure 1b. The intensity ratios of the aromatic protons and the aliphatic protons were equal to the expected values assuming a quantitative reaction. Furthermore, the elemental analysis of **3a** was in reasonable agreement with the calculated values. Thus, it was proved that the reaction of **1** with **2a** proceeded “quantitatively”.

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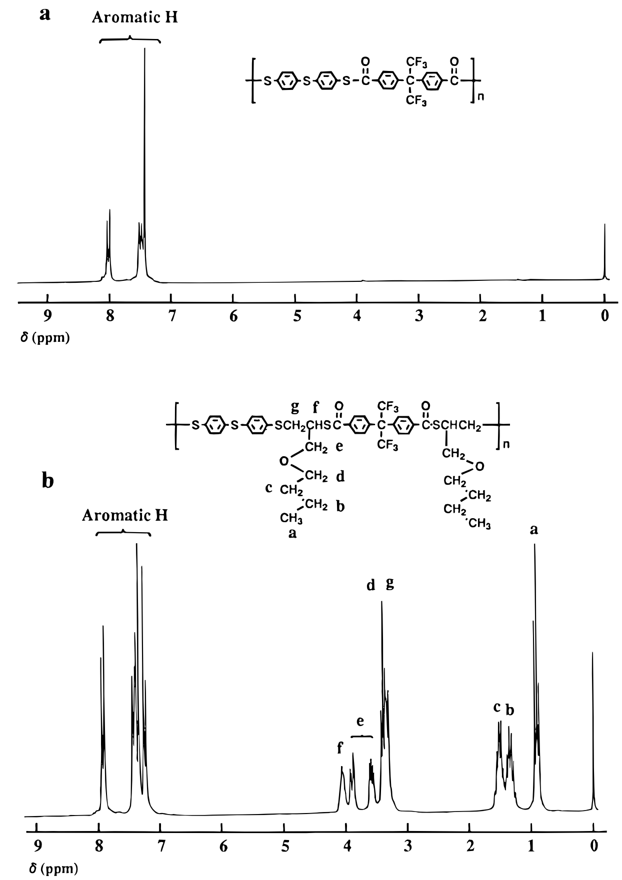

Figure 1. ^{1}H NMR spectra of **1** (a) and **3a** (b).

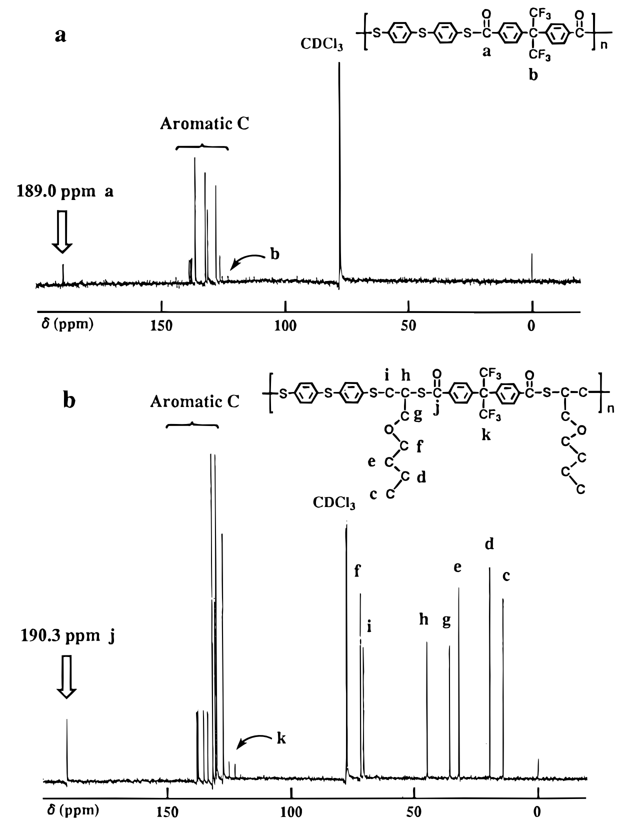

Figure 2. ^{13}C NMR spectra of **1** (a) and **3a** (b).

Table 1. Insertion Reaction of Various Thiiranes into 1[a]

run	thiirane	yield[b] (%)	DI[c] (%)	$S\beta$[d]	M_n ($\times 10^{-4}$)[e]	M_w/M_n[e]
1	**2a**	88	100	100	1.36	1.83
2	**2b**	98	100	100	1.25	1.79
3	**2c**[f]	99	100		1.50	1.77
4	**2d**[f]	95	92		1.55	2.95

[a] The reaction was carried out with **1**(1 mmol, $M_n = 0.78 \times 10^4$, $M_w/M_n = 2.16$) and thiiranes (2 mmol) using TBAC (0.1 mmol) in DMAc (5 mL) at 70 °C for 24 h. [b] Recovered yield. [c] Degree of insertion calculated from ^{1}H NMR. [d] Selectivity of β-addition which was determined by ^{1}H and ^{13}C NMR. [e] Estimated by GPC based on polystyrene standards. [f] Using **1** ($M_n = 1.08 \times 10^4$, $M_w/M_n = 2.00$).

The ^{13}C NMR spectra of **1** and **3a** are exhibited in parts a and b of Figure 2, respectively. The signals corresponding to the structure of **3a** are observed in Figure 2b. Furthermore, the signal of the C=O carbon at 189.0 ppm of **1** shifted to 190.3 ppm due to the C=O of the *S*-alkyl thioester as one signal. This means that the reaction of **1** with **2a** proceeded "regioselectively"; that is, β-addition of **2a** occurred selectively, to give the polymer with the multisequence of —○—◁—□—▷—. Therefore, it was demonstrated that the regioselective and quantitative transformation of polymer **1** by the insertion reaction with **2a** provided the sequence-ordered polymer successfully.

The transformation of **1** was carried out with a variety of thiiranes in the presence of TBAC in DMAc at 90 °C for 24 h. The reaction with **2a** or 3-phenoxypropylene sulfide (**2b**) proceeded regioselectively and quantitatively to give the targeted polymer **3a** or **3b**. In the case of the reaction with cyclohexylene sulfide (**2c**), the corresponding polymer **3c** was also obtained in quantitative yield. The IR, ^{1}H NMR, and ^{13}C NMR spectra of the resulting polymers proved that the reactions proceeded selectively and quantitatively as did the reaction using **2a** to give the corresponding sequence-ordered polymers. When the reaction was carried out with 3-methoxypropylene sulfide (**2d**), however, the degree of insertion (DI) of **2d** was 92%. All of the obtained polymers had molecular weights higher than that of the starting polymer **1**. This means that the transformation of **1** by the insertion with the thiiranes proceeded without side reactions such as the cleavage of the *S*-thioester group in the polymer main chain.

In summary, the present study has demonstrated a successful synthesis of polymers with ordered multisequence of —○—◁—□—▷— by the insertion of thiiranes into the poly(*S*-aryl ester) catalyzed by quaternary ammonium salts. The transformation of the polymer main chain is a novel approach to achieve the synthesis of multisequence-ordered polymers.

References and Notes

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(11) Identification. IR (film, cm^{-1}): 1679 ($\nu_{\mathrm{C=O}}$). ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, TMS): δ 7.46 (s, 8 H, Ar$-H$), 7.53 (d, J = 8.3 Hz, 4 H, Ar$-H$), 8.04 (d, J = 8.3 Hz, 4 H, Ar$-H$). ^{13}C NMR (125 Hz, $\mathrm{CDCl_3}$, TMS): δ 123.63 ($C\mathrm{F}_3$), 125.83, 127.37, 130.66, 131.60, 135.66, 137.06, 137.52, 138.21 (Ar$-C$), 189.00 (C=O). Anal. Calcd for $\mathrm{C_{29}H_{16}F_6O_2S_3}$: C, 54.72; H, 2.66. Found: C, 54.27; H, 2.75.

(12) The reaction was carried out with **1** (1 mmol, $M_\mathrm{n} = 0.78 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 2.16$) and **2a** (2 mmol) using TBAC (0.1 mmol) in DMAc (5 mL) at 70 °C for 6 h. The reaction mixture was poured into methanol to precipitate a white polymer, and then the obtained polymer was purified twice by reprecipitation using chloroform and methanol. Yield: 98%.

(13) Identification. IR (film, cm^{-1}): 1662 ($\nu_{\mathrm{C=O}}$), 1117 ($\nu_{\mathrm{C-O-C}}$). ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, TMS): δ 0.91 (t, J = 6.8 Hz, 6 H, $\mathrm{C}H_3$), 1.34 (sex, J = 6.8 Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.54 (sep, J = 6.8 Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 3.20$-$3.50 (m, 8 H, ArS$-\mathrm{C}H_2$, and $\mathrm{OC}H_2$ of Bu), 3.60 (dd, J = 9.8 Hz, J = 4.4 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CHS(C{=}O)}$), 3.92 (dd, J = 9.8 Hz, J = 3.4 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CHS(C{=}O)}$), 4.00$-$4.10 (m, 2 H, $\mathrm{C}H\mathrm{S(C{=}O)}$), 7.27 (d, J = 7.8 Hz, 4 H, Ar$-H$), 7.39 (d, J = 7.8 Hz, 4 H Ar$-H$), 7.45 (d, J = 8.5 Hz, 4 H, Ar$-H$), 7.95 (d, J = 8.5 Hz, 4 H, Ar$-H$). ^{13}C NMR (125 Hz, $\mathrm{CDCl_3}$, TMS): δ 13.91 ($C\mathrm{H_3}$), 19.27 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 31.59 ($C\mathrm{H_2CH_2CH_3}$), 35.25 ($\mathrm{CH_2O}C\mathrm{H_2}$-CH), 44.34 ($\mathrm{OCH_2}C\mathrm{H}$), 70.06 (ArS$C\mathrm{H_2}$), 71.24 ($\mathrm{O}C\mathrm{H_2CH_2}$-$\mathrm{CH_3}$), 123.63 ($C\mathrm{F_3}$), 127.16, 129.82, 130.45, 131.54, 133.51, 135.15, 137.39, 137.92 (Ar$-C$), 190.30 (C=O). Anal. Calcd for $\mathrm{C_{43}H_{44}F_6O_4S_5}$: C, 57.68; H, 4.97. Found: C, 57.44; H, 4.93.

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