Synthesis and Photopolymerization of Multifunctional Propenyl Ether Monomers

J. V. Crivello[a]; Whan-Gi Kim[a]

[a] Department of Chemistry, Center for Polymer Synthesis Rensselaer Polytechnic Institute, Troy, New York

PLEASE SCROLL DOWN FOR ARTICLE

SYNTHESIS AND PHOTOPOLYMERIZATION OF MULTIFUNCTIONAL PROPENYL ETHER MONOMERS

J. V. CRIVELLO and WHAN-GI KIM

Department of Chemistry
Center for Polymer Synthesis
Rensselaer Polytechnic Institute
Troy, New York 12180

Key Words: Allyl glycidyl ether; Multifunctional propenyl ethers; Cationic photopolymerization; Diaryliodonium salts

ABSTRACT

A novel and facile synthesis of aromatics containing di- and tetrafunctional propenyl ether monomers is reported. These monomers were prepared by the base-catalyzed condensation of allyl glycidyl ether with a variety of bisphenols followed by allylation of the secondary hydroxyl groups and finally isomerization of the allyl groups by a ruthenium catalyst. The cationic photopolymerization of these novel monomers to give crosslinked network polymers was carried out using a diaryliodonium salt photoinitiator. The reactivity of the multifunctional propenyl ether monomers was studied using real-time infrared spectroscopy and by differential scanning photocalorimetry.

INTRODUCTION

A major focus of recent research activity in this laboratory has been the synthesis of novel, easily-prepared multifunctional monomers which undergo rapid photoinduced cationic polymerization. There is much current interest in such monomers which can be used in a number of applications such as adhesives, coatings, and

photolithography [1, 2]. In a recent series of papers we described the synthesis and photoinduced cationic polymerization of several series of mono-, di-, tri-, and multifunctional alkyl propenyl ethers [3]. These monomers are especially attractive for the applications cited above because they display very high reactivity when irradiated in the presence of onium salt photoinitiators and yet are not susceptible to spontaneous polymerization on standing. Moreover, these monomers are readily prepared in high yields using simple, readily available starting materials.

Although multifunctional alkyl propenyl ether monomers are attractive for many applications, the resulting polymers have rather poor mechanical properties and lack sufficient toughness to meet the requirements of demanding applications such as abrasion-resistant coatings. The introduction of aromatic groups as stiffening elements into monomer units often considerably improves the mechanical characteristics and has a toughening effect on the resulting polymers. Accordingly, one strategy pursued in this laboratory has been to prepare vinyl and propenyl ether monomers containing aromatic groups [4–6]. The present article describes the design and preparation of di- and tetrafunctional monomers containing aromatic groups using novel synthetic methodology. The results of an investigation of the reactivity of these monomers in photoinduced cationic polymerization are also presented.

EXPERIMENTAL

General Methods

^{1}H-NMR spectra were recorded in CDCl$_3$ solution on a Varian XL-200 MHz instrument, and the chemical shifts given in parts per million (ppm) downfield from tetramethylsilane as an internal standard. Allyl glycidyl ether (1-allyloxy-2,3-epoxy-propane), phenol, 2,6-dimethylphenol, hydroquinone, 4,4′- isopropylidenediphenol, 4,4′-biphenol, 4,4′-sulfonyldiphenol, and [(C$_6$H$_5$)$_3$P]$_3$RuCl$_2$ were purchased from Aldrich Chemical Co. and used without further purification. The cationic photoinitiator, (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate, was prepared as described previously [7].

Polymer Characterization Methods

Real-time infrared spectroscopy (RTIR) was performed on a Buck Scientific Model 500 Infrared Spectrometer equipped with a UVEXS Co. SCU 110 UV lamp fitted with a fiber optic cable.

Differential scanning photocalorimetry (DSP) was performed using a Perkin-Elmer Series 7 Thermal Analysis System equipped with a DPA-7 ultraviolet photo-accessory (DPS) module fitted with a 100 W Hg arc lamp. Photopolymerizations were conducted using 0.45–0.50 mg samples of the monomer **VId** containing 1.0 mol% photoinitiator.

Monomer Synthesis

1-Propenyloxy-2,6-dimethylbenzene

Into a 100-mL round-bottom flask fitted with a magnetic stirrer, reflux condenser, and nitrogen inlet were placed 2,6-dimethylphenol (5 g, 0.041 mol), allyl bromide (5 g, 0.041 mol), tetra-*n*-butylammonium bromide (0.9 g, 2.87 mmol),

NaOH (2.5 g, 0.0625 mil), and toluene (15 mL). The reaction mixture was heated to 90°C and held at that temperature for 10 hours. After cooling, the mixture was filtered to remove the inorganic salts. The filtrate was poured into 300 mL distilled water, and the layers were separated by means of a separatory funnel. The aqueous layer was extracted with toluene, and all the toluene solutions were combined. The toluene was removed on a rotary evaporator, giving allyloxy-2,6-dimethylbenzene as an oil in 61% yield.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 2.31 (s, 6H, C$\underline{H}_3$); 4.32 (2d, 2H, 2$\underline{H}_2$); 5.26–5.51 (q, 2H, C$\underline{H}_2$); 6.05–6.24 (m, 1H, C$\underline{H}$), 6.83–7.08 (m, 3H, Ph).

A mixture of allyloxy-2,6-dimethylbenzene (5 g, 0.03 mol) and [(C$_6$H$_5$)$_3$P]$_3$-RuCl$_2$ (0.28 g, 0.1 mol %) was stirred in a 25-mL round-bottom flask fitted with a reflux condenser and thermometer. The reaction mixture was heated in an oil bath at 130°C for 5 hours. Analysis by ^{1}H NMR showed that the allyl group was 65% isomerized to the propenyl group; after 17 hours the reaction had proceeded to 85% completion. An additional 0.28 g [(C$_6$H$_5$)$_3$P]$_3$RuCl$_2$ was added, and the reaction mixture was held at 130°C for 40 hours to bring the reaction to 95% completion. Both Z and E isomers of propenyl-2,6-dimethylbenzene were produced with an E:Z composition ratio of 60:40. The pure product, consisting of a mixture of both isomers, was obtained by vacuum distillation (bp 75°C/1.0 mmHg) in 82% overall yield.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 1.54 (d, CH—C$\underline{H}_3$, E isomer); 1.80 (d, CH—C$\underline{H}_3$, Z isomer); 2.23 (d, 6H, Ph—C$\underline{H}_3$); 4.53–4.78 (m, 1H, CH—C$\underline{H}_3$); 5.99 (2d, O—C$\underline{H}$, Z isomer); 6.37 (2d, 1H, O—C$\underline{H}$, E isomer); 6.83–7.08 (m, 3H, Ph).

1-Allyloxy-3-phenoxy-2-propanol (I)

A mixture of allyl glycidyl ether (11.41 g, 0.1 mol), phenol (9.41 g, 0.1 mol), and potassium hydroxide (0.17 g, 3 mmol) was placed in a 100-mL round-bottomed flask equipped with a condenser, nitrogen inlet, and magnetic stirrer. The reaction mixture was heated in an oil bath under a slow stream of nitrogen. When the temperature reached approximately 110°C, an exothermic reaction set in and the temperature spontaneously rose to 130°C. After the exotherm had subsided, heat was applied to maintain the reaction mixture at 130°C for 4 hours. Then the reaction mixture was cooled and poured into a mixture of 100 mL water and 50 mL chloroform. The organic layer was separated and washed three times with 100 mL portions of water. The solvent was removed using a rotary evaporator, and the remaining oil was vacuum distilled. The fraction boiling at 80°C (1.0 mmHg) was found to consist of pure I.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 3.01 (s, 1H, OH); 3.53–3.70 (m, 2H, C$\underline{H}_2$—O—); 4.03 (m, 4H, PhO—C$\underline{H}_2$, O—C$\underline{H}_2$—CH=CH$_2$); 4.13–4.23 (q, 1H, CH$_2$—C$\underline{H}$—CH$_2$); 5.28–5.34 (2d, 2H, CH=C$\underline{H}_2$); 5.80–6.01 (m, 1H, C$\underline{H}$=CH$_2$); 6.90 (t, 3H, Ph); 7.28 (t, 2H, Ph).

1,2-Diallyloxy-3-phenoxy-propane (II)

Into a 250-mL flask equipped with a condenser, magnetic stirrer, nitrogen inlet, and thermometer were placed 1-allyloxy-3-phenoxy-2-propanol (I) (10 g, 0.04 mol), allyl bromide (4.84 g, 0.04 mol), tetra-n-butylammonium bromide (0.64 g, 2 mmol), NaOH (2.08 g, 0.052 mol), and toluene (30 mL). The reaction mixture was

heated at 70°C for 10 hours. After cooling, the reaction mixture was poured into 100 mL distilled water, and the organic and aqueous layers were separated by means of a separatory funnel. The aqueous layer was extracted with toluene, and the toluene was combined with the organic layer. The combined organic layers were then extracted with three 100-mL portions of distilled water to remove the remaining tetra-*n*-butylammonium salt. After drying the organic phase over anhydrous magnesium sulfate, the product, **II**, was isolated in 85% yield by fractional vacuum distillation (bp 95°C/0.7 mmHg).

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 3.61–3.67 (m, 2H, C$\underline{H}_2$—O); 3.85–3.94 (q, 1H, C$\underline{H}_2$—CH—CH$_2$); 4.01–4.10 (m, 2H, PhO—C$\underline{H}_2$); 4.19–4.12 (2d, 2H, CH$_2$—O—C$\underline{H}_2$—CH=CH$_2$); 4.51–4.57 (2d, 2H, CH—O—C$\underline{H}_2$—CH=CH$_2$); 5.16–5.49 (m, 4H, —CH=C$\underline{H}_2$); 5.82–6.17 (m, 2H, —C$\underline{H}$=CH$_2$); 6.91 (t, 3H, Ph): 7.29 (t, 2H, Ph).

1,2-Dipropenyloxy-3-phenoxy-propane (III)

A mixture of 1,2-diallyloxy-3-phenoxy-propane, **II** (10 g, 0.04 mol), and tris-(triphenylphosphine)ruthenium(II) dichloride (1.0 mol%) was placed in a 50-mL round-bottom flask equipped with a thermometer, magnetic stirrer, and reflux condenser. The reaction mixture was immersed in an oil bath and heated at 130°C for 7 hours. The course of the reaction was followed using ^{1}H NMR by monitoring the bands centered at 5.25 and 6.00 ppm due, respectively, to the CH$_2$ and the olefinic CH protons of the allyl groups. When the aforementioned bands had disappeared, the reaction mixture was allowed to cool to room temperature and then subjected to vacuum distillation. The resulting product, **III**, was isolated (bp 90°C/1.0 mmHg) in 80% yield.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 1.56 (2t, 6H, —C$\underline{H}_3$); 3.85 (m, 1H CH$_2$—C$\underline{H}$—CH$_2$); 3.93 (m, 2H, C$\underline{H}_2$—O); 4.03–4.15 (m, 2H, PhO—C$\underline{H}_2$); 4.35–4.53 (m, C$\underline{H}$—CH$_3$, *Z* isomer); 4.73–5.19 (m, C$\underline{H}$—CH$_3$, *E* isomer); 5.97–6.02 (m, C$\underline{H}$—O, *Z* isomer); 6.19–6.29 (m, C$\underline{H}$—O, *E* isomer); 6.90 (m, 3H, Ph); 7.29 (t, 2H, Ph).

Analysis: Calculated for C$_{15}$H$_{20}$O$_3$: C, 72.54%; H, 8.12%. Found: C, 72.12%; H, 8.07%.

Preparation of Tetrafunctional Propenyl Ether Monomers

The synthetic procedure given below for **VIa** is typical of that used for all of the tetrafunctional propenyl ether monomers (**VIa–d**) prepared during this investigation.

Preparation of VIa

A mixture of hydroquinone (5.5 g, 0.05 mol), allyl glycidyl ether (11.4 g, 0.1 mol), and potassium hydroxide (0.2 g, 3.6 mmol) was stirred under nitrogen at 130°C for 5 hours. The reaction was monitored by following the disappearance of the epoxy protons and the appearance of secondary hydroxyl protons of **IVa** by ^{1}H-NMR spectroscopy. The reaction mixture was cooled to room temperature and a quantitative yield of the bisadduct, *IVa*, was obtained.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 2.84 (s, 2H, OH); 3.52-3.65 (m, 4H, C$\underline{H}_2$—O—); 4.00 (m, 8H, PhO—C$\underline{H}_2$, O—C$\underline{H}_2$—CH=CH$_2$); 4.12 (m, 2H, CH$_2$—C$\underline{H}$—CH$_2$); 5.14-5.32 (2d, 4H, CH=C$\underline{H}_2$); 5.80-6.00 (m, 2H, C$\underline{H}$=CH$_2$); 6.81 (s, 4H, Ph).

Without isolation or further purification, a mixture of allyl bromide (15.72 g, 0.13 mol), tetra-n-butylammonium bromide (1.0 g, 3.1 mmol), NaOH (8 g, 0.2 mol), and toluene (30 mL) was added into the reaction mixture. The reaction mixture was heated to 90°C and held at that temperature for 12 hours. After cooling, the mixture was poured into distilled water and the layers separated using a separatory funnel. The aqueous layer was extracted with toluene and the toluene combined with the previously separated organic layer. The toluene was removed on a rotary evaporator yielding a liquid product (**Va**) in 90% yield.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 3.58 (m, 4H, C$\underline{H}_2$—O); 3.83 (m, 2H, CH$_2$—C$\underline{H}$—CH$_2$); 3.96-4.07 (m, 8H, PhO—C$\underline{H}_2$ and CH$_2$—O—C$\underline{H}_2$—CH=CH$_2$); 4.26 (m, 4H, CH—O—C$\underline{H}_2$—CH=CH$_2$); 5.15-5.48 (m, 8H, —CH=C$\underline{H}_2$); 5.80-6.13 (m, 4H, —C$\underline{H}$=CH$_2$); 6.91 (s, 2H, Ph).

A mixture of **Va** (10 g, 0.04 mol) and tris(triphenylphosphine)ruthenium(II) dichloride (1.0 mol%) was heated at 130°C for 8 hours. To remove the catalyst, the product, **VIa**, a free-flowing oil, was purified by chromatography using a 9:1 mixture of n-hexane and ethyl acetate as the eluant solvent. An overall yield of 86% of **VIa** was obtained for the three steps from the starting materials.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 1.51-1.62 (2t, 12H, C$\underline{H}_3$); 3.81 (m, 4H, C$\underline{H}_2$—O); 3.92 (m, 2H, CH$_2$—C$\underline{H}$—CH$_2$); 3.97-4.18 (m, 4H, PhO—C$\underline{H}_2$—); 4.34-4.52 (m, C$\underline{H}$—CH$_3$, Z isomer); 4.73-5.15 (m, C$\underline{H}$—CH$_3$, E isomer); 5.94-6.01 (m, C$\underline{H}$—O, Z isomer); 6.05-6.27 (m, C$\underline{H}$—O, E isomer); 6.81 (s, 5H, Ph).

Analysis: Calculated for C$_{24}$H$_{34}$O$_6$: C, 68.86%; H, 8.19%. Found: C, 68.81%; H, 8.24%.

Preparation of **VIb**

VIb was prepared in 83% yield as described above and purified by column chromatography using a mixture of n-hexane and ethyl acetate (8:2) as the eluant.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 1.51-1.62 (t, 12H, —CH$_3$); 3.83 (m, 4, —C$\underline{H}_2$—O—); 3.92 (m, 2H, CH$_2$—C$\underline{H}$—CH$_2$); 4.08-4.20 (m, 4H, PhO—C$\underline{H}_2$—); 4.47-4.58 (m, C$\underline{H}$—CH$_3$, Z isomer); 4.74-5.09 (m, C$\underline{H}$—CH$_3$, E isomer); 5.95-6.02 (m, C$\underline{H}$—O, Z isomer); 6.10-6.29 (m, C$\underline{H}$—O, E isomer); 6.81 (d, 4H, Ph); 7.46 (d, 4H, Ph).

Analysis: Calculated for C$_{33}$H$_{44}$O$_6$: C, 73.85%; H, 8.26%. Found: C, 74.13%; H, 8.26%.

Preparation of **VIc**

The tetrafunctional monomer, **VIc**, was obtained in 85% yield as a free-flowing oil and was purified by column chromatography as described for **VIa**.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 1.53-1.68 (m, 18H, CH$_3$); 3.87 (m, 4H, C$\underline{H}_2$—O); 3.95 (m, 2H, CH$_2$—C$\underline{H}$—CH$_2$); 4.05-4.18 (m, 4H, PhO—C$\underline{H}_2$); 4.37-

4.56 (m, C$\underline{\text{H}}$—CH$_3$, Z isomer); 4.73-5.17 (m, C$\underline{\text{H}}$—CH$_3$, E isomer); 5.96-6.02 (m, C$\underline{\text{H}}$—O, Z isomer); 6.09-6.28 (m, C$\underline{\text{H}}$—O, E isomer); 6.81 (d, 2H, Ph); 7.12 (d, 2H, Ph).

Analysis: Calculated for C$_{30}$H$_{38}$O$_6$: C, 72.84%; H, 7.75%. Found: C, 72.88%; H, 7.75%.

Preparation of VId

Monomer **VId** was a low melting glassy solid which was purified by chromatography using a mixture of n-hexane and ethyl acetate (7:3) as an eluant. An 81% yield of **VId** was obtained.

^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 1.50-1.61 (2t, 12H, CH$_3$); 3.81 (m, 4H, CH$_2$—O); 3.91 (m, 2H, CH$_2$—C$\underline{\text{H}}$—CH$_2$); 4.08-4.19 (m, 4H, PhO—C$\underline{\text{H}}_2$—); 4.34-4.52 (m, C$\underline{\text{H}}$—CH$_3$, Z isomer); 4.68-5.14 (m, C$\underline{\text{H}}$—CH$_3$, E isomer); 5.88-6.24 (m, C$\underline{\text{H}}$—O, Z isomer); 6.05-6.27 (m, C$\underline{\text{H}}$—O, E isomer); 6.98 (d, 2H, Ph); 7.31 (d, 2H, Ph).

Analysis: Calculated for C$_{30}$H$_{38}$O$_8$S: C, 64.49%; H, 6.86%. Found: C, 64.61%; H, 6.92%.

General Photopolymerization of Monomers

Photopolymerizations of monomers **VIa-d** were carried out by spreading the bulk monomers containing 0.5 mol% (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate as a photoinitiator as a thin film onto glass plates. Then the films were irradiated using a Fusion Systems, Inc. Laboratory UV Cure Processor fitted with a microwave activated 300 W UV lamp aligned perpendicular to the travel of the conveyor belt and mounted at a distance of 10 cm from the belt. Irradiation times were of the order of 0.5-1 second.

Real-Time Infrared (RTIR) Measurements

The conversions of monomers **VIa-d** to crosslinked polymers were measured by RTIR spectroscopy. The measurements were performed in air at room temperature on samples of monomers containing 0.5 mol% dissolved (4-decyloxyphenyl)-phenyliodonium hexafluoroantimonate coated onto polyethylene films. The samples were irradiated at an UV intensity of 5 mW/cm^2 at a probe distance of 5 cm from the sample. The photopolymerizations were monitored by following the decrease in the intensity of the 1660-1680 cm^{-1} (propenyl ether) absorption band upon UV exposure as a function of time. The conversions of the monomers were calculated by comparing the initial and final absorbances.

RESULTS AND DISCUSSION

Preliminary Studies

An important factor which must be considered in the design and synthesis of multifunctional propenyl ethers containing aromatic groups is the tendency of aryl-vinyl and propenyl ethers to undergo undersirable Claisen-type rearrangements

during polymerization to give low molecular weight polymers containing pendant phenolic hydroxyl groups [8, 9]. An example of this reaction is

eq. 1
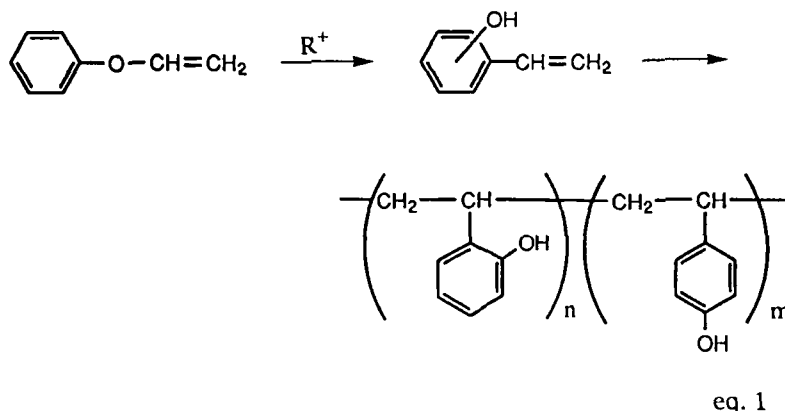
In an attempt to avoid this reaction, the synthesis of the model compound, 1-propenoxy-2,6-dimethylbenzene, in which both ortho positions are blocked, was carried out as depicted in Scheme 1. The desired compound was prepared in high yield by the reaction of 2,6-dimethylphenol with allyl bromide, tetra-*n*-butylammonium bromide, and NaOH in toluene (Eq. 2), followed by isomerization with 0.2 mol% ruthenium catalyst for 40 hours at 130°C (Eq. 3). However, when cationic photopolymerization of this monomer was attempted, a polymer was not obtained nor did rearrangement occur. Instead, 2,6-dimethylphenol was observed, possibly due to facile acid-catalyzed hydrolysis of the aryl propenyl ether bond as shown in Eq. (4).
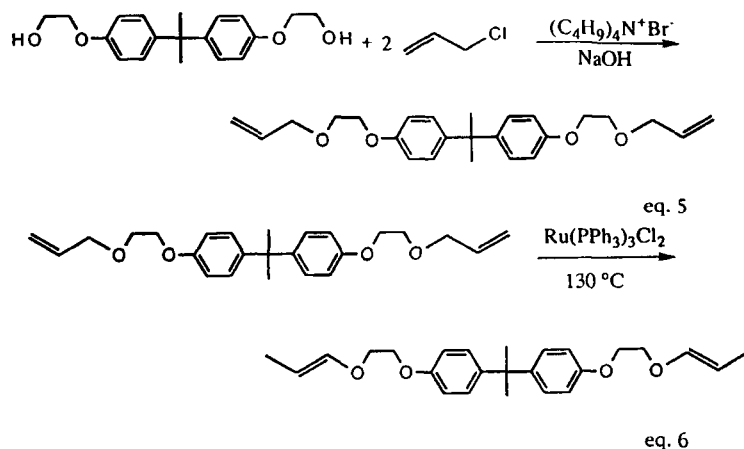

eq. 2

eq. 3

eq. 4
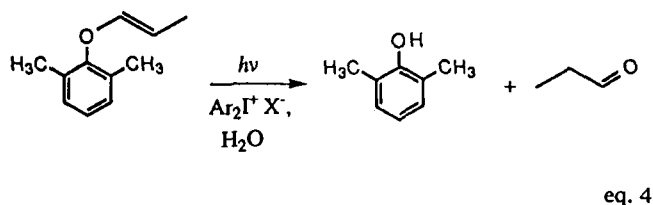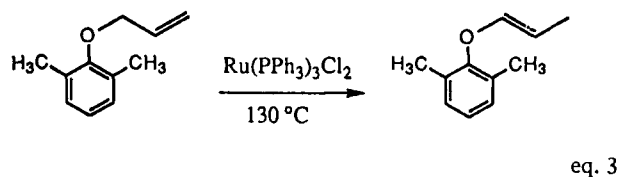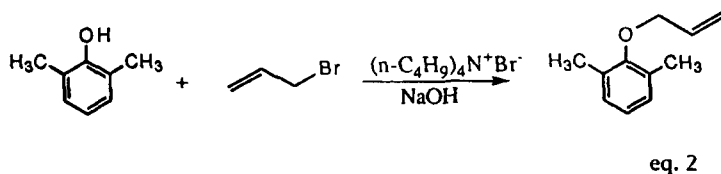
SCHEME 1.

Thus, the direct attachment of the propenyl ether groups to aromatic rings has to be avoided both to prevent rearrangement and rapid hydrolysis during poly-merization. One successful approach to the synthesis of mono- and polyfunctional propenyl ethers containing aromatic groups is shown in Scheme 2 [5]. In this scheme, a spacer was inserted between the aromatic ring and the propenyl ether group which effectively prevents both hydrolysis and rearrangement (Eq. 5). A key step in the above synthetic sequence is the facile isomerization of the bisallyl ether to the corresponding bispropenyl ether in the presence of a ruthenium(II) catalyst (Eq. 6).
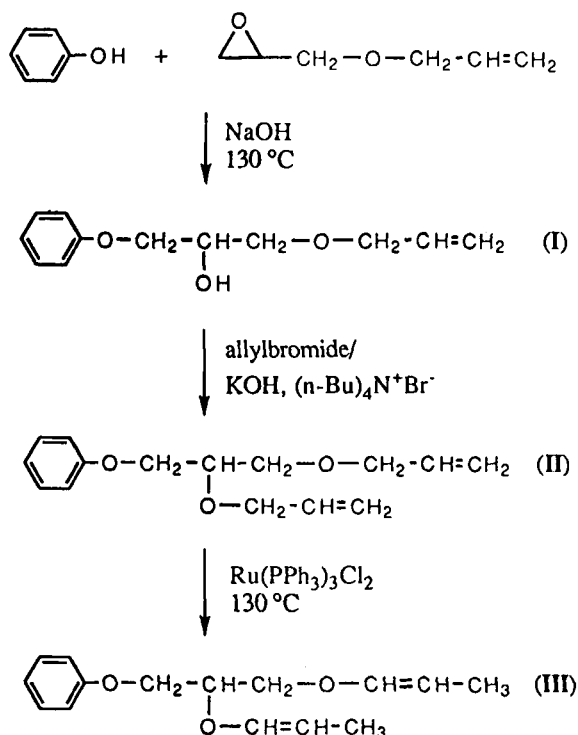
Synthesis of Multifunctional Propenyl Ethers

A different synthetic approach was employed in the present investigation and is shown in Scheme 3 for the preparation of the difunctional monomer, 1,2-dipro-penoxy-3-phenoxypropane (**III**). First, the base-catalyzed condensation of allyl glycidyl ether and phenol was carried out in the absence of solvent at 130°C. The resulting adduct, 1-allyloxy-3-phenoxy-2-propanol (**I**), was obtained in 85% yield. Further condensation of the secondary hydroxyl group with allyl bromide in the presence of NaOH and tetra-n-butylammonium bromide in toluene at 70°C gave **II**. In a subsequent reaction, the allyl groups were isomerized using tris(triphenyl-phosphine)ruthenium(II) dichloride as a catalyst.

The isomerization of allyl to propenyl ether groups was conveniently moni-tored by following the decrease in the ^{1}H-NMR band at $\delta = 5.30$ ppm due to the protons attached to the terminal carbon of the allyl group or the appearance and increase of the band at $\delta = 1.56$ ppm due to the methyl protons of the propenyl ether groups which are formed. Alternatively, the increase in the bands at 1660–1680 cm^1 in the infrared due to the propenyl ether double bonds could be monitored. The ruthenium-catalyzed isomerization **II** proceeds quantitatively to give **III** as a colorless, low viscosity oil simply by heating in the absence of a solvent at 130°C for 8 hours. Figure 1 shows the ^{1}H-NMR spectra of **II** and **III**. As can be seen in the

eq. 5

eq. 6

SCHEME 2.

C$_6$H$_5$—OH + (epoxide)—CH$_2$—O—CH$_2$-CH=CH$_2$

↓ NaOH 130 °C

C$_6$H$_5$—O-CH$_2$-CH-CH$_2$—O—CH$_2$-CH=CH$_2$ (I)
|
OH

↓ allylbromide/ KOH, (n-Bu)$_4$N$^+$Br$^-$

C$_6$H$_5$—O-CH$_2$-CH-CH$_2$—O—CH$_2$-CH=CH$_2$ (II)
|
O—CH$_2$-CH=CH$_2$

↓ Ru(PPh$_3$)$_3$Cl$_2$ 130 °C

C$_6$H$_5$—O-CH$_2$-CH-CH$_2$—O—CH=CH-CH$_3$ (III)
|
O—CH=CH-CH$_3$

eq. 7-9

SCHEME 3.

spectra, **III** consists of a mixture of two isomers with E and Z configurations (ratio: ~40:60) about the propenyl ether double bond.

This synthetic approach is very broad and can be applied to the preparation of a wide variety of monomers with differing structures. In this investigation a series of four novel tetrafunctional propenyl ethers was prepared as depicted in Scheme 4 using the indicated bisphenol precursors. Monomers **VIa-c** were colorless, free-flowing liquids, while **VId** was a low-melting glassy solid. The ^{1}H-NMR spectra of tetrapropenyl ether **VIa** and its tetraallyl precursor **Va** are shown in Fig. 2. Again, both E and Z isomers are evident in the spectrum of **VIa** in a ratio of 40:60.

Cationic Photopolymerization of Multifunctional Propenyl Ethers

Photopolymerizations of di- and tetrafunctional monomers were undertaken in the presence of onium salt cationic initiators. Aromatic propenyl ether monomers were found to be poor solvents for diaryliodonium and triarylsulfonium salt photoinitiators. However, diaryliodonium salts bearing long-chain alkoxy groups exhibited quite good solubility in these monomers and showed high efficiency in the initiation of cationic polymerization. Typical cationic photopolymerizations were
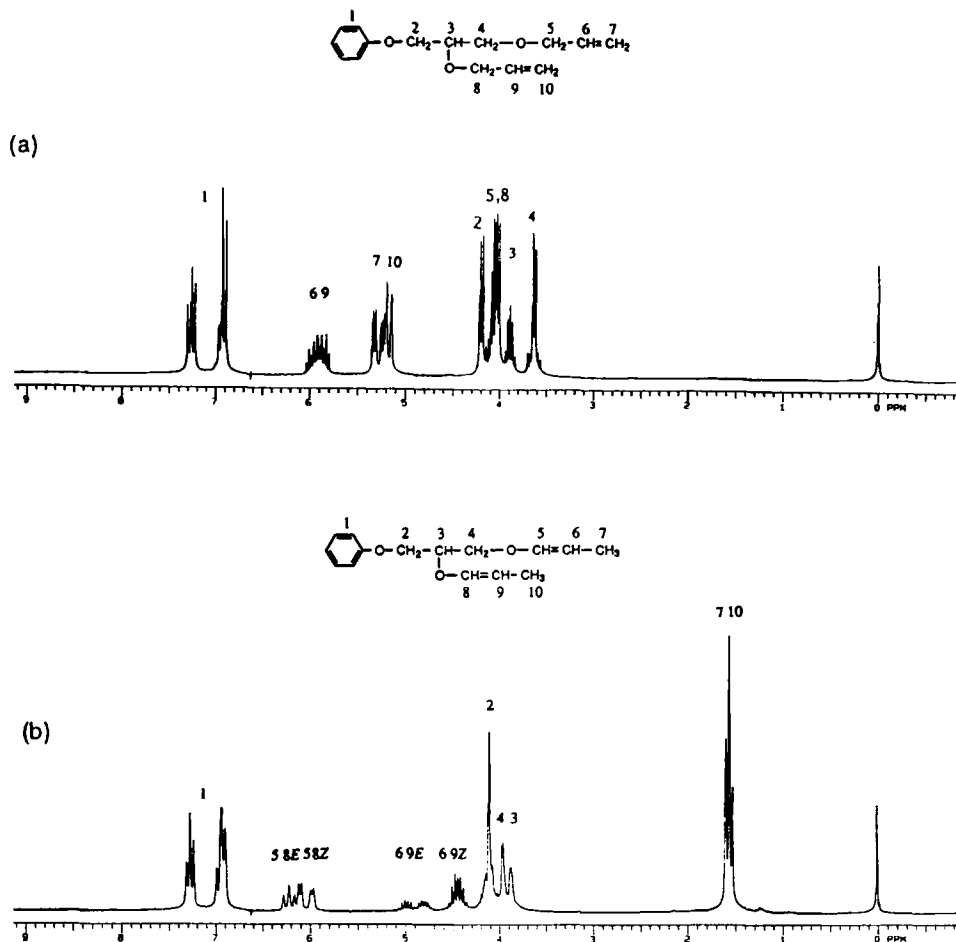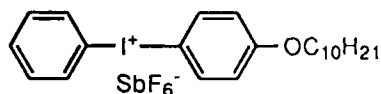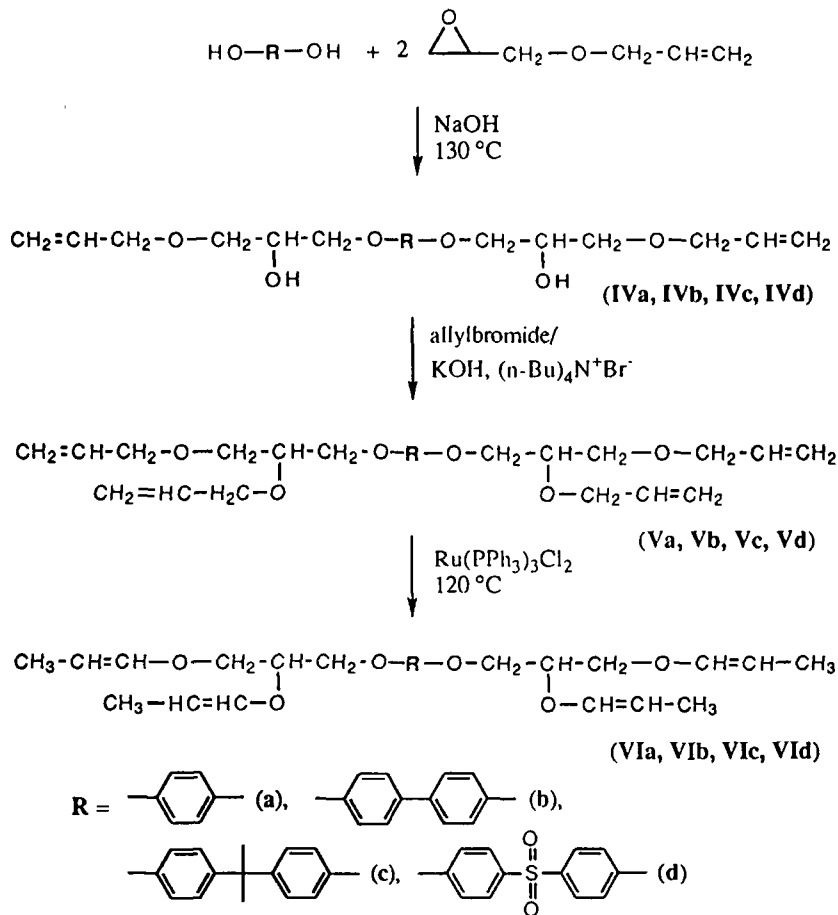
FIG. 1. ^{1}H-NMR spectra **II** (A) and **III** (B) in CDCl$_3$.

carried out at room temperature in bulk monomers with 0.5 mol% (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate as a photoinitiator whose structure is

In all cases, irradiation for 1–2 seconds using a 300-W Hg arc lamp was sufficient to convert the liquid monomers to pale yellow, transparent, brittle solids. After irradiation, the polymers were insoluble in all common solvents, indicating that they were crosslinked.

To determine the rate of conversion of propenyl ether functional groups in the various monomers to polymers during cationic photopolymerization, real-time infrared spectroscopy (RTIR) studies were carried out at room temperature. This

$$HO-R-OH \ + \ 2 \ \overset{O}{\triangle}-CH_2-O-CH_2-CH=CH_2$$

$$\downarrow \ \begin{array}{l} NaOH \\ 130\,°C \end{array}$$

$$CH_2=CH-CH_2-O-CH_2-\underset{\underset{OH}{|}}{C}H-CH_2-O-R-O-CH_2-\underset{\underset{OH}{|}}{C}H-CH_2-O-CH_2-CH=CH_2$$

(IVa, IVb, IVc, IVd)

$$\downarrow \ \begin{array}{l} allylbromide/ \\ KOH, \ (n\text{-}Bu)_4N^+Br^- \end{array}$$

$$CH_2=CH-CH_2-O-CH_2-\underset{\underset{CH_2=HC-H_2C-O}{|}}{C}H-CH_2-O-R-O-CH_2-\underset{\underset{O-CH_2-CH=CH_2}{|}}{C}H-CH_2-O-CH_2-CH=CH_2$$

(Va, Vb, Vc, Vd)

$$\downarrow \ \begin{array}{l} Ru(PPh_3)_3Cl_2 \\ 120\,°C \end{array}$$

$$CH_3-CH=CH-O-CH_2-\underset{\underset{CH_3-HC=HC-O}{|}}{C}H-CH_2-O-R-O-CH_2-\underset{\underset{O-CH=CH-CH_3}{|}}{C}H-CH_2-O-CH=CH-CH_3$$

(VIa, VIb, VIc, VId)

$$R = \ -\langle\bigcirc\rangle- \ (a), \quad -\langle\bigcirc\rangle-\langle\bigcirc\rangle- \ (b),$$

$$-\langle\bigcirc\rangle-\overset{|}{\underset{|}{C}}-\langle\bigcirc\rangle- \ (c), \quad -\langle\bigcirc\rangle-\overset{O}{\underset{O}{\overset{||}{\underset{||}{S}}}}-\langle\bigcirc\rangle- \ (d)$$

eq. 10-12

SCHEME 4.

method involves monitoring the decrease or increase of distinctive infrared bands with time during simultaneous UV irradiation. The IR spectra of propenyl ether monomers showed characteristic absorptions due to the carbon—carbon double bond of the propenyl ether group at 1660–1680 cm^{-1}, and this band was monitored during the RTIR studies.

In Fig. 3 are shown are shown conversion versus time plots for various propenyl ether monomers in the RTIR studies. Inspection of this figure leads to the conclusion that the difunctional propenyl ether, **III**, is much more reactive and proceeds to a higher conversion than the corresponding tetrafunctional propenyl ether monomers. Among the tetrapropenyl ether monomers, **VIa** has the highest polymerization rate and proceeds to the greatest extent of conversion. In the case of the three remaining monomers, **VIb–d**, the increased rigidity of the resulting network structures due to the presence of the bisaromatic units may be responsible for
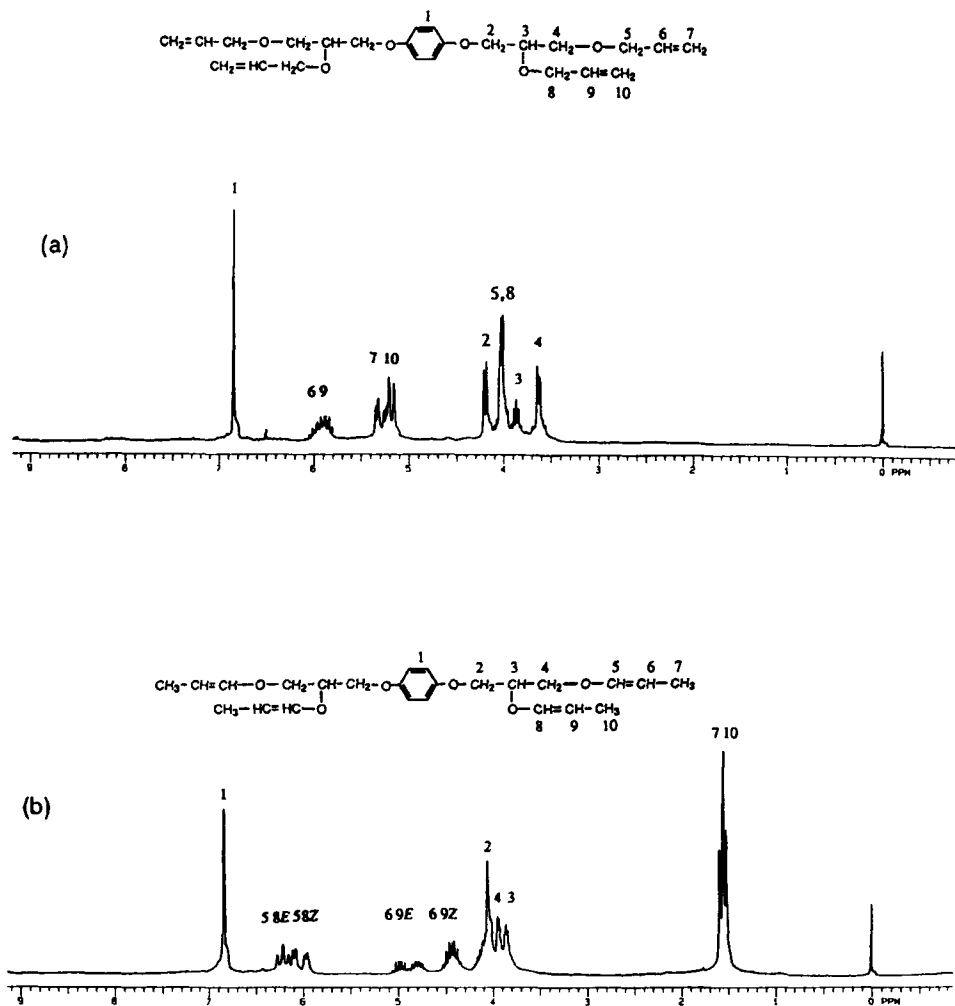
FIG. 2.   ¹H-NMR spectra **Va** (A) and **VIa** (B) in CDCl₃.

the markedly lower reactivity and conversions at room temperature. Rigid groups would be expected to raise the glass transition temperature of the network which is formed, thereby immobilizing and decreasing the reactivity of the remaining pro-penyl ether groups at lower conversions. Since monomers containing bisaromatic units also have strong absorptions in the 240–300 nm region of the UV, they would also be expected to effectively screen the photoinitiators which absorb in this same region.

The rate of photopolymerization and conversion at any moment of the reac-tion depends on the concentration of photoinitiators. Figure 4 shows an RTIR study of the reactivity of the three tetrafunctional monomers **VIb**, **VIc**, and **VId** using 1.0 mol% of the diaryliodonium salt. In all cases, higher rates of polymerization and conversions of the propenyl ethers were observed with the higher photoinitiator contents.
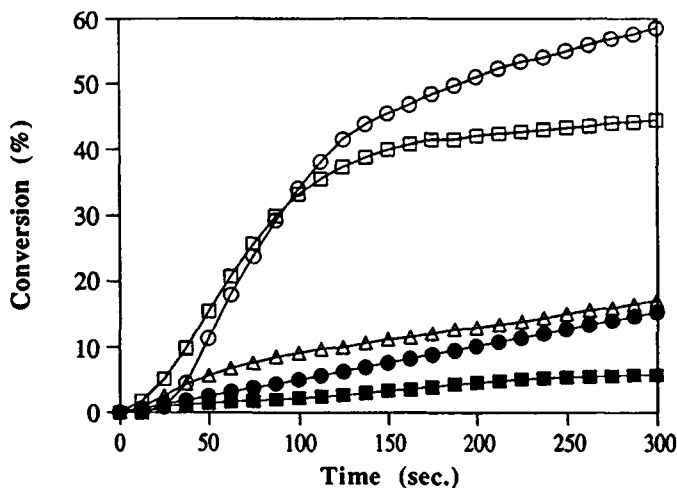
FIG. 3.   RTIR study of the rates of photopolymerization of di- and tetrafunctional monomers (○, **III**; □, **VIa**; △, **VIb**; ●, **VIc**; ■, **VId**) with 0.5 mol% (4-decyloxyphenyl)-phenyliodonium hexafluoroantimonate.

The sulfone-containing monomer **VId** undergoes very slow polymerization at room temperature because of its high viscosity and due to the poor solubility of the photoinitiator in the monomer at 25°C. For this reason the photopolymerization was followed by differential scanning photocalorimetry (DSP) at four different temperatures (40, 60, 80, and 100°C). The radiation intensity of the lamp was measured at 357 mJ/cm², and the sample weights were carefully controlled to be in
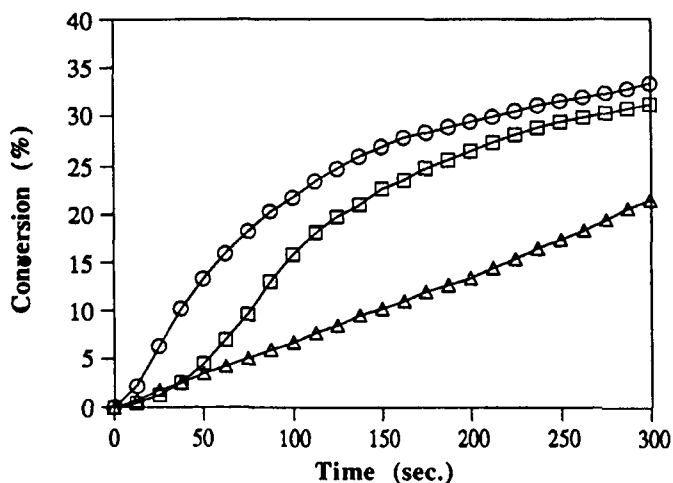

FIG. 4.   RTIR study of the rates of photopolymerization of tetrafunctional monomers (○, **VIb**; □, **VIc**; △, **VId**) with 1.0 mol% (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate.
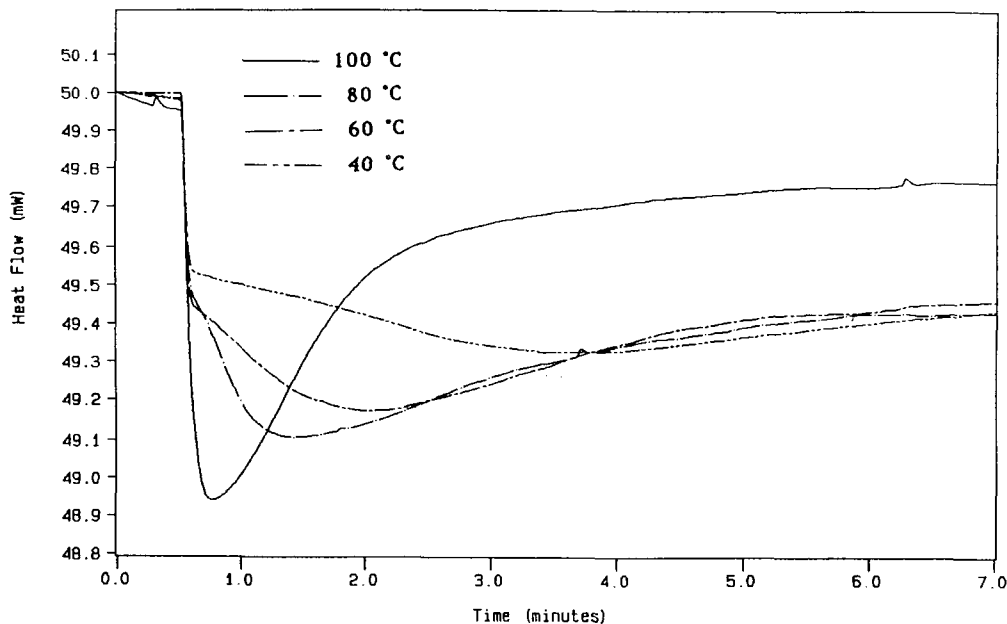
FIG. 5.   DSP study of the photopolymerization of tetrafunctional monomer **VId** at various temperatures using 1.0 mol% (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate as a photoinitiator.

the range of 0.45 to 0.50 mg to allow direct comparison of the DSP curves. The experiments were conducted in the presence of 1.0 mol% of the diaryliodonium salt photoinitiator. As shown in Fig. 5, an increase in the temperature produces a concomitant increase in the rate and degree of photopolymerization of this tetrafunctional monomer. At 40°C the evolution of the heat of polymerization is very slow, while at 100°C there is a marked increase in the rate and quantity of heat evolved. Both the DSP and RTIR results indicate rather low ultimate conversions of propenyl ether groups to polymer during photopolymerization for all the tetrafunctional monomers studied in this investigation. This is in accord with earlier observations made with other multifunctional propenyl ethers [3] and may be ascribed to the rapid formation of a tightly crosslinked network in which the mobility of the remaining unreacted propenyl ether groups is severely restricted. The properties of the polymers appear to closely resemble those of the related aromatic bispropenyl ethers [5].

CONCLUSIONS

Aromatic di- and tetrafunctional propenyl ethers were prepared by a stepwise synthesis involving as the key step a facile, high yield rearrangement of the corresponding allyl ethers using tris(triphenylphosphine)ruthenium(II) dichloride as a catalyst. These monomers underwent UV-induced cationic photopolymerization in

the presence of a diaryliodonium salt photoinitiator to give crosslinked polymers. Photopolymerizations were studied using real-time infrared spectroscopy and differential scanning photocalorimetry techniques. The conversions of aromatic tetrapropenyl ether monomers were lower than those of difunctional propenyl ethers and depended on the specific types of aromatic groups present in the monomers.

REFERENCES

[1]   C. C. Roffey, *Photopolymerization of Surface Coatings*, Wiley, Chichester, 1982.
[2]   K. Moussa and C. Decker, *J. Polym., Sci., Polym. Chem. Ed.*, *31*, 2197 (1993).
[3]   J. V. Crivello and K. D. Jo, *Ibid.*, *31*, 1473, 1483, 2143 (1993).
[4]   J. V. Crivello and D. A. Conlon, *Ibid.*, *21*, 1785 (1983).
[5]   J. V. Crivello and D. A. Conlon, *Ibid.*, *22*, 2105 (1984).
[6]   D. H. Suh and J. H. Crivello, *Chem. Mater.*, *5*, 210 (1993).
[7]   J. V. Crivello and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed.*, *27*, 3951 (1989).
[8]   J. B. Niederl and E. A. Storch, *J. Am. Chem. Soc.*, *55*, 284 (1933); *60*, 1905 (1938).
[9]   K. Yamamoto and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, *12*, 613 (1974).