Synthesis of Polyfunctional Vinyl Ether Derivatives by the Regioselective Addition Reaction of Glycidyl Vinyl Ether with Acyl Chlorides and Their Photoinitiated Cationic Polymerization

Hideyuki Itoh, Atsushi Kameyama, and Tadatomi Nishikubo*

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

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ABSTRACT: New di- or trifunctional vinyl ether monomers were successfully synthesized by the regioselective addition reaction of glycidyl vinyl ether **1** with di- or triacyl chlorides using tetrabutylammonium bromide (TBAB) as a catalyst. Polycondensations of the vinyl ether monomers having chloromethyl groups with terephthalic acid were carried out using 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) to afford polyester oligomers carrying pendant vinyl ether moieties. The vinyl groups of the monomers and the oligomers reacted rapidly, when cationic polymerization was conducted in bulk using photoinitiators upon UV irradiation.

Introduction

Polyfunctional acrylate monomers and oligomers have been mostly used for UV curing systems. Since the acrylates undergo photoinitiated radical polymerizations with high reaction rates, the UV curing of polyfunctional acrylates has been widely used for coatings, printing inks, adhesives, and solder masks.[1] Although acrylates are extremely useful and versatile materials for polymer chemistry and industry, the radical polymerizations of acrylates are usually inhibited by atmospheric oxygen.[2] It has been known that some polyfunctional acrylate monomers have high skin irritabilities, which are unfavorable problems for handling in various processes.

Meanwhile, cationic polymerization has attracted much attention over the last several years. Some polyfunctional epoxide and vinyl ether compounds were used for UV curing processes. Although many UV curing systems using epoxides have been reported, the reaction rates of commercially available epoxy compounds are essentially lower than that of the acrylate monomers.[3,4] On the other hand, vinyl ethers have relatively high reactivity in cationic polymerization and are not inhibited by atmospheric oxygen.[5] Therefore, vinyl ether monomers and oligomers are expected to be useful materials as an alternative for new cationic photocuring systems.

Many difunctional vinyl ethers have been synthesized by the reaction of a vinyl ether carrying chloromethyl groups with difunctional phenols and carboxylic acids.[6,7] Crivello et al. reported the synthesis of photopolymerizable difunctional 2-propenyl ether derivatives by the isomerization of difunctional allyl compounds.[8,9] Lapin reported radiation-induced cationic polymerization of vinyl ether monomers[10] and oligomers[11] using photoinitiators such as sulfonium salts. However, most of the reported vinyl ethers having low molecular weights have been used as diluents of acrylates or epoxides as base materials in the UV curing. Therefore, it is considered that polyfunctional vinyl ether compounds with a rigid structure and a large molecular weight as base resins are well suited for the cationic UV curing systems.

The authors recently reported the selective polymerization of glycidyl vinyl ether (**1**), which is a very interesting functional monomer having both epoxy and vinyl groups, to synthesize reactive polymers containing pendant epoxy or vinyl groups.[12,13] It is also found that the addition reaction of epoxy compounds with acyl chlorides proceeded using quaternary onium halides to give corresponding ester derivatives.[14] The characteristics of the reaction are as follows. (1) The addition reaction with the catalysts proceeds smoothly and selectively under neutral conditions. (2) The resulting products containing chloromethyl groups are easily modified by conventional reactions. From this background, we designed a new synthesis of polyfunctional vinyl ether monomers based on the regioselective addition reaction of **1** with polyfunctional acyl chlorides.

In this study, new di- or trifunctional vinyl ether monomers applicable for the cationic curing system as base resins were synthesized by the regioselective addition reaction of **1** with di- or triacyl chlorides catalyzed by the quarternary onium salt. The polycondensation of difunctional vinyl ether monomers containing chloromethyl groups with terephthalic acid was carried out using 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) to afford oligomers containing pendant vinyl ether moieties. Furthermore, the polymerizations of the obtained vinyl ether monomers and oligomers in bulk induced by the cationic photoinitiators were also investigated.

Experimental Section

Materials. Glycidyl vinyl ether (**1**), which was provided by Seimi Chemical Co. Ltd., was purified by distillation on CaH_2 *in vacuo*. Terephthaloyl chloride (**2a**) and isophthaloyl chloride (**2b**) were purified by recrystallization from dry hexane. Adipoyl chloride (**2c**) and sebacoyl chloride (**2d**) were purified by distillation *in vacuo*. 2,2-Bis(4-chlorocarboxyphenyl)hexafluoropropane (**2e**) was prepared in 64% yield from the reaction 2,2-bis(4-carboxyphenyl)hexafluoropropane with thionyl chloride according to the reported method[15] and purified by recrystallization from dry hexane. Reagent grade trimesoyl chloride (**2f**) and terephthalic acid (**4**) were used without further purification. Tetra-*n*-butylammonium bromide (TBAB) was purified by recrystallization from dry ethyl acetate. DBU and dimethyl sulfoxide (DMSO) were purified by distillation *in vacuo*. Toluene was dried over sodium metal and distilled before use. Bis-[4-(diphenylsulfonio)phenyl] sulfide–bis(hexafluorophoshate), DPSP (KI85B from Degussa), *N*-morpholino-2,5-dibutoxybenzenediazonium hexafluorophosphate (MDBZ, from Sanbo Chemical Co.), bis(4-*tert*-butylphenyl)-iodonium hexafluorophosphate (BBI, from Midori Chemical

* To whom all correspondence should be addressed.

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Co.), and (η-cyclopentadiene)(η-1-isopropylbenzene)iron(II) hexafluorophosphate (CBI, from Ciba-Geigy), were used as commercial grade. Triethylene glycol divinyl ether (TEGVE, from ISP) and 1,4-cyclohexanedimethanol divinyl ether (CHVE, from ISP) were obtained as commercial grade.

Measurement. IR spectra were recorded on a JASCO FT-IR 5300 spectrometer. ^{1}H-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 chloroform-*d*. GLC analysis was carried out on a Shimadzu Model GC-9AM gas chromatograph equipped with a 3 mm × 2.6 m column packed with 3% silicon UV-101 on Shimalite W (AW-DMCS). Gel-permeation chromatography (GPC) was performed with a TOSOH HLC-8020 GPC unit using TSK Gel columns (eluent, *N,N*-dimethylformamide (DMF); calibration, polystyrene standards). Melting points were measured with a Yanaco NP-500D micro melting point apparatus. Viscosities were measured with a Nihon Keiki E-type viscosimeter at 25 °C. UV light intensity was measured using an ORC UV-M30.

Synthesis of Bis[1-(chloromethyl)-2-(vinyloxy)ethyl] Terephthalate (3a). A typical procedure for the addition reaction of glycidyl vinyl ether (**1**) with terephthaloyl chloride (**2a**) is as follows: **1** (1.001 g, 10 mmol), **2a** (1.015 g, 5 mmol), and TBAB (0.161 g, 0.5 mmol) were dissolved in toluene (5 mL); then the solution was heated at 90 °C for 24 h with stirring. The reaction mixture was poured into water and extracted with chloroform. After the chloroform layer was dried using $MgSO_4$, the solvent was evaporated under reduced pressure to obtain the product. Yield: 1.81 g (90%). The product was purified by silica gel chromatography using methylene chloride as an eluent. IR (neat, cm^{-1}): 1726 ($\nu_{C=O}$), 1619 ($\nu_{C=C-O-}$), 1200 (ν_{C-O-C}), 760 (ν_{C-Cl}). ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 3.87 (dd, J = 2.4 Hz, J = 5.4 Hz, 3.8 H, $-CH_2Cl_2$), 4.04 (dd, J = 1.0 Hz, J = 5.0 Hz, 3.8 H, $-CH_2-O-$), 4.09 (dd, J = 2.4 Hz, J = 6.8 Hz, 2.0 H, $-CH=CH_2$), 4.27 (dd, J = 2.6 Hz, J = 14.2 Hz, 2.0 H, $-CH=CH_2$), 5.49 (m, 2.0 H, $-C-CH-C-$), 6.48 (dd, J = 6.8 Hz, J = 14.2 Hz, 2.0 H, $-CH=CH_2$), 8.14 (s, 4.0 H, Ar). Anal. Calcd for $C_{18}H_{20}O_6Cl_2$: C, 53.61; H, 5.00. Found: C, 53.30; H, 4.95.

Synthesis of Bis[1-(chloromethyl)-2-(vinyloxy)ethyl] Isophthalate (3b). The addition reaction was carried out with **1** (1.001 g, 10 mmol) and **2b** (1.015 g, 5 mmol) in the presence of TBAB (0.161 g, 0.5 mmol) similar to the synthesis of **3a**. Yield: 1.65 g (82%). IR (neat, cm^{-1}): 1726 ($\nu_{C=O}$), 1619 ($\nu_{C=C-O-}$), 1200 (ν_{C-O-C}), 760 (ν_{C-Cl}). ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 3.88 (dd, J = 2.6 Hz, J = 5.2 Hz, 3.8 H, $-CH_2Cl_2$), 4.08 (m, 3.8 H, $-CH_2-O-$), 4.09 (dd, J = 2.4 Hz, J = 6.8 Hz, 2.0 H, $-CH=CH_2$), 4.19 (dd, J = 2.4 Hz, J = 14.4 Hz, 2.0 H, $-CH=CH_2$), 5.51 (m, 2.0 H, $-C-CH-C-$), 6.49 (dd, J = 6.8 Hz, J = 14.4 Hz, 2.0 H, $-CH=CH_2$), 7.57 (t, J = 7.8 Hz, 1.0 H, Ar), 8.28 (dd, J = 1.6 Hz, J = 7.8 Hz, 2.0 H, Ar), 8.73 (s, 1.0 H, Ar). Anal. Calcd for $C_{18}H_{20}O_6Cl_2$: C, 53.61; H, 5.00. Found: C, 53.32; H, 4.97.

Synthesis of Bis[1-(chloromethyl)-2-(vinyloxy)ethyl] Adipate (3c). The reaction of **1** (1.001 g, 10 mmol) and **2c** (0.900 g, 5 mmol) catalyzed by TBAB (0.161 g, 0.5 mmol) was used for the synthesis of **3a**. Yield: 1.66 g (87%). IR (neat, cm^{-1}): 1742 ($\nu_{C=O}$), 1619 ($\nu_{C=C-O-}$), 1200 (ν_{C-O-C}), 760 (ν_{C-Cl}). ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 1.60–1.80 (m, 4.4 H, $-C-CH_2-CH_2-C-$), 2.20–2.40 (m, 4.2 H, $-OC-CH_2-C-$), 3.72 (t, J = 5.4 Hz, 3.8 H, $-CH_2Cl_2$), 3.88 (d, J = 4.8 Hz, 3.8 H, $-CH_2-O-$), 4.07 (dd, J = 2.4 Hz, J = 6.8 Hz, 2.0 H, $-CH=CH_2$), 4.23 (dd, J = 2.4 Hz, J = 14.2 Hz, 2.0 H, $-CH=CH_2$), 5.24 (m, 2.0 H, $-C-CH-C-$), 6.45 (dd, J = 7.0 Hz, J = 14.2 Hz, 2.0 H, $-CH=CH_2$). Anal. Calcd for $C_{16}H_{24}O_6Cl_2$: C, 50.14; H, 6.31. Found: C, 49.72; H, 6.23.

Synthesis of Bis[1-(chloromethyl)-2-(vinyloxy)ethyl] Sebacate (3d). The reaction took place using **1** (1.001 g, 10 mmol), **2d** (1.196 g, 5 mmol), and TBAB (0.161 g, 0.5 mmol) in the same way like for the synthesis of **3a**. Yield: 1.85 g (84%). IR (neat, cm^{-1}): 1742 ($\nu_{C=O}$), 1619 ($\nu_{C=C-O-}$), 1200 (ν_{C-O-C}), 760 (ν_{C-Cl}). ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 1.31 (s, 8.6 H, $-C-CH_2-CH_2-CH_2-CH_2-C-$), 1.50–1.70 (m, 4.3 H, $-C-CH_2-C-$), 2.20–2.36 (m, 4.4 H, $-OC-CH_2-C-$), 3.72 (t, J = 5.4 Hz, 3.8 H, $-CH_2Cl_2$), 3.88 (d, J = 4.8 Hz, 3.8 H, $-CH_2-O-$), 4.07 (dd, J = 2.4 Hz, J = 6.8 Hz, 2.0 H, $-CH=CH_2$), 4.23 (dd, J = 2.4 Hz, J = 14.2 Hz, 2.0 H, $-CH=CH_2$), 5.23 (m, 2.0 H, $-C-CH-C-$), 6.45 (dd, J = 7.0 Hz, J = 14.2 Hz, 2.0 H, $-CH=CH_2$). Anal. Calcd for $C_{24}H_{32}O_6Cl_2$: C, 54.67; H, 7.34. Found: C, 54.61; H, 7.36.

Synthesis of 2,2-Bis[4-[[[1-(chloromethyl)-2-(vinyloxy)ethyl]oxy]carbonyl]phenyl]-1,1,1,3,3,3-hexafluoropropane (3e). **3e** was obtained by the reaction of **1** (1.001 g, 10 mmol) with **2e** (2.146 g, 5 mmol) using TBAB (0.161 g, 0.5 mmol) as a catalyst. Yield: 2.24 g (71%). IR (neat, cm^{-1}): 1726 ($\nu_{C=O}$), 1619 ($\nu_{C=C-O-}$), 1200 (ν_{C-O-C}), 7.60 (ν_{C-Cl}). ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 3.86 (dd, J = 2.6 Hz, J = 4.8 Hz, 3.8 H, $-CH_2Cl_2$), 4.03 (dd, J = 1.6 Hz, J = 4.8 Hz, 3.8 H, $-CH_2-O-$), 4.09 (dd, J = 2.4 Hz, J = 6.8 Hz, 2.0 H, $-CH=CH_2$), 4.26 (dd, J = 2.4 Hz, J = 14.6 Hz, 2.0 H, $-CH=CH_2$), 5.49 (m, 2.0 H, $-C-CH-C-$), 6.48 (dd, J = 6.8 Hz, J = 14.2 Hz, 2.0 H, $-CH=CH_2$), 7.48 (d, J = 8.4 Hz, 4.1 H, Ar), 8.09 (d, J = 8.4 H, 4.2 H, Ar). Anal. Calcd for $C_{27}H_{24}O_6Cl_2F_6$: C, 51.53; H, 3.84. Found: C, 51.36; H, 3.79.

Synthesis of 1,3,5-Tris[[[1-(chloromethyl)-2-(vinyloxy)ethyl]oxy]carbonyl]benzene (3f). The addition reaction of **1** (1.502 g, 15 mmol) with **2f** (1.327 g, 5 mmol) was carried out using TBAB (0.242 g, 0.75 mmol) to obtain **3f** using the same method as for the synthesis of **3a**. Yield: 2.24 g (53%). Mp: 74–76 °C. IR (KBr, cm^{-1}): 1729 ($\nu_{C=O}$), 1619 ($\nu_{C=C-O-}$), 1200 (ν_{C-O-C}), 760 (ν_{C-Cl}). ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 3.89 (dd, J = 2.4 Hz, J = 5.4 Hz, 5.7 H, $-CH_2Cl_2$), 3.95 (d, J = 4.8 Hz, 5.8 H, $-CH_2-O-$), 4.03 (dd, J = 2.4 Hz, J = 6.8 Hz, 3.1 H, $-CH=CH_2$), 4.11 (dd, J = 2.4 Hz, J = 14.2 Hz, 2.0 H, $-CH=CH_2$), 5.54 (m, 3.0 H, $-C-CH-C-$), 6.49 (dd, J = 6.8 Hz, J = 14.2 Hz, 3.0 H, $-CH=CH_2$), 8.91 (s, 2.9 H, Ar). Anal. Calcd for $C_{24}H_{27}O_9Cl_3$: C, 50.95; H, 4.81. Found: C, 50.63; H, 4.73.

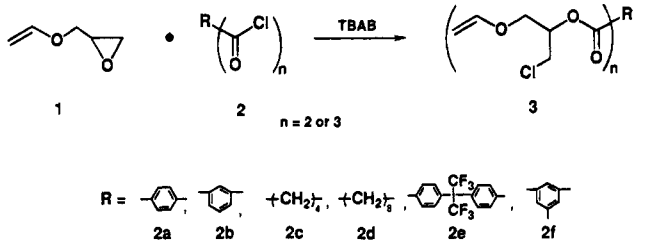
Synthesis of Polyfunctional Vinyl Ether Oligomer 5. A typical procedure for the polycondensation of **3a** with **4** is as follows: **3a** (0.807 g, 2 mmol), **4** (0.166 g, 1 mmol), and DBU (0.304 g, 2 mmol) were dissolved in DMSO (5 mL), with stirring, and the solution was heated at 70 °C for 48 h. The reaction mixture was then poured into water and extracted with chloroform. The combined chloroform layer was washed with aqueous 0.1 N HCl solution and dried using $MgSO_4$. The solvent was removed by evaporation under reduced pressure to obtain the product. Yield: 0.848 g (94%). $\bar{M}_n$ = 4400, $\bar{M}_w/\bar{M}_n$ = 1.47. IR (neat, cm^{-1}): 1730 ($\nu_{C=O}$), 1619 ($\nu_{C=C-O-}$), 1200 (ν_{C-O-C}), 760 (ν_{C-Cl}). ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): 3.86 (dd, J = 2.5 Hz, J = 5.0 Hz, 2 H, $-CH_2Cl_2$), 4.02–4.13 (m, 13 H, $-CH_2-O-$), 4.23–4.31 (m, 4 H, $-CH=CH_2$), 4.61–4.79 (m, 4 H, $-CH_2-O-$), 5.46–5.51 (m, 2 H, $-C-CH-C-$), 5.60–5.80 (m, 2 H, $-C-CH-C-$), 6.42–6.56 (m, 4 H, $-CH=CH_2$), 8.06 (s, 4 H, Ar), 8.13 (s, 8 H, Ar).

Isolation of Trimer 5g from the Reaction Product of 3a with 4. Trimer **5g** was isolated from **5e** (0.80 g) by silica gel chromatography using methylene chloride as an eluent. Isolated yield: 0.12 g. IR (neat, cm^{-1}): 1740 ($\nu_{C=O}$), 1619 ($\nu_{C=C-O-}$), 1200 (ν_{C-O-C}), 760 (ν_{C-Cl}). ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 3.87 (dd, J = 2.4 Hz, J = 5.0 Hz, 4 H, $-CH_2Cl_2$), 4.02–4.11 (m, 8 H, $-CH_2-O-$), 4.23 (d, J = 2.4 Hz, 8 H, $-CH=CH_2$), 4.30–4.70 (m, 4 H, $-CH_2-O-$), 5.46–5.71 (m, 4 H, $-C-CH-C-$), 6.42–6.56 (m, 4 H, $-CH=CH_2$), 8.05–8.12 (m, 12 H, Ar).

Solubility of Photoinitiators in the Synthesized Vinyl Ether Monomers. Each photoinitiator (concentation is 1 mol % per vinyl group of a monomer) was added to the monomers and the mixture was well stirred. Their solubility was evaluated in three stages as follows: (○) soluble at room temperature; (△) partially soluble or swelling; (×) insoluble.

Typical Procedure for Photoinitiated Cationic Polymerization. DPSP (0.015 g, 0.01 mmol) was dissolved in **3a** (0.201 g, 0.5 mmol). The reaction of the viscous liquid mixture film formed on the KBr plate was performed upon UV irradiation with a 250 W high-pressure mercury lamp (Ushio Electric Co., SPOT CURE) at a distance of 10 cm (UV light intensity: 6.7 mW/cm^2 at 360 nm) in air. Then the conversion of the vinyl group of **3a** was monitored by a decrease in the absorption peak at 1619 cm^{-1} due to $\nu_{C=C}$ in the FT-IR spectrum.

Scheme 1



1 2 3

Table 1. Synthesis of Polyfunctional Vinyl Ether Monomers by the Addition Reaction of 1 with Acyl Chlorides Using TBAB[a]

run	product	yield (%)	α:β[b]	viscosity[c] (P s)	characteristic state
1	**3a**	90	7:93	24	liquid
2	**3b**	82	4:96	24	liquid
3	**3c**	87	4:96	12	liquid
4	**3d**	84	4:96	12	liquid
5	**3e**	71	7:93	55	liquid
6	**3f**	53	7:93		powder

[a] The reaction was carried out with **1** and each chloride using 5 mol % TBAB in toluene (5 mL) at 90 °C for 24 h. [b] Selectivities of addition on the epoxy groups determined by ^{1}H-NMR. [c] Measured by an E-type viscosimeter (25 °C).

Table 2. Synthesis of Polyfunctional Vinyl Ether Oligomers[a]

run	feed ratio **3a**:**4**	product	reaction time (h)	yield (%)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	VEEW[c] (g/VE)
7	1:1	**5a**	48	89	5800	1.53	246
8	1:1	**5b**	96	96	7300	1.94	246
9	3:2	**5c**	48	96	4900	1.52	220
10	3:2	**5d**	96	98	6600	1.75	220
11	2:1	**5e**	48	94	4400	1.47	206
12	2:1	**5f**	96	95	6200	2.07	206

[a] The reaction was carriedout with **3a** and **4** using DBU in DMSO (5 mL) at 70 °C. [b] Estimated by GPC on the basis of polystyrene standards (cf. **3a** = 2.1×10^3, PSt base). [c] Vinyl ether equivalent weight. It is the molecular weight per a vinyl group in the oligomer.

Results and Discussion

Synthesis of Di- or Trifunctional Vinyl Ether Monomers. The addition reactions of **1** with acyl chlorides were carried out using 5 mol % TBAB as a catalyst in toluene at 90 °C for 24 h (Scheme 1). The results are summarized in Table 1. The reaction of **1** with **2a** proceeded smoothly to give a product in 90% isolated yield. The structure of the obtained product was confirmed by IR, ^{1}H-NMR spectra, and elemental analysis. The IR spectrum of the product shows characteristic absorption peaks based on $\nu_{C=O}$ of the ester group at 1726 cm^{-1}, $\nu_{C=C}$ of the vinyl ether moiety at 1619 cm^{-1}, and ν_{C-Cl} at 760 cm^{-1}, respectively. Figure 1 shows the ^{1}H-NMR spectrum of the product with corresponding assignments. In the ^{1}H-NMR spectrum, the signals of the methine protons ***c*** due to the vinyl group and methylene protons ***f*** due to the chloromethyl group were observed at 6.48 and 3.87 ppm, respectively. And the intensity ratios of ***f*** to ***c*** were 1.86 compared to the expected value (2.0) assuming that only β-addition of the epoxy groups occurred. Therefore, it was found that the selectivity of the β-addition of the epoxy groups of **3a** was 93%.

Figure 2 shows the time course of the addition reaction of **1** with **2a** monitored by gas chromatography. **1** was consumed completely at 90 °C after 1 h in the reaction. The GC yield of the 1-1 adduct reacted 70%

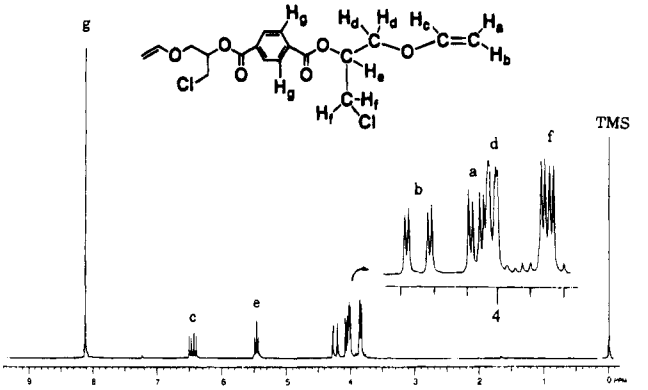


Figure 1. ^{1}H-NMR spectrum of **3a** with the assignment for various signals.

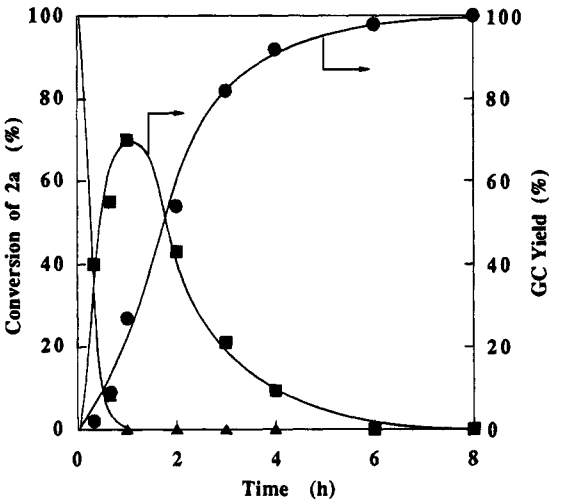
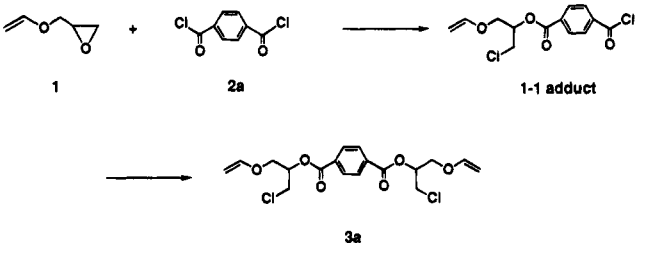


Figure 2. Time course of the reaction of **1** with **2a** using 5 mol % TBAB in toluene at 90 °C: (●) **3a**; (■) 1-1adduct; (▲) **2a**.

Scheme 2



at 1 h, and then the reaction of the 1-1 adduct with **1** gradually proceeded to give **3a** (Scheme 2). It is considered that the slow reaction of **1** with the 1-1 adduct is related to the lower reactivity of the acyl group of the 1-1 adduct and a reduced concentration of **1**. Thus, it was found that the addition reaction requires 8 h to proceed quantitatively.

The effect of reaction temperature on the addition reaction of **1** with **2a** in toluene for 24 h is shown in Figure 3. The reaction above 80 °C gave **3a** in 90% yield, which means the isolated yield, although **3a** was obtained in about 50% yield from the reaction at 60 °C. This result means that temperatures over 80 °C are suitable to prepare **3a** in good yield.

Various di- or trifunctional vinyl ether monomers were also prepared successfully by the reaction of **1** with the corresponding di- or trifunctional acyl chlorides under the same reaction conditions. The reaction of **1** with **2b** gave the targeted **3b** in 82% yield. Difunctional

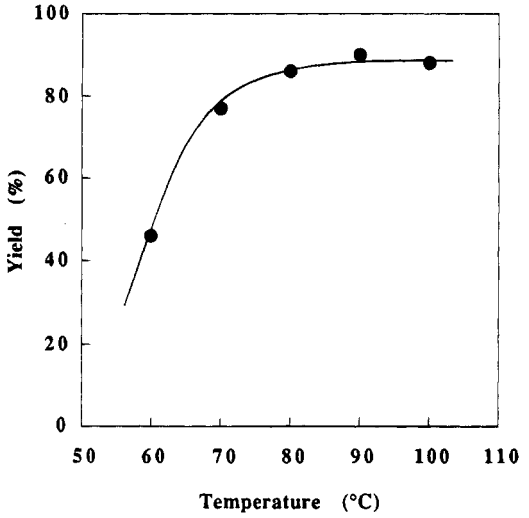


Figure 3. Effect of the reaction temperature on the reaction of **1** with **2a** using 5 mol % TBAB in toluene for 24 h.

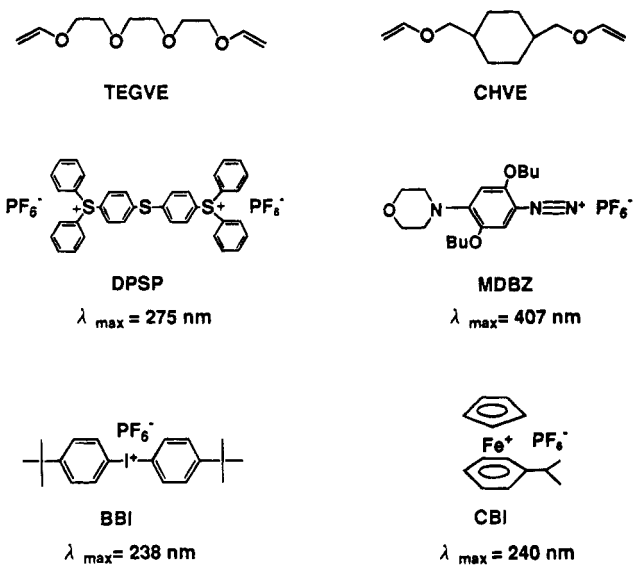


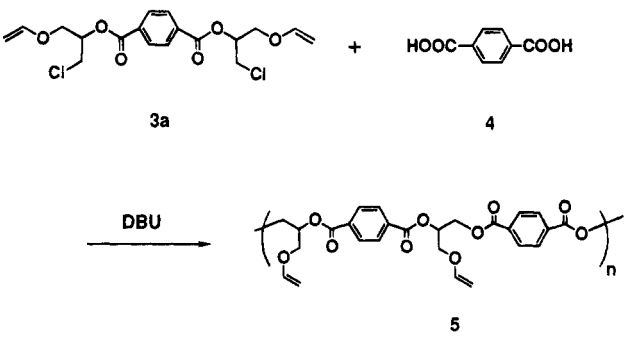
Figure 4. Structures of commercial viny ether monomers and photoinitiators.

vinyl ethers **3c**, **3d**, and **3e** were prepared in 87, 84, and 71% yields by the addition reactions with **2c**, **2d**, **2e**, respectively. The reaction of **1** with trimesoyl chloride (**2f**) also proceeded to afford **3f** in 53% yield. All of the ^{1}H-NMR spectra of these products suggested that the addition reactions proceeded regioselectively to give the targeted vinyl ether monomers with the structures shown in Scheme 1.

The viscosity of the obtained vinyl ethers is an important physical property for photocuring materials to produce a thick coating and for handling. The viscosity of the difunctional vinyl ethers was measured using an E-type viscosimeter. The viscosities of both **3a** and **3b** were 24 P s. The viscosities of **3c** and **3d** with aliphatic chains in their structures were 12 P s. The viscosity of **3e** with two aromatic rings was 55 P s. On the other hand, the trifunctional vinyl ether **3f** was a solid powder at room temperature (mp = 74–76 °C). These results suggest that the viscosities of the vinyl ether monomers are affected by the main skeleton derived from the used acyl chlorides.

Synthesis of Polyfunctional Vinyl Ether Oligomers. The polycondensation of dicarboxylic acids with alkylene dihalides using DBU as base is a useful

Scheme 3



reaction[16] for the synthesis of polyesters. Since the difunctional vinyl ethers have reactive chloromethyl groups, oligomers carrying pendant vinyl ether moieties are prepared readily by polycondensation of the difunctional vinyl ethers with dicarboxylic acids using DBU. The polycondensation of **3a** with terephthalic acids **4** was carried out using DBU in DMSO at 70 °C for 48 h to give a semisolid product **5a** in 89% yield (Scheme 3). The $\bar{M}_n$ of the product was estimated by GPC to be 5800 g/mol. The IR spectrum of the product showed characteristic peaks based on $\nu_{C=O}$ of the ester group in the main chain at 1730 cm^{-1}, $\nu_{C=C}$ at 1619 cm^{-1} of the vinyl group, and ν_{C-Cl} at 760 cm^{-1} of the chloromethyl group, respectively. It was also suggested that carboxyl groups remain due to the small broad peak of the OH group at 3200–3400 cm^{-1}. In the ^{1}H-NMR spectrum of the product, signals due to vinyl protons and methylene protons of the chloromethyl groups were observed at 6.4–6.6 and 3.86 ppm, respectively. It was presumed that the observed carboxyl and chloromethyl groups would exist at the terminals of the oligomers. From these data, it was found that the polycondensation of **3a** with **4** proceeded to give the oligomer **5a**. The reaction of **3a** with **4** for 96 h under the similar condition gave **5b** with an $\bar{M}_n$ of 7300 g/mol.

To obtain an oligomer with lower molecular weights and fewer terminal carboxyl groups, the reaction was also carried out with an excess **3a** to **4**. In the case of the feed ratio (**3a**/**4**) being 3/2, oligomers **5c** with an $\bar{M}_n$ of 4900 g/mol and **5d** with $\bar{M}_n$ of 6600 g/mol were obtained from the reaction for 48 and 96 h, respectively. The reaction using twice the amount of **3a** to **4** by mole for 48 h gave the oligomer **5e** with an $\bar{M}_n$ of 4400 g/mol, in which the terminal OH of the carboxyl groups was not observed in the IR spectrum. It was found that the oligomers with various molecular weights and chloromethyl terminals were easily prepared by controlling the feed ratio and the reaction time.

Solubility of Photoinitiator in the Difunctional Vinyl Ethers. The solubility of photoinitiators into curing materials is a very important factor for photocuring. The solubility of the photoinitiators in synthesized, and two commercially available difunctional vinyl ethers were examined qualitatively. As summarized in Table 3, the sulfonium salt DPSP was easily miscible with aromatic divinyl ether compounds such as **3a**, **3b**, and **3e**. However, DPSP was not miscible with alphatic divinyl ether compounds such as **3c**, **3d**, and CHVE. Although diazonium salt MDBZ was soluble in **3a**, **3b**, and TEGVE, the solubility of MDBZ was not enough in **3c**, **3d** and **3f**. The solubility of BBI with the diphenyliodonium structure is very poor in most vinyl ethers except TEGVE. On the other hand, iron–arene complex CBI has excellent solubility in all of the vinyl ether monomers.

Table 3. Solubility of Photoinitiators in the Vinyl Ether Monomers[a]

vinyl ether	photoinitiator			
	DPSP	MDBZ	BBI	CBI
3a	○	○	△	○
3b	○	○	△	○
3c	×	△	△	○
3d	×	△	△	○
3e	○	△	△	○
3f				
TEGVE	○	○	○	○
CHVE	×	×	△	○

[a] Solubility at room temperature (1 mol % to the vinyl groups): (○) soluble, (△) partially soluble or swelling, (×) insoluble.

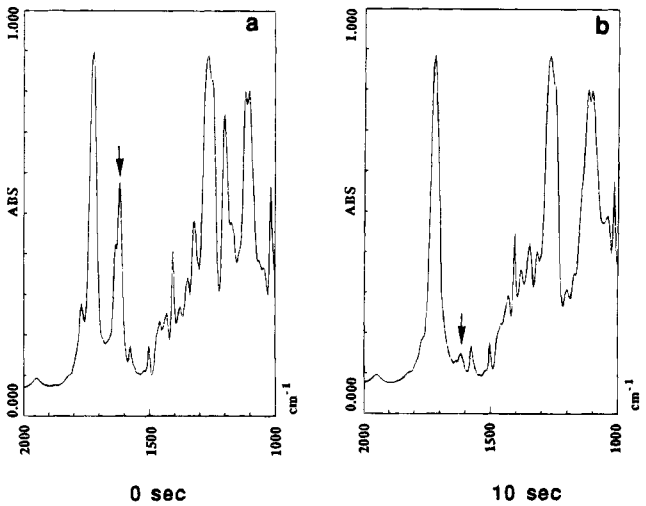


Figure 5. IR spectral changes of **3a** in the presence of 1 mol % DPSP upon UV irradiation: (a) 0 s of irradiation; (b) 10 s of irradiation.

Photoinitiated Cationic Polymerization of Difunctional Vinyl Ether Monomers. The photoinitiated polymerization of **3a** was carried out in bulk using 1 mol % of DPSP upon UV irradiation using a 250 W high-pressure mercury lamp. The conversion of the vinyl groups was estimated from the decrease of the absorbance at 1619 cm^{-1} in the FT-IR spectra. Figure 5 demonstrates a rapid decrease of the vinyl groups of **3a** in the FT-IR.

The photoinitiated reaction of **3a** was performed with 1 mol % of photoinitiators under the same conditions. The absorption band of the photoinitiators was covered with the wavelength band of the irradiation. The polymerization of **3a** with DPSP proceeded very quickly, and the conversion of the vinyl groups was nearly 100% for 30 s (Figure 6). The reaction using CBI and MDBZ which produced Lewis acids[17] upon UV irradiation was relatively slower than that with DPSP. The reaction with BBI scarcely proceeded. It seems that BBI showed a lower activity for the reaction because of its poor miscibility with **3a**. Therefore, it was demonstrated that the sulfonium salt DPSP initiated efficiently the polymerization of **3a** in bulk upon UV irradiation.

The effect of DPSP concentration on the reaction of **3a** was exhibited in Figure 7. The reaction of **3a** proceeded smoothly with even 0.1 mol % DPSP and the conversion was 83% at 60 s. The reaction rate increased with an increase of the DPSP concentration; the reaction with 0.5 mol % DPSP gave 80% conversion for 20 s of irradiation. The conversion of the vinyl groups reached 95% for 20 s when the reaction was carried out with 1 mol % DPSP.

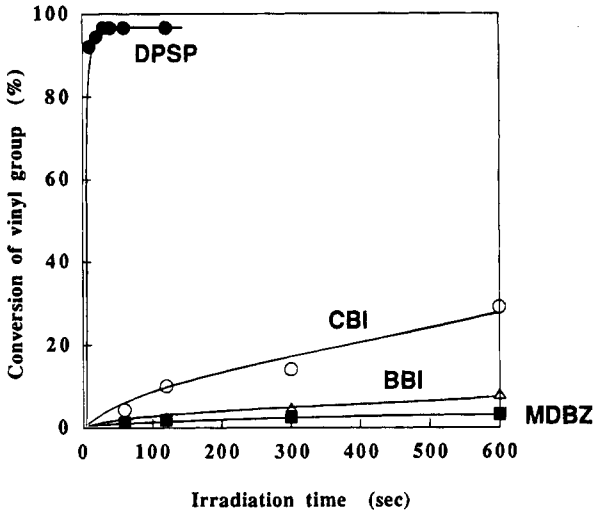


Figure 6. Photoinitiated cationic polymerization of **3a** using various photoinitiators (1 mol % to the vinyl groups): (●) DPSP; (■) MDBZ; (△) BBI; (○) CBI.

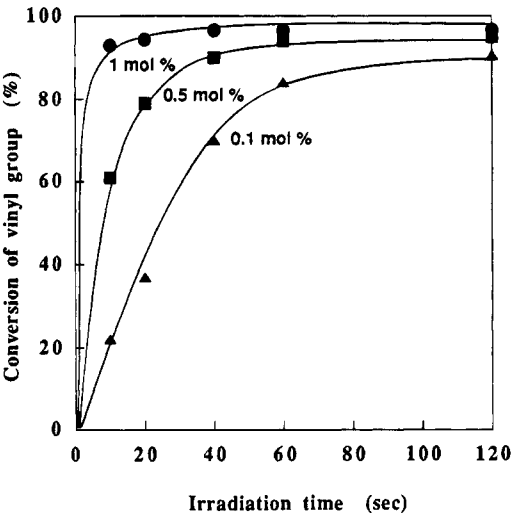


Figure 7. Photoinitiated cationic polymerization of **3a** using DPSP: (▲) 0.1 mol %; (■) 0.5 mol %; (●) 1 mol %.

The photoinitiated reaction of the synthesized monomers **3a**, **3b**, and **3e** using 1 mol % DPSP were investigated under the same conditions. As shown in Figure 8, it was found that **3b** has a high reactivity as well as **3a**. Although the reaction of **3e** proceeded rapidly similar to the reaction of **3a** and **3b** in the initial stage, the conversion scarcely increased after 10 s. Taking account of the viscosity of the difunctional monomers, the reactions would be influenced by diffusions of propagating spices during the polymerizations. The lower density of the vinyl groups of **3e** compared with **3a** and **3b** would also be another factor of the lowering of the conversion of the vinyl groups. These results suggest that monomer **3a** and **3b** have a high reactivity in the photoinitiated cationic polymerization to achieve quantitative conversions of the vinyl groups upon UV irradiation.

Photoinitiated Cationic Polymerization of Polyfunctional Vinyl Ether Oligomers. The photoinitiated reaction of the liquid oligomer **5e** ($\bar{M}_n$ = 4400 g/mol) having pendent vinyl ether moieties using 1 mol % DPSP took place under the conditions similar to those of the reaction of **3a**. Figure 9 shows the time course of the photopolymerization of **5e**; for comparison, those of **3a** and trimer **5g** which was isolated from **5e** (see

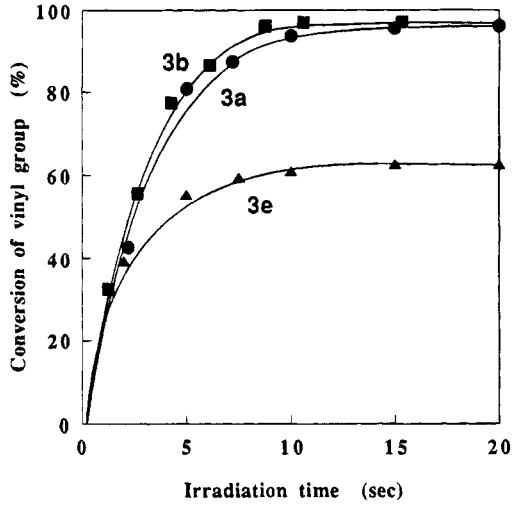


Figure 8. Photoinitiated cationic polymerization of various vinyl ether monomers using 1 mol % DPSP: (●) **3a**; (■) **3b**; (▲) **3e**.

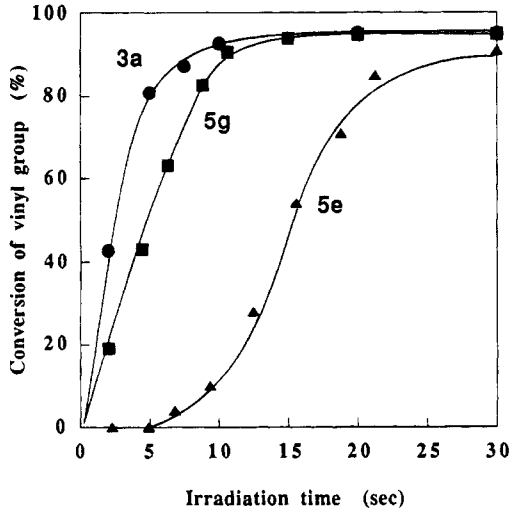
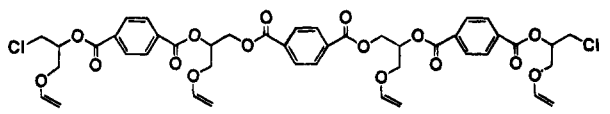


Figure 9. Photoinitiated cationic polymerization of vinyl ether monomer and oligomers using 1 mol % DPSP: (●) **3a**; (■) **5g**; (▲) **5e**.



5g

Figure 10. Polyfunctional vinyl ether oligomer (trimer).

Figure 10) by column chromatography were also exhibited. **5g** showed good reactivity in the photopolymerization and about 90% of the pendent vinyl groups were reacted for 30 s of UV irradiation. It was also found that **5e** had an induction period of about 5 s in the reaction, although similar induction periods were not observed in the reaction of **3a** and **5g** at all. An inhibition of photoinitiated cationic polymerization owing to a small amount of carboxyl groups[18] in a reaction system has been suggested. As a control experiment, the photopolymerization of **3a** was carried out in the presence of 1 mol % heptanoic acid under the same conditions and an induction period was observed in the initial stage (Figure 11). This result suggests indirectly that carboxyl groups remaining slightly at the terminals of **5e** inhibit the photoinitiated cationic polymerization. The reaction of the solid oligomer **5b** with $\bar{M}_n$ = 7300

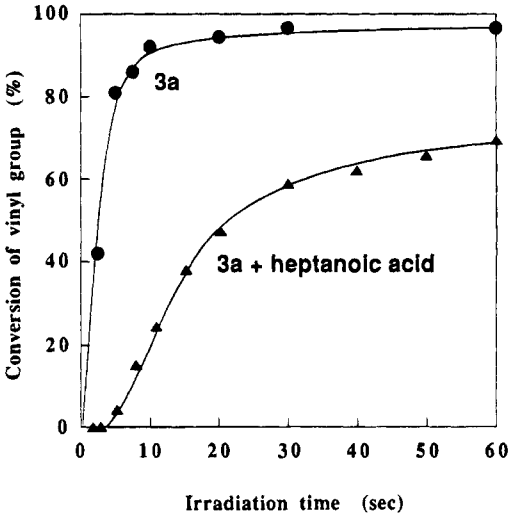


Figure 11. Retarding effect of carboxylic acid on the photoinitiated cationic polymerization of **3a** using 1 mol % DPSP: (●) **3a**; (▲) **3a** + 1 mol % heptanoic acid.

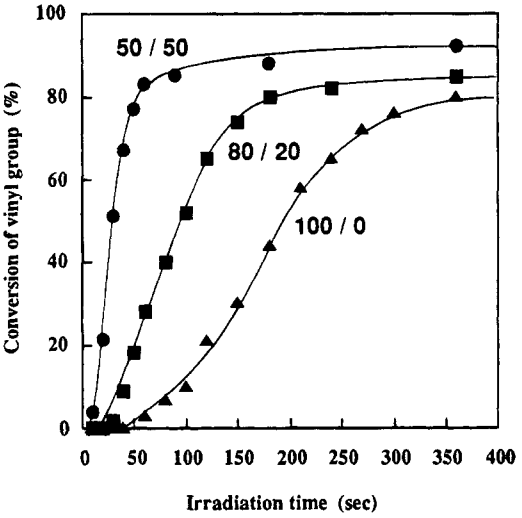


Figure 12. Addition effect of **3a** on the photoinitiated cationic polymerization of polyfunctional vinyl ether **5b** using 1 mol % DPSP: (●) **5b/3a** = 50/50; (■) 80/20; (▲) 100/0 (wt/wt).

g/mol prepared by equimolar reaction of **3a** with **4** was also examined. The dichloromethane solution containing **5b** and 1 mol % DPSP was cast on a KBr plate to be irradiated under the same conditions. As shown in Figure 12, the reaction of **5b** proceeded relatively slowly showing about 30 s of induction periods. The low reactivity of **5b** might be caused by its solid state. However, the photopolymerization was accelerated effectively by the addition of monomer **3a**. The reaction rate of vinyl groups in the mixture of **5b** and **3a** increased and the induction period decreased with the increase of **3a** content in the mixture. The conversions of the all vinyl groups in the reaction of the mixture of **5b** involving 20 wt % of **3a** at 50 s of UV irradiation was 10 times that of **5b**. In the case of the reaction of the mixture prepared from equivalent weights of **5b** and **3a**, the induction period was 10 s and the conversion at 50 s was 83%, which corresponds to 40 times that of **5b**. These results demonstrate that the combination of appropriate amounts of polyfunctional vinyl ether oligomers and monomers can be used to achieve high reactivity for the photoinitiated cationic polymerization.

From all these results the following conclusions can be obtained. (1) Novel di- or trifunctional vinyl ether

monomers carrying a chloromethyl group were successfully synthesized by the regioselective addition reaction of **1** with various acyl chlorides. (2) Oligomers carrying pendent vinyl ether moieties with appropriate molecular weights were readily prepared by the polycondensation of the synthesized vinyl ether monomers with dicarboxylic acids using DBU. (3) Difunctional vinyl ether monomers **3a** and **3b** having phthalate structures indicated excellent reactivity in the photopolymerization using sulfonium salt photoinitiator DPSP. (4) Oligomers with low molecular weights polymerized smoothly upon UV irradiation. Therefore, the new vinyl ether compounds are useful materials for photoinitiated cationic polymerization.

References and Notes

(1) Nishikubo, T., Ed. *Synthesis and Application of Photosensitive Polymers*; CMC: Tokyo, 1979; p 37.
(2) Decker, C.; Moussa, K. *Makromol. Chem.* **1988**, *189*, 2381.
(3) Decker, C.; Moussa, K. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3429.
(4) Ito, H.; Kidokoro, N.; Ishikawa, N. *J. Photopolym. Sci. Technol.* **1992**, *5*, 235.
(5) Crivello, J. V.; Lee, J. L.; Colon, D. A. *Radiation Curing VI: Conference Proceedings*; Association for Finishing Processes: Chicago, 1982; pp 4–28.
(6) Crivello, J. V.; Conlon, D. A. *J. Polym. Sci., Part A: Polym. Chem.* **1983**, *21*, 1785.
(7) Gallucci, R. R.; Going, R. C. *J. Org. Chem.* **1983**, *48*, 342.
(8) Crivello, J. V.; Jo, K. D. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1473.
(9) Crivello, J. V.; Jo, K. D. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1483.
(10) Lapin, S. C. *Radiation Curing: Conference; General Review*; New York, 1992; pp 241–271.
(11) Brautigam, R. J.; Lapin, S. C.; Synder, J. R. *RadTech '90 North America, Conference Proceeding*; 1990; Vol. 1, pp 99–110.
(12) Sasano, M.; Nishikubo, T. *Kobunshi Ronbunshu* **1990**, *47*, 597.
(13) Sasano, M.; Nishikubo, T. *Kobunshi Ronbunshu* **1990**, *48*, 477.
(14) Nishikubo, T.; Kameyama, A. *Prog. Polym. Sci.* **1993**, *18*, 969.
(15) Helferich, B.; Schaefer, W. *Org. Synth.* **1941**, *1*, 147.
(16) Nishikubo, T.; Ozaki, K.; Kameyama, A. *Polym. J.* **1994**, *26*, 593.
(17) Meier, K.; Zweifel, H. *J. Radiat. Curing* **1986**, *26* (4), 13.
(18) Shimokawa, T.; Nishikubo, T. *Kobunshi Ronbunshu* **1987**, *44*, 641.

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