

Synthesis and Photoinitiated Cationic Polymerization of Polyfunctional 1-Propenyl Ether Monomers and Polymers Containing Phosphonate Linkage in the Main Chain

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ABSTRACT: Polyfunctional 1-propenyl ether monomers (**1a–c**) were synthesized by the regioselective addition reaction of 1-propenyl glycidyl ether (PGE) with certain phosphonic dichlorides using quaternary onium salts as catalysts. The reaction of PGE with phenylphosphonic dichloride (PPDC) gave bis[1-(chloromethyl)-2-(propenyloxy)ethyl]phenylphosphonate (**1a**) in 82% yield. Polycondensation of **1a** with terephthalic acid (TPC) was also carried out using 1, 8-diazabicyclo[5.4.0]undecene-7 (DBU) as a base to afford the corresponding polymer containing 1-propenyl ether groups (**2a**). A multifunctional monomer (**3a**) containing both 1-propenyl ether groups as Vc and methacrylate groups as Vr was prepared by the reaction of **1a** with methacrylic acid (MA) using DBU. Photoinitiated cationic polymerization of these 1-propenyl ether compounds proceeded rapidly using bis[4-(diphenylsulfonio)phenyl]sulfide bis(hexafluorophosphate) (DPSP), as a cationic photoinitiator without solvent upon UV irradiation.

KEY WORDS 1-Propenyl Glycidyl Ether / Phosphonic Dichloride / Polyfunctional 1-Propenyl Ether Monomers / Polymers Containing 1-Propenyl Ether Groups / Photoinitiated Cationic Polymerization /

It is well known that polymers containing phosphorus atom in the backbone have excellent flame retardant property.¹ Polyphosphonates and polyphosphates are ordinary synthesized by either melt or interfacial polycondensation of diols with phosphonic dichlorides and dichlorophosphates, respectively.^{2,3} Polyphosphonates with high molecular weight were also synthesized by the polycondensation of phosphonic dichlorides with certain diols using phase transfer catalysis.^{4,5}

The authors recently found new regioselective polyaddition of bis(epoxide)s with phosphonic dichlorides or dichlorophosphates, which proceed smoothly using quaternary onium salts as catalysts at elevated temperature to give the corresponding polyphosphonates or polyphosphates containing phosphorus groups in the polymer main chain and halogen atoms in the side chain, respectively.⁶ This reaction system has the possibility of extending polyadditions of reactive inorganic halide compounds or metal halide compounds with bis(epoxide)s to produce the corresponding inorganic or organometallic polymers with reactive pendant chloromethyl groups.⁷

Meanwhile, in the UV-curing fields, photoinitiated cationic polymerization of epoxides or vinyl ether compounds has become a candidate of the new UV-curing system,⁸ because these monomers do not receive any inhibition on the polymerization by atmos-

pheric oxygen.⁹ It is also well known that vinyl ethers have higher curing speed than epoxides under UV irradiation.¹⁰ One of highly reactive cationically polymerizable monomers is 1-propenyl ether same as vinyl ether. Crivello *et al.*^{11,12} have recently reported the synthesis of such monomers. A wide variety of monomers having the 1-propenyl ether groups can be prepared from the corresponding 2-propenyl ethers by the isomerization reaction.

Nishikubo *et al.*¹³ recently reported the synthesis of polyfunctional vinyl ether derivatives by the regioselective addition reaction of glycidyl vinyl ether (GVE) with acyl chlorides and their photoinitiated cationic polymerization. Furthermore, they succeeded in the synthesis of new hybrid monomers and polymers containing both cationic and radical polymerizable vinyl groups.¹⁴ Recently, they also reported the synthesis of silicon-containing divinyl ether monomers with chloromethyl groups by the reaction of GVE with various silyl dichlorides, the synthesis of silicon-containing polymers with vinyl ether groups by the reaction of the above reaction products with a dicarboxylic acid, and the synthesis of a silicon-containing multifunctional monomer by the reaction of the obtained silicon-containing divinyl ether monomer with potassium methacrylate.¹⁵ From this background information, we designed a new phosphorous-containing vinyl compounds for cationic UV-curing.

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This article reports on the synthesis of phosphorus-containing 1-propenyl ether monomers by the addition reaction of 1-propenyl glycidyl ether with various phosphonic dichlorides and dichlorophosphates, the synthesis of phosphorus-containing polymers with 1-propenyl ether groups by the polycondensation of the above product with dicarboxylic acids, and the synthesis of a phosphorus-containing multifunctional monomer by the condensation reaction of the obtained phosphorus-containing 1-propenyl ether monomer with methacrylic acid. Furthermore, the photoinitiated cationic polymerizations of thus obtained phosphorus-containing 1-propenyl monomers and polymers were also examined.

EXPERIMENTAL

Materials

Reagent grade phenylphosphonic dichloride (PPDC) was purified by distillation under reduced pressure. Tetrabutylammonium bromide (TBAB) was purified by recrystallization from dry ethyl acetate. Toluene was dried over sodium metal and distilled before use. 1,8-Diazabicyclo[5.4.0.]undecene-7 (DBU) and dimethylsulfoxide (DMSO) were purified by distillation under reduced pressure. Terephthalic acid (TPA), isophthalic acid (IPA), adipic acid (AA), and fumaric acid (FA) were purified by recrystallization from appropriate solvents. Phenylphosphonic dichloride (PDCP), propylphosphonic dichloride (PrPDC), allyl glycidyl ether, tris(triphenylphosphino)ruthenium(II) dichloride, triethylamine (TEA), tetrabutylphosphonium chloride (TBAB), phenothiazine, methacrylic acid (MA), bis[4-(diphenylsulfonio)phenyl]sulfide bis(hexafluorophosphate) (DPSP),¹⁶ *N*-morpholino-2,5-dibutoxybenzenediazonium hexafluorophosphate (MDBZ), (η -cyclopentadiene) (η -1-isopropylbenzene)iron(II) hexafluorophosphate (CBI), and 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1 (MMP) were used without further purification.

Measurements

IR spectra were measured on a JASCO FT/IR-5300 or a JASCO IR-700 spectrometer. ¹H NMR spectra were obtained on a JEOL FX-200 operating in the pulsed Fourier Transform (FT) modes, using tetramethylsilane (TMS) as an internal standard in CDCl₃. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymers were measured with a TOSOH HLC-8020 GPC unit equipped with a refractive index detector using TSKgel GMHXL as gel columns (eluent, DMF; calibration, polystyrene standards). Elemental analyses were measured on a PE-2400 Series II CHNS/O Analyzer.

UV light intensity was monitored using ORC UV-M30 radiometer.

Synthesis of 1-Propenyl Glycidyl Ether (PGE) from Isomerization Reaction of Allyl Glycidyl Ether

PGE was prepared with 69% yield, according to the reported method by Crivello *et al.*^{11c} The *E/Z* ratio determined by ¹H NMR was 4/6.

Synthesis of 1-Propenyl Ether Monomer (**1a**) from PGE with PPDC

A typical procedure for the reaction of PGE with PPDC is as follows: PGE (1.141 g, 10 mmol), PPDC (0.975 g, 5 mmol), and TBAB (0.161 g, 0.5 mmol) were dissolved in toluene (5 mL), and the solution was stirred at 90 °C for 24 h. The reaction mixture was diluted with ethyl acetate/TEA (7/0.7 mL), washed three times with small amounts (4 mL) of water. The reaction mixture was dried with MgSO₄, and then the solvent was evaporated *in vacuo*. The crude product obtained was purified by silica gel column chromatography using the mixed solvent of methyl ethyl ketone and *n*-hexane (1:3, v/v) as the eluent. The isolated yield of the resulting adduct **1a** was 1.74 g (82%). IR (neat, cm⁻¹): 1667 (ν C=C; 1-propenyl ether), 1439 (ν C=C; aromatic), 1254 (ν C-O-C), 1182 (ν P=O), 1065 (ν P-O-C), and 748 (ν C-Cl). ¹H NMR (200 MHz, CDCl₃, TMS): δ 1.32–1.75 (m, 6 H, CH₃), 3.54–4.14 (m, 8.0 H, O-CH₂-CH, CH₂-Cl), 4.25–4.99 (m, 4.0H, CH₃-CH=CH, CH₂-CH-O), 5.73–6.31 (m, 2.0H, CH=CH-O), and 7.33–8.07 ppm (m, 5.0H, aromatic protons). *Anal.* Calcd for C₁₈H₂₅O₅PCl₂: C, 51.08; H, 5.95. Found: C, 51.35; H, 5.68.

Synthesis of 1-Propenyl Ether Monomer (**1b**) from PGE with PDCP

The reaction of PGE (1.141 g, 10 mmol) and PDCP (1.055 g; 5 mmol) was performed using TBPC (0.147 g, 0.5 mmol) as the catalyst in toluene (5 mL) at 90 °C for 48 h in a sealed tube under stirring. The reaction mixture was diluted with ethyl acetate/TEA (7/0.7 mL), washed three times with water (4 mL), and the product was purified by the same procedure as described above. The yield of **1b** was 1.05 g (48%). IR (neat, cm⁻¹): 1668 (ν C=C; 1-propenyl ether), 1490 (ν C=C; aromatic), 1280 (ν C-O-C), 1182 (ν P=O), 1139 (ν P-O-C), and 758 (ν C-Cl). ¹H NMR (200 MHz, CDCl₃, TMS): δ 1.38–1.68 (m, 6 H, CH₃), 3.60–4.09 (m, 8.0 H, O-CH₂-CH, CH₂-Cl), 4.30–5.07 (m, 4.0 H, CH₃-CH=CH, CH₂-CH-O), 5.70–6.33 (m, 2.0 H, CH=CH-O), and 7.12–7.41 ppm (m, 5.0 H, aromatic protons). *Anal.* Calcd for C₁₈H₂₅O₆PCl₂: C, 49.22; H, 5.74. Found: C, 49.49; H, 5.59.

Synthesis of 1-Propenyl Ether Monomer (1c) from PGE with PrPDC

PGE (1.141 g, 10 mmol) was made to react with PrPDC (0.805 g; 5 mmol) in the presence of TBAB (0.161 g, 0.5 mmol) in toluene (5 mL) at 90 °C for 24 h. The product was purified by the same procedure as described above. The yield of **1c** was 1.12 g (57%). IR (neat, cm^{-1}): 1668 (ν C=C; 1-propenyl ether), 1257 (ν C–O–C), 1183 (ν P=O), 1139 (ν P–O–C), and 723 (ν C–Cl). $^1\text{H NMR}$ (200 MHz, CDCl_3 , TMS): δ 0.84–1.15 (m, 3H, $\text{CH}_3\text{--CH}_2\text{--CH}_2$), 1.45–2.19 (m, 10.0H, $\text{CH}_3\text{--CH=CH}$, $\text{CH}_3\text{--CH}_2\text{--CH}_2$), 3.53–4.10 (m, 8.0H, O– $\text{CH}_2\text{--CH}$, $\text{CH}_2\text{--Cl}$), 4.35–4.97 (m, 4.0H, $\text{CH}_3\text{--CH=CH}$, $\text{CH}_2\text{--CH--O}$), and 5.86–6.31 (m, 2.0H, CH=CH--O). Anal. Calcd for $\text{C}_{15}\text{H}_{27}\text{O}_5\text{PCl}_2$: C, 46.29; H, 6.99. Found: C, 46.03; H, 6.85.

Synthesis of Polymer Containing 1-Propenyl Ether Groups (2a₃) from 1a with TPA

A typical procedure for the polycondensation of **1a** with TPA is as follows: **1a** (0.847 g, 2 mmol), TPA (0.166 g, 1 mmol), and DBU (0.304 g, 2 mmol) were dissolved in DMSO (5 mL). The solution was stirred at 70 °C for 48 h. The reaction mixture was diluted with chloroform (10 mL), washed six times with small amount (20 mL) of water, and the combined chloroform layer was dried using MgSO_4 . The solvent was evaporated *in vacuo*. The isolated yield of the resulting polymer **2a₃** was 0.90 g (94%). M_n of the polymer determined by GPC was 3,700 ($M_w/M_n = 1.03$). IR (neat, cm^{-1}): 1722 (ν C=O), 1668 (ν C=C; 1-propenyl ether), 1438 (ν C=C; aromatic), 1256 (ν C–O–C), 1182 (ν P=O), 1131 (ν P–O–C), and 749 (ν C–Cl). $^1\text{H NMR}$ (200 MHz, CDCl_3 , TMS): δ 1.32–1.75 (m, 12H, $\text{CH}_3\text{--CH=CH}$), 3.51–5.32 (m, 24.0H, $\text{CH}_3\text{--CH=CH--O--CH}_2\text{--CH--O--P=O}$, $\text{CH}_2\text{--O--C=O}$ and $\text{CH}_2\text{--Cl}$; terminal groups), 5.68–6.38 (m, 4.0H, $\text{CH}_3\text{--CH=CH}$), and 7.12–8.29 ppm (m, 14.0H, aromatic protons).

Synthesis of Polymer Containing 1-Propenyl Ether Groups (2b) from 1a with IPA

The reaction of **1a** (0.847 g, 2 mmol) and IPA (0.166 g, 1 mmol) was performed using DBU (0.304 g, 2 mmol) in DMSO (5 mL) at 70 °C for 48 h in a sealed tube under stirring, and the product was purified by the same procedure as described above. The yield of **2b** was 0.87 g (92%). M_n of the polymer determined by GPC was 3,500 ($M_w/M_n = 1.03$). IR (neat, cm^{-1}): 1728 (ν C=O), 1668 (ν C=C; 1-propenyl ether), 1438 (ν C=C; aromatic), 1236 (ν C–O–C), 1182 (ν P=O), 1131 (ν P–O–C), and 748 (ν C–Cl). $^1\text{H NMR}$ (200 MHz, CDCl_3 , TMS): δ 1.28–1.75 (m, 12H, $\text{CH}_3\text{--CH=CH}$), 3.44–5.24 (m, 24.0H, $\text{CH}_3\text{--}$

$\text{CH=CH--O--CH}_2\text{--CH--O--P=O}$, $\text{CH}_2\text{--O--C=O}$ and $\text{CH}_2\text{--Cl}$; terminal groups), 5.66–6.39 (m, 4.0H, $\text{CH}_3\text{--CH=CH}$), and 7.05–8.93 ppm (m, 14.0H, aromatic protons).

Synthesis of Polymer Containing 1-Propenyl Ether Groups (2c) from 1a with AA

1a (0.847 g, 2 mmol) was made to react with AA (0.146 g; 1 mmol) in the presence of DBU (0.304 g, 2 mmol) in DMSO (5 mL) at 70 °C for 48 h. The product was purified by the same procedure as described above. The yield of **2c** was 0.81 g (87%). M_n of the polymer determined by GPC was 3,900 ($M_w/M_n = 1.03$). IR (neat, cm^{-1}): 1739 (ν C=O), 1668 (ν C=C; 1-propenyl ether), 1438 (ν C=C; aromatic), 1253 (ν C–O–C), 1178 (ν P=O), 1131 (ν P–O–C), and 748 (ν C–Cl). $^1\text{H NMR}$ (200 MHz, CDCl_3 , TMS): δ 1.21–1.96 (m, 20H, $\text{CH}_3\text{--CH=CH}$, methylenes of adipate unit), 3.56–5.12 (m, 24.0H, $\text{CH}_3\text{--CH=CH--O--CH}_2\text{--CH--O--P=O}$, $\text{CH}_2\text{--O--C=O}$ and $\text{CH}_2\text{--Cl}$; terminal groups), 5.66–6.39 (m, 4.0H, $\text{CH}_3\text{--CH=CH}$), and 7.31–8.00 ppm (m, 10.0H, aromatic protons).

Synthesis of Polymer Containing 1-Propenyl Ether Groups (2d) from 1a with FA

The polyaddition of **1a** (0.847 g, 2 mmol) and SA (0.116 g; 1 mmol) was carried out in the presence of DBU (0.304 g, 2 mmol) in DMSO (5 mL) at 70 °C for 48 h. The contents were washed six times with water. The yield of **2d** was 0.67 g (74%). M_n of the polymer determined by GPC was 3,600 ($M_w/M_n = 1.03$). IR (neat, cm^{-1}): 1725 (ν C=O), 1669 (ν C=C; 1-propenyl ether), 1438 (ν C=C; aromatic), 1253 (ν C–O–C), 1180 (ν P=O), 1131 (ν P–O–C), and 748 (ν C–Cl). $^1\text{H NMR}$ (200 MHz, CDCl_3 , TMS): δ 1.30–1.76 (m, 12H, $\text{CH}_3\text{--CH=CH}$), 3.44–5.12 (m, 24.0H, $\text{CH}_3\text{--CH=CH--O--CH}_2\text{--CH--O--P=O}$, $\text{CH}_2\text{--O--C=O}$ and $\text{CH}_2\text{--Cl}$; terminal groups), 5.65–6.33 (m, 4.0H, $\text{CH}_3\text{--CH=CH}$), 6.33–7.02 (m, 2.0H, methyne of fumarate unit), and 7.30–8.03 ppm (m, 10.0H, aromatic protons).

Synthesis of Hybrid Monomer Containing both 1-Propenyl Ether and Methacrylate Groups (3a) from 1a with MA

A typical procedure for the reaction of **1a** with MA is as follows: **1a** (0.847 g, 2 mmol), MA (0.517 g, 6 mmol), a micro spatula of phenothiazine as an inhibitor of the radical polymerization, and DBU (0.913 g, 6 mmol) were dissolved in DMSO (5 mL). The solution was stirred at 70 °C for 24 h. The reaction mixture was poured into water and extracted with chloroform (10 mL). The combined chloroform layer was washed with aqueous 0.1 N HCl solutions, and dried with

MgSO₄. The solvent was evaporated *in vacuo*. The product was purified by the silica gel chromatography using chloroform/acetone (v/v = 20/1) as an eluent. The isolated yield of the resulting hybrid monomer (**3a**) was 0.51 g (48%). IR (neat, cm⁻¹): 1721 (ν C=O), 1667 (ν C=C; 1-propenyl ether), 1636 (ν C=C; methacryloyl), 1439 (ν C=C; aromatic), 1255 (ν C-O-C), 1164 (ν P=O), and 1130 (ν P-O-C). ¹H NMR (200 MHz, CDCl₃, TMS): δ 1.33–1.72 (m, 6.0H, CH₃-CH=CH), 1.72–2.09 (m, 6.0H, CH₂=C(CH₃)-C=O), 3.79–5.04 (m, 12.0H, CH₃-CH=CH and O-CH₂-CH-CH₂-O-C=O), 5.33–5.69 (m, 2.0H, CH₃-CH=CH), 5.71–6.32 (m, 4.0H, CH₂=C(CH₃)-C=O), and 7.31–7.9 ppm (m, 5H, aromatic protons). *Anal.* Calcd for C₄₄H₅₄O₁₄P₂: C, 56.24; H, 5.79. Found: C, 56.31; H, 5.75.

Typical Procedure for the Photoinitiated Cationic Polymerization

1 Mol% (for 1-propenyl ether group of **3a**) of DPSP was dissolved in **3a** (0.523 g, 1 mmol). The photochemical reaction of the viscous liquid mixture on the KBr plate was performed upon UV irradiation with a 250 W high-pressure mercury lamp at a distance of 10 cm (UV light intensity: 6.8 mW/cm² at 360 nm) in air. Then the conversion of the 1-propenyl

ether group of the hybrid monomer was monitored by the decrease in the absorption peak at 1667 cm⁻¹ due to ν C=C (1-propenyl ether group) in the FT-IR spectrum.

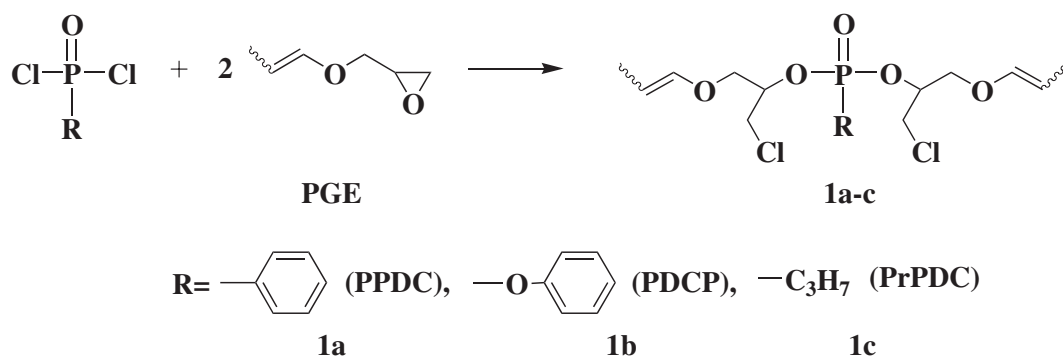
Typical Procedure for Photoinitiated Radical Polymerization

5 Mol% (for methacryloyl of **3a**) of MMP was dissolved in **3a** (0.523 g, 1 mmol). The reaction to form the viscous liquid mixture on the KBr plate was conducted under the same conditions. Then the conversion of the methacryloyl group of the hybrid monomer was monitored by observing the decrease of the absorption peak at 1636 cm⁻¹ due to ν C=C (methacryloyl group) in the FT-IR spectrum.

RESULTS AND DISCUSSION

Synthesis of Phosphorus-containing 1-Propenyl Ether Monomers and Polymers

The addition reactions of PGE with certain phosphonic dichlorides or dichlorophosphate were carried out for the synthesis of the 1-propenyl ether monomers **1a–c** (Scheme 1), and the results are summarized in Table I. As for the addition reaction of PGE with PPDC, it was referred to addition reaction of phenyl



Scheme 1.

Table I. Synthesis of 1-prppenyl ether monomers^a

No.	Dichlorides	Feed Ratio		Catalyst	Time (h)	Yield (%) ^b
		PGE	Dichloride			
1	PPDC	2	1	TBAB	24	82
2	PDCP	2	1	TBAB	24	0
3	PDCP	2	1	TBPC	48	48
4	PDCP	3	1	TBPC	48	58
5	PDCP	4	1	TBPC	48	71
6	PrPDC	2	1	TBAB	24	57
7	PrPDC	2	1	TBPC	48	75
8	PrPDC	3	1	TBPC	48	76
9	PrPDC	4	1	TBPC	48	78

^aThe reaction was carried out with PGE and dichlorides using various catalysts (5 mol% for PGE) in toluene at 90 °C. ^bIsolated yield.

glycidyl ether with PPDC reported previously.⁶ The addition reaction of PGE with PPDC proceeded very smoothly using 5 mol% of TBAB as a catalyst in toluene at 90 °C for 24 h to give the corresponding 1-propenyl ether monomer **1a** with 82% yield. The structure of the obtained **1a** was confirmed by IR and ¹HNMR spectra. The IR spectrum of **1a** showed absorption peaks at 1667, 1439, 1254, 1182, 1065, and 748 cm⁻¹ due to C=C; 1-propenyl ether, C=C; aromatic, C–O–C, P=O, P–O–C, and C–Cl stretching, respectively. The ¹HNMR spectrum of **1a** exhibited the corresponding proton signals at 1.32–1.75 ppm due to CH₃, at 3.54–4.14 ppm due to O–CH₂–CH, CH₂–Cl, at 4.25–4.99 ppm due to CH₃–CH=CH, CH₂–CH–O, at 5.73–6.31 ppm due to CH=CH–O, and at 7.33–8.07 ppm due to aromatic protons.

According to the information obtained from the addition reaction of PGE with PPDC, addition reactions of PGE with PDCP or PrPDC were performed with 5 mol% of TBAB at 90 °C for 24 h. When the addition reaction of PGE with PDCP was carried out with 5 mol% of TBAB at 90 °C for 24 h, the corresponding 1-propenyl ether monomer **1b** was not obtained. The addition reaction of PGE with PrPDC produced the corresponding 1-propenyl ether monomer **1c** with comparatively high yield (66%) under the same conditions. The reaction of PGE with PDCP was examined in the presence of TBPC as a catalyst at 90 °C for 48 h. The yield of the resulting **1b** was 48%. The effect of charge of a PGE/PDCP ratio was examined to obtain **1b** with high yields. This result suggests that yield of **1b** improved gradually with increasing of PGE ratio. Particularly, when the reaction of PGE with PDCP at molar ratio of 4/1 was performed, the targeted product **1b** was obtained in good yield (71%). On the other hand, when the addition reaction of PGE with PrPDC was carried out in the presence of TBPC, the yield of **1c** was improved. That is, when a PGE/PrPDC ratio was 2/1, 3/1, and 4/1, 75, 76, and 78% yields of **1b** were obtained, respectively. From these results, it seems that the reactivity of PPDC to the epoxide group was higher than that of PrPDC, and the reactivity of PDCP was lower than that of PrPDC.

All of the IR and ¹HNMR spectra of the obtained products suggested that the addition reactions gave the corresponding 1-propenyl ether monomers **1a–c**. Nishikubo *et al.* reported¹⁷ the mechanism of the addition reaction of epoxy compound with acyl chloride catalyzed by quaternary onium salts or crown ether complexes based on the kinetic data. We assumed that a similar mechanism for the addition reaction of epoxide with phosphonic dichlorides and dichlorophosphates catalyzed by quaternary onium salts or crown ethers shown in Scheme 2.

The catalyst first attacks epoxide to produce active intermediate **I** as Eq. 1. The intermediate **I** reacts with phosphonic dichlorides to form unstable adduct **II** as Eq. 2, and the adduct **II** decomposes spontaneously to produce the product releasing the catalyst as Eq. 3. As for the reactivity as electrophilic reagent (such as phosphonic dichlorides and dichlorophosphates), the stability of adduct **II** is influenced by substituents greatly. As for the reactivity of epoxide to phosphonic dichlorides and dichlorophosphates, it is caused by balance with leaving ability (of Cl⁻ as leaving group) and electrophilicity of phosphorus-containing dichlorides.

Polycondensations of **1a** with certain dicarboxylic acids were conducted using DBU as a base in DMSO at 70 °C to give the polymers (Scheme 3).

As summarized in Table II, when the reaction of **1a** with TPA was performed with 2/1 ratio for 48 h, the polymer (**2a₃**) with *M_n* of 3,700 was obtained in 94% yield. The structure of the obtained polymer **2a₃** was confirmed by IR and ¹HNMR spectra. The IR spectrum of **2a₃** showed characteristic absorption peaks on ν C=O of the ester groups at 1722 cm⁻¹, and on ν C=C of the 1-propenyl ether moiety at 1668 cm⁻¹. In the ¹HNMR spectrum of the polymer **2a₃**, the signal of a methyl proton adjacent to 1-propenyl ether was confirmed at 1.24–1.83 ppm. The signals based on 1-propenyl ether groups were exhibited at 5.73–6.45 ppm. The signals of aromatic protons were observed at 7.09–8.38 ppm. In the case that the ratios of **1a**/TPA were 1/1 and 3/2, solid polymer **2a₁** with *M_n* of 6200 and semi-solid polymer **2a₂** with *M_n* of 4,100 were obtained, respectively. This means that liquid polymer, which is the suitable form for photopolymerization without solvent, was easily prepared by the condensation reaction using double amount **1a** as TPA. This result also shows that the molecular weights of phosphorus-containing polymer with 1-propenyl ether groups can be controlled by the feed ratio. Furthermore, it was proved that the polycondensations of **1a** with dicarboxylic acids such as IPA, AA, and FA proceeded smoothly with DBU to give the corresponding polymers containing 1-propenyl ether groups (**2b–d**). The structures of the resulting polymers were confirmed by IR and ¹HNMR spectra.

The reaction of **1a** with MA was examined using DBU in DMSO at 70 °C (Scheme 4). The reaction of **1a** with MA at a **1a**/MA ratio = 1/3 gave 48% isolated yield of the corresponding hybrid monomer (**3a**) after 24 h. The structure of **3a** was confirmed by IR and ¹HNMR spectra. The IR spectrum of **3a** showed absorption peaks at 1721, 1667, 1636, 1255, 1164, and 1130 cm⁻¹ due to C=O, C=C; 1-propenyl ether, C=C; methacryloyl, C–O–C, P=O, and P–O–C stretching, respectively. In particular, the absorption

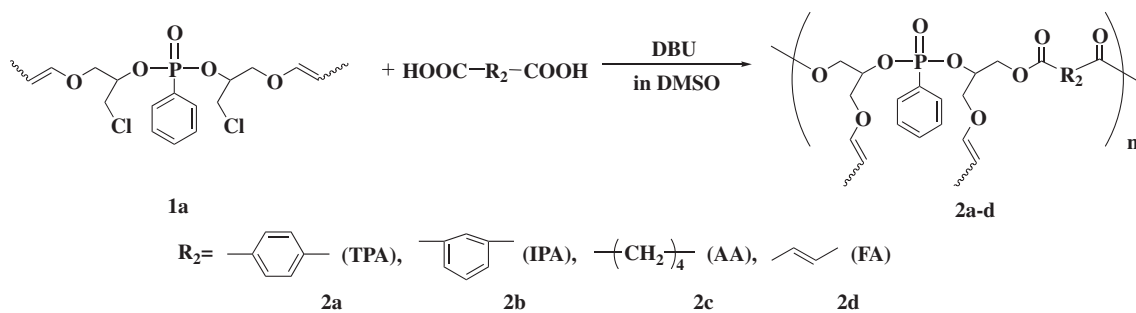
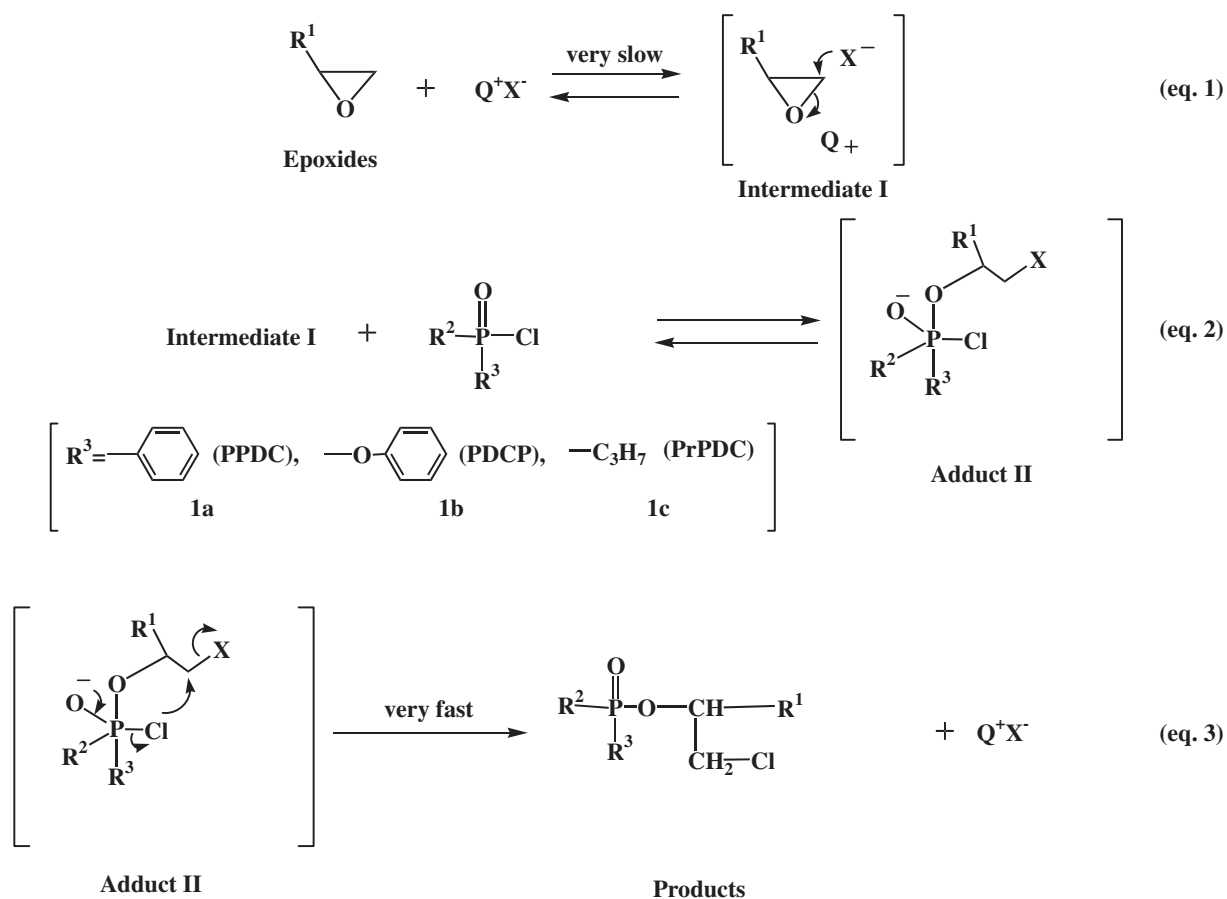
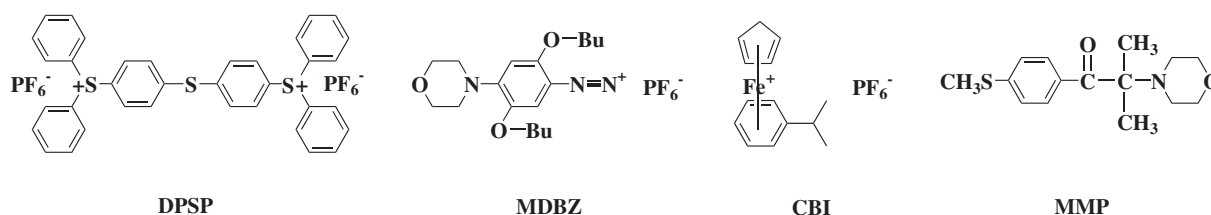
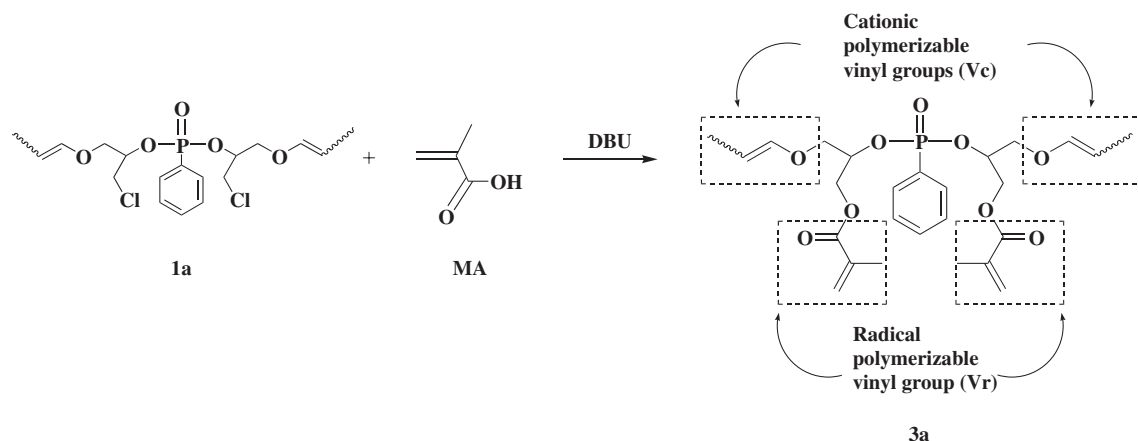


Table II. Synthesis of polymer containing 1-propenyl ether groups^a

Dicarboxylic acid	Feed ratio 1a:2	Oligomer	Yield (%)	M_n^b	Characteristic
TPA	1:1	2a ₁	87	6200	Solid
TPA	3:2	2a ₂	88	4100	Semi-solid
TPA	2:1	2a ₃	94	3700	Liquid
IPA	2:1	2b	92	3500	Liquid
AA	2:1	2c	87	3900	Liquid
FA	2:1	2d	84	3600	Liquid

^aThe reaction was carried out with **1a** and dicarboxylic acids using DBU in DMSO (5 mL) for 48 h at 70 °C.

^bEstimated by GPC (DMF) based on polystyrene standards.



peak due to C–Cl stretching of **1a** at 748 cm^{-1} disappeared, and a new absorption peak due to C=O stretching was observed at 1721 cm^{-1} .

Photoinitiated Cationic Polymerization of Phosphorus-containing 1-Propenyl Ether Monomers and Polymers

The photoinitiated cationic polymerization of **1a** with 1 mol% of certain catalysts was carried out in bulk upon UV irradiation using a 250 W high-pressure mercury lamp. Figure 1 showed the structure of catalysts. The conversion of the 1-propenyl ether groups was estimated from the decrease of the absorbance at 1667 cm^{-1} in the FT-IR spectrum. The polymerization of **1a** with DPSP proceeded very quickly, and the conversion of the 1-propenyl ether groups was 84% at 30 s (Figure 2). DPSP underwent irreversible fragmentation with the formation of bronsted acid upon UV irradiation (Scheme 5).

On the other hand, when CBI and MDBZ which produce Lewis acids¹⁸ upon UV irradiation were used as the catalysts, the reaction did not proceed at all. MDBZ contains a morpholino group that would be expected to interfere with cationic polymerization. In the case of CBI, substitution reaction of aromatic would occur by UV irradiation. And then, the proposed mechanism requires coordination by the monomer. However, it seems to be impossible that 1-propenyl ether group coordinates. From these results, it was found that DPSP has good activity as a photo-acid

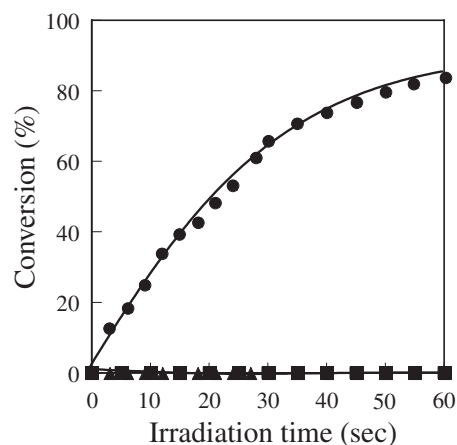
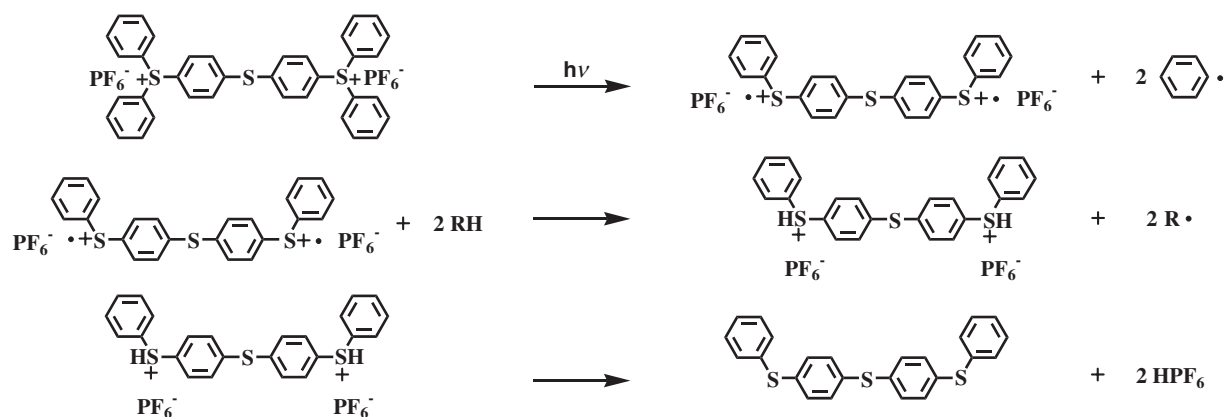


Figure 2. Photoinitiated cationic polymerization of 1-propenyl ether monomer **1a** using certain photo-acid generators (1 mol%). ●: DPSP, ▲: MDBZ, ■: CBI.

generator to the 1-propenyl ether group in **1a**.

The photoinitiated cationic polymerization of 1-propenyl ether monomers **1b** and **1c** with 1 mol% of DPSP took place under the same conditions as applied to the reaction of **1a** (Figure 3). The reaction of **1b** proceeded rapidly with DPSP and the conversion was 81% at 60 s. The **1b** showed almost the same good characteristic of photoinitiated cationic polymerization as the **1a** did. On the other hand, conversion of the **1c** was less than 35% by the irradiation at 60 s, because the **1c** have poor miscibility with DPSP. As for the substituent of phosphorus-containing 1-propenyl



Scheme 5.

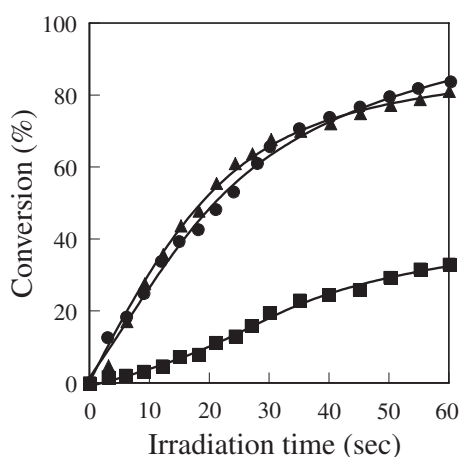


Figure 3. Photoinitiated cationic polymerization of 1-propenyl ether monomers using DPSP (1 mol%). ●: **1a**, ▲: **1b**, ■: **1c**.

ether monomers, the monomer with propyl moiety (**1c**) showed a lower photoreactivity than monomers with phenyl moiety (**1a**) and phenoxy moiety (**1b**), which may be due to the miscibility of the monomers and DPSP.

The photoinitiated cationic polymerization of polymers **2a₃**, **2b**, **2c**, and **2d** with 1 mol% DPSP was also examined under the same conditions. The conversions of 1-propenyl ether groups in the polymers measured by the FT-IR were shown in Figure 4. This result shows that the reaction rates of **2a₃**, **2b**, and **2c** were almost the same, and the conversion of 1-propenyl ether groups reached about 80% after 300 s of the irradiation. However the conversion of 1-propenyl ether groups in polymer **2d**, which has C=C bonds in the main chain and 1-propenyl ether moieties on the side chain, reached only 50% after 300 s of the irradiation. Because, unsaturated C=C bonds in the main chain reacted with radicals and cations which produced dur-

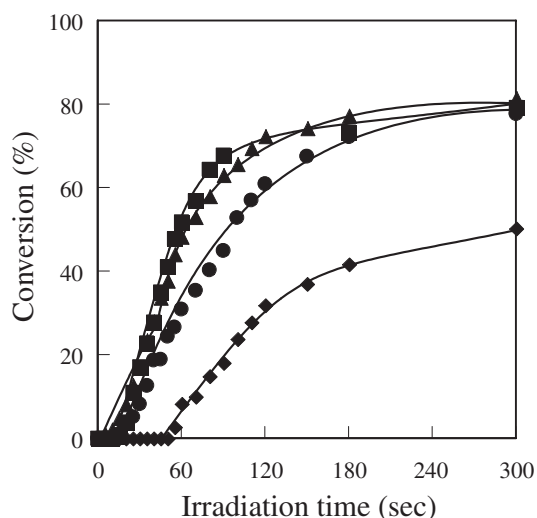


Figure 4. Photoinitiated cationic polymerization of polymers containing 1-propenyl ether groups using DPSP (1 mol%). ●: **2a₃**, ▲: **2b**, ■: **2c**, ◆: **2d**.

ing the photodecomposition process of DPSP.

As shown in scheme 4, the synthesized phosphorus-containing hybrid 1-propenyl monomers **3a** had both cationically polymerizable 1-propenyl ether groups (Vc) and radically polymerizable methacrylate groups (Vr). The polymerization behavior of the multifunctional monomers was investigated using either cationic or radical photoinitiators. The sulfonium salt DPSP as cationic photoinitiators and MMP as radical photoinitiators were used for the polymerization of **3a**, respectively. Photoinitiated cationic or radical polymerizations of **3a** were carried out with 1 mol% of DPSP or 5 mol% of MMP, respectively, upon UV irradiation using a 250 W high pressure mercury lamp. The conversions of 1-propenyl ether groups as Vc and methacrylate group as Vr of **3a** were estimated from the decrease of absorption at 1667 cm^{-1} and 1636 cm^{-1} , respectively, in the FT-IR spectrum.

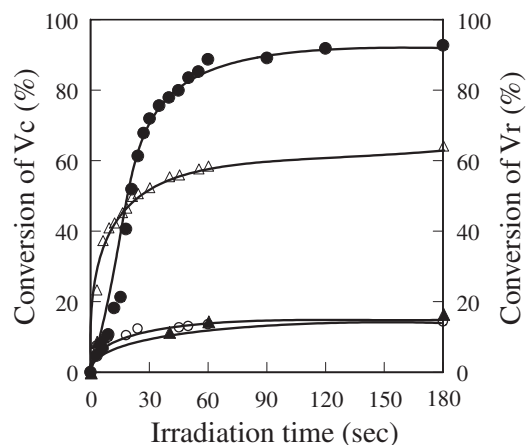


Figure 5. Photoinitiated polymerization of hybrid-type 1-propenyl monomer **3a**; ●: 1-propenyl ether groups with DPSP (1 mol%), ▲: methacryloyl groups with DPSP (1 mol%), ○: 1-propenyl ether groups with MMP (5 mol%), △: methacryloyl groups with MMP (5 mol%). Irradiation condition was 6.8 mW/cm² at 360 nm.

As shown in Figure 5, the conversions of Vc were about 90% at 180 s, when the polymerization of **3a** was carried out with 1 mol% of DPSP under UV irradiation. After 180 s of the irradiation, the conversion of Vr in **3a** reacted 17% to give a cured film. On the other hand, the conversion of Vr at 180 s was 64%, when the photopolymerization of **3a** with 5 mol% of MMP took place under similar conditions. In addition, about 10% of Vc converted for 180 s under UV irradiation due to the photoinitiated radical copolymerization with methacryloyl groups in monomer **3a**. These demonstrate that the photopolymerizations of the phosphorus-containing hybrid 1-propenyl ether monomers proceed effectively using either cationic or radical photoinitiator to give the cured film.

CONCLUSIONS

From all these results, following conclusions are obtained. (1) Phosphorus-containing 1-propenyl ether monomers **1a–c** were successfully synthesized by the addition reaction of PGE with certain phosphonic dichlorides or dichlorophosphate using quaternary onium salts as the catalysts. (2) The polycondensation of **1a** with dicarboxylic acids using DBU gave phosphorus-containing polymers with 1-propenyl ether groups **2a–d**. (3) Multifunctional monomer **3a** containing both 1-propenyl ether group as Vc and methacrylate group as Vr was also prepared by the condensation reaction of **1a** with MA. (4) It was found that the photoinitiated cationic polymerization of the resulting 1-propenyl ether derivatives proceeded smoothly in bulk using DPSP as a cationic photoinitiator.

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