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A Novel Synthesis of Poly(phosphonate) by the Addition Reaction of Diepoxide with Phenylphosphonic Dichloride

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It is well-known[1] that poly(phosphonate)s have a flame-retardant property, and this property is enhanced by the combination of halogen atoms. The poly(phosphonate)s are ordinarily synthesized by either melt or interfacial polyconsensation[2,3] of phosphonic dichlorides with diols. Recently, poly(phosphonate)s with high molecular weight have been synthesized[4,5] by the polycondensation of phosphonic dichlorides with certain diols using phase-transfer catalysts. However, these poly(phosphonate)s have contained only phosphorus atoms in the polymer chain, because halogen atoms have been removed by the condensation reaction.

Recently, the authors found that the polyaddition of diepoxides[6] or bisoxetanes[7] with diacyl chlorides proceeded very smoothly to give reactive poly(ester)s containing pendant chloromethyl groups as did the polyaddition[8] of diepoxide with active diesters using quaternary onium salts as catalysts. More recently, we also reported[9] the synthesis of poly(silyl ether)s by the regioselective addition reaction of diepoxide with dichlorosilane compounds at room temperature using the same catalysts. This paper reports on the novel synthesis of poly(phosphonate) containing both phosphorus and halogen atoms in the polymer main chain and side chain, respectively, by polyaddition of a diepoxide, Bisphenol A diglycidyl ether (BPGE), with phenylphosphonic dichloride (PPDC) using quaternary onium salts as catalysts.

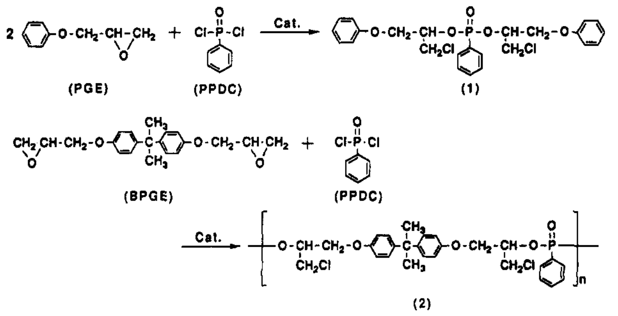
The addition reaction of phenyl glycidyl ether (PGE) [1.50 g (10 mmol)] with PPDC [0.98 g (5 mmol)] was carried out in toluene (5 mL) using tetrabutylammonium chloride [TBAC; 6.95 mg (0.25 mmol)] as a catalyst at 90 °C for 24 h. The reaction mixture was washed twice with small amounts (4 mL) of water, and the solvent was evaporated *in vacuo*. The yield of crude product thus obtained was 2.28 g (92.1%). The product (1) was purified by silica gel column chromatography using the mixed solvent of methyl ethyl ketone and hexane (1:2, v/v) as the eluent. The IR spectrum of 1 showed absorption peaks at 1240 (COC), 1170 (P=O), 990 (POC), and 770 cm^{-1} (CCl). The ^{1}H NMR (90 MHz, $CDCl_3$, TMS) of this compound showed proton signals at δ 3.65–4.05 (m, 4H, CH_2Cl), 4.04–4.50 (m, 4H, CH_2O), 4.75–5.35 (m, 2H, CH), and 6.65–8.25 (m, 15H, aromatic protons). This result means that the addition reaction of PGE with PPDC, which is a model reaction of polyaddition, proceeds smoothly and regioselectively.

Table 1. Polyaddition of BPGE with PPDC Using Various Catalysts in Certain Solvents[a]

run no.	catalyst	solvent	yield (%)	M_n[b] (×10^{-4})	M_w/M_n
1	none	toluene	22	0.80	1.28
2	TBAC	toluene	95	1.63	1.36
3	TBAB	toluene	90	1.73	1.37
4	TBPC	toluene	91	1.22	1.25
5	TBPB	toluene	96	1.46	1.33
6	TEA	toluene	63	0.61	1.02
7	TPP	toluene	90	0.94	1.19
8	18-C-6/KCl	toluene	74	0.47	
9	TBAC	anisole	84	1.44	1.29
10	TBAC	*o*-dichlorobenzene	89	1.70	1.31
11	TBAC	DMAc	95	0.49	
12	TBAC	DMF	81	0.46	
13	TBAC	NMP	84	0.55	

[a] The reaction was carried out with 2 mmol of BPGE and 2 mmol of PPDC in the solvent (1 mL) using 5 mol % of the catalyst at 90 °C for 24 h. [b] Estimated by GPC based on polystyrene standards.

Scheme 1



On the basis of the above result, polyaddition of BPGE [0.681 g (2 mmol)] with PPDC [0.390 g (2 mmol)] was performed in toluene (2 mL) in the presence of 5 mol % of TBAC at 90 °C for 24 h (run no. 2). The reaction mixture was washed twice using small amounts (4 mL) of water and then poured into hexane. The polymer obtained was reprecipitated twice from chloroform by hexane and dried *in vacuo* at 60 °C. Yield of the polymer was 1.018 g (95%). M_n of this polymer, estimated by GPC based on polystyrene standards, was 1.63×10^4. The IR spectrum of this polymer (2) film cast on a KBr plate showed absorption peaks at 1250 (COC), 1180 (P=O), 990 (POC), and 750 cm^{-1} (CCl). The ^{1}H NMR spectrum (90 MHz, $CDCl_3$, TMS) of this polymer showed proton signals at δ 1.6 (s, 6H, CH_3), 3.59–4.00 (m, 4H, CH_2Cl), 4.00–4.50 (m, 4H, CH_2O), 4.70–5.18 (m, 2H, CH), and 6.90–8.10 (m, 13H, aromatic protons). This result suggests that a new poly(phosphonate) with relatively high molecular weight was prepared by the polyaddition of BPGE with PPDC using TBAC as a catalyst (Table 1).

On the other hand, the yield and molecular weight of the polymer was very low, when the reaction was carried out without any catalyst under the same reaction conditions (run no. 1). Polyaddition of BPGE with PPDC was also examined using various other catalysts. The reaction also proceeded very smoothly to give polymer 2 in high yield using tetrabutylammonium bromide (TBAB), tetrabutylphosphonium chloride (TBPC), and tetrabutylphosphonium bromide (TBPB) as catalysts (see run nos. 3–5).

Polymer 2 was obtained in high yield when triphenylphosphine (TPP) was used as a catalyst; however, when triethylamine (TEA) was used as a catalyst, polymers 2 with low molecular weight were obtained in 63% yield (run nos. 6 and 7). Polymer 2 with relatively low molecular weight was prepared in 74% yield catalyzed by the complex of 18-crown-6 (18-C-6) with KCl (run no. 8).

The polyaddition of BPGE with PPDC was performed in various solvents. As summarized in Table 1, the polymers with relatively high molecular weight were synthesized in hydrophobic solvents such as toluene, anisole, and *o*-dichlorobenzene (run nos. 2, 9, and 10).

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Polymer **2** was prepared in high yield when the reaction was carried out in aprotic polar solvents such as DMAc, DMF, and NMP; however, the molecular weight of the obtained polymers was very low (run nos. 11–13).

These results suggest that, although a new poly(phosphonate) was synthesized by the polyaddition of BPGE with PPDC catalyzed by quaternary onium salts, *tert*-amine, *tert*-phosphine, and a crown ether complex, the molecular weight and the yield of the resulting polymer were strongly affected by the catalyst and reaction solvent.

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