Novel Syntheses of Poly(phosphonate)s and Poly(phosphate)s by Addition Reactions of Bisepoxides with Phosphonic Dichlorides and Dichlorophosphates

Tadatomi Nishikubo,* Atsushi Kameyama, and Shoji Minegishi

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

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ABSTRACT: Poly(phosphonate)s and poly(phosphate)s with reactive pendant chloromethyl groups were synthesized by polyadditions of bisepoxides with phosphonic dichlorides and dichlorophosphates, respectively. The polyaddition of Bisphenol A diglydcidyl ether (BPGE) with phenylphosphonic dichloride (PPDC) occurred without any catalyst at 90 °C for 24 h in toluene; however, the yield and molecular weight of the resulting polymer were relatively low. On the other hand, the polyadditions of BPGE with PPDC proceeded very smoothly and regioselectively with high yields (90–96%) to give the polymers with relatively high molecular weights in toluene at 90 °C for 24 h when quaternary ammonium or phosphonium salts were used as catalysts. The polyaddition was enhanced by the addition of triethylamine, triphenylphosphine, or crown ether complex; however, the catalytic activities of these compounds were lower than those of quaternary onium salts. Polyadditions of bisepoxides such as BPGE and ethylene glycol diglycidyl ether with certain phosphonic dichlorides and dichlorophosphates also proceeded smoothly and regioselectively to give the corresponding polymers under the same reaction conditions.

Introduction

It is well-known[1] that poly(phosphonate)s and poly(phosphate)s have an excellent flame-retardant property, and this property is enhanced by the addition of halogen atoms. The poly(phosphonate)s and poly(phosphate)s are ordinarily synthesized by either melt or interfacial polycondensation[2,3] of diols with phosphonic dichlorides and dichlorophosphates, respectively. Poly(thiophosphonate)s and poly(thiophosphate)s can also be synthesized[4] by the interfacial polycondensation of dithiols. Recently, poly(phosphonate)s with high molecular weight have been synthesized[5,6] by the polycondensation of phosphonic dichlorides and dichlorophosphates with certain diols using phase-transfer catalysts. The poly(phosphonate)s and poly(phosphate)s can also be synthesized by the ring-opening polymerization of cyclic phosphonate,[7] phosphate,[8] or phosphonite[9] monomers.

Recently, the authors found that the polyaddition of bisepoxides[10] or bisoxetanes[11] with diacyl chlorides proceeded very smoothly to give reactive poly(ester)s containing pendant chloromethyl groups, as did the polyaddition[12] of bisepoxide with active diesters using quaternary onium salts as catalysts. More recently, we also reported[13] the synthesis of poly(silyl ether)s by the regioselective addition reaction of bisepoxide with dichlorosilanes at room temperature using the same catalysts. However, there has been no report of the synthesis of poly(phosphonate) by polyaddition of bisepoxide with phosphonic dichloride except our recent short paper.[14]

This paper reports in detail novel syntheses of poly(phosphonate)s and poly(phosphate)s containing both phosphorus and halogen atoms in the polymer main chain and side chain by polyaddition of bisepoxides with certain phosphonic dichlorides or dichlorophosphates, respectively, using quaternary onium salts as catalysts.

Experimental Section

Materials. Solvents were dried using P_2O_5, CaH_2, or Na metal wire and purified in the usual way before use. Reagent-grade phenylphosphonic dichloride (PPDC) was purified by vacuum distillation. Methylphosphonic dichloride (MPDC), phenyl dichlorophosphate (PDCP), and methyl dichlorophosphate (MDCP) were used without further purification. Bisphenol A diglycidyl ether (BPGE) was recrystallized four times from the mixed solvent of methanol and methyl ethyl ketone (4:1, v/v). Phenyl glycidyl ether (PGE) and ethylene glycol diglycidyl ether (EGGE) were purified twice by distillation under reduced pressure. Tetrabutylammonium bromide (TBAB) was recrystallized from ethyl acetate. Triphenylphosphine (TPP) was purified by recrystallization from methanol. Triethylamine (TEA) was purified by distillation under reduced pressure. Tetrabutylammonium chloride (TBAC), tetrabutylphosphonium chloride (TBPC), tetrabutylphosphonium bromide (TBPB), 18-crown-6 (18-C-6), and potassium chloride (KCl) were used without further purification.

Measurement. Infrared (IR) spectra were measured on a Jasco Model IR-700 spectrometer. The ^{1}H NMR spectra were recorded on JEOL Models JNM EX-90 (90 MHz) and JNM α-500 (500 MHz) instruments in $CDCl_3$ with 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-8020 GPC equipped with a refractive index detector using TSK gel columns (eluent: DMF, calibrated with narrow molecular weight polystyrene standards).

Addition Reaction of PGE with PPDC. The addition reaction of PGE (1.5018 g, 10 mmol) with PPDC (0.9750 g, 5 mmol) was carried out in toluene (5 mL) using TBAC (69.5 mg, 0.25 mmol) as a catalyst at 90 °C for 24 h. The reaction mixture was diluted with ethyl acetate (10 mL) and washed twice with small amounts (2 mL) of water, and the solvent was evaporated *in vacuo*. The crude product thus obtained was purified by silica gel column chromatography using the mixed solvent of methyl ethyl ketone and hexane (1:2, v/v) as the eluent, and the final yield of adduct **1** was 2.2811 g (92%). IR (neat): 1240 (C–O–C), 1170 (P=O), 990 (P–O–C), 770 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 3.79–4.03 (m, 4H, CH_2Cl), 4.03–4.35 (m, 4H, CH_2–O), 4.93–5.08 (m, 2H, CH–O), 6.72–7.93 (m, 15H, aromatic protons). Anal. Calcd for $C_{24}H_{25}O_5PCl_2$: C, 58.20; H, 5.09. Found: C, 57.97; H, 5.05.

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* To whom all correspondence should be addressed.

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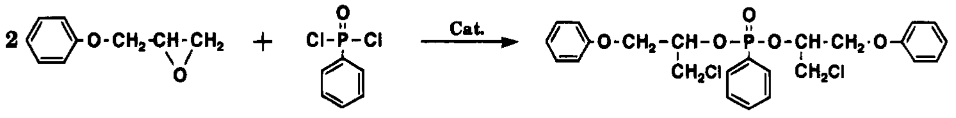
Scheme 1



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Synthesis of Poly(phosphonate) (2a) from BPGE with PPDC. A typical procedure for polyaddition of BPGE with PPDC was as follows: BPGE (0.6809 g, 2 mmol), PPDC (0.3900 g, 2 mmol), and TBAC (27.8 mg, 0.1 mmol), were dissolved in toluene (2 mL), and then the reaction was carried out at 90 °C for 24 h. The reaction mixture was diluted by the addition of chloroform (10 mL) and washed with water (2 mL), and then some amount of chloroform was evaporated. The concentrated polymer solution was poured into hexane (100 mL), reprecipitated twice from chloroform into hexane, and dried *in vacuo* at 60 °C. The yield of polymer **2a** was 1.018 g (95%). The number-average molecular weight (M_n) of the polymer determined from GPC was 1.63×10^4. IR (film): 1250 (C−O−C), 1180 (P=O), 990 (P−O−C), 750 (C−Cl) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, TMS) δ 1.60 (s, 6H, CH_3), 3.59−4.00 (m, 4H, CH_2Cl), 4.00−4.50 (m, 4H, CH_2−O), 4.70−5.18 (m, 2H, CH−O), 6.90−8.10 (m, 13H, aromatic protons). Anal. Calcd for $C_{27}H_{29}O_5PCl_2$: C, 60.57; H, 5.46. Found: C, 60.59; H, 5.74.

Synthesis of Poly(phosphonate) (2b) from BPGE with MPDC. BPGE (0.6809 g, 2 mmol) was made to react with MPDC (0.2658 g, 2 mmol) in the presence of TBAC (27.8 mg, 0.1 mmol) in toluene (2 mL) at 90 °C for 24 h. The reaction mixture was diluted with chloroform and washed with water, and some amount of chloroform was evaporated. The polymer solution was poured into hexane, reprecipitated twice from chloroform into hexane, dried *in vacuo* at 60 °C. The yield of polymer **2b** was 0.596 g (63%). M_n of the polymer determined from GPC was 2.31×10^4. IR (film): 1244 (C−O−C), 1182 (P=O), 981 (P−O−C), 731 (C−Cl) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ 1.61 (s, 6H, CH_3), 1.63 (dt, $J = 2.20$ Hz and 18.02 Hz, 3H, P−CH_3), 3.49−4.05 (m, 4H, CH_2Cl), 4.05−4.30 (m, 4H, CH_2−O), 4.70−5.20 (m, 2H, CH−O), 6.95−7.21 (m, 8H, aromatic protons). Anal. Calcd for $C_{22}H_{27}O_5PCl_2$: C, 55.83; H, 5.75. Found: C, 56.22; H, 5.97.

Synthesis of Poly(phosphate) (2c) from BPGE with PDCP. The polyaddition of BPGE (0.6809 g, 2 mmol) and PDCP (0.4220 g, 2 mmol) was carried out in the presence of TBAC (27.8 mg, 0.1 mmol) in toluene (2 mL) at 90 °C for 24 h, and the product was purified by the same procedure as described for **2a**. The yield of polymer **2c** was 0.993 g (90%). M_n of the polymer determined from GPC was 0.66×10^4. IR (film): 1245 (C−O−C), 1182 (P=O), 950 (P−O−C), 757 (C−Cl) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ 1.60 (s, 6H, CH_3), 3.30−3.98 (m, 4H, CH_2Cl), 3.98−4.31 (m, 4H, CH_2−O), 4.55−5.31 (m, 2H, CH−O), 6.60−7.55 (m, 13H, aromatic protons). Anal. Calcd for $C_{27}H_{29}O_6PCl_2$: C, 58.81; H, 5.30. Found: C, 59.33; H, 5.85.

Synthesis of Poly(phosphonate) (2e) from EGGE with PPDC. EGGE (0.3484 g, 2 mmol), PPDC (0.3900 g, 2 mmol), and TBAC (27.8 mg, 0.1 mmol) were dissolved in toluene (2 mL), and the solution was stirred at 90 °C for 24 h. The yield of polymer **2e** was 0.702 g (95%). M_n of the polymer determined from GPC was 1.01×10^4. IR (film): 1252 (C−O−C), 1130 (P=O), 990 (P−O−C), 731 (C−Cl) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ 3.19−4.01 (m, 12H, CH_2Cl and CH_2−O), 4.41−5.18 (m, 2H, CH−O), 7.30−8.00 (m, 5H, aromatic protons). Anal. Calcd for $C_{14}H_{19}O_5PCl_2$: C, 45.55; H, 5.19. Found: C, 45.48; H, 5.16.

Synthesis of Poly(phosphonate) (2f) from EGGE with MPDC. EGGE (0.3484 g, 2 mmol) was allowed to react with MPDC (0.2658 g, 2 mmol) in the presence of TBAC (27.8 mg, 0.1 mmol) in toluene (2 mL) at 90 °C for 24 h. The yield of polymer **2f** was 0.491 g (80%). M_n of the polymer determined from GPC was 1.96×10^4. IR (film): 1244 (C−O−C), 1130 (P=O), 992 (P−O−C), 744 (C−Cl) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ 1.62 (dt, $J = 2.74$ Hz and 18.02 Hz, 3H, CH_3), 3.39−4.01 (m, 12H, CH_2Cl and CH_2−O), 4.50−5.10 (m, 2H, CH−O).

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

run no.	catalyst	yield, %	M_n[b] $\times 10^{-4}$	M_w/M_n[b]
1	none	22	0.80	1.28
2	TEA	63	0.61	
3	TPP	90	0.94	1.19
4	18-C-6/KCl	74	0.47	
5	TBAB	90	1.73	1.37
6	TBAC	95	1.63	1.36
7	TBPB	96	1.46	1.33
8	TBPC	91	1.22	1.25

[a] The reactions were carried out with 2 mmol of BPGE and 2 mmol of PPDC in toluene (2 mL) using the catalyst (0.1 mmol) at 90 °C for 24 h. [b] Estimated by GPC based on polystyrene standards.

Synthesis of Poly(phosphate) (2g) from EGGE with PDCP. To EGGE (0.3484 g, 2 mmol) in toluene (2 mL) was added PDCP (0.4220 g, 2 mmol) and TBAC (27.8 mg, 0.1 mmol). The mixture was stirred at 90 °C for 24 h. The yield of polymer **2g** was 0.647 g (84%). M_n of the polymer determined from GPC was 0.43×10^4. IR (film): 1287 (C−O−C), 1130 (P=O), 941 (P−O−C), 763 (C−Cl) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ 3.30−4.90 (m, 12H, CH_2Cl and CH_2−O), 4.50−5.10 (m, 2H, CH−O), 7.12−7.53 (m, 5H, aromatic protons).

Results and Discussion

The addition reaction of PGE with PPDC was carried out as a model reaction for the polyaddition of bisepoxides with phosphonic dichlorides or dichlorophosphates. The reaction proceeded very smoothly using 5 mol % of TBAC as a catalyst in toluene at 90 °C for 24 h to give the corresponding adduct **1** with 92% yield. The structure of the obtained adduct **1** was determined by IR and ^1H NMR spectra. The IR spectrum of **1** showed absorption peaks at 1240, 1170, 990, and 770 cm^{-1} due to C−O−C, P=O, P−O−C, and C−Cl stretching, respectively. The ^1H NMR spectrum of adduct **1** exhibited the corresponding proton signals at 3.79−4.03 ppm due to the CH_2Cl, at 4.03−4.35 ppm due to the CH_2−O, at 4.93−5.08 ppm due to the CH−O, and at 6.72−7.93 ppm due to the aromatic protons. Furthermore, from the intensity ratio of methine protons at 4.93−5.08 ppm vs aromatic protons at 6.72−7.93 ppm, β-scission of the epoxy group of PGE was calculated as 100%. These results show that the addition reaction of PGE with PPDC proceeded very smoothly and regioselectivity to give adduct **1** as shown in Scheme 1.

As summarized in Table 1, when the reaction of BPGE with PPDC was performed without any catalyst in toluene at 90 °C for 24 h, poly(phosphonate) (**2a**) with relatively low molecular weight was obtained with 22% yield. Polymers **2a** were obtained with 62, 90, and 74% yields using 5 mol % of TEA, TPP, and 18-C-6/KCl complex as catalysts, respectively. However, increase of the molecular weight of the resulting polymers did not occur. On the other hand, polymers **2a** with relatively high molecular weight were synthesized with 89−96% yields under the same reaction conditions when 5 mol % of TBAB, TBAC, TBPC, and TBPB were used as catalysts.

Scheme 2

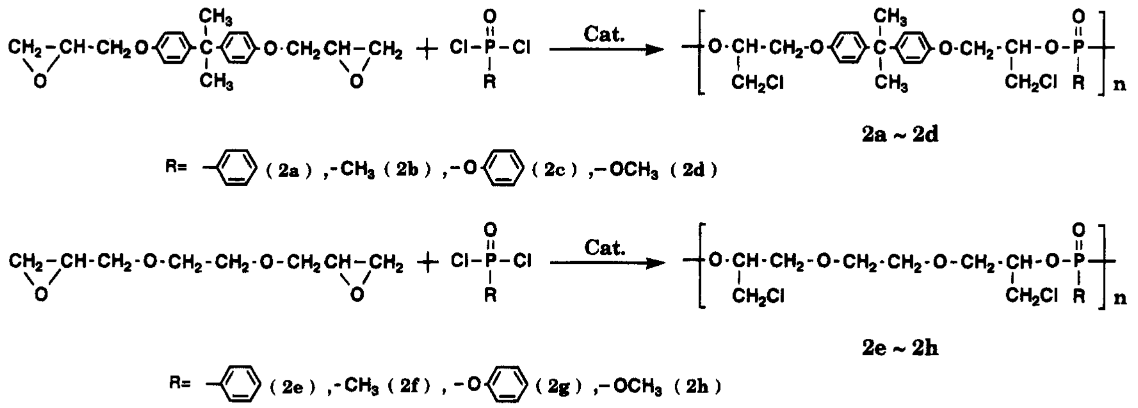

Table 2. Polyaddition of BPGE with PPDC in Various Solvents[a]

run no.	solvent	yield, %	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$
9	toluene	95	1.63	1.36
10	anisole	84	1.44	1.29
11	*o*-dichlorobenzene	89	1.70	1.31
12	THF	94	1.20	1.26
13	acetonitrile	81	1.76	1.39
14	DMF	81	0.46	
15	DMAc	95	0.48	
16	NMP	84	0.55	

[a] The reactions were carried out with 2 mmol of BPGE and 2 mmol of BPGE in the solvent (2 mL) using TBAC (0.1 mmol) as a catalyst at 90 °C for 24 h. [b] Estimated by GPC based on polystyrene standards.

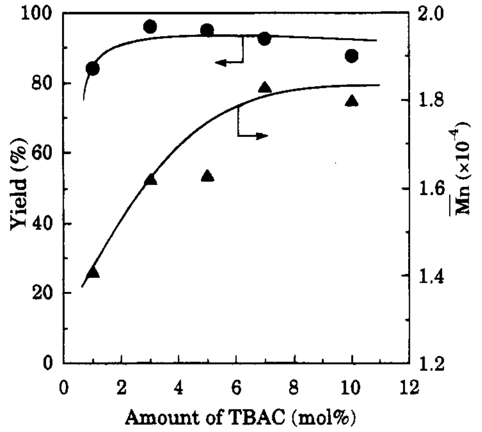

Figure 1. Effect of the TBAC concentration on the reaction of BPGE (2 mmol) with PPDC (2 mmol) in toluene (2 mL) at 90 °C for 24 h.

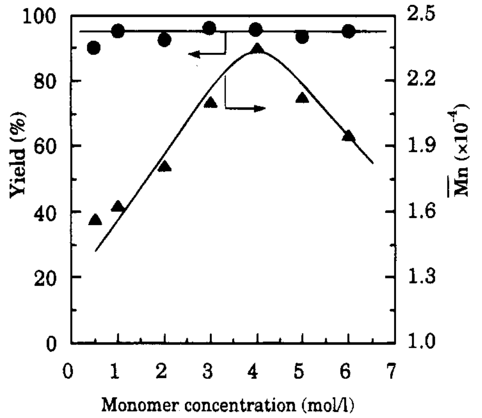

Figure 2. Effect of the monomer concentration on the reaction of BPGE with PPDC in toluene using 5 mol % of TBAC as the catalyst at 90 °C for 24 h.

This result shows that, although the polyaddition of BPGE with PPDC proceeded using TEA, TPP, 18-C-6/KCl, or quaternary onium salts as catalysts, quaternary onium salts such as TBAC, TBAB, TBPB, and TBPC have higher catalytic activity than TEA, TPP, and 18-C-6/KCl complex.

The structure of this polymer was confirmed by IR and ^{1}H NMR spectra. In the IR spectrum of **2a**, certain characteristic absorption peaks showed at 1250, 1180, 990, and 750 cm^{-1} due to C−O−C, P=O, P−O−C, and C−Cl stretching, respectively. In the ^{1}H NMR spectrum of **2a**, the corresponding proton signals were observed at 1.60 (C−CH$_3$), 3.59−4.00 (CH$_2$Cl), 4.00−4.50 (CH$_2$−O), 4.70−5.18 (CH−O), 6.90−8.10 (aromatic protons), respectively. The intensity ratio calculated from methine protons at 4.70−5.18 ppm vs aromatic protons at 6.90−8.10 ppm was 1.0. These results mean that poly(phosphonate) **2a** with pendant chloromethyl groups was synthesized by the regioselective polyaddition of BPGE with PPDC using appropriate catalysts as shown in Scheme 2.

The polyaddition of BPGE with PPDC also took place using 5 mol % of TBAC as the catalyst at 90 °C for 24 h in certain organic solvents. As summarized in Table 2, polymers **2a** with relatively high molecular weight were obtained in good yields, when the reactions were carried out in toluene, anisole, *o*-dichlorobenzene, acetonitrile, and THF. However, molecular weights (M_n) of the prepared polymers in DMF, DMAc, and NMP were lower than those of the polymer obtained in the former solvents. It seems that small amounts of water contained in polar solvents, which could not be removed completely, caused the hydrolysis of PPDC before the reaction.

The effect of the catalyst concentration was examined on the polyaddition of BPGE with PPDC in the presence of TBAC in toluene at 90 °C for 24 h. As shown in Figure 1, no remarkable difference of the yield of polymer **2a** was observed; however, the number-average molecular weight of polymer **2a** increased with the catalyst concentration. This result means that the rate of polyaddition of BPGE with PPDC was strongly affected by the catalyst concentration.

As shown in Figure 2, although the yield of the polymer was not related to the examined monomer concentration, the molecular weight of the resulting polymer was strongly affected by the monomer concentration on the polyaddition of BPGE with PPDC in toluene using 5 mol % of TBAC as the catalyst at 90 °C for 24 h. That is, the number-average molecular weight of polymer **2a** increased with monomer concentration and showed the highest molecular weight at 4 mol/L of

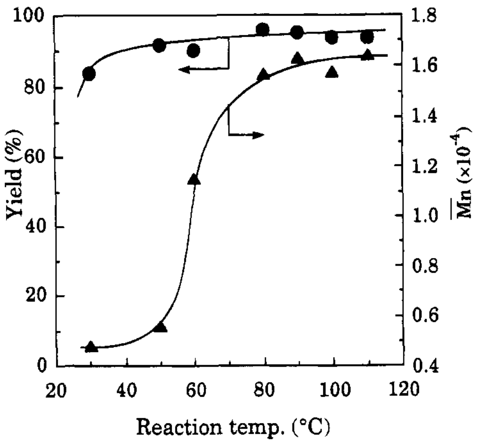

Figure 3. Effect of the reaction temperature on the reaction of BPGE (2 mmol) with PPDC (2 mmol) in toluene (2 mL) using 5 mol % of TBAC for 24 h.

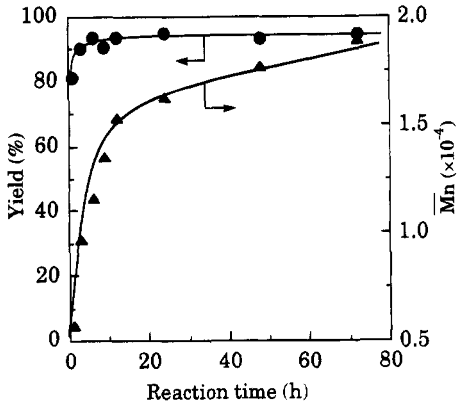

Figure 4. Effect of the reaction time on the reaction of BPGE (2 mmol) with PPDC (2 mmol) in toluene (2 mL) using 5 mol % of TBAC at 90 °C.

the monomer concentration. However, the molecular weight of the polymer decreased gradually with increasing the monomer concentration.

This result means that, although higher monomer concentration enhanced the rate of polyaddition of BPGE with PPDC at the initial stage, further polyaddition of terminal reactive groups in the polymer chains was hindered due to the high viscosity when the reaction was performed under high monomer concentration.

The effect of the reaction temperature on the polyaddition of BPGE with PPDC was examined in toluene in the presence of 5 mol % of TBAC as the catalyst at 90 °C for 24 h. As shown in Figure 3, no remarkable difference of the yield of polymer **2a** was observed except at 30 °C. On the other hand, the number-average molecular weight of polymer **2a** increased dramatically at 80 °C. This result shows that the polyaddition of BPGE with PPDC was strongly affected by the reaction temperature and that appropriate temperatures for this reaction are in the 80–110 °C range.

The effect of the reaction time on the polyaddition of BPGE with PPDC was investigated using 5 mol % of TBAC as the catalyst in toluene at 90 °C. As shown in Figure 4, the yield of polymer **2a** peaked at 10 h; however, the molecular weight of the resulting polymer continued to increase gradually with reaction time. This is a typical characteristic result of consecutive polymerization.

Table 3. Synthesis of Poly(phosphonate)s and Poly(phosphate)s[a]

polym no.	monomer		yield, %	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$
	bisepoxide	phosphonic dichloride			
2a	BPGE	PPDC	95	1.63	1.36
2b	BPGE	MPDC	63	2.31	1.46
2c	BPGE	PDCP	90	0.66	1.45
2d	BPGE	MDCP		gel	
2e	EGGE	PPDC	95	1.01	1.22
2f	EGGE	MPDC	80	1.96	1.51
2g	EGGE	PDCP	84	0.43	
2h	EGGE	MDCP		gel	

[a] The reactions were carried out with 2 mmol of bisepoxide and 2 mmol of phosphonic dichloride in toluene (2 mL) using TBAC (0.1 mmol) as a catalyst at 90 °C for 24 h. [b] Estimated by GPC based on polystyrene standards.

According to the obtained information for the polyaddition of BPDE with PPDC, polyadditions of various bisepoxides with dichlorophosphines or dichlorophosphate were performed with 5 mol % of TBAC as the catalyst at 90 °C for 24 h. As summarized in Table 3, the polyaddition of BPGE with PPDC gave the corresponding poly(phosphonate) **2a** with relatively high molecular weight (M_n = 16 300). The polyaddition of BPGE with MPDC produced the corresponding poly(phosphonate) **2b** with higher molecular weight (M_n = 23 100) than that of **2a**. Poly(phosphate) **2c** was also synthesized by the polyaddition of BPGE with PDCP; however, the molecular weight of the resulting polymer was not high enough. When the polyaddition of BPGE with MDCP was carried out under the same conditions, gelation occurred during the reaction and no soluble polymer **2d** was obtained. Poly(phosphonate)s **2e** and **2f** with M_n = 10 100 and 19 600 were also synthesized in 95 and 80% yields by the polyaddition of aliphatic bisepoxide EGGE with PPDC and MPDC, respectively. Although poly(phosphate) **2g** was obtained with 84% yield, the molecular weight of the resulting polymer was relatively low. On the other hand, when the polyaddition of EGGE with MDCP was performed under the same conditions, a gelation occurred as with the reaction of BPGE with MDCP and no soluble polymer **2h** resulted. From these results, it seems that the reactivity of MPDC to the epoxide group was higher than that of PPDC, and the reactivity of PDCP was lower than that of PPDC. However, the cause of the gel production from the reaction with MPDC is unclear.

The solubility of the poly(phosphonate)s (**2a**, **2b**, **2e**, and **2f**) and poly(phosphate)s (**2c** and **2g**) was examined. As summarized in Table 4, all of the polymers were insoluble in hexane. Polymers **2a** and **2b** were insoluble in methanol. However, polymers **2c** and **2e** swelled in methanol, and polymers **2f** and **2g** were soluble in methanol. Although polymers **2a–c** prepared by the reaction with BPGE having a bisphenol backbone swelled in acetonitrile, polymers **2e–g** prepared by the reaction of EGGE with an alkylene glycol segment were very soluble in acetonitrile.

On the other hand, all the obtained poly(phosphonate)s and poly(phosphate)s were soluble in various organic solvents such as acetone, ethyl acetate, dichloromethane, toluene, anisole, *o*-dichlorobenzene, THF, DMF, NMP, and DMSO. This result means that poly(phosphonate)s and poly(phosphate)s with pendant chloromethyl groups synthesized by the polyaddition of bisepoxides with phosphonic dichlorides and dichlorophosphate had very good solubility in common organic solvents due to the poly(phosphonate) or poly(phosphate) linkages, while polymers **2e–g** due to the oxy-

Table 4. Solubility of Poly(phosphonate)s and Poly(phosphate)s[a]

	polymer					
solvent	**2a**	**2b**	**2c**	**2e**	**2f**	**2g**
hexane	−	−	−	−	−	−
methanol	−	−	+−	+−	++	++
acetonitrile	+−	+−	+−	++	++	++
acetone	++	++	++	++	++	++
ethyl acetate	++	++	++	++	++	++
dichloromethane	++	++	++	++	++	++
toluene	++	++	++	++	++	++
anisole	++	++	++	++	++	++
o-dichlorobenzene	++	++	++	++	++	++
THF	++	++	++	++	++	++
DMF	++	++	++	++	++	++
NMP	++	++	++	++	++	++
DMSO	++	++	++	++	++	++

[a] + +: soluble at room temperature. +: soluble by heating. + −: partially soluble or swelling. −: insoluble.

ethylene chain showed higher solubility than polymers **2a–c** with a Bisphenol A skeleton in the main chain.

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