Macromolecules **1992,** *25,* 2307–2311

Synthesis of Reactive Polyesters by a Regioselective Addition Reaction of Diepoxides with Diacyl Chlorides and Their Chemical Modification

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Received August 8, 1991; Revised Manuscript Received January 13, 1992

ABSTRACT: The polyaddition of diepoxides with diacyl chlorides using quaternary ammonium salts as a catalyst proceeded regioselectively under mild conditions to afford polyesters having pendant chloromethyl groups. Quaternary ammonium halides such as tetrabutylammonium chloride and bromide were very effective catalysts for the polyaddition, and polyesters with high molecular weight were obtained using these catalysts. The resulting polyesters exhibited excellent solubility characteristics to common organic solvents. The chemical modification of the pendant chloromethyl group by a substitution reaction with nucleophilic reagents, sodium dithiocarbamate (NaDC), sodium azide (NaN_3), and potassium 3-phenyl-2,5-norbornadienecarboxylate (KNBD), was performed using a phase-transfer catalyst to give modified polyesters with high conversion.

Introduction

Polyesters have been mainly prepared by a condensation reaction of dicarboxylic acid derivatives with diols or metal diolates and by the reaction of bis(metal carboxylates) with alkylene dihalides using phase-transfer catalysts[1] as well as the condensation reaction of dicarboxylic acids with alkylene dihalides using 1,8-diazabicyclo[5.4.0]undec-7-ene.[2] Furthermore, polyesters have been prepared by the anionic ring-opening polymerization of lactones, the radical ring-opening polymerization of cyclic ketene acetals,[3] and the anionic ring-opening alternating copolymerization of carboxylic anhydrides with epoxides.[4]

Meanwhile, reactions of epoxy compounds with active carboxylic acid derivatives such as acyl chlorides or active esters are regarded as elementary reactions for the polyaddition reaction of diepoxides with active biscarbonyl compounds to give polyesters and have been widely investigated using various catalysts in the field of organic synthesis. The addition reaction of epoxides with aryl carboxylates has proceeded in the presence of tertiary amine or metal *tert*-butoxides as a catalyst at relatively high temperatures.[5] Baba et al. have reported that the reaction of epoxides with benzoyl chloride using an organotin halide–triphenylphosphine complex as a catalyst proceeded smoothly under mild conditions to afford the corresponding addition products.[6] Noncatalyzed reactions of epoxides with acyl chlorides or bromides under high-pressure conditions were reported.[7] Polyester synthesis by polyaddition of diepoxides with diacyl chlorides, or bis(aryl carboxylates), has been also performed. Vashchuk et al. reported the synthesis of polyesters by a polyaddition reaction of diepoxides with diacyl chlorides using pyridine as the catalyst in bulk.[8] However, the scission mode of the epoxy group of the diepoxides and the structure of the resulting polymer were not discussed in their study. Polyester synthesis from diepoxides with bisphenyl esters at elevated temperature has also been reported by Funahashi.[9]

Recently, we have studied the addition reaction of epoxy compounds with active carbonyl compounds, such as active esters[10] or acyl chlorides,[11] and found that the addition reaction proceeded regioselectively under mild conditions using quaternary ammonium salts, quaternary phosphonium salts, or crown ether complexes as catalysts to obtain the corresponding products, esters with functional groups (Scheme I). We have also reported that the addition reaction of diepoxides with bisphenyl esters was catalyzed by quaternary ammonium salts under mild conditions to afford polyesters.[12]

From this background information, we designed a one-step synthesis of reactive polyesters having chloromethyl groups by the regioselective polyaddition of diepoxides with diacyl chlorides using quaternary ammonium salts as catalysts. In the reaction, the pendant chloromethyl groups are introduced simultaneously with the formation of an ester linkage in the main chain of the polyesters. This polyaddition reaction is a unique and successful method for the synthesis of reactive polymers compared with the conventional method of reactive polymer synthesis, because reactive polymers have been predominantly prepared by selective polymerization of the monomers having polymerizable and reactive groups.

In this study, the polyaddition reaction of diepoxides with diacyl chlorides using quaternary ammonium salts as catalysts was investigated in detail; the catalytic activity of quaternary ammonium salts, the solvent effect, and the scission mode of the epoxy group in the polyaddition were examined. Furthermore, the chemical modification of the resulting polyesters was successfully performed with some nucleophiles using phase-transfer catalysts (Scheme II).

Experimental Section

Materials. Bisphenol A diglycidyl ether (BPGE) was recrystallized four times from methanol/methyl ethyl ketone [4:1, v/v, epoxy equivalent (EQ) 171.1, purity 99.6%]. Ethylene glycol diglycidyl ether was purified three times by distillation [70–71 °C (0.06–0.07 mmHg), EQ 90.6, purity 96.1%]. 4-(*N*,*N*-Dimethylamino)pyridine was recrystallized from tetrachloromethane. 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. Potassium 3-phenyl-2,5-norbornadienecarboxylate was prepared by a reported method.[14] Tributylamine, pyridine, tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), and the solvents used for polyaddition were purified by a conventional method. Other reagents were used as commercial grades.

Measurement. IR spectra were recorded by using a Jasco A-202 spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ using JEOL JMS-PS100 (100 MHz) or EX-90 (90 MHz) spectrometers.

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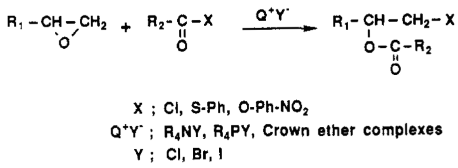
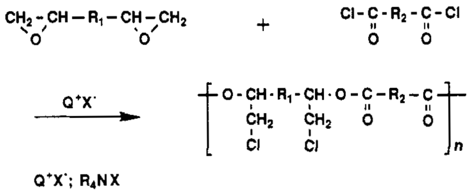
Scheme I

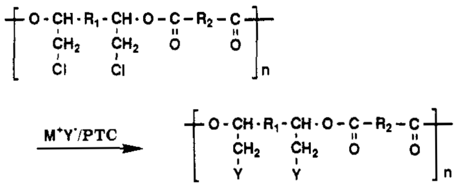


Scheme II

Polymer synthesis



Chemical modification



Synthesis of Polyester P-1 from BPGE with TPC. A typical procedure for the polyaddition of Bisphenol A diglycidyl ether (BPGE) with terephthaloyl chloride (TPC) is as follows: BPGE (1.702 g, 5 mmol), TPC (1.015 g, 5 mmol), and TBAB (0.080 g, 0.25 mmol) were dissolved in toluene (2.5 mL), and the solution was heated at 100 °C for 15 h. Then tetrahydrofuran (THF; 30 mL) was added to the reaction mixture, and the diluted solution was poured into 500 mL of methanol (MeOH) to precipitate polymer. The obtained polymer was reprecipitated twice in THF/MeOH and then collected by filtration and dried at 60 °C for 24 h in vacuo to give the polymer in 96% yield. The reduced viscosity of the resulting polymer (P-1) was 0.44 dL/g in *N,N*-dimethylformamide (DMF; conc = 0.5 g/dL) at 30 °C. IR (film): 1728 ($\nu_{C=O}$), 1255 (ν_{COC}), 728 cm^{-1} (ν_{CCl}). ^{1}H NMR (100 MHz, CDCl$_3$, TMS): δ 1.62 (s, 6.0 H, CCH_3), 3.96 (d, J = 5.0 Hz, 4.0 H, CH_2Cl), 4.30 (d, J = 5.0 Hz, 4.0 H, CH_2O), 5.36–5.68 (m, 2.0 H, OCH), 6.80 (d, J = 9.0 Hz, 4.0 Hz, Ar), 7.12 (d, J = 9.0 Hz, 4.0 H, Ar), 8.06 (s, 4.0 H, Ar).

Synthesis of Polyester P-2 from BPGE with Isophthaloyl Chloride (IPC). The polymerization was carried out similarly to the synthesis of P-1 with IPC (1.015 g, 5 mmol). Yield: 94%. $\eta_{sp/c}$: 0.35 dL/g (in DMF, conc = 0.5 g/dL, 30 °C). IR (film): 1729 ($\nu_{C=O}$), 1228 cm^{-1} (ν_{COC}). ^{1}H NMR (100 MHz, CDCl$_3$, TMS): δ 1.62 (s, 6.0 H, CH_3), 3.98 (d, J = 5.0 Hz, 4.0 H, CH_2Cl), 4.33 (d, J = 5.0 Hz, 4.0 H, CH_2O), 5.42–5.84 (m, 2.0 H, OCHO), 6.88 (d, J = 8.0 Hz, 4.0 H, Ar), 7.23 (d, J = 8.0 Hz, 4.0 H, Ar), 7.45–7.80 (m, 1.0 H, Ar), 8.23–8.58 (m, 2.0 H, Ar), 8.82 (s, 1.0 H, Ar).

Synthesis of Polyester P-3 from BPGE with Adipoyl Chloride (APC). The polymerization was carried out similarly to the synthesis of P-1 with APC (0.915 g, 5 mmol). Yield: 81%. $\eta_{sp/c}$: 0.22 dL/g (in DMF, conc = 0.5 g/dL, 30 °C). IR (film): 1740 ($\nu_{C=O}$), 1250 cm^{-1} (ν_{COC}). ^{1}H NMR (100 MHz, CDCl$_3$, TMS): δ 1.50–1.95 (m, 10.0 H, CH_3, CH_2CC(=O)O), 2.15–2.60 (m, 4.0 H, CH_2C(=O)O), 3.73 (d, J = 5.0 Hz, 4.0 H, CH_2Cl), 4.05 (d, J = 5.0 Hz, 4.0 H, CH_2O), 5.05–5.45 (m, 1.92 H, CHO), 6.70 (d, J = 8.0 Hz, 4.0 H, Ar), 7.03 (d, J = 8.0 Hz, 4.0 H, Ar).

Synthesis of Polyester P-4 from BPGE with Sebacoyl Chloride (SCC). The polymerization was carried out similarly to the synthesis of P-1 with SCC (1.196 g, 5 mmol). Yield: 85%. $\eta_{sp/c}$: 0.39 dL/g (in DMF, conc = 0.5 g/dL, 30 °C). IR (film): 1740 ($\nu_{C=O}$), 1250 cm^{-1} (ν_{COC}). ^{1}H NMR (100 MHz, CDCl$_3$, TMS): δ 1.18–1.54 (m, 8.0 H, CCH_2C), 1.67 (s, 10.0 H, CH_3, CH_2CC(=O)O), 2.23–2.61 (m, 4.0 H, CH_2C(=O)O), 3.38 (d, J = 5.0 Hz, 4.0 H, CH_2O), 5.25–5.63 (m, 1.91 H, CH), 6.88 (d, J = 8.0 Hz, 4.0 H, Ar), 7.24 (d, J = 8.0 Hz, 4.0 H, Ar).

Table I
Polyaddition of BPGE with TPC Using Various Catalysts[a]

catalyst	yield, %	$\eta_{sp/c}$,[b] dL/g
none	trace	
Bu$_4$NCl (TBAC)	96	0.61
Bu$_4$NBr (TBAB)	96	0.44
Bu$_4$NI (TBAI)	87	0.31
Bu$_4$NClO$_4$	9	0.06
Bu$_3$N	84	0.15
pyridine	74	0.29
DMAP[c]	gel	

[a] The reaction was carried out with BPGE (5 mmol) and TPC (5 mmol) using 5 mol % of catalysts in toluene (2.5 mL) at 100 °C for 15 h. [b] Measured at 0.5 g/dL in DMF at 30 °C. [c] (Dimethylamino)pyridine.

Synthesis of Polyester P-5 from Ethylene Glycol Diglycidyl Ether (EGGE) with TPC. The polymerization was carried out similarly to the synthesis of P-1 with EGGE (0.871 g, 5 mmol). Yield: 87%. $\eta_{sp/c}$: 0.16 dL/g (in DMF, conc = 0.5 g/dL, 30 °C). IR (film): 1725 ($\nu_{C=O}$), 1275 cm^{-1} (ν_{COC}). ^{1}H NMR (100 MHz, CDCl$_3$, TMS): δ 3.52–4.00 (m, 12.0 H, OCH_2CH_2O, OCH_2CH, CH_2Cl), 5.20–5.50 (m, 1.71 H, CH), 8.45 (s, 4.0 H, Ar).

Synthesis of Polyester P-6 from EGGE with IPC. The polymerization was carried out similarly to the synthesis of P-5 with EGGE (0.871 g, 5 mmol) and IPC (1.015 g, 5 mmol). Yield: 59%. $\eta_{sp/c}$: 0.14 dL/g (in DMF, conc = 0.5 g/dL, 30 °C). IR (film): 1725 ($\nu_{C=O}$), 1235 cm^{-1} (ν_{COC}). ^{1}H NMR (100 MHz, CDCl$_3$, TMS): δ 3.56–4.00 (m, 12.0 H, OCH_2CH_2O, OCH_2CH, CH_2Cl), 5.20–5.50 (m, 1.75 H, CH), 7.36–7.60 (m, 1.0 H, Ar), 8.10–8.28 (m, 2.0 H, Ar), 8.64 (s, 1.0 H, Ar).

Polymer Reaction of P-1 with Sodium *N,N*-Diethyldithiocarbamate (NaDC). The toluene solution (4 mL) containing P-1 (0.544 g, 1 mmol of chloromethyl group, $\eta_{sp/c}$ = 0.48 dL/g) prepared by the reaction of BPGE with TPC, NaDC (0.4506 g, 2 mmol), and TBAB (0.064 g, 0.1 mmol) was heated at 50 °C for 24 h. After the reaction, the reaction mixture was poured into methanol (500 mL) to precipitate, and then the resulting polymer was purified twice by reprecipitation from THF/water to obtain the substituted polymer in 0.65-g yield. The degree of substitution of the pendant chloromethyl group (DS) was estimated by elemental analysis to be 97%. The reduced viscosity of the resulting polymer was 0.36 dL/g in DMF (conc = 0.5 g/dL) at 30 °C. ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 1.24 (t, J = 7.0 Hz, 11.3 H, NCCH_3), 1.59 (s, 6.0 H, CCH_3), 3.35–4.21 (m, 15.3 H, –CH_2S, CH_2S, CH_2Cl, NCH_2CH$_3$), 4.30 (d, J = 9.0 Hz, 4.0 H, Ar), 7.11 (d, J = 9.0 Hz, 4.0 H, Ar), 8.08 (s, 4.0 H, Ar).

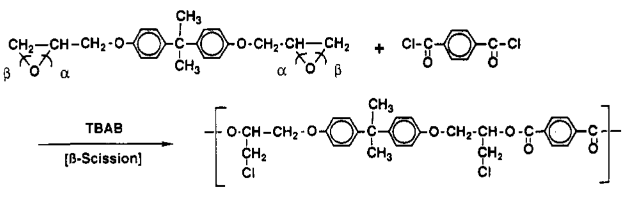
Reaction of P-1 with Sodium Azide (NaN$_3$). The reaction was carried out similarly to the reaction with NaN$_3$ (0.130 g, 2 mmol) in DMSO (4 mL). Yield: 0.44 g. DS: 38% (estimated by elemental analysis). $\eta_{sp/c}$: 0.54 dL/g (DMF, conc = 0.5 g/dL, 30 °C). IR (film): 2100 cm^{-1} (ν_{N_3}), ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 1.61 (s, 6.0 H, CH_3), 3.60–3.84 (m, 1.5 H, CH_2N$_3$), 3.84–4.10 (m, 2.5 H, CH_2Cl), 4.10–4.52 (m, 4.0 H, CH_2O), 5.35–5.75 (m, 2.0 H, CHO), 6.82 (d, J = 8.5 Hz, 4.0 H, Ar), 8.12 (s, 4.0 H, Ar).

Reaction of P-1 with Potassium 3-Phenyl-2,5-norbornadienecarboxylate (KNBD). The reaction was carried out similarly to the reaction with NaDC using P-1 (0.272 g, 0.5 mmol of chloromethyl group), KNBD (0.250 g, 1 mmol), and TBAB (0.032 g, 0.05 mmol). Yield: 0.340 g. DS: 100% (estimated by ^{1}H NMR). $\eta_{sp/c}$: 0.46 dL/g (DMF, conc = 0.5 g/dL, 30 °C). IR (film): 1723 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 1.61 (s, 6.0 H, CH_3), 1.98–2.37 (m, 4.0 H, NBD bridge), 3.80–4.53 (m, 12.0 H, CCH_2O, OCH(CH_2)C, CH of NBD), 5.40–5.72 (m, 2.0 H, CH), 6.69–7.39 (m, 22.0 H, CH=CH of NBD, Ar), 7.9–8.25 (m, 4.0 H, Ar).

Results and Discussion

Polyaddition of Bisphenol A diglycidyl ether (BPGE) with terephthaloyl chloride (TPC) was carried out without any catalyst at 100 °C for 15 h; however, polymer was not obtained at all (see Table I). On the contrary, the polyaddition did proceed when a tertiary amine such as tributylamine (Bu$_3$N) was added. When Bu$_3$N was used as the catalyst, the polyester with 0.15 dL/g of reduced viscosity was obtained in 84% yield. In the case of the reaction using pyridine, the reduced viscosity of the resulting

Scheme III



polyester was 0.29 dL/g, although it has been reported that the polyester with 0.33 dL/g was prepared with pyridine in bulk at 120 °C. When the reaction was carried out using 4-(*N,N*-dimethylamino)pyridine as the catalyst for 15 h, a gel polymer was yielded which would be produced by cross-linking between intermolecular chloromethyl groups and DMAP.

Quaternary ammonium halides, tetrabutylammonium chloride (TBAC), bromide (TBAB), and iodide (TBAI), were more efficient than tributylamine or pyridine in the polyaddition of BPGE with TPC. The polyaddition was catalyzed efficiently by TBAB to afford a polymer with a 0.44 dL/g reduced viscosity. TBAC was the most suitable catalyst for the reaction, yielding a polymer with the highest molecular weight (0.61 dL/g reduced viscosity). In the case of the reaction using tetrabutylammonium perchlorate, little polymerization was evident. The nucleophilicity of the counteranion of the quaternary ammonium salts is very important for the catalytic activity in the polyaddition of diepoxides with diacyl chlorides. The catalytic activity of tetrabutylammonium halides increased in the following order, $I^- < Br^- < Cl^-$. These results suggest that quarternary ammonium halides, particularly, chlorides or bromides, are suitable catalysts for the synthesis of the reactive polyesters having a pendant chloromethyl group.

The structure of the polyester P-1 prepared from BPGE with TPC was confirmed by IR and ^1H NMR spectra. P-1 showed the peaks based on ester groups at 1728 (C=O) and 1275 (C(=O)O–) cm^{-1} in the IR spectrum. In the ^1H NMR spectrum of P-1, the signals based on each monomer unit were observed. The signal of methine proton from the epoxy group of BPGE was exhibited at 5.36–5.68 ppm, and the signal based on the chloromethyl group was observed at 3.96 ppm. In addition, their intensity ratios to aromatic protons were equal to the expected value (4.0), assuming that only β-scission of the epoxy group proceeded. From these spectra data, it was found that β-scission of the epoxy group of BPGE selectively occurred in the polyaddition of BPGE with TPC in the presence of TBAB (Scheme III).

The effect of the concentration of the catalyst (TBAB) on the polyaddition of BPGE with TPC in toluene at 100 °C is shown in Figure 1. The molecular weight of the resulting polyester increased with TBAB concentration, and the polymer with ca. 0.7 was afforded using 10 mol % of TBAB for the monomers.

The reaction of BPGE with TPC was conducted with 5 mol % of TBAB in toluene at various temperatures for 15 h. The reduced viscosity of the obtained polymer increased with reaction temperature and reached more than 0.4 dL/g at 100 °C (Figure 2).

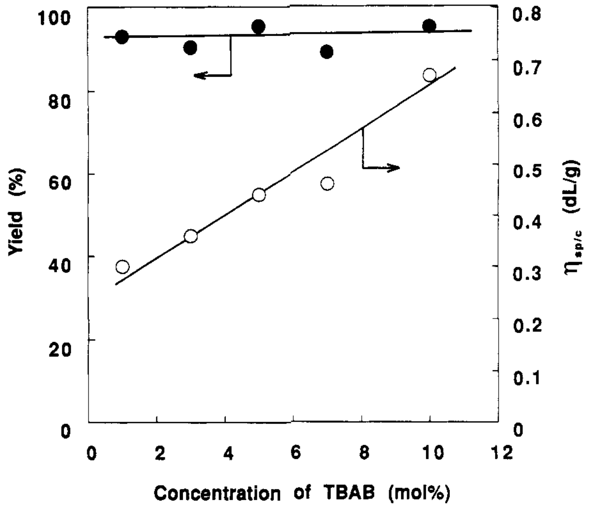


Figure 1. Effect of the TBAB concentration on the reaction of BPGE with TPC in toluene at 100 °C for 15 h.

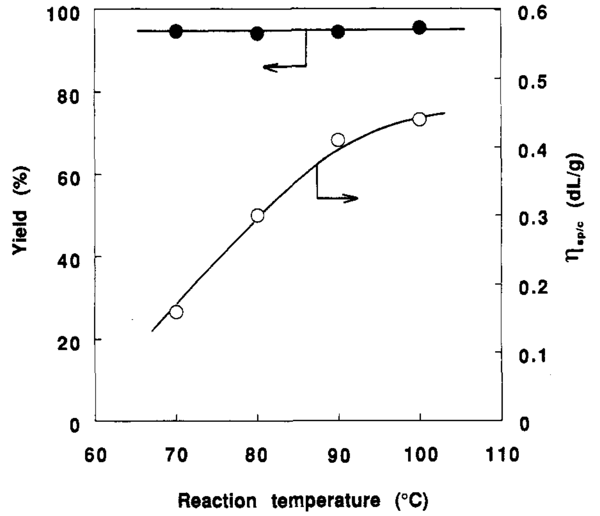


Figure 2. Effect of the reaction temperature on the reaction of BPGE with TPC using 5 mol % of TBAB in toluene for 15 h.

Table II
Solvent Effect on the Polyaddition of BPGE with TPC[a]

solvent	yield, %	$\eta_{sp/c}$,[b] dL/g
DMF	72	0.15
DMAc	43	0.09
NMP	59	0.08
sulfolane	82	0.26
cyclohexanone	58	0.10
diglyme	87	0.17
anisole	94	0.28
o-dichlorobenzene	97	0.31
toluene	96	0.44

[a] The reaction was carried out with BPGE (5 mmol) and TPC (5 mmol) using 5 mol % of TBAB in toluene (2.5 mL) at 100 °C for 15 h. [b] Measured at 0.5 g/dL in DMF at 30 °C.

The polyaddition of BPGE with TPC in the presence of 5 mol % of TBAB at 100 °C was investigated in various solvents (Table II). When the reaction was carried out in aliphatic solvents such as diglyme and cyclohexanone, the yield and the reduced viscosity of the resulting polymer were not satisfactory. In the case of reaction in such aprotic polar solvents as DMF, *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP), which are expected to be suitable media for the polyaddition, the polyester with a low molecular weight was obtained in moderate yield. On the contrary, use of aromatic solvents was effective for the polyaddition; for example, *o*-dichlorobenzene afforded the polymer with 0.31 dL/g. Toluene, particularly, was the most suitable solvent for polyaddition among the examined solvents, yielding a polymer with the highest molecular weight. The interaction between the acyl chloride moiety of TPC and TBAB seemed to be stronger in aromatic solvents than in aprotic polar solvents. In addition, for aprotic polar solvents, such as DMAc, trace water contained in the solvents could not be removed completely; therefore, hydrolysis of the acyl chlorides seems to occur slightly as a side reaction.

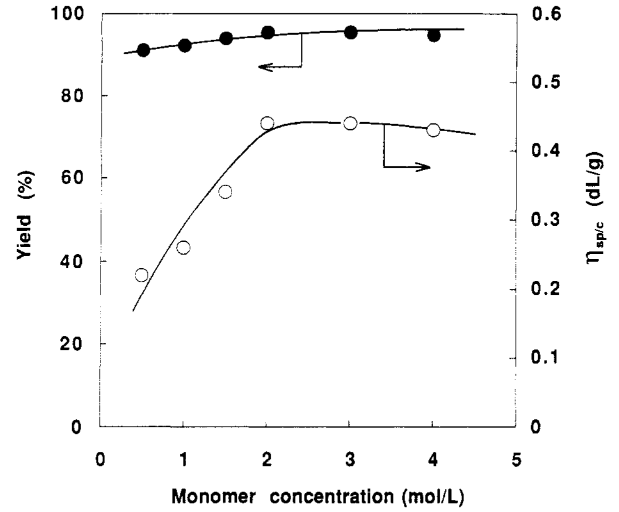


Figure 3. Effect of the monomer concentration on the reaction of BPGE with TPC using 5 mol % of TBAB in toluene at 100 °C for 15 h.

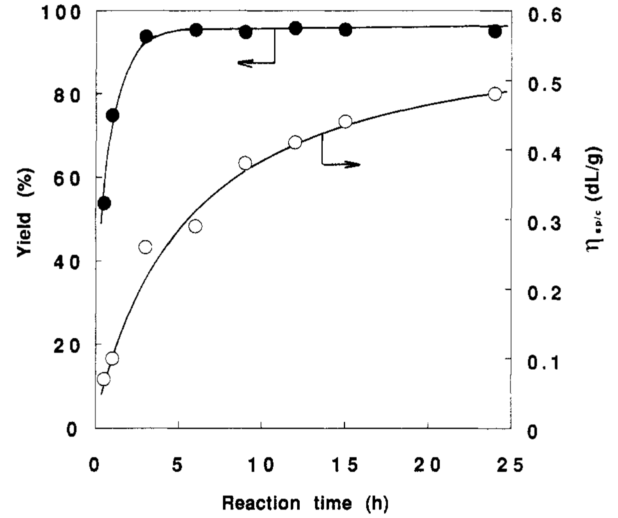


Figure 4. Effect of the reaction time on the reaction of BPGE with TPC using 5 mol % of TBAB in toluene at 100 °C.

Figure 3 shows the effect of monomer concentration in the polyaddition of BPGE with TPC using 5 mol % of TBAB in toluene at 100 °C for 15 h. The reduced viscosity of the polymer increased with an increase in the monomer concentration until 2 mol/L, but a further positive effect was not observed above 2 mol/L. The reaction between the end functional groups of propagating polymer chains did not proceed well in the late stage of the polyaddition because of viscosity effects; that is, the reaction solution was not well mixed.

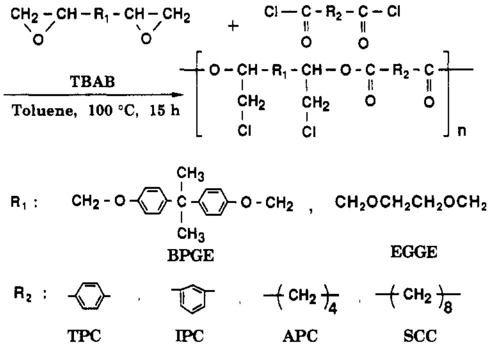
The correlation between the reduced viscosity of the resulting polymer and the reaction time on the reaction of BPGE with TPC was investigated (Figure 4). The yield of the resulting polymer reached more than 95% in 3 h. The reduced viscosity increased gradually with the reaction time and went up to about 0.5 dL/g for 24 h.

Table III
Polyaddition of Various Diepoxides with Diacyl Chlorides[a]

monomer		polymer			
diepoxide	dichloride		yield, %	$\eta_{sp/c}$,[b] dL/g	S_β,[c] %
BPGE	TPC	P-1	93	0.44	100
	IPC	P-2	94	0.35	100
	APC	P-3	81	0.22	96
	SCC	P-4	85	0.39	96
EGGE	TPC	P-5	87	0.16	85
	IPC	P-6	59	0.14	88

[a] The reaction was carried out with 5 mmol of each monomer using 5 mol % of TBAB in toluene (2.5 mL) at 100 °C for 15 h. [b] Measured at a concentration of 0.5 g/dL in DMF at 30 °C. [c] Selectivity of β-scission of the epoxy group.

Scheme IV



Polyadditions of various diacyl chlorides with diepoxides were performed using 5 mol % of TBAB in toluene at 100 °C for 15 h (Table III). The polyaddition of BPGE with aliphatic dichloride, i.e., adipoyl chloride (APC) and sebacoyl chloride (SCC), gave the corresponding polyesters with 0.22 and 0.39 dL/g in good yield, respectively. From the polyaddition of BPGE with aromatic dichlorides, IPC and TPC, polymers with 0.35 and 0.44 dL/g were obtained, respectively. In the case of the reaction of aliphatic diepoxide, EGGE, with TPC or IPC, the reduced viscosities of the resulting polyesters were low (0.16 and 0.14 dL/g). Particularly, the yield of the polymer from the reaction with IPC was also relatively low (59%). Since each monomer was not recovered from the filtrate of the precipitation mixture, the recovered materials showed the same IR spectrum as the obtained polyester P-6. It seems that the polyaddition proceeded with a production of oligomers or macrocyclic compounds (Scheme IV).

The ^{1}H NMR spectrum of P-1 exhibits a signal at 5.36–5.68 ppm (multiplet) based on the methine proton, which arises from the methine of the epoxy group of BPGE, and the intensity ratio of the methine proton to the aromatic one is 4.0. Subsequently, it was demonstrated that the epoxy group of BPGE underwent selectively β-scission in the polyaddition of BPGE with TPC. In the case of ^{1}H NMR of P-5 (from EGGE and TPC), the intensity of the methine proton observed at 5.20–5.50 (multiplet) was estimated to be 85% of the expected value assuming that only the β-scission of the epoxy group of EGGE occurred in the polyaddition of EGGE with TPC. Therefore, it is found that the selectivity of the β-scission of the epoxy group of EGGE is 85%. Similarly, the selectivities of the β-scission of the epoxy groups of the diepoxides in the other polyadditions were estimated from the intensity of the methine proton signals in their ^{1}H NMR as follows; 100% for the reaction of BPGE with TPC, 96% for that of BPGE with APC, 96% for that of BPGE with SCC, and 88% for that of EGGE with IPC. It was, consequently, proven that these polyadditions of diepoxides with diacyl chlorides using TBAB did proceed regioselectively to afford polyesters containing pendant chloromethyl groups.

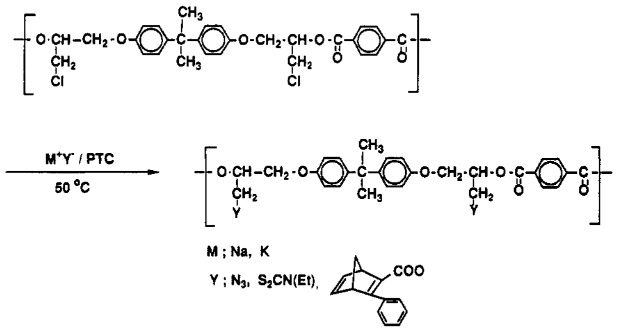
The solubility of the polymers is summarized in Table IV. All of the polymers are insoluble in methanol, ethanol, *n*-hexane, and cyclohexanone. However, these polymers are soluble in various organic solvents including ketones, halogenated hydrocarbons, aromatic solvents, and tetrahydrofuran. This means that the polyesters have excellent solubility, because intermolecular interaction of polymers would be inhibited by the bulkiness of the pendant chloromethyl groups.

Table IV
Solubility of Various Polyesters[a]

solvent/polyester	P-1	P-2	P-3	P-4	P-5	P-6
methanol	–	–	–	–	–	–
ethanol	–	–	–	–	–	–
isopropanol	–	–	–	–	–	–
n-hexane	–	–	–	–	–	–
cyclohexane	–	–	–	–	–	–
dichloromethane	++	++	++	++	++	++
trichloromethane	++	++	++	++	++	++
tetrachloromethane	++	++	++	++	+–	+–
acetone	++	++	++	++	++	++
MEK	++	++	++	++	++	++
ethyl acetate	++	++	++	++	++	++
benzene	++	++	++	++	++	++
toluene	++	++	++	++	++	++
o-dichlorobenzene	++	++	++	++	++	++
anisole	++	++	++	++	++	++
diglyme	++	++	++	++	++	++
dioxane	++	++	++	++	++	++
THF	++	++	++	++	++	++
acetonitrile	+–	+–	+–	+–	++	++
DMF	++	++	++	++	++	++
DMAc	++	++	++	++	++	++
NMP	++	++	++	++	++	++
DMSO	++	++	+	+	++	++
sulfolane	++	++	++	++	++	++

[a] ++, soluble at room temperature; +, soluble by heating; +–, partially soluble or swelling; –, insoluble.

Scheme V



Chemical Modification of the Pendant Chloromethyl Group. Substitution reactions of the pendant chloromethyl group of polymers with various nucleophilic reagents using phase-transfer catalysts have been reported.[13] The chloromethyl group of the polyesters prepared by the polyaddition of diepoxides with diacyl chlorides is also expected to participate in a nucleophilic substitution reaction. Thus, the substitution reaction of the pendant chloromethyl group with some nucleophiles, sodium dithiocarbamate (NaDC), sodium azide (NaN_3), and potassium 3-phenyl-2,5-norbornadienecarboxylate (KNBD), was performed by using a phase-transfer catalyst (Scheme V).

The reaction of the pendant chloromethyl group of P-1 with nucleophiles was carried out using 10 mol % of TBAB as a phase-transfer catalyst (Table V). The substitution reaction of P-1 with NaDC proceeded smoothly in the presence of 10 mol % of TBAB in dimethyl sulfoxide (DMSO), and the degree of substitution of the chloromethyl group (DS) after 24 h was determined by elemental analysis to be 91%. Use of toluene as the reaction medium enhanced DS to 97%. The reaction of P-1 with NaN_3 was conducted similarly to the reaction with NaDC in toluene for 24 h; however, the reaction was scarcely proceeded. When the reaction was carried out in DMSO, DS increased to 38%. The reactions did not proceed efficiently because of the low solubility of NaN_3 into these reaction solvents. Furthermore, the reaction of P-1 with KNBD proceeded smoothly in DMSO at 50 °C for 48 h to give the photofunctional polyester, in which the pendant chloromethyl group was completely substituted by a NBD residue. To our knowledge, this polymer is the first example of the photofunctional polyester having a NBD moiety, which has the function of converting light energy to strain of quadricyclanes.[14] Thus, it is demonstrated that the pendant chloromethyl group has a high reactivity to the substitution reaction with nucleophiles. The polyester having a pendant chloromethyl group from the reaction of BPGE with TPC is promising the synthesis of functional polymers.

Table V
Substitution Reaction of P-1 with Nucleophilic Reagents[a]

run	reagent	solvent, mL	time, h	DS,[b] %
1	NaDC[c]	toluene	24	97[d]
2	NaDC[c]	DMSO	24	91[d]
3	NaN_3	toluene	24	3[d]
4	NaN_3	DMSO	24	38[d]
5	NBD[e]	DMSO	48	100[f]

[a] Substitution reaction of P-1 ($\eta_{sp/c}$ = 0.48 dL/g, 2 mmol) with reagents was carried out using 10 mol % of TBAB in solvent (4 mL) at 50 °C. [b] Degree of substitution. [c] $(Et)_2NCSSNa{\cdot}3H_2O$. [d] Determined by elemental analysis. [e] Potassium 3-phenyl-2,5-norbornadiene-2-carboxylate. [f] Determined by ^1H NMR.

In conclusion, reactive polyesters with pendant chloromethyl groups were successfully synthesized by the regioselective polyaddition reaction of diepoxides with diacyl chlorides in the presence of quaternary ammonium halides. Among quaternary ammonium halides, tetrabutylammonium chloride and bromide were very effective catalysts for the synthesis of high molecular weight polyesters. Furthermore, it was demonstrated that the pendant chloromethyl group was highly reactive to the substitution reaction using phase-transfer catalysts.

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Registry No. P-1 (copolymer), 42814-89-1; P-1 (SRU), 139704-39-5; P-2 (copolymer), 139704-35-1; P-2 (SRU), 139704-40-8; P-3 (copolymer), 53223-19-1; P-3 (SRU), 139704-41-9; P-4 (copolymer), 139704-36-2; P-4 (SRU), 139704-42-0; P-5 (copolymer), 139704-37-3; P-5 (SRU), 139704-43-1; P-6 (copolymer), 139704-38-4; P-6 (SRU), 139704-44-2; TBAC, 1112-67-0; TBAB, 1643-19-2; TBAI, 311-28-4; DMAP, 57951-36-7; DMF, 68-12-2; DMAc, 127-19-5; NMP, 872-50-4; Bu_4NClO_4, 1923-70-2; Bu_3N, 102-82-9; pyridine, 110-86-1; sulfolane, 126-33-0; cyclohexanone, 108-94-1; diglyme, 111-96-6; anisole, 100-66-3; *o*-dichlorobenzene, 95-50-1; toluene, 108-88-3.