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New Synthesis of Poly(*S*-thioester)s by Regioselective Addition Reaction of Bis(thiirane)s with Diacyl Chlorides Using Quaternary Onium Salts

Atsushi Kameyama, Yasuhiro Kimura, and Tadatomi Nishikubo*

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221, Japan

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ABSTRACT: Poly(*S*-thioester)s were successfully synthesized by a new addition reaction of bis(thiirane)s with diacyl chlorides catalyzed by quaternary onium salts or crown ether complexes. The polyaddition of Bisphenol A bis(2,3-epithiopropyl) ether (BPTE) or butanediol bis(2,3-epithiopropyl) ether with certain diacyl chlorides proceeded smoothly using quaternary onium chlorides to give the corresponding poly(*S*-thioester)s with relatively high molecular weights. When the reaction of BPTE with terephthaloyl chloride or isophthaloyl chloride was carried out using 5 mol % of tetrabutylammonium chloride (TBAC) or tetrabutylphosphonium chloride (TBPC) in anisole at 90 °C for 24 h, the poly(*S*-thioester) with a number-average molecular weight of 40 000 was obtained. The reaction was enhanced more efficiently in aromatic solvents such as toluene or anisole than in aprotic polar solvents. It was proven that the reaction proceeded regioselectively to give the poly(*S*-thioester)s with the pendant chloromethyl group, which was introduced simultaneously with the formation of a *S*-thioester linkage in the polymer backbone during the reaction.

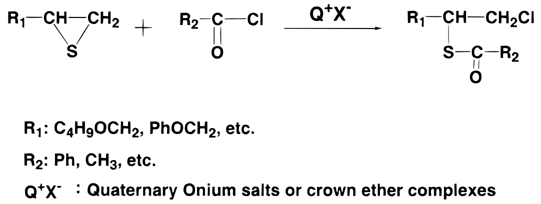
Introduction

Although poly(*S*-thioester)s are a new class of polymers analogous to polyesters, the reports of synthesis and characterization of poly(*S*-thioester)s are fewer compared with those of polyesters. Poly(*S*-thioester)s have been prepared by the condensation[1] of dithiols with dicarboxylic acid chlorides, diphenyl dicarboxylates, addition of carboxylic thioacids with diolefines,[2] or the ring-opening polymerization of β-thiopropiolactones,[3] δ-thiovalerolactones,[4] and ϵ-thiocaprolactones[5] using strong bases. In these polymer synthesis, monomers containing sulfur are restricted by thiols or thiolactones.

Meanwhile, the authors found that the reaction of thiiranes[6] with carboxylic acid derivatives such as acyl chlorides or *S*-phenyl thioesters using quaternary onium salts or crown ether complexes proceeded smoothly and regioselectively under mild conditions to provide the carboxylic acid *S*-thioesters as products (Scheme 1). A remarkable advantage of the reactions using the catalysts is the selective transformation of thiiranes under mild conditions. That is to say that although the thiiranes are well-known as useful monomers for synthesis of polysulfides by ring-opening polymerizations using cationic or anionic catalysts, any polymerizations of the used thiiranes do not occur during the reactions with the neutral catalysts.

The reaction of thiiranes with carboxylic acid derivatives is successfully applied to achieve a novel group transfer polymerization[7] of the thiiranes using *S*-phenyl thioesters as initiators and the quaternary onium salts catalysts, in which an acyl group transfers in each propagating process. In addition, a new approach toward the synthesis of sequence-ordered polymers by the transformation of polymer backbones[8] based on the quantitative and regioselective reaction of thiiranes with *S*-phenyl thioesters under mild conditions was reported. These mean that the reaction of thiiranes with the reagents catalyzed by quaternary onium salts is a very useful method for a novel polymer synthesis, in particular for the molecular design of macromolecules with well-defined structures.

Scheme 1



Our research group has also reported that synthesis of polyesters[9] could be achieved by the polyaddition of bisoxiranes with reactive dicarboxylic acid esters using quaternary onium salts or crown ether complexes. Recently, polyesters with high molecular weights were synthesized by the polyaddition of bis(cyclic ether)s such as bis(oxirane)s[10] or bis(oxetane)s[11] with diacyl chlorides using the catalysts. Interestingly, the polymerization process forms a reactive chloromethyl group in the side chains. Thus, it was demonstrated that the polyaddition of bis(cyclic ether)s with dicarboxylic acid derivatives is classified as a novel method toward polyester synthesis.

In a series of studies on new polymer synthesis based on selective transformation of thiiranes under neutral conditions, we designed a synthesis of poly(*S*-thioester)s by the addition reaction of thiiranes with acyl chlorides. In this paper, a novel synthesis of poly(*S*-thioester)s by the polyaddition of bis(thiirane)s with diacyl chlorides using quaternary onium salts as catalysts was described. The behavior of the polymerization was investigated in detail.

Experimental Section

Materials. Bisphenol A diglycidyl ether (BPGE) was recrystallized four times from methanol/methyl ethyl ketone (4:1, v/v). Butanediol diglycidyl ether was purified by distillation *in vacuo*. Terephthaloyl chloride (TPC) was purified by recrystallization from *n*-hexane; isophthaloyl chloride (IPC), adipoyl chloride (APC), and sebacoyl chloride (SCC) were purified by distillation *in vacuo*. Tetra-*n*-butylammonium bromide (TBAB) was recrystallized from dried ethyl acetate.

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* To whom all correspondence should be addressed.

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Solvents used for polyaddition were purified by conventional method. Other reagents were used as commercial grades.

Measurements. ^{1}H NMR spectra were obtained on a JEOL FX-200 or a JEOL 500-α 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, *N*,*N*-dimethylformamide (DMF); calibration, polystyrene standards).

Synthesis of Bisphenol A Bis(2,3-epithiopropyl) Ether (BPTE). BPTE was prepared using thiourea according to the reported method.[12] Yield: 69%. IR (KBr, cm^{-1}): 3032, 2964 (ν_{C-H}), 1510 ($\nu_{C=C}$ of Ph), 1246 (ν_{C-O-C}). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.62 (s, 6.0 H, CH_3), 2.28−2.30 (m, 2.0 H, CH_2 of thiirane), 2.56−2.59 (m, 2.0 H, CH_2 of thiirane), 3.20−3.27 (m, 2.0 H, CH of thiirane), 3.82−4.00 (m, 2.0 H, C-CH_2-O), 4.11−4.20 (m, 2.0 H, C-CH_2-O). 6.78−6.82 (m, 4.0 H, ArH), 7.10−7.15 (m, 4.0 H, ArH). Anal. calucd. for $C_{21}H_{24}O_2S_2$: C, 67.74; H, 6.45. Found: C, 67.45; H, 6.55.

Synthesis of Butanediol Bis(2,3-epithiopropyl) Ether (BDTE). BDTE was also prepared from butanediol diglycidyl ether with ammonium thiocyanate according to the reported method.[13] Yield: 45%. IR (neat, cm^{-1}): 3062, 2984, 2940 (ν_{C-H}), 1100 (ν_{C-O-C}). ^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ 2.25 (dd, $J = 1.1$ Hz, $J = 5.4$ Hz, 2.0 H, CH_2 of thiirane), 2.52 (d, $J = 5.8$ Hz, 2.0 H, CH_2 of thiirane), 2.91−3.21 (m, 2.0 H, CH of thiirane), 3.31−3.76 (m, 8.0 H, CH_2−O), 5.55−5.78 (m, 4.0 H, CH_2).

Synthesis of Poly(*S*-thioester) P-1. A typical procedure for the polyaddition of BPTE with TPC is as follows: BPTE (0.4469 g, 1.2 mmol), TPC (0.2436 g, 1.2 mmol), and TBPC (17.7 mg, 0.06 mmol) were dissolved in toluene (0.6 mL) and then the reaction was carried out at 90 °C for 24 h. The reaction mixture was diluted with chloroform and then poured into methanol (300 mL), reprecipitated twice from chloroform into methanol, and dried *in vacuo* at 60 °C. The yield of polymer was 0.677 g (98%). The number-average molecular weight (M_n) of the polymer determined by GPC was 3.03×10^4. M_w/M_n: 1.54. IR (film, cm^{-1}): 1665 ($\nu_{C=O}$), 1237 (ν_{C-O-C}). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 1.63 (s, 6.0 H, CH_3), 3.86−4.10, (br, 3.8 H, CH_2−Cl), 4.12−4.28 (br, 2.1 H, O−CH_2), 4.32−4.64 (br, 4.1 H, O−CH_2, S−CH−C), 6.86 (d, $J = 8.2$ Hz, 4.0 H, ArH), 7.16 (d, $J = 8.2$ Hz, 4.0 H, ArH), 8.03 (s, 4.0 H, ArH).

Synthesis of Poly(*S*-thioester) P-2. The polyaddition of BPTE with IPC was carried out in the same way as the synthesis of **P−1**. Yield: 97%. M_n: 4.03×10^4. M_w/M_n: 1.77. IR (film, cm^{-1}): 1668 ($\nu_{C=O}$), 1242 (ν_{C-O-C}). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 1.64 (s, 6.0 H, CH_3), 3.86−4.04 (br, 3.8 H, CH_2−Cl), 4.12−4.28 (br, 2.1 H, O−CH_2), 4.31−4.52 (br, 4.0 H, O−CH_2, S−CH−C), 6.87 (d, $J = 8.8$ Hz, 4.0 H, ArH), 7.16 (d, $J = 8.8$ Hz, 4.0 H, ArH), 7.57 (t, $J = 7.8$ Hz, 1.0 H, ArH), 8.17 (d, $J = 9.4$ Hz, 2.0 H, ArH), 8.53 (s, 1.0 H, ArH).

Synthesis of Poly(*S*-thioester) P-3. The polyaddition of BPTE with APC was carried out as the synthesis of **P−1.** Yield: 94%. M_n: 3.21×10^4. M_w/M_n: 1.59. IR (film, cm^{-1}): 1692 ($\nu_{C=O}$), 1241 (ν_{C-O-C}). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 1.62 (s, 6.0 H, CH_3), 1.71, (br, 4.0 H, CH_2), 2.60 (br, 4.0 H, CH_2), 3.68−4.40 (m, 9.8 H, O−CH_2, S−CH, CH_2−Cl), 6.82 (d, $J = 8.8$ Hz, 4.0 H, ArH), 7.13 (d, $J = 8.4$ Hz, 4.0 H, ArH).

Synthesis of Poly(*S*-thioester) P-4. The polyaddition of BPTE with SCC was carried out as the synthesis of **P-1.** Yield: 87%. M_n: 1.92×10^4. M_w/M_n: 1.44. IR (film, cm^{-1}): 1693 ($\nu_{C=O}$), 1242 (ν_{C-O}). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 1.30 (br, 9.2 H, CH_2), 1.51−1.78 (m, 10.0 H, CH_3, CH_2), 2.57 (t, $J = 7.8$ Hz, 4.0 H, CH_2−C(=O)), 3.74−4.18 (m, 9.7 H, CH_2−CH, C−CH_2−O, CH), 6.98 (d, $J = 8.0$ Hz, 4.0 H, ArH), 7.13 (d, $J = 8.0$ Hz, 4.0 H, ArH).

Synthesis of Poly(*S*-thioester) P-5. The polyaddition of BDTE with TPC was carried out as the synthesis of **P-1**. Yield: 89%. M_n: 1.82×10^4. M_w/M_n: 1.51. IR (film, cm^{-1}): 1664 ($\nu_{C=O}$), 1203 (ν_{C-O-C}). ^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ 1.70 (bs, 9.2 H, CH_2), 3.28−4.38 (m, 14.0 H, CH_2, CH), 8.02 (s, 4.0 H, ArH).

Synthesis of Poly(*S*-thioester) P-6. The polyaddition of BPTE with IPC was carried out as the synthesis of **P-1**. Yield: 87%. M_n: 1.76×10^4. M_w/M_n: 1.49. IR (film, cm^{-1}): 1666 ($\nu_{C=O}$), 1147 (ν_{C-O-C}). ^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ 1.70 (s, 4.0 H, CH_2), 3.32−4.41 (m, 14.0 H, CH_2, CH), 7.56 (t, $J = 8.4$ Hz, 1.0 H, ArH), 8.16 (d, $J = 9.0$ Hz, 2.0 H, ArH), 8.50 (s, 1.0 H, ArH).

Table 1. Polyaddition of BPTE with TPC Using Various Catalysts[a]

catalysts	yield, %[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n[c]
none	0		
TBAC[d]	98	2.54	1.48
TBAB[e]	98	2.13	1.54
TBAI[f]	96	2.03	1.69
THAB[g]	76	1.34	1.38
TPPB[h]	85	0.72	1.09
TBPC[i]	98	3.03	1.54
TBPB[j]	97	1.91	1.49
18-C-6[k]/KCl	0		
DMAP[l]	0		
TEA[m]	0		

[a] The reaction was carried out with BPTE (1.2 mmol) and TPC (1.2 mmol) using 5 mol % of catalysts in toluene (0.6 mL) at 90 °C for 24 h. [b] Insoluble parts in methanol. [c] Determined by GPC based on polystyrene standards. [d] TBAC: tetrabutylammonium chloride. [e] TBAB: tetrabutylammonium bromide. [f] TBAI: tetrabutylammonium iodide. [g] THAB: tetrahexylammonium bromide. [h] TPPB: tetraphenylphosphonium bromide. [i] TBPC: tetrabutylphosphonium chloride. [j] TBPB: tetrabutylphosphonium bromide. [k] 18-C-6: 18-crown-6. [l] DMAP: (dimethylamino)pyridine. [m] TEA: triethylamine.

Synthesis of Poly(*S*-thioester) P-7. The polyaddition of BPTE with APC was carried out as the synthesis of **P-1**. Yield: 76%. M_n: 1.60×10^4. M_w/M_n: 1.42. IR (film, cm^{-1}): 1692 ($\nu_{C=O}$), 1114 (ν_{C-O-C}). ^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ 1.42−1.89 (m, 8.0 H, CH_2), 2.59 (br, 4.0 H, CH_2), 3.05−4.31 (m, 14.0 H, CH_2, CH).

Synthesis of Poly(*S*-thioester) P-8. The polyaddition of BPTE with SCC was carried out as the synthesis of **P-1.** Yield: 76%. M_n: 2.13×10^4. M_w/M_n: 1.49. IR (film, cm^{-1}): 1695 (νC=O), 1114 (νC−O−C). ^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ 1.29 (s, 4.0 H, CH_2), 1.64 (br, 4.0 H, CH_2), 2.57 (t, $J = 15.6$ Hz, 4.0 H, CH_2−C(=O)), 3.23−4.22 (m, 14.0 H, CH_2, CH).

Results and Discussion

The polyaddition of BPTE with TPC using various catalysts was examined in toluene at 90 °C for 24 h. The results are summarized in Table 1. The reaction did not proceed without catalysts under the same conditions. In the case of the reaction using triethylamine or 4-(*N*,*N*′-dimethylamino)pyridine, no polymer resulted. This means that the organic bases used did not catalyze the reaction, even though the reaction of bis(oxirane)s[10] with diacyl chlorides proceeded using the organic bases as the catalysts. On the other hand, reactions using quaternary ammonium or phosphonium salts proceeded very smoothly to provide polymers. When the reaction was carried out with tetra-*n*-butylammonium chloride (TBAC), bromide (TBAB), or iodide (TBAI) or tetra-*n*-butylphosphonium bromide (TBPB), polymers with number-average molecular weights (M_n) of 20 000−25 000 were obtained. Concerning the counteranions of tetrabutylammonium salts, TBAC provided a higher molecular weight compared with TBAB and TBAI. The reaction using other quaternary onium bromides such as tetra-*n*-hexylammonium bromide (THAB) or tetraphenylphosphonium bromide (TPPB) provided polymers with lower M_ns than that from the reaction using tetra-*n*-butylammonium halides. The polymer with the highest M_n of 30 000 was obtained from the reaction with tetra-*n*-butylphosphonium chloride (TBPC) under the same reaction conditions. This

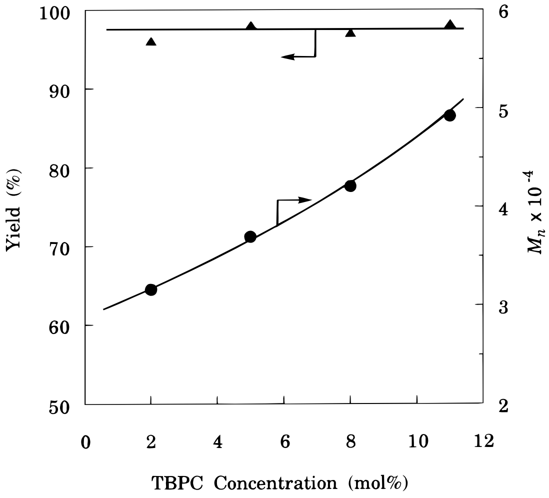

Figure 1. Effect of TBPC concentration on the reaction of BPTE (1.2 mmol) with TPC (1.2 mmol) in toluene (0.6 mL) at 90 °C for 24 h: (▲) yield; (●) M_n.

means that the catalysts with chloride as the counteranion have a higher activity than those with bromide or iodide. It was suggested[6] that characters of the halides of quaternary onium salts such as the nucleophilicity and the ability as a leaving group were very important in a process in which the halides activate thiiranes. It is also showed that catalytic activity of the quaternary onium salts is affected by the nature of quaternary onium cations such as hydrophobicity and bulkiness due to their substituents.

The reaction of BPTE with TPC in toluene at 90 °C was efficiently enhanced by the concentration of TBPC as the catalyst (Figure 1). The molecular weight of the obtained polymer increased with the concentration of TBPC. That is to say that the M_ns of the polymer increased from 30 000 to 50 000 when the concentration of TBPC increased from 2 mol % to 11 mol %.

The structure of the polymer obtained from the reaction of BPTE with TPC was confirmed by IR and ^1H NMR spectroscopies. In the IR spectrum, a characteristic peak due to $C{=}O$ stretching of the *S*-thioester group was observed at 1665 cm^{-1}. The ^1H NMR spectral data supported the structure of the targeted polymer. In addition, the signal due to the protons of the chloromethyl group was observed from 3.86−4.10 ppm with the intensity ratio of 3.8. Thus, the selectivity of β-addition of acyl group to thiirane ring on the reaction was estimated as 95% based on the expected intensity ratio of 4.0. This means that the reaction of BPTE with TPC using TBPC proceeded regioselectivity to afford the poly(*S*-thioester) with the chloromethyl group in the side chain as shown in Scheme 2.

The reaction with 5 mol % of TBPC was conducted in various solvents at 90 °C for 24 h (Table 2). The polymer with a moderate M_n was produced from the reaction in *N*,*N*′-dimethylacetamide (DMAc), *N*-methyl-2-pyrolidone (NMP), hexamethylphosphoric triamide (HMPA), or diglyme. The reaction in aromatic solvents such as toluene or *o*-dichlorobenzene provided polymers with high molecular weights. In particular, the polymer with the highest M_n of 40 000 resulted from the reaction using anisole. This suggests that the aromatic solvents, which are less polar than aprotic polar solvents such as DMAc and HMPA, are suitable reaction media for the reaction of bis(thiirane)s with diacyl chlorides.

The effect of temperature on the reaction of BPTE with TPC in the presence of 5 mol % of TBAB catalyst was examined in toluene for 24 h. As shown in Figure 2, the reaction proceeded easily even at 70 °C to provide the polymer with M_n of 20 000 in quantitative yield. The reaction was effectively enhanced by elevating the reaction temperature to obtain the polymer with a higher molecular weight. A polymer with a M_n of 42 000 was obtained from the reaction at 110 °C. The IR and ^1H NMR spectral data of the obtained polymer proved that the reaction proceeded without any side reactions at elevated temperatures to produce the desired polymer.

Figure 3 shows the time-course of the reaction using 5 mol % of TBPC in toluene at 90 °C. The yield of a polymer insoluble in methanol reached 98% in 4 h. The M_ns of the obtained polymer increased gradually to

Scheme 2

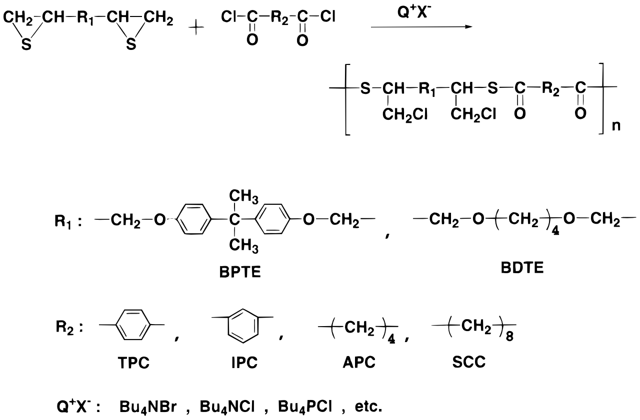

Table 2. Solvent Effect on the Polyaddition of BPTE with TPC[a]

solvent	yield, %[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n[c]
toluene	98	3.03	1.54
anisole	98	3.99	2.01
o-dichlorobenzene	96	2.87	1.66
diglyme	98	2.25	1.63
DMAc[d]	94	1.68	1.45
NMP[e]	98	2.28	1.58
HMPA[f]	97	2.07	1.57

[a] The reaction was carried out with BPTE (1.2 mmol) and TPC (1.2 mmol) using 5 mol% of TBPC in solvent (0.6 mL) at 90 °C for 24 h. [b] Insoluble parts in methanol. [c] Determined by GPC based on polystyrene standards. [d] DMAc: *N*,*N*′-dimethylacetamide. [e] NMP: *N*-methylpyrrolidone. [f] HMPA: hexamethylphosphoric triamide.

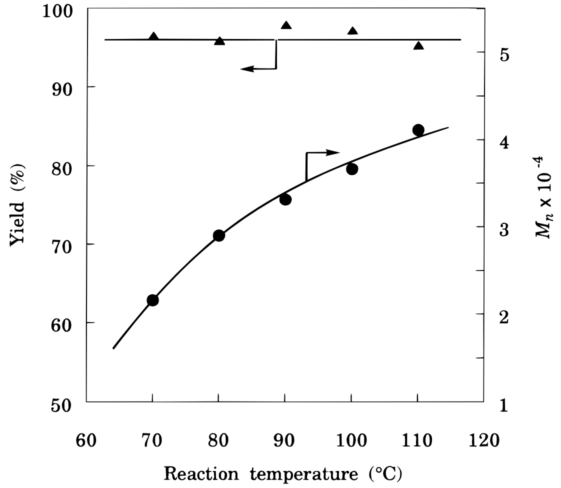

Figure 2. Effect of reaction temperature on the reaction of BPTE (1.2 mmol) with TPC (1.2 mmol) using 5 mol % of TBAB in toluene (0.6 mL) for 24 h: (▲) yield; (●) M_n.

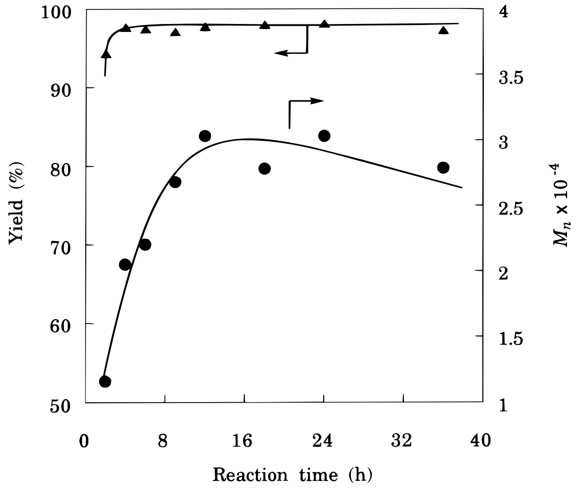

Figure 3. Time-course of the reaction of BPTE (1.2 mmol) with TPC (1.2 mmol) using 5 mol % of TBPC in toluene (0.6 mL) at 90 °C for 24 h: (▲) yield; (●) M_n.

Table 3. Synthesis of Various Poly(S-thioester)s[a]

polymers	bis(thiirane)s	dichlorides	yield, %[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n [c]	S.β., %[d]
P-1	BPTE	TPC[e]	98	3.99	2.01	95
P-2	BPTE	IPC[f]	97	4.03	1.77	95
P-3	BPTE	APC[g]	94	3.21	1.59	
P-4	BPTE	SCC[h]	87	3.07	1.58	
P-5	BDTE	TPC	89	1.82	1.51	
P-6	BDTE	IPC	87	1.76	1.49	
P-7	BDTE	APC	76	1.60	1.42	
P-8	BDTE	SCC	76	2.13	1.49	

[a] The reaction was carried out with bis(thiirane)s (1.2 mmol) and dichlorides (1.2 mmol) using 5 mol % of TBPC in anisole (0.6 mL) at 90 °C for 24 h. [b] Insoluble parts in methanol. [c] Determined by GPC based on polystyrene standards. [d] Selectivity of β-addition which was determined by ^{1}H NMR. [e] Terephtharoyl chloride. [f] Isophtharoyl chloride. [g] Adipoyl chloride. [h] Sebacoyl chloride.

30 000, and decreased slightly after about 20 h. Thus, this suggests that a cleavage of S-thioester group in the polymer backbone would proceed slowly at a prolonged reaction time such as 36 h.

The polyaddition of BPTE with various diacyl chlorides using 5 mol % of TBPC was performed in anisole at 90 °C for 24 h (Table 3). The reaction with aliphatic diacyl chlorides such as adipoyl chloride (APC) or sebacoyl chloride (SCC) produced the corresponding polymer with M_n of 30 000. The reaction of BPTE with TPC or isophthaloyl chloride (IPC) proceeded very efficiently to produce the polymer with relatively high molecular weights (M_n: 40 000). When the reaction of butanediol bis(2,3-epithiopropyl) ether (BDGE) with TPC, IPC, APC, or SCC was carried out under the same conditions, corresponding polymers with M_n of 16 000–21 000 were obtained, respectively. In the case of the reaction of BDGE with APC or SCC, the yields of the resulting polymers were relatively lower (76%) than those obtained from the reaction of TPC or IPC. It seems that cyclic oligo-S-thioesters would be produced in the reaction of aliphatic bis(thiirane)s with aliphatic diacyl chlorides. It also suggests that aromatic diacyl chlorides are more efficient at producing the poly(S-thioester)s with high molecular weights than aliphatic ones. The spectral data of the obtained poly(S-thioester)s proved that all of the prepared poly(S-thioester)s have the chloromethyl group in the side chains. Therefore, it is clear that the polyaddition of the bis(thiirane)s with diacyl chlorides proceeded to form a pendant chloromethyl group.

The solubilities of the obtained poly(S-thioester)s were examined. All of the poly(S-thioester)s are insoluble in methanol, ethanol, and n-hexane and are partially soluble in acetone. On the other hand, the polymers showed good solubility in common solvents including halogenated hydrocarbones, aromatic solvents, etc. The excellent solubility of the high-molecular weight polymers would be ascribed to the pendant chloromethyl group, which inhibit an intermolecular interaction due to their bulkiness.

It is concluded that the polyaddition of bis(thiirane)s with diacyl chlorides proceeded smoothly and regioselectively using quaternary onium salts or crown ether complexes to obtain the poly(S-thioester)s with a chloromethyl group in the side chain. It was also found that TBAC or TBPC catalyzed efficiently the reaction in aromatic solvents to provide the poly(S-thioester)s with high molecular weights. The polyaddition of bis(thiirane)s with diacyl chlorides using quaternary onium salts is classified as a new synthetic method for poly(S-thioester)s.

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