SYNTHESIS AND CATIONIC PHOTOPOLYMERIZATION OF OLIGOMERS BEARING TERMINAL AND INTERNAL ENOL ETHER GROUPS

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ABSTRACT

The synthesis of multifunctional oligomers containing cationically polymerizable enol ether groups at the terminal positions and along the backbone was achieved through the use of simple, straightforward reaction chemistry. This involves first, the etherification of 2-butene-1,4-diol with α,ω-dibromoalkanes or an alkyl ether linking group followed by an end capping reaction with allyl bromide. Thereafter, the base catalyzed isomerization of the allylic double bonds was carried out to afford the desired enol ether oligomers. The cationic photopolymerizations of these oligomers were studied using onium salt photoinitiators. While crosslinked polymers were obtained in all cases, the rates of polymerization were found to be strongly dependent on the character of the linking group.

Key Words: Cationic photopolymerization; Enol ethers; Enol ether oligomers.

INTRODUCTION

The development of efficient, high quantum yield onium salt photoinitiators for photoinitiated cationic polymerization has resulted in the rapid adoption of this chemistry for many practical applications including photocurable printing inks, adhesives and coatings for wood, plastics and metals [1] Although considerable

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487

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efforts are in progress to develop still other new classes of cationic photoinitiators [2], the primary direction of research in this laboratory in recent years has been in the design and synthesis of novel cationically photopolymerizable monomers and oligomers. To this end, we have reported the preparation of several new classes of mono- and multifunctional epoxide [3], 1-propenyl ether [4], 1-butenyl ether [5], ketene acetal [6], and allene ether [7], monomers.

In the applications cited above, the main objective of the photopolymerization is to achieve the conversion of a bulk liquid monomer or oligomer to a solid, cross-linked polymer as rapidly and with as little expenditure of energy as possible. From a practical point of view, this requires at the outset the selection of monomers or oligomers that incorporate the most reactive functional groups known in cationic polymerization. In addition, such polymerizable substrates should be multifunctional to maximize the crosslinking efficiency and to ensure complete incorporation of the substrate into the crosslinked matrix polymer during photopolymerization. Additionally, the polymerizable substrate should be nonvolatile, nontoxic, colorless and odorless, possess a relatively low viscosity and high adhesion to the substrate. To meet these criteria, reactive oligomers are often employed in commercial applications [8]. While the strategy of the use of photocurable reactive oligomers is often applied in free radical photopolymerizations, little work has been directed towards the development of reactive oligomers polymerizable by photocationic methods.

In this paper, we describe the preparation of a series of liquid oligomers that bear highly reactive enol ether groups. The results of the study of the photopolymerizations of these oligomers using typical onium salt cationic photoinitiators are also presented.

EXPERIMENTAL

Materials and Methods

Allyl bromide, methyl iodide, *cis*-2-butene-1,4-diol, the α,ω-dibromoalkanes and ethers, as well as the solvents and reagents were used as received from the Aldrich Chemical Company (St Louis, MO). Triethylene glycol divinyl ether (DVE-3) was received as a gift from International Specialties Products Company (Wayne, NJ). The photoinitiator, (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (**IOC10**) was prepared as described previously [9]. Routine infrared spectra were obtained using a Midac-M1300 Fourier transform Infrared spectrometer. ^{1}H-NMR experiments were carried out using either a Varian XL-200 (200 MHz) or an Inova-300 (300 MHz) spectrometer at room temperature using CDCl$_3$ as the solvent and employing tetramethylsilane (TMS) as an internal standard. Gel Permeation Chromatography (GPC) carried out with the aid of a Hewlett Packard, Gel Permeation Chromatograph equipped with a refractive index detector and a μ-styragel column (particle size 5 μm, mixed 24–34 Å pores). THF was used as the eluent at a flow rate of 1.0 mL/min. Elemental analyses (EA) were performed by Atlantic Microlabs, Norcross, GA.

Synthesis of Monomers and Model Compounds

The following representative general experimental procedures are given for the oligomers prepared during the course of this work. Due to the presence of multiple isomers in all cases and the resulting complexity of the ^{1}H-NMR spectra, only the chemical shifts of key functional groups are reported. Coupling constants for the resonances were not reported.

Synthesis of Model Compound IIa

Into a 100 mL round-bottom two-neck round bottom flask equipped with a condenser and a thermometer were placed 10 g (0.11 mol) of *cis*-2-butene-1,4-diol, 36 g (0.3 mol) of allyl bromide 50 mL of toluene and 11 g (0.27 mol, 2.5 equivalent) of sodium hydroxide. There were added 1.3 g of tetra-n-butyl-ammonium bromide as a phase transfer catalyst and the mixture slowly heated to reflux and maintained at that temperature for 20 hours. The reaction mixture was cooled and poured into 100 mL of distilled water. The organic layer was separated and the aqueous layer was extracted with fresh toluene. The combined organic layers were washed with aqueous 0.15 N HCl and then with an aqueous solution of Na_2CO_3 to remove traces of acid. The organic phase was dried over CaH_2 and the excess allyl bromide and toluene were removed using a rotary evaporator. The product IIa was isolated as a pale yellow viscous oil (yield 69%).

The same reaction conditions were employed for the synthesis of all the oligomeric precursors (IVa-VIIa).

Isomerizations of IIa, IVa-VIIa

Into a 100 mL round-bottom-flask fitted with a magnetic stirrer, reflux condenser and nitrogen inlet were placed 5.0 g of the respective synthesized oligomer, 3.0 g of potassium-t-butoxide and 25 mL of DMSO. The reaction mixture was stirred at 130°C for 1 hour. After cooling to room temperature, the reaction mixture was poured into 100 mL of water and extracted with Et_2O. The organic layer was then washed three times with distilled water to remove DMSO, and then stripped of solvent using a rotary evaporator. The structures and yields of the isomerized oligomers are given in Table 1.

Photopolymerization Studies Using Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR)

Cationic photopolymerizations of the enol ether oligomers were monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). A Midac M-1300 FTIR spectrometer (Midac Corp., Irvine, CA) equipped with a liquid nitrogen cooled mercury-cadmium-telluride detector was used. The instrument was fitted

with a UVEXS Model SCU-110 mercury arc lamp (Sunyvale, CA) equipped with a flexible liquid optic wand. The end of this wand was directed at an incident angle of 45° onto the sample window and the distance from the window varied from 6–18 cm to control the light intensity. UV light intensities were measured with the aid of a UV Process Supply, Inc. radiometer (Chicago, IL) at the sample window. The light intensity used in these studies was 30 mW/cm^2 (1800 mJ/cm^{2}sec).

Photopolymerizations were carried out at room temperature in solutions of the epoxide monomers containing various concentrations (in wt%) of **IOC10** as the photoinitiator. Irradiations were carried out using broadband UV irradiation. The monomer/photoinitiator solutions were coated onto 12 μm oriented and corona treated polypropylene films (General Electric Capacitor Dept., Hudson Falls, NY), covered with an identical polypropylene film, and then mounted in 5 cm × 5 cm slide frames. The thickness of the liquid monomer films was estimated at 10–25 μm. Infrared spectra were collected at a rate of 1 spectrum per second using LabCalc, data acquisition software obtained from the Galactic Industries Corp. (Salem, NH) and were processed using GRAMS-386 software from the same company. During irradiation, the decrease in the absorbance due to the internal enol ether groups at 1643 cm^{-1} and the terminal 1-propenyl ether groups at 1666 cm^{-1} were simultaneously monitored. Data analysis and subsequent conversion versus time plots were obtained using Excel (Microsoft Corp., Redmond, WA) software.

RESULTS AND DISCUSSION

Among the most reactive monomers known to polymerize by a cationic chain mechanism are vinyl ethers [10]. Work in this laboratory has shown that multifunctional vinyl ethers undergo exceedingly rapid photoinitiated cationic polymerization using diaryliodonium and triarylsulfonium salt photoinitiators [11]. In several papers [12, 13, 14], we have described the synthesis of analogous types of highly reactive enol ether monomers, specifically, 1-propenyl ethers by two simple, direct preparative methods involving the isomerization of the corresponding allyl ethers. This chemistry is depicted in Scheme 1.

Allyl ethers can be prepared in quantitative yields by the tetraalkylammonium bromide (TBAB) catalyzed Williamson ether synthesis (Equation 1). These ethers can be quantitatively isomerized to 1-propenyl ethers by heating for a short time at 120–130°C in the presence of potassium tert-butoxide and dimethylsulfoxide (Equation 2). This method generally affords mainly the *cis*-1-propenyl ether. Alternatively, catalytic isomerization of an allyl ether can be achieved by treatment with tristriphenylphosphineruthenium(I) dichloride (Equation 3). Under these conditions, a mixture of *cis*- and *trans*-1-propenyl ether isomers is usually obtained.
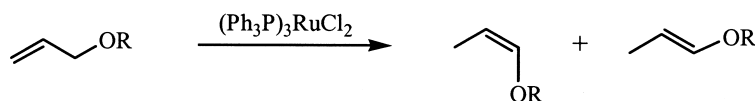
A further development in this chemistry showed that the same synthetic methodology could be applied to compounds bearing internal (i.e., non-terminal)
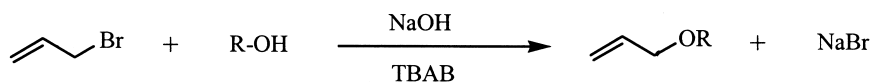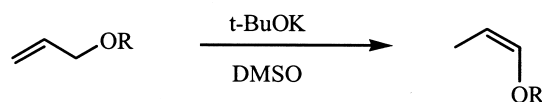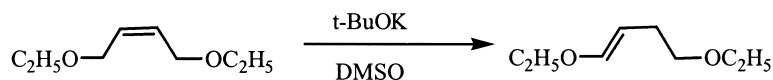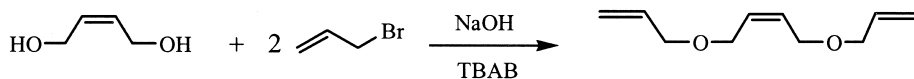
Scheme 1.

allylic ethers [15]. For example, the isomerization of the diethyl ether of *cis*-2-butene-1,4 diol was readily carried out to give the desired enol ether, **I**, in good yield (Equation 4). Moreover, we were able to show that this and other similar enol ether monomers exhibited excellent reactivity in photoinitiated cationic polymerization.


Based on these results, it was decided to attempt to prepare oligomeric polyethers bearing internal allylic ether groups and to carry out their isomerizations to the corresponding oligomeric enol ethers. The synthetic strategy we employed (Scheme 2) was based on the readily available and inexpensive *cis*-2-butene-1,4-diol which is prepared by the condensation of acetylene with formaldehyde followed by platinum catalyzed hydrogenation of the resulting 2-butyne-1,4-diol.
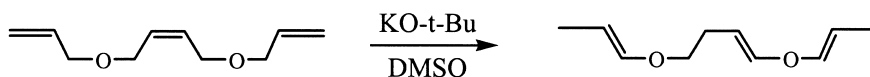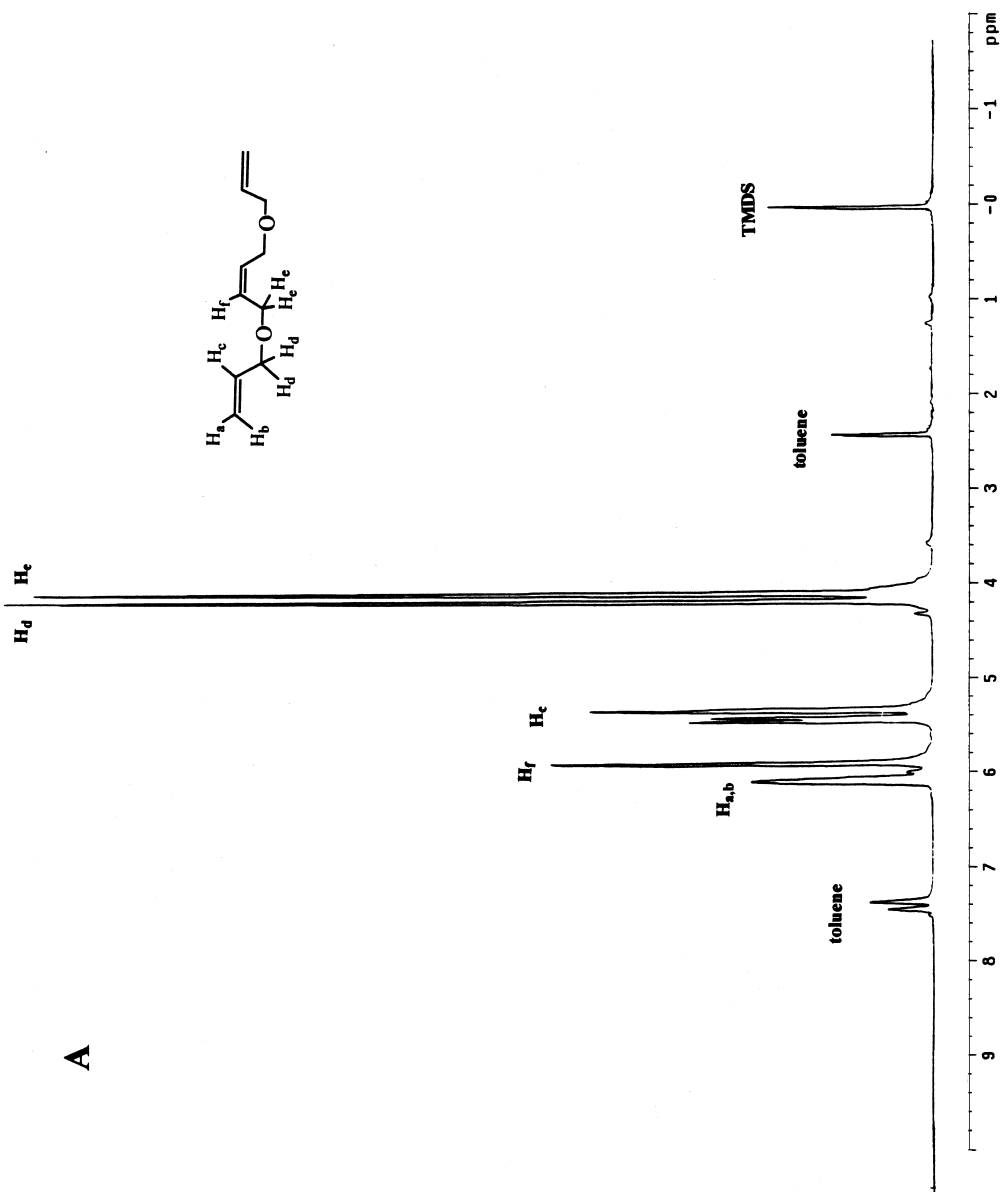

Scheme 2.

Figure 1. ¹H-NMR spectrum of IIa A before isomerization and B after isomerization.
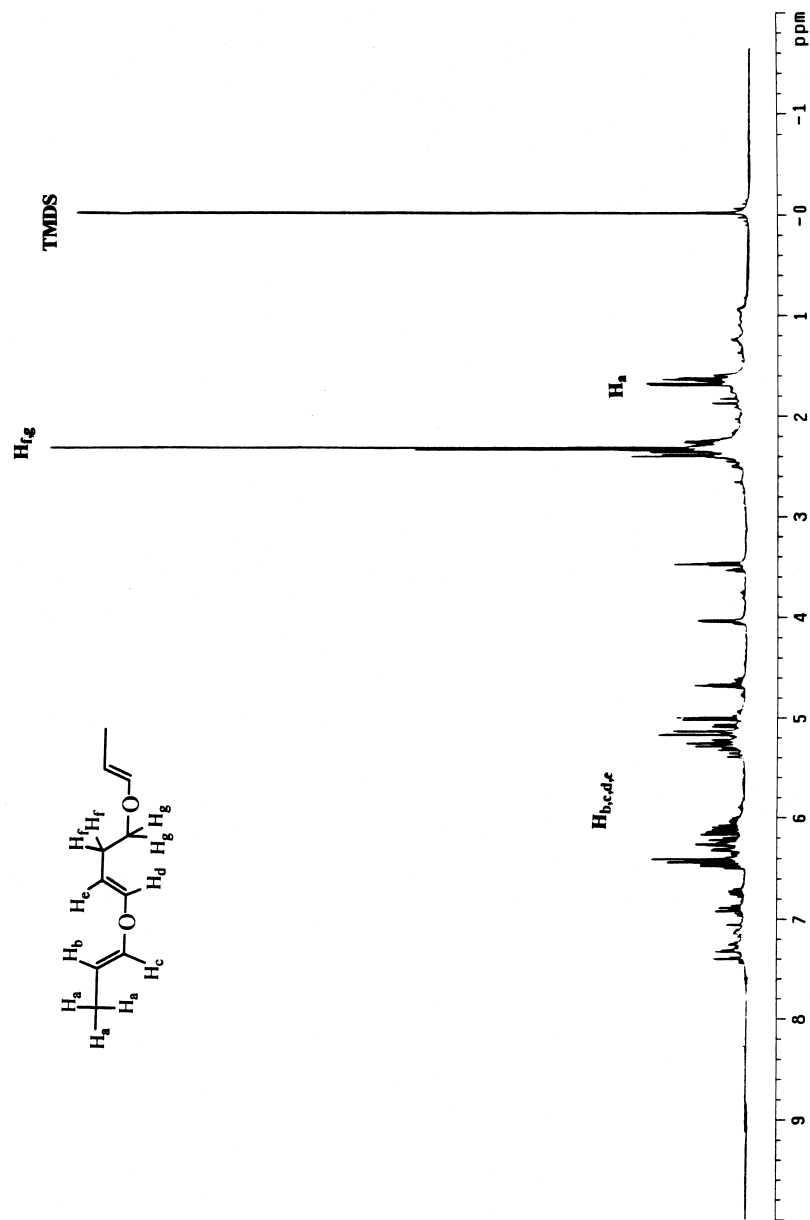
B

Figure 1. Continued

This process yields predominantly the *cis*-2-butene-1,4-diol isomer. The Williamson ether condensation of *cis*-2-butene-1,4-diol with a two-fold stoichiometric amount of allyl bromide was carried out under phase transfer conditions in the presence of TBAB as a catalyst (Equation 5) to give model compound **IIa**.

Subsequent base catalyzed isomerization of the internal and terminal allylic double bonds (Equation 6) afforded the desired oligomer, **IIb**, containing three enol ether groups. The progress of the isomerization reaction was readily monitored using ^{1}H-NMR by following the simultaneous decrease in the resonance (5.63 ppm) due to protons of the double bond of the 1,4-dioxy-2-butene units as the *cis* and *trans* enol ether double bonds (*trans*, 4.60, 6.18; *cis*, 4.23, 5.85 ppm) of **IIb** are formed. Figure 1 shows the ^{1}H-NMR spectra of **IIa** and **IIb** together with the assignments of the salient bands. While equation 6 depicts only the *trans-trans-trans* isomer, as the NMR clearly shows, the mixture consists of six isomers with all possible *cis* and *trans* double bond configurations.
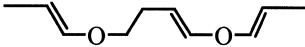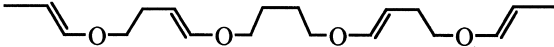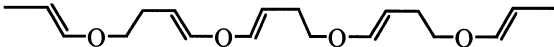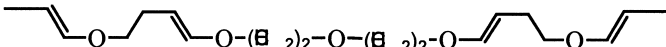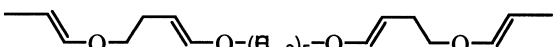
Based on these results, the stoichiometric condensation of *cis*-2-butene-1,4-diol with 1,4-dibromobutane was carried out to give an oligomer **IIIa** of approximately five repeat units. IR spectroscopy (3000–3500 cm^{-1}) revealed that the oligomer was hydroxyl terminated. Isomerization under basic conditions proceeded as described above to give the corresponding enol ether polymer **IIIb**. Attempts to photopolymerize this oligomer showed that it displayed very sluggish reactivity under the usual polymerization conditions. As cationic photopolymerization proceeds, these groups disappear. One possible explanation for the poor reactivity of **IIIb** is that the hydroxyl groups undergo a well-known acid catalyzed addition to the enol ether groups in the presence of acid catalysts. This condensation reaction proceeds preferentially instead of cationic chain polymerization in the case of enol ether monomers bearing hydroxyl groups [16]. The photopolymerization reactivity of oligomer **IIIb** was markedly improved by capping it by reaction with methyl iodide.

To avoid this difficulty, a series of low molecular weight oligomers were prepared by the condensation of a 2:1 molar ratio of *cis*-2-butene-1,4-diol and various α,ω-dibromoalkanes or α,ω-dibromoalkenes. Using a one-pot, two-step procedure, the resulting diol was capped with allyl bromide resulting in the generation of the oligomeric precursors. Further reaction to simultaneously isomerize the internal and terminal allylic double bonds was carried out in the presence of potassium t-butoxide and DMSO to give the reactive oligomers shown in Table 1. The oligomers were isolated as pale yellow colored low viscosity liquids. Although the idealized structures shown in Table 1 depict the isomerization of the

$$H-\left[O-\diagup\!\!\diagup\!\!\diagdown\!\!-O-(CH_2)_4\right]_n OH \qquad\qquad H-\left[O-\diagup\!\!\diagdown\!\!\diagup-O-(CH_2)_4\right]_n OH$$

IIIa   **IIIb**

Scheme 3.

Table 1. Synthesis of Enol Ether Oligomers

Notation	Structure	Yield (%)
IIb		83
IVb		73
Vb		75
VIb		80
VIIb		68

internal double bonds as taking place only in one direction, migration of the double bonds occurs in both directions. In addition, both *cis* and *trans* enol ether double bonds are formed at each enol ether site. This leads to a large number of isomeric structures for each oligomer shown in Table 1. For example, there are 96 isomers of tetrafunctional oligomers **IVb**, **VIb,** and **VIIb** while in the case of pentafunctional oligomer **Vb**, 132 isomers are present. In Table 1, for the sake of simplicity, we have chosen to depict only one of the all *trans* substituted isomers for each oligomer. As a result of the presence of isomers, the ^{1}H-NMR spectra of the oligomers are very complex. Figure 2 gives the spectrum of **IVb**. Nevertheless, during isomerization the disappearance of the protons of the internal double bonds at 5.37 ppm as well as the methylene protons of both internal and terminal allyl groups at 3.82 and 3.95 respectively, together with the appearance of the methyl group resonances at 1.2 ppm are indicative of the formation of the desired enol ether oligomers.

Photopolymerization of Enol Ether Oligomers

The cationic photopolymerization of model oligomer **IIb** was carried out in the presence of 1.0% of (4-n-decyloxyphenyl)phenyliodonium hexafluroantimonate (IOC10).

The progress of the polymerization was monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). This analytical method consists of following the evolution of characteristic IR bands associated with the functional groups undergoing cationic photopolymerization [17, 18]. In the studies reported in this paper, the disappearance of the IR band of the internal enol ether double bonds at 1643 cm^{-1} and the terminal enol ether groups at 1666 were simultaneously monitored. The UV light intensity was kept low (30 mW/cm^2, 1500 mJ/cm^2
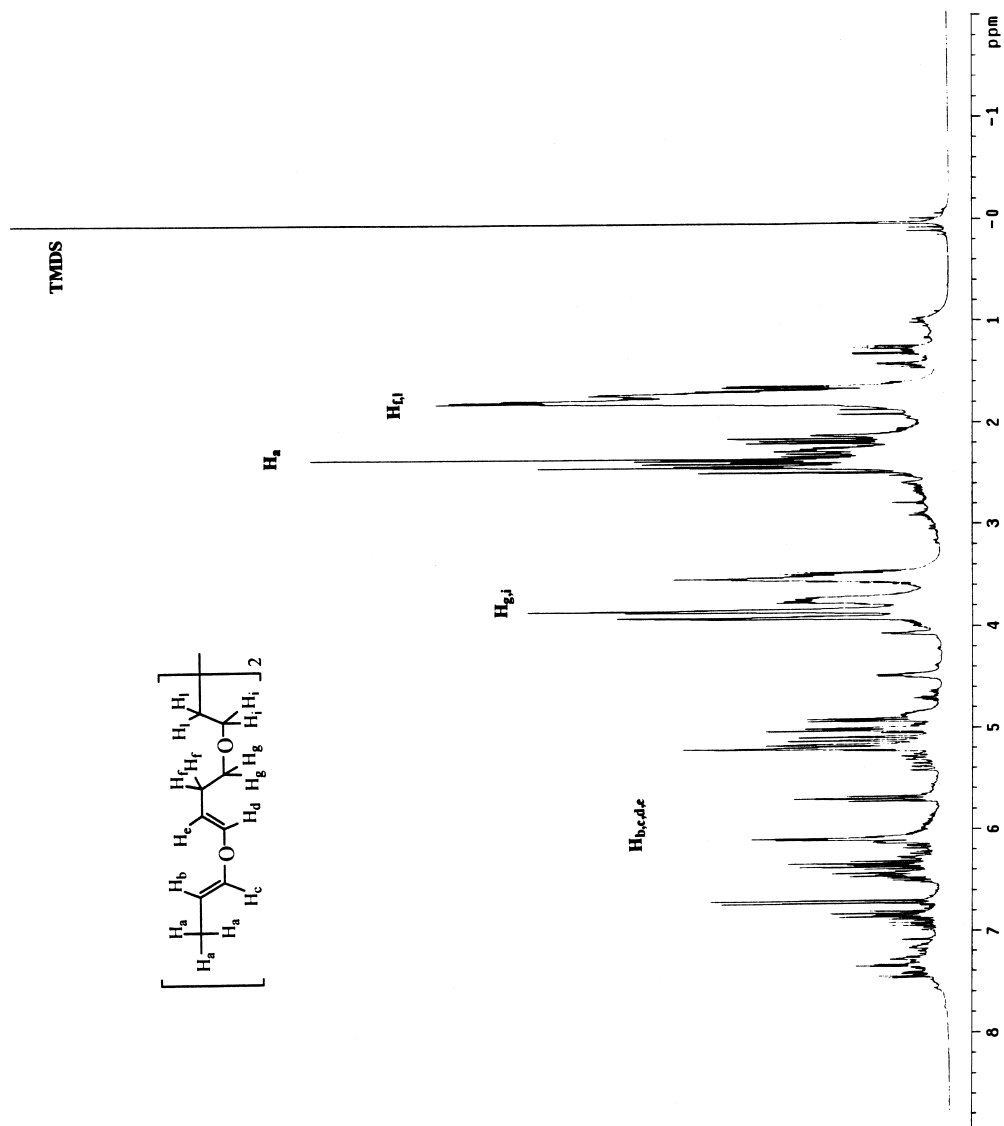
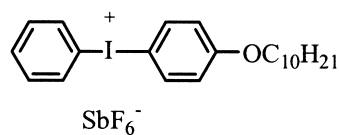*Figure 2.* ¹H-NMR spectrum of IVb in CDCl₃.

IOC10

Scheme 4.

min) to provide a slow enough polymerization rate to allow the reaction rates to be accurately and conveniently monitored. Figure 3 shows the results of the polymerization of model oligomer **IIb** under these conditions. The photopolymerization proceeds smoothly under these conditions with an ultimate enol ether double bond conversion after 200 seconds continuous irradiation of approximately 80%. It is interesting to note that both internal and terminal enol ether groups have nearly the same reactivity even though there are twice as many of the latter groups as the former and these would be expected to be somewhat less hindered.

FT-RTIR studies of the cationic photopolymerization of oligomers **IVb–VIIb** are respectively shown in Figures 4–7 in which the disappearances of both the terminal and internal enol ether groups are monitored. The results show a dependence on the structure of the linking group used in the oligomer. Oligomer **IVb** displays good reactivity with the terminal enol ether double bonds considerably more reactive than the internal ones. Similar results were observed in the
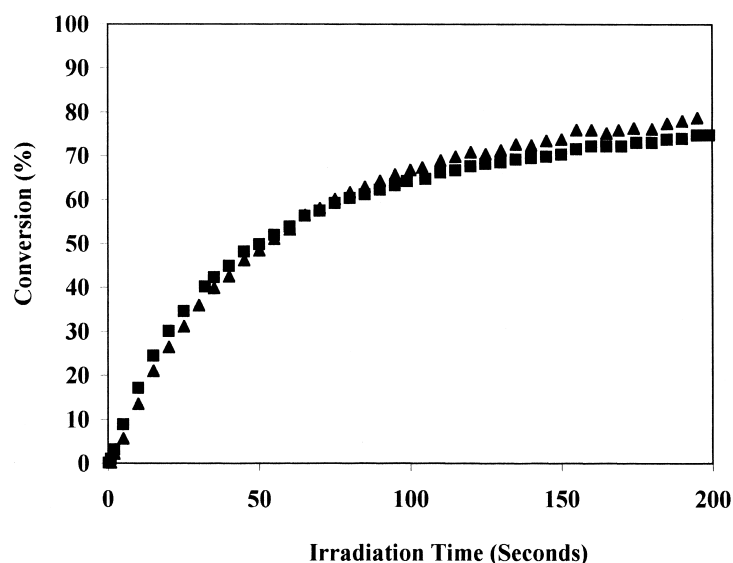
Figure 3. FT-RTIR study of the photopolymerization of model oligomer IIb in the presence of 1.0% IOC10. (▲) 1666 cm^{-1} band (terminal enol ether groups) and (■) 1643 cm^{-1} band (internal enol ether groups).
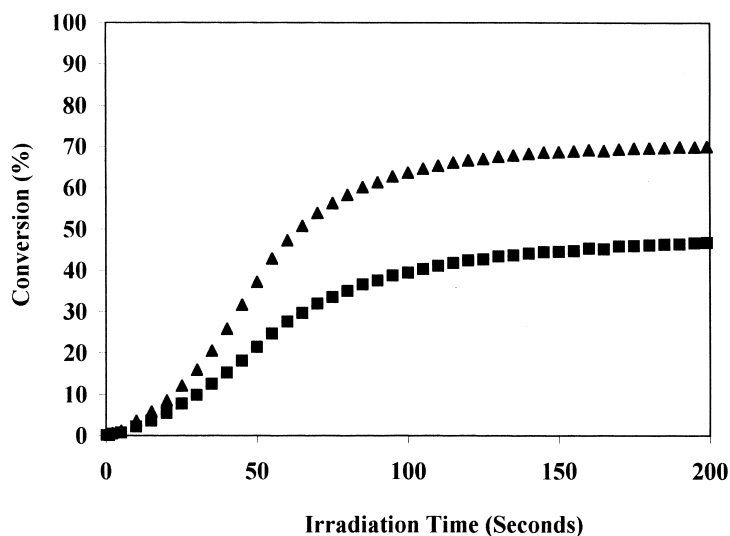
Figure 4. Photopolymerization of oligomer IVb using 1.0% IOC10 as photoinitiator. (▲) 1666 cm^{-1} band and (■) 1643 cm^{-1} band).

cases of oligomers **Vb** and **VIIb**. However, oligomer **VIb** containing the very flexible ether linkage displayed very high reactivity as may be noted by the rapid rise of the slope of the initial portion of the kinetic curve. In this case, as with model oligomer **IIb**, both types of enol ether groups in the molecule appear to have the same polymerization rates.
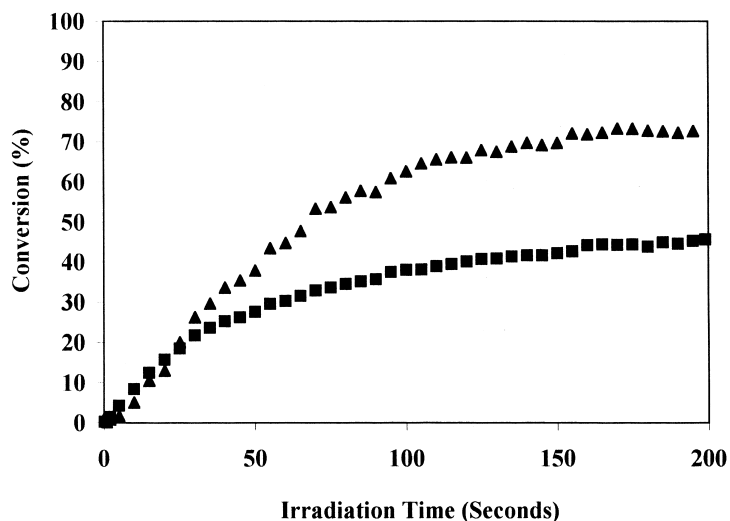

Figure 5. Study of the photopolymerization of Vb (▲) 1666 cm^{-1} band and (■) 1643 cm^{-1} band using 1.0% IOC10.
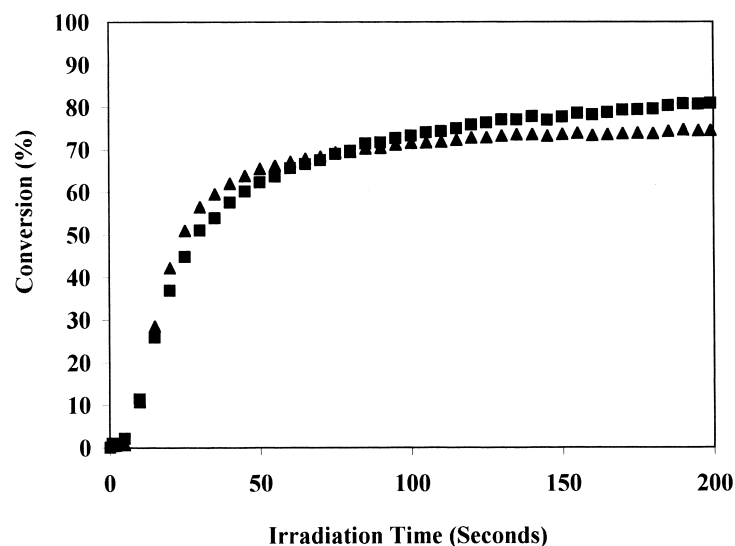
Figure 6. Study of the photopolymerization of VIb (▲) 1666 cm^{-1} band and (■) 1643 cm^{-1} band using 1.0% IOC10.

Figure 8 shows a study of the copolymerization of model oligomer **IIb** conducted in the presence of 50 wt% triethyleneglycol divinyl ether (DVE-3). A complimentary study of the photopolymerization of oligomer **IVb** and DVE-3 is depicted in Figure 9. The IR band at 1643 cm^{-1} for the internal enol ether groups of the oligomer was monitored. Very similar curves were obtained when the 1666
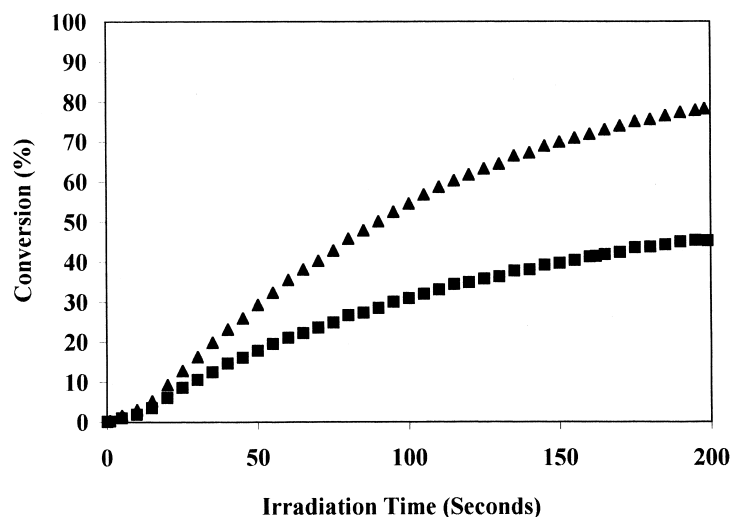

Figure 7. Study of the photopolymerization of VIIb (▲) 1666 cm^{-1} band and (■) 1643 cm^{-1} band using 1.0% IOC10.

Figure 8. Comparison of the photopolymerization of IIb alone (▲) and as a 50:50 w% mixture of IIb and DVE-3 (■). (1643 cm^{-1} band using 1.0% IOC10.)

cm^{-1} band was monitored. In both cases, the curves for the photopolymerization of the pure oligomers are also included for comparison. It may be noted that the polymerization rates of the oligomer are only slightly elevated in the presence of DVE-3. This may be due to a decrease in the viscosity of the medium. This further
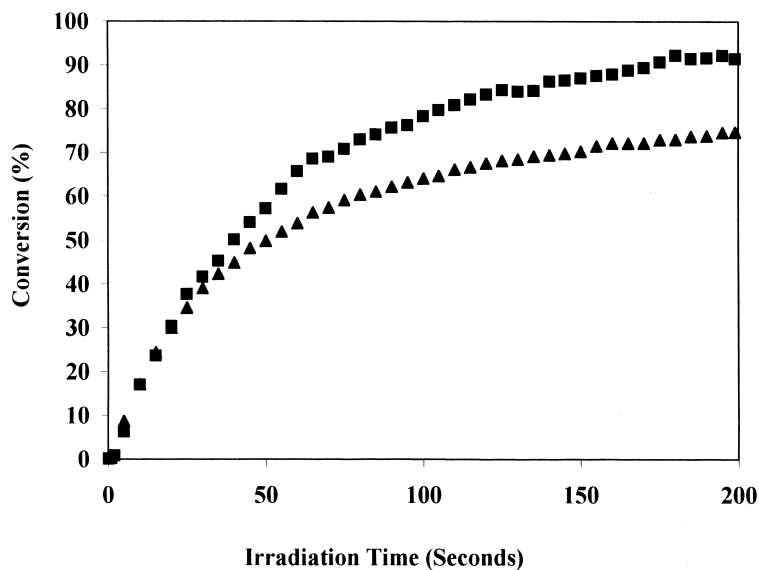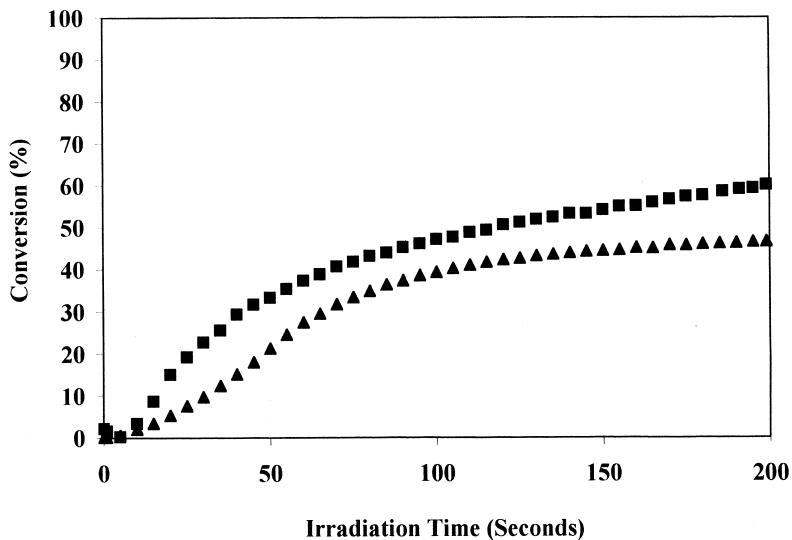
Figure 9. Comparison of the photopolymerization of IVb alone (▲) and as a 50:50 w% mixture of IVb and DVE-3 (■). (1643 cm^{-1} band using 1.0% IOC10.)

suggests that the reactivity of the 1,2-disubstituted enol ether and vinyl ether groups have similar reactivities. In a previous paper [19] we have already made this same observation.

CONCLUSION

A series of five reactive liquid oligomers bearing internal and terminal enol ether groups were prepared using a straightforward two-step synthetic approach from readily available and inexpensive starting materials. First, an oligomer containing terminal and internal allylic ethers was synthesized using the Williamson ether synthesis. Then the allylic double bonds were isomerized in the presence of a strong base to give the desired oligomers bearing both terminal and internal enol ether groups. We have shown that such oligomers readily undergo cationic photopolymerization. Those oligomers that incorporate a flexible linking group in their backbone appear to have higher reactivities and conversions of the double bonds during polymerization. We speculate that these effects are due to the high flexibility in the latter oligomers that results in a lowering of the glass transition temperature. This, in turn, delays the onset of vitrification during the photoinduced crosslinking reaction. The low volatility and high molecular weight together with low toxicity of the oligomers described here have many potential applications such as in coatings, printing inks, resists for micromachining and adhesives.

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