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Synthesis and Cationic Polymerization of Open-Chain and Cyclic Enol Ethers

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SYNTHESIS AND CATIONIC POLYMERIZATION OF OPEN-CHAIN AND CYCLIC ENOL ETHERS

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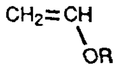
Key Words: Photoinitiated cationic polymerization; Enol ethers; Cyclic enol ethers; Polymerization reactivity

ABSTRACT

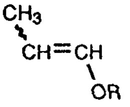
Several new open-chain and cyclic enol ether monomers were prepared using simple, straightforward procedures. The reactivities of these monomers were compared using both differential scanning photocalorimetry and Fourier transform real-time infrared spectroscopy. In general, these new monomers were found to possess excellent reactivity in photoinitiated cationic polymerization using a diaryliodonium salt photoinitiator.

INTRODUCTION

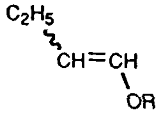
The development of onium salts as efficient photoinitiators for cationic polymerization has led to the use of these photoinitiators in a large number of commercial applications in imaging systems and for rapidly polymerizable coatings, adhesives, and printing inks. In this laboratory we have been exploring the use of these photoinitiators with various cationically polymerizable monomer types. For example, we have employed a wide variety of commercially available mono-, di-, and multifunctional epoxide [1] and vinyl ether monomers [2]. At the same time, we have been engaged in the search for novel chemistries leading to the preparation of new types of cationically photopolymerizable monomers. Two such classes of novel monomers are 1-propenyl [3-5] and 1-butenyl [6] ethers. These monomers are readily prepared in good yield by simple, straightforward methods. Moreover, they possess excellent reactivity in photoinitiated cationic polymerization which is similar to that of the vinyl ethers. These three types of related monomers, whose structures are shown below, can all be considered to belong to the class of compounds known as enol ethers.



vinyl ether

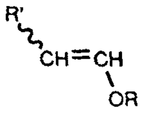


1-propenyl ether



1-butenyl ether

Two additional classes of structurally related monomers which similarly possess highly electron-rich double bonds are open-chain and cyclic enol ethers with the following structures.



open chain enol ether

cyclic enol ethers

In the above structures, R and R′ are aliphatic groups which may or may not contain other functional groups.

In this paper we report the synthesis of several prototypical examples of these latter monomers from readily available starting materials. As part of this investigation, a study of the reactivity of these monomers in photoinduced cationic polymerization using a typical diaryliodonium salt photoinitiator was also undertaken to determine their reactivity.

EXPERIMENTAL

All the organic reagents employed in this investigation were purchased from the Aldrich Chemical Co. and used as received unless otherwise noted. 2,3-Dihydropyran was distilled from solid powdered sodium hydroxide before use. (4-*n*-Decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10) was prepared as described previously [7]. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5890 Gas Chromatograph equipped with a high performance capillary HP-1 (5% phenylmethyl silicone) column and a flame ionization detector. ^{1}H-NMR spectra were obtained on a Varian XL-200 MHz Spectrometer at room temperature in deuterochloroform. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

Synthesis of Open-Chain and Cyclic Enol Ether Monomers

The procedures given below are typical for those used for the synthesis of all of the cyclic and open-chain allylic ether precursors shown in Table 1.

Preparation of 1-Allyloxy-2(2-methoxyethoxy)ethane (**Ia**)

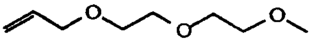
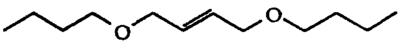
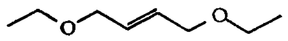
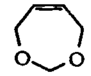
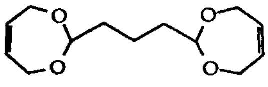
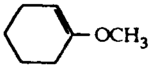
Into a 250-mL two-neck round-bottom flask equipped with a magnetic stirrer, a nitrogen inlet, and a reflux condenser were placed 56 g (0.47 mol) di(ethylene glycol) monomethyl ether, 24 g (0.2 mol) allyl bromide, 9 g (0.225 mol) sodium hydroxide, and 50 mL toluene. The reaction mixture was stirred at room temperature for a short time, and then 1.3 g (4 mmol) tetra-*n*-butylammonium bromide was added. The reaction mixture was slowly heated to reflux and maintained at reflux overnight. On cooling, the reaction mixture was poured into 100 mL distilled water, the organic layer was separated, and the aqueous layer was extracted with fresh toluene. The combined organic layers were washed with three 100 mL portions of distilled water and dried over anhydrous sodium sulfate. Then the excess allyl bromide and toluene were removed using a rotary evaporator, and the liquid residue was subjected to fractional vacuum distillation. There were obtained 19.55 g (61% yield) of a fraction boiling at 64°C/0.25 mmHg whose ^{1}H-NMR spectrum indicated that it was pure **Ia**.

^{1}H-NMR (200 MHz, $CDCl_3$), δ (ppm) 5.13-5.3 (m, 2H, $C\mathit{H}_2{=}CH-$); 5.8-6.1 (m, 1H, $CH_2{=}C\mathit{H}-$); 4.05 (m, 2H, $CH_2{=}CH-C\mathit{H}_2-$); 3.55-3.7 (m, 8H, $O-C\mathit{H}_2-C\mathit{H}_2-O$); 3.78 (s, 3H, $O-CH_3$).

Preparation of *cis*-1,4-Dibutoxy-2-butene (**IIa**)

Into a 250-mL round-bottom two-neck flask equipped with condenser and nitrogen inlet were placed 26.4 g (0.3 mol) *cis*-2-butene-1,4-diol, 123 g (0.9 mol) *n*-butyl bromide, 50 mL toluene, and 24.8 g (0.72 mol) sodium hydroxide. The

TABLE 1. Synthesis of Cyclic and Open-Chain Allyl Ether Precursors

Notation	Monomer structure	Boiling point, °C/mmHg
Ia		64/0.25
IIa		87/0.25
IIIa		45/0.25
IVa		70-72/0.25
Va		126.5-128/760
VIa		99-100/0.25
VIIa		145/760

reaction mixture was stirred at room temperature for approximately 0.5 hour, then 1.3 g (4 mmol) tetra-*n*-butylammonium bromide was added, and the reaction mixture was slowly heated to reflux and maintained at that temperature overnight. The reaction mixture was poured into 100 mL distilled water, the organic layers were separated, and the aqueous layer was extracted with fresh toluene. The combined organic layers were washed with three 100-mL portions of distilled water, and the organic phase was dried over anhydrous sodium sulfate. Then the excess *n*-butyl bromide and toluene were removed using a rotary evaporator, and the resulting oil was subjected to vacuum distillation. Fractional distillation gave 83% 1,4-dibutoxy-2-butene (**IIa**) with a boiling point of 87°C/0.25 mmHg.

^{1}H-NMR (200 MHz, $CDCl_3$), δ (ppm) 0.9 (t, 6H, CH_3); 1.4 (m, 4H, $CH_3-CH_2-CH_2$); 1.55 (m, 4H $CH_3-CH_2-CH_2$); 3.4 (t, 4H, CH_2-O); 4.0 (d, 4H, $O-CH=CH_2$); 5.7 (t, 2H, $-CH=CH-$).

Preparation of 5,6-Dihydro-1,3-dioxepin (Va)

The synthesis given below for 5,6-dihydro-1,3-dioxepin (**Va**) was also employed for disubstituted 5,6-dihydro-1,3-dioxepin (**VIa**).

A mixture of 58.15 g (0.66 mol) *cis*-2-butene-1,4-diol, 18 g (0.6 mol) paraformaldehyde, 40 g benzene, and 0.3 g *p*-toluenesulfonic acid was refluxed using a Dean-Stark trap until the theoretical amount of water was collected. Distillation of the mixture, after removal of benzene, gave 35 g (85%) of **Va** (bp 126.5-128°C).

^{1}H-NMR (200 MHz, $CDCl_3$), δ (ppm) 4.2 (s, 4H, $CH=CH_2-O$); 4.88 (s, 2H, $O-CH_2-O$); 5.72 (t, 2H, $-CH=CH-$).

Synthesis of 2,2′-Trimethylene-bis(4,5-dihydro-1,3-dioxepin (VIa)

A mixture of 40 g (0.45 mol) *cis*-2-butene-1,4-diol, 40 g (0.2 mol) of a 50% aqueous solution of glutaric dialdehyde, 50 g benzene, and 0.36 g *p*-toluenesulfonic acid was refluxed, and the water formed was collected in a Dean-Stark trap. When the theoretical amount of water had been collected, the reaction mixture was cooled and washed with a 1 N sodium hydroxide solution followed by washing with distilled water. The organic phase was dried over anhydrous sodium sulfate, and the benzene was removed on a rotary evaporator. The resulting oil was subjected to fractional vacuum distillation to give 31 g (65% yield) **VIa** with bp 99-100/0.25 mmHg.

^{1}H-NMR (200 MHz, $CDCl_3$), δ (ppm) 1.4-1.8 (m, 6H, $-(CH_2)_3-$); 4.1-4.5 (m, 8H, $-CH=CH-CH_2$); 4.72-4.8 (t, 2H, $O-CH-O$); 5.72 (t, 4H, $CH=CH$).

Preparation of 1-Metnoxy-1-cyclohexene (VIIa)

A mixture of 49 g (0.4 mol) cyclohexanone and 63.67 g (0.6 mol) trimethyl orthoformate was dissolved in methanol and placed in a 100-mL round-bottom flask fitted with a magnetic stirrer and a reflux condenser. The mixture was cooled in an ice bath, and 0.1 g *p*-toluenesulfonic acid was added slowly (the reaction was very exothermic). Then the solution was refluxed for 3 days. After cooling to room temperature, the reaction mixture was neutralized with methanolic sodium methoxide. The solvent and excess trimethyl orthoformate were removed using a rotary evaporator, and the desired product, 1,1-dimethoxycyclohexane (**VIIa**), was obtained by distillation (58%, bp 38-39°C/0.25 mmHg).

Under an atmosphere of nitrogen, a 150-mL reaction vessel was charged with 6.24 g (79.4 mmol) *N,N*-diisopropylethylamine (DIPEA), 5.7 g (39.5 mmol) 1,1-

dimethoxycyclohexene, and 80 mL methylene chloride. After the reaction mixture was cooled to −20°C, 10 g (44.8 mmol) trimethylsilyl triflate was added dropwise to the solution using a syringe. During the addition a pale yellow color developed. The solution was allowed to warm to room temperature over the course of 3 hours. The reaction mixture was quenched by the addition of aqueous sodium hydroxide, diluted with 100 mL hexane, and refrigerated overnight to precipitate the trialkylammonium triflate salt which was removed by filtration. The solution was dried over anhydrous sodium carbonate. After removal of the solvent on a rotary evaporator, the product was passed through a column of basic alumina to remove residual DIPEA using hexane as the eluent. The hexane was removed on a rotary evaporator, and the resulting oil was fractionally distilled. There were obtained 3.84 g (87%) **VIIa** with a bp 145°C/760 mmHg.

^{1}H-NMR (200 MHz, $CDCl_3$), δ (ppm) 1.5–1.7 (m, 4H, $-CH_2-$); 2.0–2.1 (m, 4H, $CH_2-CH=CH$); 3.5 (s, 3H, $O-CH_3$); 4.62 (t, 1H, $CH_2-CH=C$).

General Procedures for Isomerizations

See Table 2.

Method 1: Base-Catalyzed Isomerization

Into a 100-mL round-bottom flask fitted with a magnetic stirrer, reflux condenser, and nitrogen inlet were placed 10 g (50 mmol) 1,4-dibutoxy-2-butene (**IIa**), 5.6 g (50 mmol) potassium *t*-butoxide, and 50 mL dimethylsulfoxide (DMSO). The reaction mixture was stirred at room temperature, and then the dark brown mixture was heated to 135°C and held at that temperature for 2 hours. After cooling to room temperature, the reaction mixture was poured into 100 mL distilled water, and the organic layer was extracted into ethyl ether. Then the layers were separated. The organic layer was washed three times with distilled water to remove DMSO, then stripped of solvents using a rotary evaporator. Fractional vacuum distillation gave 40% 1,4-dibutoxy-1-butene (**IIe**) (bp 83°C/0.25 mmHg).

Method 2: Ruthenium-Catalyzed Isomerization

Isomerization of **IIa**. Into a 100-mL round-bottom flask fitted with a magnetic stirrer, reflux condenser, and nitrogen inlet were placed 10 g (50 mmol) **IIa** and 0.024 g (0.05 mmol) tris(triphenylphosphine)ruthenium(II) dichloride. The mixture was heated to 150°C for 2 hours. Fractional distillation gave **IIe** (bp 83°C/0.25 mmHg) in 63% yield.

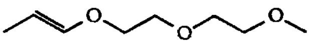
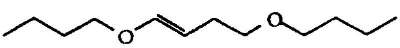
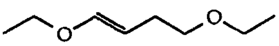
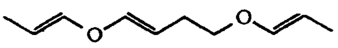
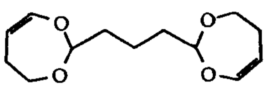
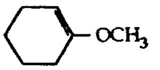
Isomerization of VIa: Into a 25-mL two-neck round-bottom flask fitted with a magnetic stirrer, reflux condenser, and nitrogen inlet was placed 3 g (12.5 mmol) **VIa** and 72 mg (0.015 mmol) tris(triphenylphosphine)ruthenium(II) dichloride. The reaction mixture was heated to 135°C for 6 days. The product was distilled using a Büchi microdistillation apparatus to give a 15% yield of **VIe**.

^{1}H-NMR (200 MHz, $CDCl_3$), δ (ppm) 1.5–1.8 (m, 6H, $-(CH_2)_3-$); 2.15 and 2.50 (2 m, 4H, $CH_2-CH=$); 3.26 and 4.13 (t and m, 4H, $O-CH_2-CH=$); 4.45 (m, 2H, $-CH=CH-O$); 4.85 (m, 2H, $O-CH-O$); 6.37 (m, 2H, $O-CH=CH$).

Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR)

This method involves the monitoring of an appropriate IR band due to the polymerizing enol ether group while simultaneously irradiating a thin film sample of a monomer with UV light. Measurements were performed on a Midac Corp.

TABLE 2. Syntheses of Open-Chain and Cyclic Enol Ethers

Notation	Monomer structure	Yield, %	Elemental analysis			bp, °C/mm
				% C	% H	
Ie		57[a]	Cal:	59.97	10.07	62/0.25
			Fnd:	58.78	9.83	
IIe		40[b]	Cal:	71.95	12.07	83/0.25
			Fnd:	69.79	11.83	
IIIe		69[b]	Cal:	66.63	11.18	46/0.25
			Fnd:	66.47	10.81	
IVe		45[a]	Cal:	71.39	9.59	70/0.25
			Fnd:	69.94	9.28	
Ve		71[a]	Cal:	59.98	8.05	127/760
			Fnd:	59.60	7.76	
VIe		15[a]	Cal:	64.98	8.39	–
			Fnd:	63.22	8.26	
VIIe		87	Cal:	74.95	10.78	145/760
			Fnd:	73.50	10.53	

[a] Ruthenium-catalyzed isomerization.
[b] Base catalyzed isomerization.

Model M-1300 Fourier Transform Infrared Spectrometer equipped with a UVEXS Co SCU 110 UV lamp fitted with a flexible liquid optic cable. The end of the probe was situated so as to direct UV irradiation at a 45° angle onto the sample window. All studies were conducted using broad band, unfiltered UV light at an intensity of 1000 mJ/cm^2·min. Samples were prepared by placing the liquid monomers containing 0.5 mol% per enol ether equivalent of (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate between two poly(vinylidene chloride) films and then mounting the resulting sandwich in 5 cm × 5 cm slide frames. The progress of the polymerizations of the monomers were determined quantitatively by monitoring the decrease of the enol ether peaks at 1640 cm^{-1}. The data were collected on a Bit-Wise Co. 486 PC computer, and reduced and plotted as conversion versus time curves with the aid of a Galactic Industries Corp. Grams 386, Version 3.0 software package. Light intensity measurements were made with the aid of an International Light Co. Control-Cure Radiometer.

Differential Scanning Photocalorimeter (DSP)

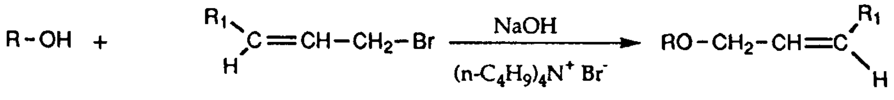
The photoinitiated polymerizations of the enol ether monomers were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a 100-W high-pressure Hg arc lamp. DSP experiments were conducted isothermally at

30°C on 0.5–1.0 mg samples of the monomer-photoinitiator solutions. The samples were placed in aluminum pans and allowed to equilibrate for several minutes. The samples were then irradiated by opening the shutter, and the course of the exothermic polymerization was followed by recording the heat evolved as a function of the irradiation time. The light flux used in these studies was 130–140 mJ/cm^2·min.

RESULTS AND DISCUSSION

Synthesis of Open-Chain and Cyclic Enol Ethers

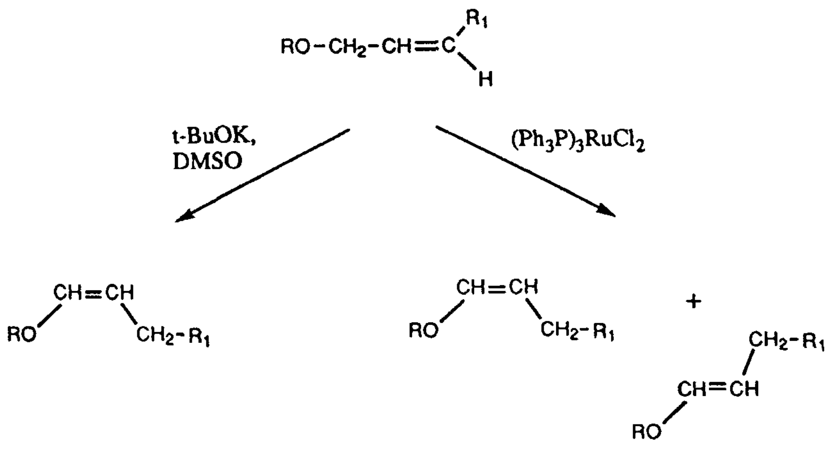
Over the years, several procedures for the preparation of enol ethers have been developed [8]. In this laboratory we have developed two synthetic methods which have been used for the preparation of 1-propenyl ethers [2–5] and 1-butenyl ethers [6] but which are widely applicable to enol ethers in general. Starting with an alcohol and an allyl or crotyl halide, the corresponding allyl or crotyl ether can be prepared in very high yields in the presence of a strong inorganic base and a phase transfer catalyst such as tetra-*n*-butylammonium bromide. This is shown in Eq. (1).



R_1 = H or CH_3

eq. 1

1-Propenyl ethers and 1-butenyl ethers can be readily prepared by a base or transition metal-catalyzed rearrangement of the corresponding allyl and crotyl ethers as depicted in Scheme 1.



eq. 2, 3

SCHEME 1.

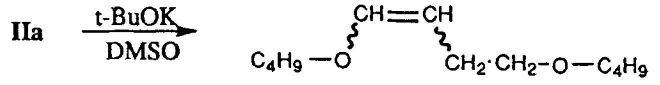
Base-catalyzed isomerization in the presence of potassium *t*-butoxide and DMSO gives almost exclusively the *cis* isomer, while isomerization in the presence of tris(triphenylphosphine)ruthenium(II) dichloride [$(Ph_3P)_3RuCl_2$] typically gives a 60:40 mixture of the *trans* and *cis* isomers, respectively.

This method has been applied to the synthesis of the linear, open-chain and cyclic enol ether monomers of the present investigation. For example, an interesting open-chain monomer may be easily prepared by the reaction of the readily available 2-butene-1,4-diol with 2 moles of butyl bromide followed by isomerization of the 1,4-dibutoxy-2-butene at 135 °C in DMSO in the presence of an equivalent of potassium *t*-butoxide (Eqs. 4 and 5).

$$HO-CH_2-CH{=}CH-CH_2-OH \quad + \quad 2\ C_4H_9\text{-}Br \xrightarrow[(n\text{-}C_4H_9)_4N^+\ Br^-]{NaOH}$$

$$C_4H_9-O-CH_2\cdot CH{=}CH-CH_2-O-C_4H_9$$

IIa eq. 4



$$\text{IIa} \xrightarrow[DMSO]{t\text{-}BuOK} C_4H_9-O-CH{=}CH-CH_2\cdot CH_2-O-C_4H_9$$

IIe eq. 5

The isomerization was conveniently monitored by ^{1}H-NMR by following the decrease in the band at δ 5.7 ppm due to the protons attached to the isolated double bond in **IIa**. Figure 1 shows the ^{1}H-NMR spectra of the reaction mixture before and after isomerization. As the spectra show, **IIa** is cleanly converted to the enol ether **IIe**. The base-catalyzed isomerization of an allyl ether usually requires 15 minutes at 110°C. The base-catalyzed isomerization of **IIa** was complete after 2 hours at 135 °C. The isomerization of **IIa** to **IIe** could also be achieved by heating **IIa** at 150°C in the presence of 0.05 mol% $(Ph_3P)_3RuCl_2$. The ^{1}H-NMR spectra of the reaction mixture after isomerization of **IIa** was essentially identical to that of Fig. 1(B). The isomer ratios observed for both base- and ruthenium-catalyzed isomerizations of **IIa** were approximately 55:45 *cis* to *trans* (*Z* to *E*). While the ruthenium-complex-catalyzed isomerization of allyl ethers is typically completed in 1-2 hours at 120°C, the isomerization of **IIa** required 2 hours at 150°C. Thus, both the base- and ruthenium-catalyzed isomerizations of internal allyl ethers require considerably more rigorous conditions than simple allyl ethers. At the same time, the ruthenium-catalyzed isomerization of crotyl (2-butenyl) ethers were isomerized only under considerably more vigorous conditions (e.g., 22 minutes at 220°C) [6]. It is possible that the milder conditions required for the isomerization of **IIa** are due to the fact that isomerization is favored since it can occur in either direction from the double bond to give the product.

Intermediate **IVa** was prepared by reaction of 2-butene-1,4-diol with allyl bromide under phase transfer conditions. Subsequently, both of the allyl groups

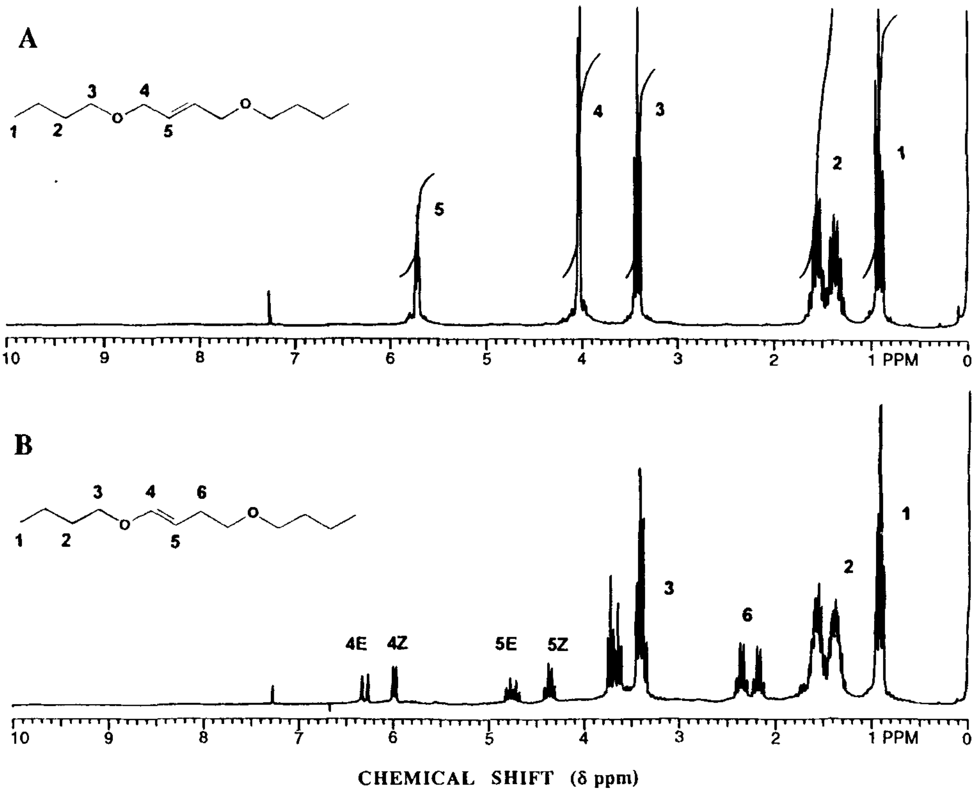
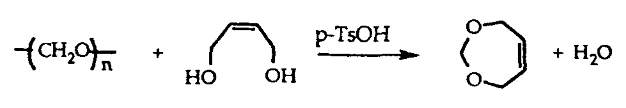


FIG. 1. ^{1}H-NMR spectra (A) before and (B) after the isomerization of 1,4-dibutoxy-2-butene (**IIa**) at 135°C in the presence of *t*-BuOK.

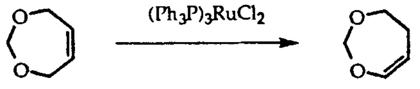
and the 2-butene group were simultaneously isomerized in the presence of $(Ph_3P)_3RuCl_2$ to give the trifunctional enol ether monomer **IVa**. **IVa** was obtained as a mixture of isomers due to *cis-trans* configurations at each of the three double bonds. In all cases with the linear enol ethers **Ie–IVe**, no attempt was made to separate the individual isomers. Rather, the isomeric mixture was carried forward into the polymerization studies.

In 1949 Copenhaver and Bigelow [9] reported that the unsaturated cyclic acetal (5,6-dihydro-1,3-dioxepin) **Va** can be easily prepared as shown in Eq. 6 from commercially available *cis*-2-butene-1,4-diol by acid-catalyzed condensation with paraformaldehyde. Best yields (25%) were obtained using an azeotroping agent for removal of the water formed during the reaction and by neutralizing the acid prior to distillation of the product [10].



Va eq. 6

Va was readily isomerized in the presence of $(Ph_3P)_3RuCl_2$ to give the cyclic enol ether **Ve** as shown in Eq. (7).



Ve eq. 7

Figure 2 shows the ^{1}H-NMR spectra of the reaction mixture before and after isomerization of **Va** to **Ve** at 115°C in the presence of 0.05 mol% $(Ph_3P)_3RuCl_2$. The double bond peak at δ 5.8 ppm completely disappears, and a new peak of vinyl ether double bond proton peak at δ 6.4 ppm appears due to the formation of cyclic vinyl ether. This isomerization was rapid and was complete after heating for 30 minutes at 115°C. Several other kinds of 2-substituted 5,6-dihydro-1,3-dioxepins were also prepared using different aldehydes including succinic dialdehyde, cyclohexane carboxaldehyde, benzaldehyde, and terephthaldehyde. Although the isomerizations of these compounds have been reported by other laboratories [11, 12], in our hands the isomerizations gave either low yields or did not take place. For example, the ruthenium-catalyzed isomerization of **VIa** to **VIe** required 1 week at

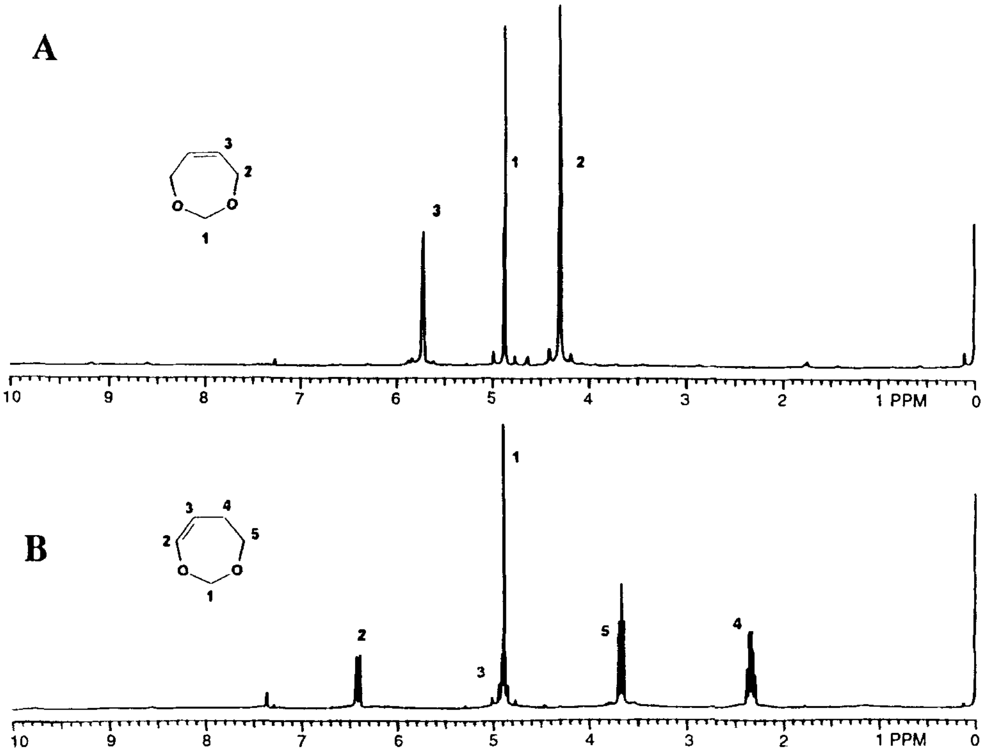
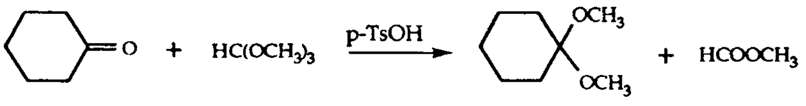


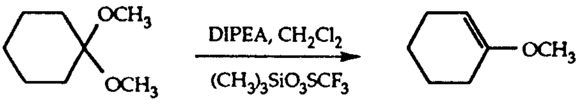
FIG. 2. ^{1}H-NMR spectra (A) before and (B) after the isomerization of 4,7-dihydrodioxepin (**Va**) at 115°C in the presence of $(Ph_3P)_3RuCl_2$.

135°C. At higher temperatures, oxidation reactions dominate, and many undesirable by-products are formed.

Lastly, cyclic enol ether monomer **VIIe** was prepared using the following sequence of reactions.



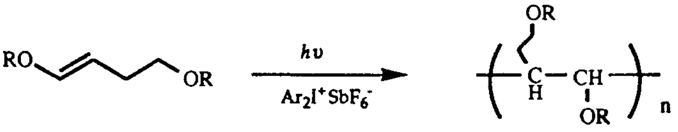
eq. 8



VIIe eq. 9

Cationic Photopolymerization of Open-Chain Enol Ethers

In recent years we have studied the reactivity of vinyl, 1-propenyl, and 1-butenyl ethers [2-5] in photoinitiated cationic polymerization. In these investigations we have employed onium salts, such as diaryliodonium salts, as stable and latent sources of cation-radicals and Brønsted acids which can be generated by photolysis. Typically, such polymerizations proceed very rapidly and exothermically. Preliminary investigations showed that the open-chain and cyclic monomers prepared and described above undergo facile photoinitiated cationic polymerization when irradiated with ultraviolet light in the presence of such onium salt photoinitiators. For example, the polymerization of open-chain enol ether monomers **IIe-IVe** takes place by a conventional cationic process as depicted in Eq. (10).



eq. 10

The initial investigation of the cationic photopolymerization of the monomers was carried out by spreading a monomer containing 0.5 mol% (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10) onto a slide glass and irradiating the monomer mixture using a Fusion Systems Inc. Laboratory UV Cure Processor. This apparatus consisted of a microwave-activated 300-W UV lamp configured perpendicular to the travel of the conveyor belt and mounted at a distance of 10 cm from the belt. While the monofunctional open-chain vinyl ether monomers **IIe** and **IIIe** became viscous after a 1-2 second irradiation, under the same conditions the trifunctional monomer, **IVe**, gave a colorless solid film which was not soluble in chloroform due to crosslinking.

In order to obtain more quantitative information, cationic photopolymerizations of the monomers were carried out using two different analytical techniques: differential scanning photocalorimetry (DSP) and Fourier transform real-time infrared analysis (FT-RTIR). Shown in Fig. 3 is a DSP profile of the polymerizations of monomer **Ie**, which is a typical example of a 1-propenyl, and open-chain enol ether **IIe**. In these and all the other polymerization studies, 0.5 mol% of (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate was used as the photoinitiator. Sharp peaks obtained immediately after opening the shutter indicate rapid, exothermic polymerizations in both cases. However, since the peak of the exothermic polymerization of **Ie** is reached after about 0.2 minute irradiation, while that of **IIe** is reached after 0.3 minute, 1-propenyl ether **Ie** is judged to be more reactive than **IIe**.

An FT-RTIR comparison of the cationic photopolymerization of four different monomers, 1-propenyl ether (**Ie**), dimethoxy-1-butene (**IIe**), dibutoxy-1-butene (**IIIe**), and trifunctional monomer (**IVe**), is given in Fig. 4. For the monofunctional monomers, **Ie** shows the highest reactivity. For the two open-chain enol ethers **IIe** and **IIIe**, both the reactivity and the conversion appear to decrease slightly as the size of β-substituent on the double bond increases. The trifunctional monomer **IVe** undergoes a comparatively rapid initial polymerization but attains a rather low conversion (60%) due to crosslinking. The above differences in the polymerization rates can be rationalized by considering the relative steric hindrance due to the size of both the alkoxy group and the β-substituent about the enol ether double bond.

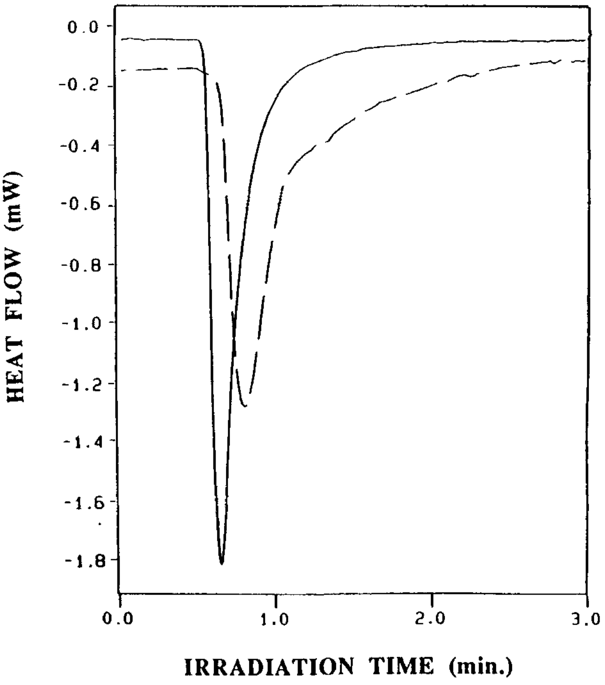


FIG. 3. Differential scanning photocalorimetric (DSP) study of the photopolymerization of propenyl ethers containing 0.5 mol% IOC 10: (—) **Ie** and (- -) **IIe**.

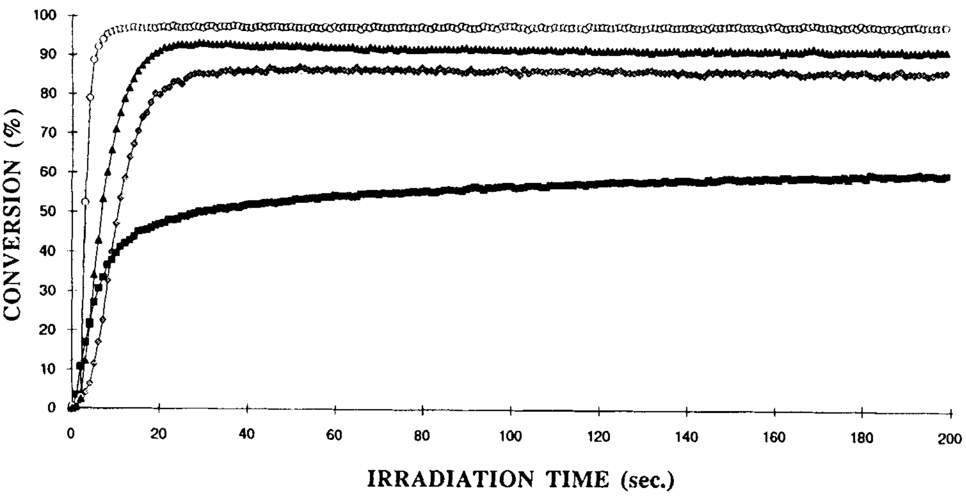
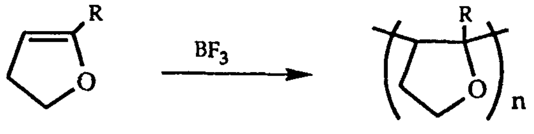


FIG. 4. FT-RTIR comparison of the photopolymerizations of (○) **Ie**, (◇) **IIe**, (△) **IIIe**, and (■) **IVe** in the presence of 0.5 mol% IOC 10.

Higashimura and coworkers [13, 14] compared the reactivities of the vinyl and β-substituted vinyl ethers in copolymerization. They observed that *cis*-1-propenyl ethers were more reactive than vinyl ethers, and that *trans*-1-propenyl ethers and vinyl ethers exhibited comparable reactivity. However, when the β-substituted alkyl group was very bulky, such as *t*-butyl, the reactivity of the *cis*-1-propenyl ether was lower than that of the corresponding vinyl ethers. Similar results were obtained for alkyl ethers with longer chain β-substituents [15]. The results of these workers appear to correlate well with ours.

Photopolymerization of Cyclic Enol Ethers

It was known [16, 17] that cyclic enol ethers such as 2,3-dihydrofuran and 5-methyl-2,3-dihydrofuran polymerize in the presence of cationic initiators to give linear polymers with heterocyclic rings in the repeat units, as, for example, shown in Eq. (11).



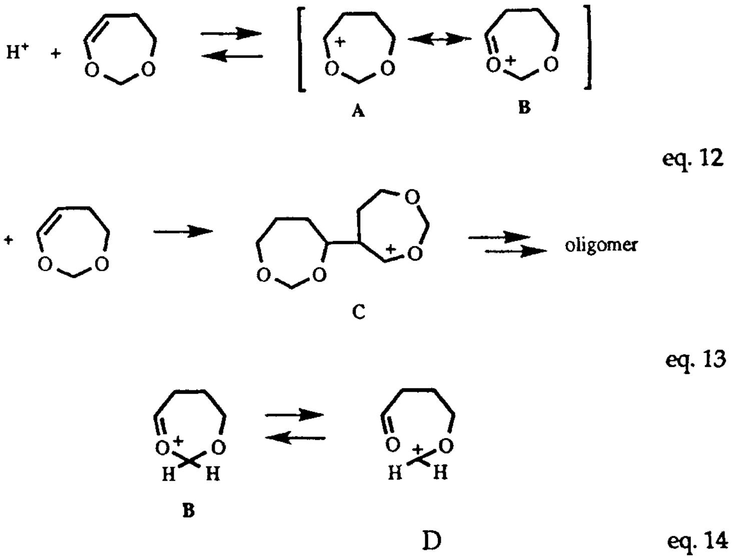
eq. 11

Yokoyama and Hall [18] reported that 5,6-dihydro-1,3-dioxepin (**Ve**) could not be homopolymerized via a free-radical polymerization but oligomerized via cationic ring-opening polymerization. Hellermann and Schulz [19] reported that the molecular weight of the polymer from **Ve** increased with decreasing temperature and concentration of the initiator: BF_3–etherate. When the cationic photopolymerization of **Ve** was carried out using the above-described Fusion System apparatus, a viscous liquid polymer was obtained. Under the same conditions the polymerization of the well-known monomer 2,3-dihydropyran give a solid, high molecular weight film of polymer. The polymer from **Ve** was characterized using ^{1}H-NMR and GPC. ^{1}H-NMR spectrum shows a prominent aldehyde resonance at δ 9.6–9.7 ppm, and the GPC indicates that the product consists primarily of a trimer. Possible explanations for the behavior of **Ve** can be drawn from a consideration of the mechanism shown in Scheme 2.

First, the *cis* enol ether double bond of **Ve** is sterically hindered and possesses considerable strain due to the seven-membered ring. The presence of the seven-membered ring prevents bond rotations from taking place which would relieve steric hindrance from intermediates such as **C**. Further, as shown in Eq. (14), ring-opening of protonated or alkylated intermediates such as **B** can give rise to aldehyde groups which may terminate chain growth. This ring-opening side-reaction is driven by relief of ring strain.

Comparing the rates of cationic photopolymerization of **Ve** and 2,2′-trimethylene bis(4,5-dihydro-1,3-dioxepin) (**VIe**) using FT-RTIR, it was observed that latter monomer was much more rapid. However, like **Ve**, the ^{1}H-NMR spectra of **VIe** after photopolymerization shows a large aldehyde resonance at δ 9.6–9.7 ppm. From these results it appears that side reactions of the type described above leading to the formation of aldehydes is also occurring in the case of this monomer. In fact, this side reaction would be expected to play a greater role in this case due to the stabilization of cation **D** by the 2-alkyl substituent.

Initial screening studies of the photopolymerizations of 2,3-dihydropyran and 1-methoxy-1-cyclohexene (**VIIe**) showed that these two monomers behaved quite differently. Whereas 2,3-dihydropyran underwent facile polymerization to high mo-



SCHEME 2.

lecular weight polymer, **VIIe** showed no tendency to polymerize. The cationic polymerization of 2,3-dihydropyran using Friedel-Crafts catalysts has been reported previously [19]. IR spectra showed that besides tetrahydropyran units there also exist repeating units with free aldehyde groups due to ring opening [20]. Thus, 2,3-dihydropyran behaves like a typical linear, β-substituted, open-chain enol ether. Figure 5 shows the ^{1}H-NMR spectra of 2,3-dihydropyran before and after photoinduced cationic polymerization. The protons of the carbon—carbon double bond at δ 6.4 ppm disappeared completely and were replaced by broad bands due to the polymer which was formed. In contrast, FT-RTIR studies confirmed that **VIIe** does not polymerize under these conditions. **VIIe** is an α,β-disubstituted enol ether and is consequently more sterically hindered than 2,3-dihydropyran. It is well known that the reactivity of α- and β-substituted vinyl ethers are influenced electronically and sterically by the substituents; as the substituents become bulky, steric hindrance becomes the dominant factor in determining the reactivity [21]. In the case of **VIIe**, due to steric hindrance, this monomer prefers to undergo side reactions rather than polymerize.

Shown in Fig. 6 is an FT-RTIR comparison of the reactivity of various open-chain and cyclic enol ether monomers under UV irradiation in the presence of 0.5 mol% (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate. It is interesting to note that all the monomers are very reactive. However, whereas monomer **IIIe**

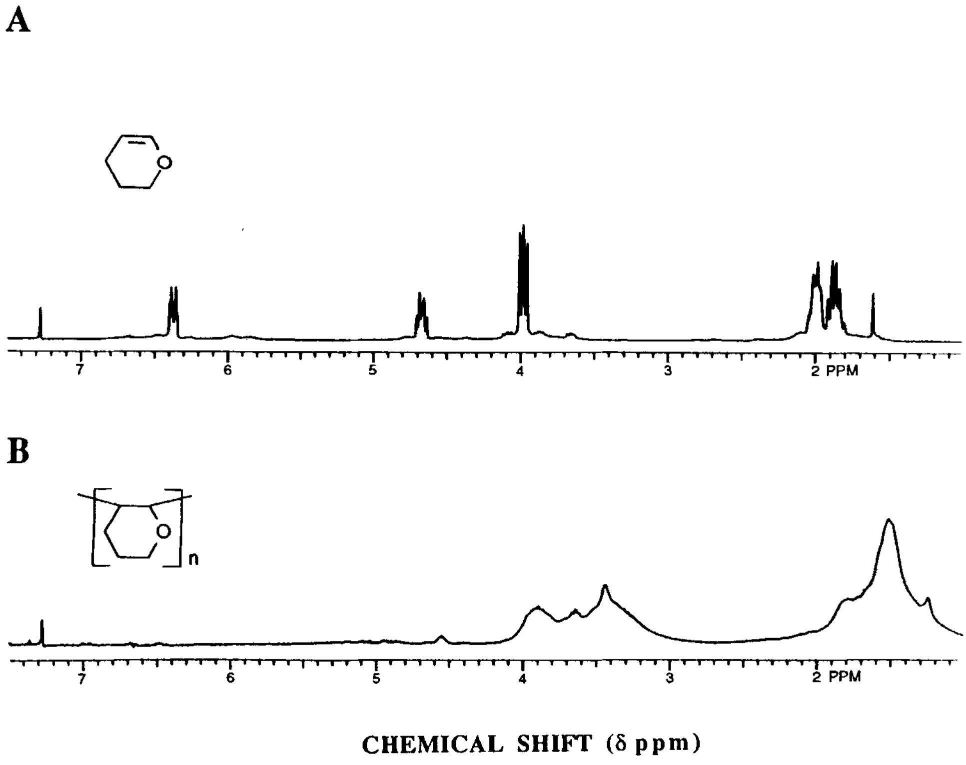


FIG. 5. ^{1}H-NMR spectra (A) before and (B) after the polymerization of 2,3-dihydropyran in the presence of 0.5 mol% IOC 10.

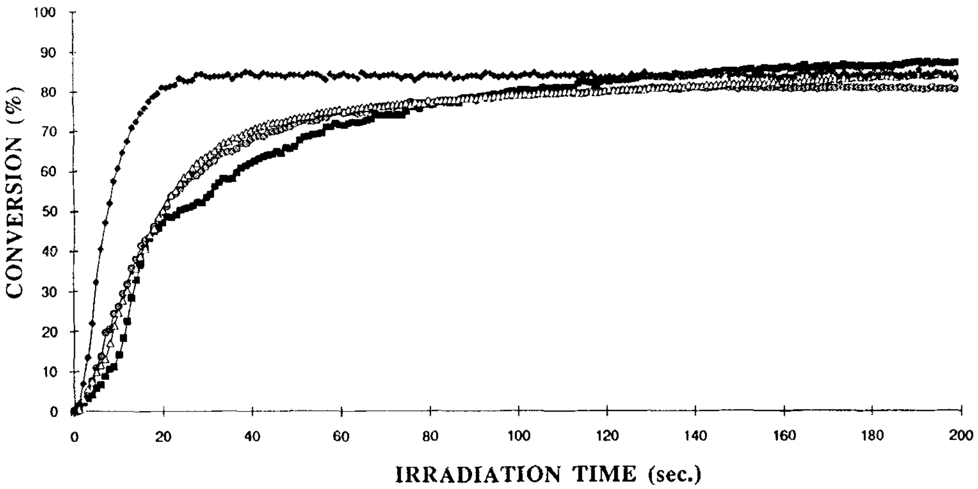


FIG. 6. FT-RTIR comparison of the photopolymerizations of (◇) **IIIe**, (○) 2,3-dihydropyran, (△) **VIIe**, and (■) **Ve** in the presence of 0.5 mol% IOC 10.

and 2,3-dihydropyran give high polymers, cyclic monomers **Ve** and **VIIe** undergo inefficient polymerization due to side reactions. Of the monomers shown in Fig. 6, open-chain monomer **IIIe** is the most reactive.

CONCLUSIONS

Open-chain and cyclic enol ether monomers were readily prepared in good yields from allyl ether precursors by either the strong base or ruthenium-complex-catalyzed isomerizations. The open-chain enol ether monomers undergo facile and rapid UV-induced photopolymerization using diaryliodonium salt photoinitiators. The polymerization rate and conversion were dependent on the presence and steric bulk of the substituents. We also briefly studied the photopolymerization of cyclic enol ethers. While the photopolymerization of 2,3-dihydropyran yields high polymers, 4,5-dihydro-1,3-dioxepin and 1-methoxy-1-cyclohexene, respectively, undergo oligomerization and no polymerization. The differences observed in the polymerizability of cyclic enol ethers appears to be mainly due to steric effects.

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