4746 *Macromolecules* **1998,** *31,* 4746−4752

A Novel Synthesis of Poly(ester-*alt*-sulfide)s by the Ring-Opening Alternating Copolymerization of Oxiranes with γ-Thiobutyrolactone Using Quaternary Onium Salts or Crown Ether Complexes as Catalysts

Tadatomi Nishikubo,* Atsushi Kameyama, and Susumu Kawakami

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

Received March 5, 1998; Revised Manuscript Received May 27, 1998

ABSTRACT: Poly(ester-*alt*-sulfide) (polymer **1**) was synthesized by the alternating copolymerization of glycidyl phenyl ether (GPE) with γ-thiobutyrolactone (TBL) catalyzed by either quaternary onium salts or crown ether complexes. The copolymerization proceeded to produce polymer **1** with good yields in neat or in various organic solvents at 30−120 °C, in which quaternary onium salts having Cl^- as a counteranion such as tetrabutylammonium chloride (TBAC) had higher activity than quaternary onium salts such as tetrabutylammonium bromide having Br^- as a counteranion. It was also found that the alternate copolymer (polymer **1**) of GPE with TBL was obtained selectively under different feed ratios of GPE and TBL, although ring-opening homopolymerizations of GPE and TBL did not proceed. Copolymerizations of various oxiranes such as butyl glycidyl ether, styrene oxide, and 1,2-hexene oxide with TBL catalyzed by TBAC also proceeded, and the corresponding poly(ester-*alt*-sulfide)s (polymers **2**, **3**, and **4**) were obtained under the same conditions as for the synthesis of polymer **1**.

Introduction

It is well-known[1] that addition reactions of oxirane with protic reagents such as amines, alcohols, thiols, phenols, and carboxylic acids using appropriate acidic or basic catalysts proceed to give the corresponding 1:1 adducts containing hydroxyl groups. These reactions have been widely used[1,2] in organic synthesis and polymer synthesis. The other interesting reaction of oxiranes is the ring-opening polymerization,[3] which proceeds smoothly to produce the corresponding polyethers when catalyzed by appropriate strong acids or bases. Oxiranes also produce the corresponding polyesters and polycarbonates by alternating copolymerization with carboxylic acid anhydrides and carbon dioxide, respectively.

Meanwhile, ring-opening polymerizations of four-, six-, and seven-membered lactones[4] and thiolactones[5−8] are also known to produce corresponding polyesters and poly(thiol ester)s, respectively, with high molecular weights under appropriate catalytic conditions. However, five-membered lactones[4] and thiolactones[5] such as γ-(thio)butyrolactones and γ-(thio)valerolactones have not been polymerized under reaction conditions similar to those applied for the polymerization of four-, six-, and seven-membered lactones and thiolactones excepting a recent paper, in which Duda et al. reported[9] that γ-butyrolactone produced corresponding homooligomer and copolymers under appropriate conditions.

We have found recently a number of novel addition reactions of oxirane[10] and thiirane[11] with certain carboxylic acid derivatives. These reactions proceed very smoothly to give the corresponding adducts using quaternary onium salts or crown ether complexes as catalysts, in which reaction products did not have any hydroxyl groups. These addition reactions of oxiranes and thiiranes with carboxylic acid derivatives can be applied widely for polymer synthesis. The first application of this reaction is the synthesis of polyesters containing pendant functional groups by the polyaddition of bis(oxirane)s with active di(ester)s[12] or acyl di(chloride)s.[13] Thus obtained functional polyesters can also be used as starting materials for the synthesis of various kinds of functional polymers.[13] The second application of this reaction is the chemical modification of polymers with pendant epoxide groups[14] such as poly(glycidyl methacrylate)s and the chemical modification of polymers with pendant active ester groups[15] such as poly(phenyl methacrylate)s. These reaction systems are very useful for the synthesis of various kinds of functional polymers. The third application of this reaction is the acyl group-transfer polymerization[16,17] of thiiranes to produce the corresponding polysulfides using carboxylic acid derivatives containing suitable leaving groups as initiators and quaternary onium salts as catalysts. This polymerization system is a new method for the synthesis of well-defined polymers and can be applied for the synthesis of living polymers, telechelic polymers, and block copolymers. The fourth application of this reaction is the insertion reactions[18] of thiiranes or oxiranes into polymer main chains such as active poly(*S*-thioester)s or active poly(ester)s using certain quaternary onium salts as catalysts. This reaction proceeds quantitatively and regioselectively. That is, this reaction system can be considered as a breakthrough in the field of synthesis of multisequence-ordered polymers. However, we had not yet studied addition reactions of oxiranes and thiiranes with cyclic (thio)carboxylic esters having suitable leaving groups. We expected still more new addition reactions of oxiranes and thiiranes.

Given this background, we examined the addition reaction of oxiranes with γ-thiobutyrolactone in the presence of quaternary onium salts or crown ether complexes as catalysts and found the corresponding poly(ester-*alt*-sulfide)s can be obtained in good yields.

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* To whom all correspondence should be addressed.

S0024-9297(98)00350-7 CCC: $15.00

Experimental Section

Materials. Solvents were dried using P_2O_5, CaH_2, or Na metal wire and purified by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized twice from ethyl acetate. Commercial reagent grades of tetrabutylammonium chloride (TBAC), tetrabutylammonium acetate (TBAAc), tetrabutylphosphonium bromide (TBPB), tetrabutylphosphonium chloride (TBPC), 18-crown-6 (18-C-6), potassium chloride (KCl), potassium *tert*-butoxide (*t*-BuOK), and potassium phenoxide (PhOK) were used without further purification. Glycidyl phenyl ether (GPE), butyl glycidyl ether (BGE), styrene oxide (SO), 1,2-hexene oxide (HO), cyclohexene oxide (CHO), and γ-thiobutyrolactone (TBL) were dried using CaH_2 and purified by distillation.

Measurement. Infrared (IR) spectra were measured on a JASCO Model IR-700 spectrometer. The ^{1}H NMR and the ^{13}C NMR spectra were recorded on a JEOL Model JNM FX-200 (200 MHz) instrument in $CDCl_3$ using Me_4Si (TMS) as an internal standard. The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of a Tosoh Model HLC-8120 GPC equipped with a refractive index detector using TSK gel columns (eluent: THF, calibrated using narrow molecular weight polystyrenes as standards).

Typical Procedure for the Alternating Copolymerization of Oxirane with TBL Catalyzed by Quaternary Onium Salt. A typical example of the copolymerization of oxirane with TBL is as follows.

Copolymerization of GPE with TBL. GPE (0.45 g; 3.0 mmol), TBL (0.31 g; 3.0 mmol), and TBAB (0.032 g; 0.1 mmol) as a catalyst were all charged into a glass tube in a drybox, after which the tube was evacuated and then sealed using a gas torch. The copolymerization of GPE with TBL was carried out in the sealed tube at 90 °C for 24 h under stirring. The reaction mixture was dissolved with 2 mL of chloroform, and then poured into methanol to precipitate the polymer. The resulting polymer was reprecipitated twice from chloroform into methanol and dried in vacuo. The yield of the corresponding poly(ester-*alt*-sulfide) (polymer **1)** was 0.76 g (97%). The number average molecular weight (M_n) of the polymer determined from GPC was 14 000 ($M_w/M_n = 2.22$). IR (film): 1735 ($\nu_{C=O}$), 1589 and 1494 ($\nu_{\text{aromatic C=C}}$), 1293 ($\nu_{Ph-O-C}$), 1243 ($\nu_{C-O-C}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 1.73−2.14 (m, 2.0H, $CH_2CH_2CH_2$), 2.21−2.53 (m, 2.0H, SCH_2CH_2), 2.53−2.68 (m, 2.0H, CH_2CH_2CO), 2.68−3.03 (m, 2.0H, $CHCH_2S$), 4.18−4.33 (m, 2.0H, $CHCH_2OPh$), 5.09−5.43 (m, 1.0H, CO_2CHCH_2), 6.66−7.48 ppm (m, 5.0H, aromatic protons). ^{13}C NMR (50 MHz, $CDCl_3$, TMS): δ 24.49 ($CH_2CH_2CH_2$), 31.74 (SCH_2CH_2), 31.97 ($CHCH_2S$), 32.87 (CH_2CH_2CO), 67.27 ($CHCH_2OPh$), 71.26 (CO_2CHCH_2), 114.61, 121.21, 129.48, 158.32 (aromatic carbons), 172.28 ppm (CH_2CO_2). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 62.12; H, 6.33.

Copolymerization of BGE with TBL. BGE (0.39 g; 3.0 mmol), TBL (0.31 g; 3.0 mmol), and TBAC (0.029 g, 0.1 mmol) were charged into a glass tube in a drybox, and then the tube was sealed as explained above. The reaction was performed at 90 °C in the sealed tube for 24 h under stirring, then the reaction mixture was dissolved with 10 mL of chloroform. The polymer solution was washed thrice with minimal amounts of water, and some chloroform was evaporated. The solution was poured into *n*-hexane to precipitate the polymer. The resulting polymer was reprecipitated from chloroform into *n*-hexane, and dried in vacuo. The yield of the corresponding poly(ester-*alt*-sulfide) (polymer **2)** was 0.47 g (64%). The M_n of the polymer determined from GPC was 8800 ($M_w/M_n =$ 1.43). IR (film): 1733 ($\nu_{C=O}$), 1230 (ν_{C-O-C}) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 0.75−1.11 (m, 3.0H, pendant CH_2-CH_3), 1.16−1.44 (m, 2.0H, pendant $OCH_2CH_2CH_2CH_3$), 1.44−1.65 (m, 2.0H, pendant $OCH_2CH_2CH_2CH_3$), 1.72−2.09 (m, 2.0H, $CH_2CH_2CH_2$), 2.28−3.88 (m, 6.0H, CH_2CH_2CO, SCH_2CH_2, and $CHCH_2S$), 3.17−3.75 (m, 4.0H, pendant CH_2OCH_2), 4.83−5.17 ppm (m, 1.0H, CO_2CHCH_2).

Table 1. Effect of Catalyst on the Copolymerization of GPE with TBL[a]

catalyst	time, h	yield,[b] %	composition[c] GPE:TBL	M_n x 10^{-4} [d]	M_w/M_n [d]
none	24	0			
TBAB	24	93	50:50	1.4	2.22
TBAC	1	93	50:50	0.95	1.99
TBPB	24	90	50:50	1.5	2.30
TBPC	1	97	50:50	0.75	1.66
18-C-6/KCl	24	98	50:50	1.7	2.24
PhOK	24	95	50:50	0.56	1.68
18-C-6/ PhOK	24	98	50:50	0.74	1.72
t-BuOK	24	91	50:50	0.75	1.48
18-C-6/*t*-BuOK	24	99	50:50	0.62	1.50

[a] The reaction was carried out with GPE (1.0 mmol) and TBL (1.0 mmol) using the catalyst (0.03 mmol) without solvent at 90 °C. [b] Insoluble part in methanol. [c] Determined by ^{1}H NMR spectrum. [d] Estimated by GPC based on polystyrene standards.

Copolymerization of SO with TBL. SO (0.36 g; 3.0 mmol) was made to react with TBL (0.31 g; 3.0 mmol) in the presence of TBAC (0.029 g; 0.1 mmol) at 90 °C in a sealed tube for 24 h. The reaction mixture was dissolved with chloroform and then washed with water. The polymer solution was poured into *n*-hexane, reprecipitated from chloroform into *n*-hexane, and dried in vacuo. The yield of the corresponding poly(ester-*alt*-sulfide) (polymer **3**) was 0.66 g (94%). The M_n of the polymer determined from GPC was 6400 ($M_w/M_n =$ 1.51). IR (film): 1733 ($\nu_{C=O}$), 1493 ($\nu_{\text{aromatic C=C}}$), 1307 ($\nu_{C-O-C}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 1.59−2.06 (m, 2.0H, $CH_2CH_2CH_2$), 2.12−2.64 (m, 6.0H, SCH_2CH_2, $CHCH_2S$, and OCH_2CH), 2.65−3.15 (m, 2.0H, CH_2CH_2CO), 4.20−4.47 (m, 0.24H, $CH_2CH(Ph)S$), 5.68−5.97 (m, 0.76H, $OCH(Ph)CH_2$), 7.05−7.53 ppm (m, 5.0H, aromatic protons).

Copolymerization of HO with TBL. The copolymerization of HO (0.30 g; 3 mmol) and TBL (0.31 g; 3 mmol) was carried out in the presence of TBAC (0.029 g; 0.1 mmol) at 90 °C in a sealed tube for 24 h, and the product was purified by the same procedure as described for polymer **2**. The final yield of the corresponding poly(ester-*alt*-sulfide) (polymer **4**) was 0.12 g (19%). The M_n of the polymer determined from GPC was 7700 ($M_w/M_n = 1.27$). IR (film): 1731 ($\nu_{C=O}$), 1234 (ν_{C-O-C}) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 0.73−1.12 (m, 3.0H, pendant CH_2CH_3), 1.12−1.47 (m, 4.0H, pendant $CH_2CH_2CH_2CH_3$), 1.47−1.83 (m, 2.0H, pendant $CHCH_2CH_2-CH_2CH_3$), 1.83−2.06 (m, 2.0H, $CH_2CH_2CH_2$), 2.22−2.88 (m, 6.0H, CH_2CH_2CO, SCH_2CH_2, and $CHCH_2S$), 4.72−5.09 ppm (m, 1.0H, CO_2CHCH_2).

Results and Discussion

The addition reaction of GPE with cyclic thioester TBL was examined using TBAB as a catalyst to obtain the expected cyclic adduct, since corresponding adducts had been obtained quantitatively and regioselectively[11] by the addition reaction of oxiranes with *S*-aryl thioesters and *S*-alkyl thioesters catalyzed by quaternary onium salts. Furthermore, it had been reported[5,8] that the ring-opening polymerization of TBL did not occur.

Surprisingly, as shown in Table 1, a new polymer with high molecular weight (number average molecular weight (M_n) =14 000) was obtained in 93% yield by the reaction of equivalent amounts of GPE and TBL without solvent using 3 mol % of TBAB as the catalyst at 90 °C for 24 h, although no corresponding cyclic adduct was obtained. The structure of the polymer was determined by the IR spectrum, ^{1}H- and ^{13}C-NMR spectra, and elemental analysis. The IR spectrum of the obtained polymer showed absorption peaks at 1735, 1589 and 1494, 1293, and 1243 cm^{-1} due to C=O, aromatic C=C, Ph−O−C, and C−O−C stretching, respectively. The ^{1}H NMR spectrum of this compound exhibited the proton

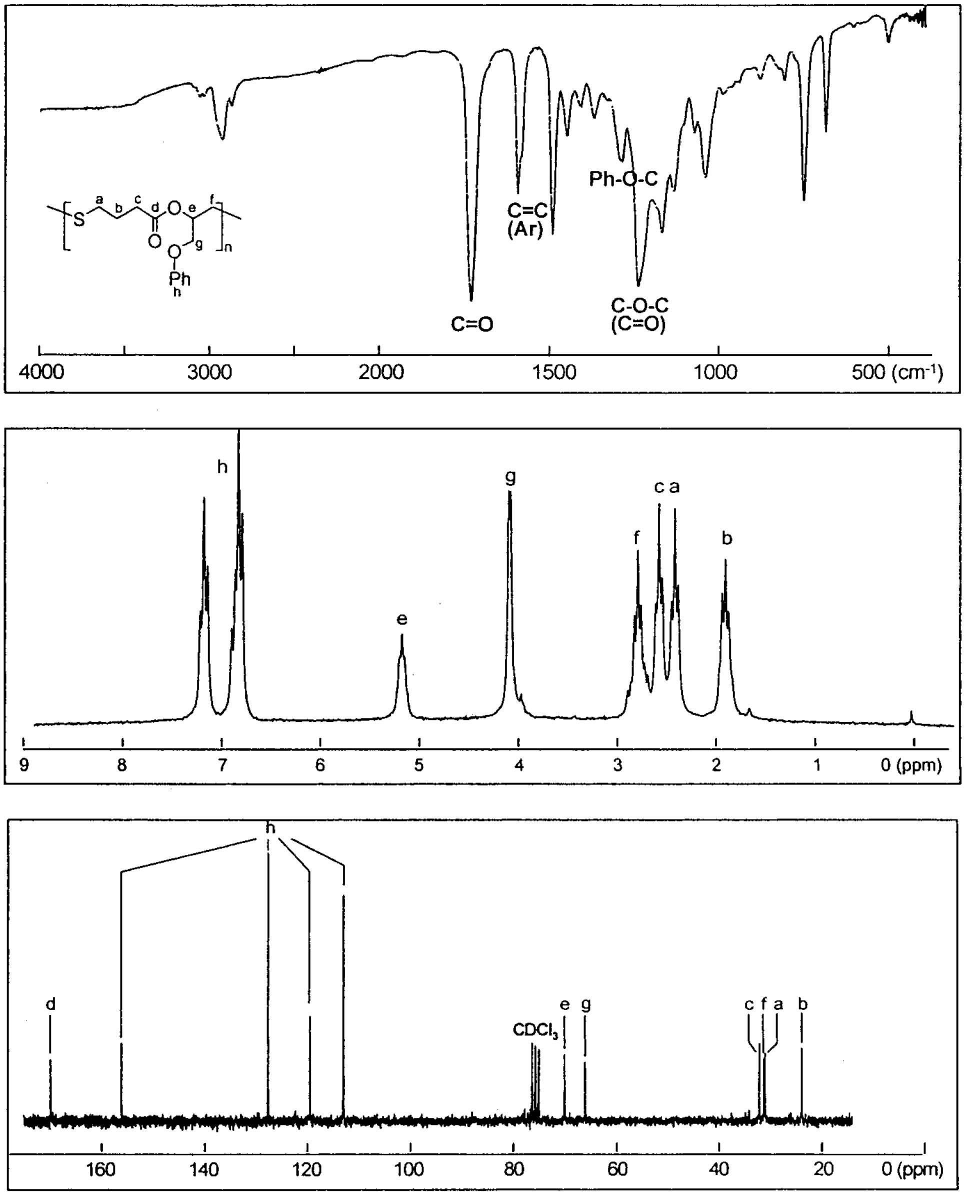
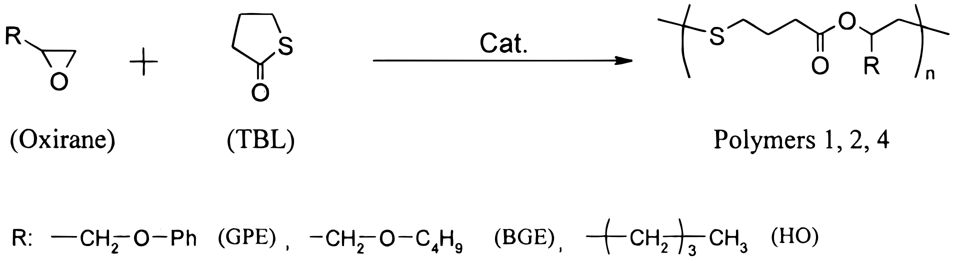


Figure 1. Spectral data of polymer **1**.

Scheme 1



signals at 1.73−2.14 due to the CCH_2C (b), at 2.21−2.53 due to the SCH_2C (a), at 2.53−2.68 due to the CCH_2CO (c), at 2.68−3.03 due to the $CHCH_2S$ (f), at 4.18−4.33 due to the CCH_2OPh (g), at 5.09−5.43 due to the CO_2CHC (e), and at 6.66−7.48 ppm due to the aromatic protons (h) (Figure 1). From the intensity ratio of methine protons (e) at 5.09−5.43 ppm vs aromatic protons (h) at 6.66−7.48 ppm, the ratio of β-cleavage of the epoxy ring of GPE was found to be 100%. The ^{13}C NMR spectrum of the polymer also showed the corresponding signals. Furthermore, elemental analysis values of C and H of the polymer agreed with calculated values. From all these results, it was confirmed that the new copolymer (polymer **1**) shown in Scheme 1 was obtained by the ring-opening alternation copolymerization of GPE with TBL using TBAB as the catalyst.

The effect of the catalyst on the copolymerization of GPE with TBL was examined without solvent at 90 °C. As summarized in Table 1, although the reaction did not proceed without a catalyst, the copolymerization proceeded smoothly to produce polymers **1** with M_n = 7500−15 000 in good yields using certain quaternary onium salts such as TBAB, TBAC, TBPB, and TBPC.

Table 2. Effect of Solvent on the Copolymerization of GPE with TBL[a]

solvent	time, h	yield,[b] %	composition[c] GPE:TBL	M_n x 10^{-4} [d]	M_w/M_n [d]
none	1	93	50:50	1.0	1.92
DMAc	24	67	50:50	0.43	1.50
DMSO	24	37	50:50	0.34	1.27
anisole	24	86	50:50	0.83	1.63
toluene	24	85	50:50	0.92	1.66

[a] The reaction was carried out with GPE (1.0 mmol) and TBL (1.0 mmol) using TBAC (0.03 mmol) in the solvent (3.0 mL) at 90 °C. [b] Insoluble part in methanol. [c] Determined by ^{1}H NMR spectrum. [d] Estimated by GPC based on polystyrene standards.

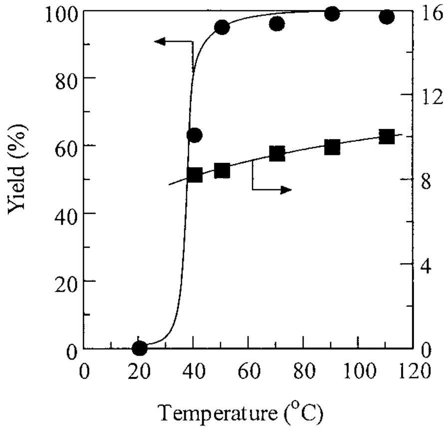


Figure 2. Effect of reaction temperature on the copolymerization of GPE (1.0 mmol) with TBL (1.0 mmol) using TBAC (0.03 mmol) without solvent for 2 h.

In this reaction system, it became clear that TBAC and TBPC having Cl$^-$ as the counteranion showed a higher activity than TBAB and TBPB having Br$^-$ as the counteranion, because alternating copolymers were obtained in quantitative yields after only 1 h using TBAC and TBPC. A complex of 18-C-6 with KCl also showed good catalytic activity. Although the copolymerization proceeded smoothly using potassium phenoxide and potassium *tert*-butoxide to produce polymer **1**, it seems from yields of the polymer that the rate of the copolymerization was enhanced using the complexes of 18-C-6 with potassium phenoxide and potassium *tert*-butoxide.

The effect of the solvent used on the copolymerization of GPE with TBL was investigated using 3 mol % of TBAC as the catalyst at 90 °C (Table 2). Polymer **1** was obtained in 93% yield when the reaction was carried out without solvent at 1 h. Yields of polymer **1** were 67, 37, 86, and 85% in DMAc, DMSO, anisole, and toluene for 24 h, respectively. This suggests that although the copolymerization of GPE with TBL proceeded smoothly without solvent, aromatic and hydrophobic solvents such as anisole and toluene were better solvents than aprotic polar solvents such as DMAc and DMSO.

The effect of reaction temperature on the copolymerization of GPE with TBL was examined without solvent for 2 h, in which 3 mol % of TBAC was used as the catalyst. As shown in Figure 2, although the copolymerization did not proceed at 20 °C, the copolymerization proceeded very smoothly at 40−120 °C, and the yield and the molecular weight of the polymer increased gradually with increasing temperature.

The effect of the feed ratio of monomers vs TBAC was examined. As shown in Figure 3, when the reaction was carried out at 90 °C for 2 h, polymers **1** were obtained in quantitative yields regardless of feed ratio. On the other hand, the molecular weight of the resulting polymers increased with an increase in monomer proportion; however, a straight line was not found in this correlation. This means that this copolymerization system has a chain-growth polymerization character induced by the quaternary onium salt as with the other ring-opening polymerization systems.

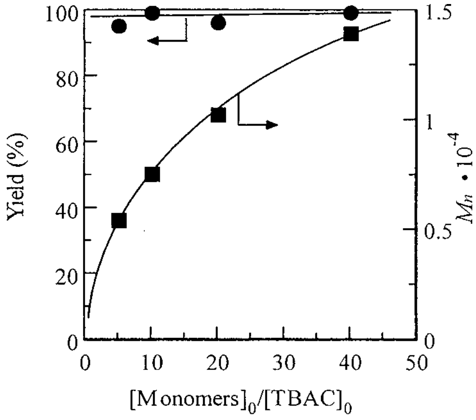


Figure 3. Effect of feed ratio of monomers for TBAC on the copolymerization of GPE (1.0 mmol) with TBL (1.0 mmol) using TBAC without solvent at 90 °C for 2 h.

As shown in Table 3, the effect of feed ratio of two monomers was investigated. The alternating copolymerization proceeded smoothly at different feed ratios of GPE and TBL to produce polymer **1** with quantitative yields using TBAC as the catalyst at 90 °C for 1 h, although no homopolymerization of GPE and TBL proceeded under the same conditions. Conversions of both monomers GPE and TBL were plotted against reaction time. As shown in Figure 4, conversions of both monomers decreased equally. This also shows that the yield of the resulting copolymer agrees with the conversion of both monomers at over time. This means that in this reaction system, the alternating copolymerization of GPE with TBL occurred selectively over time.

As shown in Figure 5, when the copolymerizations of GPE with TBL were carried out under different feed ratios, rates of decrease of both monomers were mostly the same. However, when large amounts of GPE were charged in the reaction tubes, the rate of the alternating copolymerization was relatively high. This means that the complex formation step between oxirane and the catalyst is the rate-determining factor in the reaction.

Interestingly, when the yield of the polymer increased, the M_n and the molecular weight distribution (M_w/M_n) of the resulting polymer increased. Figure 6 shows the detailed data of the correlation between the yields of the polymer with M_n and M_w/M_n on the copolymerization of GPE with TBL catalyzed by TBAC or TBAB. This shows that this ring-opening alternating copolymerization system has a step-growth polymerization character, because the M_n of the resulting polymer increased with the yield of the polymer.

The effect of the counteranion of tetrabutylammonium salts can also be found from Figure 6. When TBAB was used as the catalyst, the increase of the M_n of the polymer was higher than that of the polymer using TBAC. On the other hand, as shown in Figure 7, when TBAAc was used as the catalyst, the increase of the M_n of the polymer was lower than that of the polymer using TBAC. That is, the increase of the M_n of the resulting

Table 3. Effect of Feed Ratio of Monomer on the Copolymerization of GPE with TBL[a]

feed ratio GPE:TBL	yield,[b] % recovered	(theoretical)	composition[c] GPE:TBL	$M_n \times 10^{-4\,d}$	M_w/M_n [d]
100: 0	0	(0)			
75:25	44	(46)	50:50	0.65	1.77
50:50	93	(100)	50:50	0.95	1.99
25:75	51	(55)	50:50	0.44	1.57
0:100	0	(0)			

[a] The reaction was carried out with GPE and TBL (total 6.0 mmol) using TBAC (0.03 mmol) without solvent at 90 °C for 1 h. [b] Insoluble part in methanol. [c] Determined by ^{1}H NMR spectrum. [d] Estimated by GPC based on polystyrene standards.

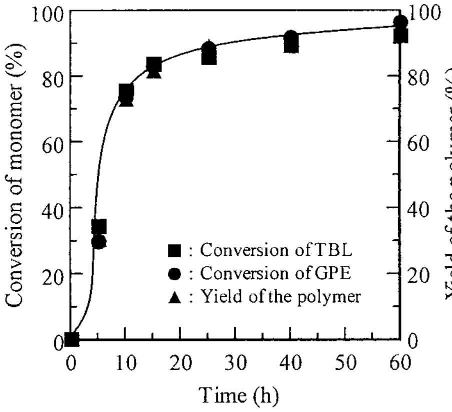


Figure 4. Time–conversion of the copolymerization of equivalent amounts of GPE (1.0 mmol) and TBL (1.0 mmol) using TBAC (0.03 mmol) without solvent at 90 °C.

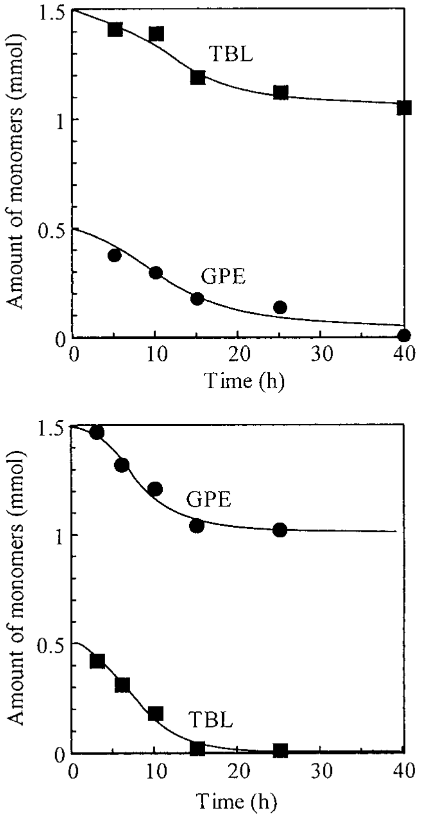


Figure 5. Time–conversion of the copolymerization of different amounts of GPE and TBL using TBAC (0.02 mmol) without solvent at 90 °C: (top) with GPE (0.5 mmol) and TBL (1.5 mmol); (bottom) with GPE (1.5 mmol) and TBL (0.5 mmol).

polymer in the last stage was related to the leaving property of these counteranions of quaternary ammonium salts. From these results, we propose the following reaction mechanisms for the alternating copolymerization of oxirane with TBL (Scheme 2). The initial step is complex formation of oxirane with the quaternary onium salt, and this complex reacts with TBL, producing an adduct with a thiolate anion. The normal next propagation step in this reaction is repetitions of the addition of oxirane and TBL to each propagating species. This reaction mechanism might account for the chain-growth polymerization character. However, a possible further propagation step in this reaction is a coupling reaction of the propagating terminal thialate anion with leaving groups of the other side of the polymer chain, in which the increase of the M_n of the polymer relates to the leaving property of the counteranion of the quaternary onium salts. This latter reaction mechanism might also account for the step-growth polymerization character.

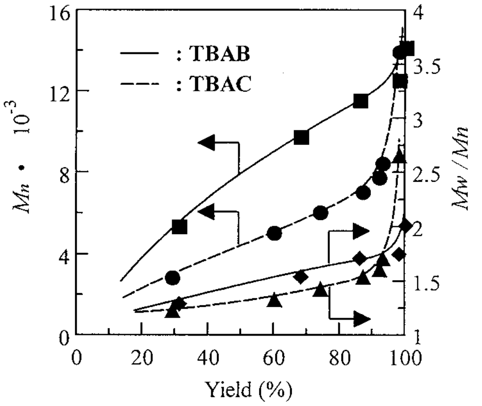


Figure 6. Correlation between yield and M_n of the polymer on the copolymerization of GPE (1.0 mmol) with TBL (1.0 mmol) using TBAC (0.03 mmol) or TBAB (0.03 mmol) without solvent at 90 °C: (●, ▲) TBAC, (■, ◆) TBAB.

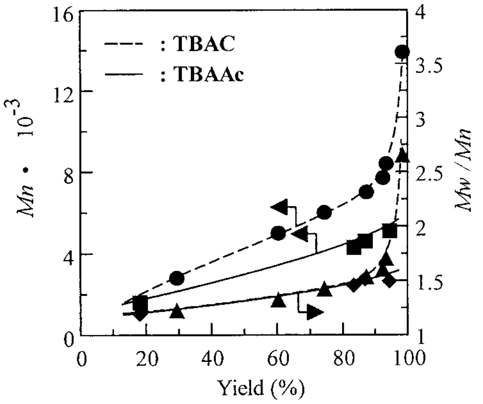
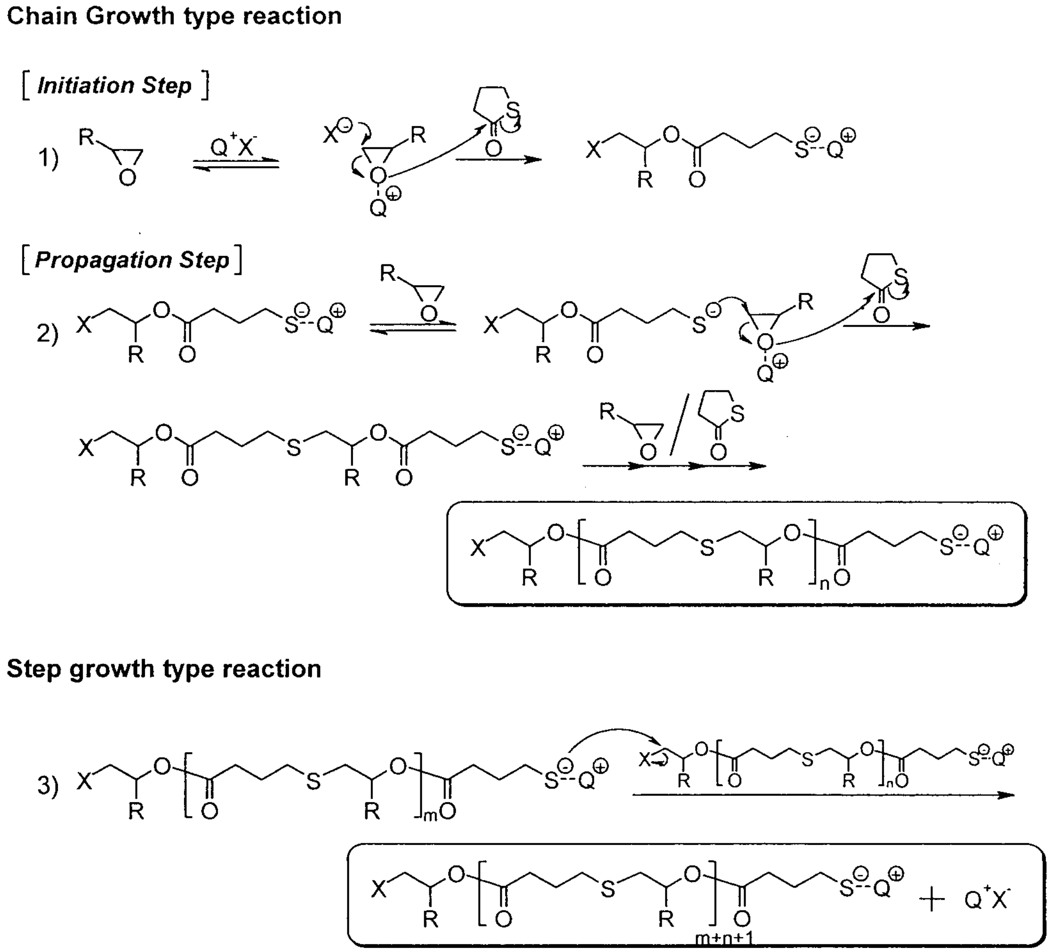


Figure 7. Correlation between yield and M_n of the polymer on the copolymerization of GPE (1.0 mmol) with TBL (1.0 mmol) using TBAC (0.03 mmol) or TBAAc (0.03 mmol) without solvent at 90 °C: (●, ▲) TBAC, (■, ◆) TBAAc.

This reaction mechanism was supported from GPC data on the copolymerization of GPE with TBL catalyzed by TBAC and TBAB. As shown in Figure 8, when TBAC was used as the catalyst, only one peak was found

Scheme 2



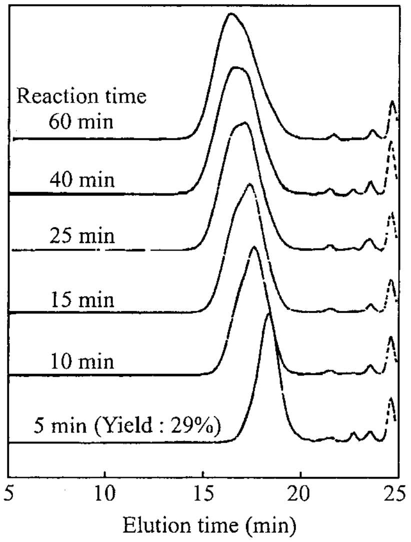


Figure 8. GPC data of polymers by the reaction of GPE (1.0 mmol) with TBL (1.0 mmol) using TBAC (0.03 mmol) without solvent at 90 °C for various reaction times.

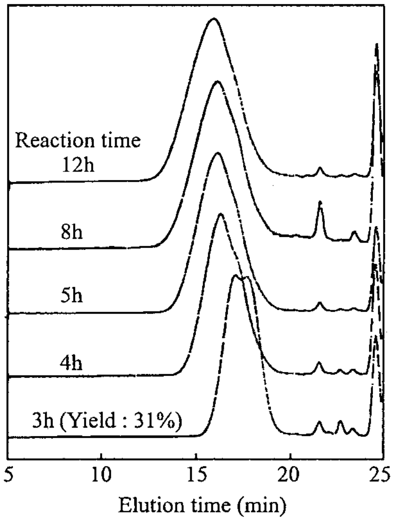


Figure 9. GPC data of polymers by the reaction of GPE (1.0 mmol) with TBL (1.0 mmol) using TBAB (0.03 mmol) without solvent at 90 °C for various reaction times.

due to chain-growth polymerization, and no shoulder was found due to the step-growth polymerization at 5 min. However, the shoulder due to the step-growth polymerization appeared with time. On the other hand, as shown in Figure 9, when TBAB was used as the catalyst, both peaks due to the chain-growth polymerization and the step-growth polymerization were found at 3 h.

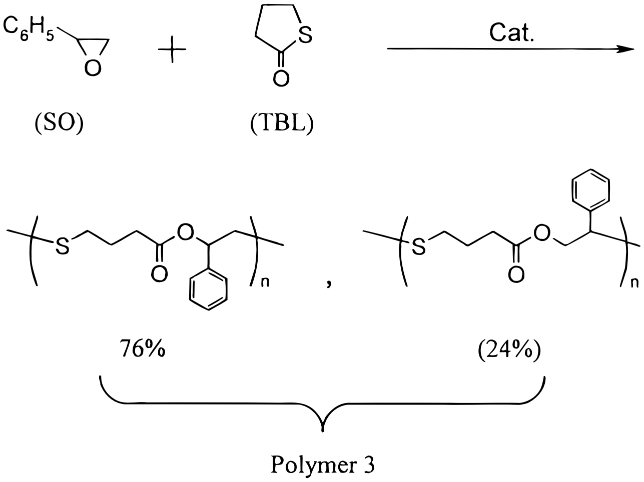
The copolymerization of TBL with certain oxiranes such as BGE, SO, HO, and CHO was examined using TBAC as the catalyst at 90 °C for 24 h. As summarized in Table 4, copolymerizations of TBL with BGE and HO proceeded to give corresponding copolymers (polymers **2** and **4**) with 64 and 19% yields, respectively. It was also found that β-cleavage of oxiranes occurred with 100% selectivity to form the polymers shown in Scheme 1. The copolymerization of SO with TBL produced the

Table 4. Copolymerizations of Various Oxiranes with TBL Using TBAC[a]

oxirane	yield,[b] %	composition oxirane:TBL	β-cleavage[c] of oxirane, %	$M_n \times 10^{-3}$ [d]	M_w/M_n [d]
BGE	64	50:50	100	8.8	1.43
SO	94	50:50	76	6.4	1.51
HO	19	50:50	100	7.7	1.27
CHO	0				

[a] The reaction was carried out with GPE (3.0 mmol) and TBL (3.0 mmol) using TBAC (0.1 mmol) without solvent at 90 °C for 24 h. [b] Insoluble part in methanol. [c] Determined from ^{1}H NMR spectrum. [d] Estimated by GPC based on polystyrene standards.

Scheme 3



corresponding polymer (polymer **3**) in 94% yield (Scheme 3). However, the selectivity of β-cleavage of SO was 76%, which was confirmed by ^{1}H NMR spectrum. It seems that higher electrophilicity of α-carbon on SO due to the resonance stability of phenyl group than that of GPE and BGE produced 24 mol % of α-adduct form, although the α-carbon on SO was sterically hindered by the directly bonded phenyl group to the oxirane ring. On the other hand, the copolymerization of TBL with CHO did not proceed to produce any polymer. It seems that CHO was a sterically hindered molecule in this reaction system.

From all these results, the following conclusion can be drawn. Novel poly(ester-*alt*-sulfide)s were obtained by the ring-opening alternating copolymerization of certain oxiranes with TBL using quaternary onium salts or crown ether complexes as catalysts, although no homopolymerization of oxiranes and TBL occurred in the presence of the same catalyst system.

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MA980350U