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Study of the Cationic Photopolymerization of Multifunctional Propenyl Ether Monomers

J. V. Crivello[a]; S. A. Bratslavsky[a]
[a] Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York

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STUDY OF THE CATIONIC PHOTOPOLYMERIZATION OF MULTIFUNCTIONAL PROPENYL ETHER MONOMERS

J. V. CRIVELLO* and S. A. BRATSLAVSKY

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180

Key Words: Propenyl ether monomers; Cationic photopolymerization; Diaryliodonium salt; Triarylsulfonium salt; Coating properties; Glycerol tripropenyl ether

ABSTRACT

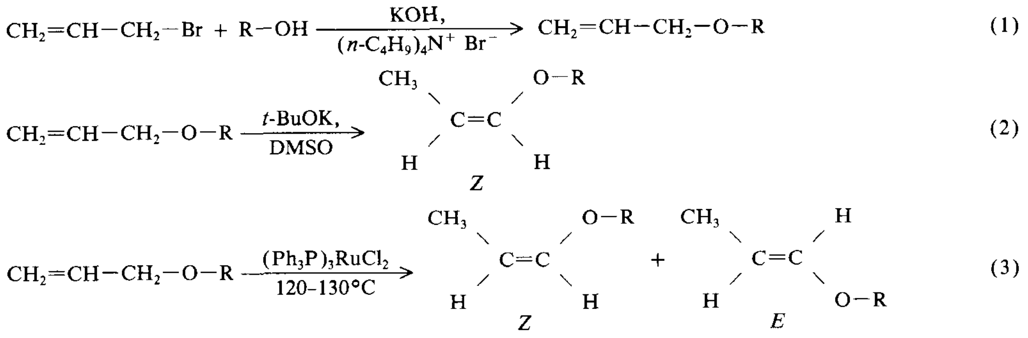
The cationic photopolymerization of a new biorenewable monomer, glycerol tripropenyl ether, was carried out to determine whether it is suitable for use in such thin film applications as photocurable inks, coatings, and adhesives. Studies of the photoinduced homopolymerization of this monomer and its copolymerizations with other mono- and difunctional propenyl ethers were conducted in the presence of diaryliodonium and triarylsulfonium salt initiators. The dependence of such properties as the gel fraction, hardness, impact, and adhesion of model coatings upon the structure and composition of the monomers used and on UV irradiation dose and postcure were investigated.

INTRODUCTION

Multifunctional monomers which can be rapidly and efficiently photopolymerized are of increasing technical importance. This is due to the widespread movement of industry away from the use of traditional solvent-based processes in compliance with the pressure applied by regulatory agencies to limit the amount of volatile organic compounds emitted into the atmosphere. Photocured multifunctional monomers produce highly crosslinked polymers which in most cases can duplicate or exceed the properties available by traditional solvent-borne thermal curing processes. In addition, photocuring provides further benefits such as reduced energy usage, higher throughput, lower capital investment, and smaller floor space requirements. Until recently, most investigations have been focused on commercially available acrylate and methacrylate monomers which can be polymerized under free-radical conditions [1–4]. In this laboratory we have been investigating the use of photoinduced cationic polymerizations and employing commercially available difunctional epoxide [5] and vinyl ether monomers [6]. At the same time, we have been engaged in the development of a general synthetic method for the preparation of a new series of multifunctional propenyl ether monomers as shown in Scheme 1 [7–9].

Mono-, di-, and multifunctional propenyl ethers were prepared by the straightforward strong base or $(Ph_3P)_3RuCl_2$-catalyzed rearrangement of the corresponding readily available allyl ethers. Base-catalyzed isomerization results in the exclusive formation of the *Z* isomer while the corresponding ruthenium-catalyzed reaction gives a mixture of *Z* and *E* isomers. The above synthetic methods are very general, and a wide variety of functional groups may be tolerated. Both natural and synthetic polyols were employed as substrates for these monomers.

Initial attempts to carry out the photoinitiated cationic polymerization of propenyl ether monomers showed they possess extremely high reactivity [7–10]. The relative order of reactivity of the propenyl ether monomers with respect to each other as well as to other cationically polymerizable monomers was investigated, using different types of diaryliodonium and triarylsulfonium salt photoinitiators. Propenyl ethers polymerized under photoinduced cationic conditions are, perhaps, the most reactive monomers yet prepared.



SCHEME 1.

For this paper an investigation was undertaken of the photoinduced cationic of the novel biorenewable monomer glycerol tripropenyl ether (GTPE) and its copolymerization with several other propenyl ether monomers. The properties of the resulting crosslinked polymers were measured and compared to determine their suitability for use in various practical applications.

EXPERIMENTAL

General

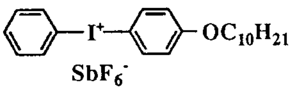
All the organic reagents were used as purchased from the Aldrich Chemical Co. without additional purification. Infrared spectra were obtained on a Buck Scientific Model 500 Spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5890 Gas Chromatograph equipped with a high performance capillary HP-1 (5% phenylmethyl silicone) column and a flame ionization detector. ^{1}H-NMR spectra were obtained using a Varian XL-200 MHz Spectrometer at room temperature in $CDCl_3$. Elemental analyses were performed by Quantitative Technologies, Inc., Bound Brook, New Jersey.

Synthesis of Propenyl Ether Monomers

The synthetic procedures and characteristics of the propenyl ether monomers used in this communication were described in detail previously [7]. All propenyl ethers were characterized by GC, ^{1}H-NMR, and elemental analyses after purification by fractional vacuum distillation. Table 1 shows the structures of the propenyl ether monomers used in this investigation.

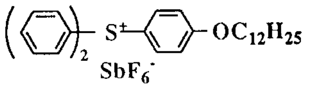
Photoinitiators

Diaryliodonium salt (IOC) and triarylsulfonium salt (SOC) were prepared as described [3, 4] and used as photoinitiators.



IOC

(λ_{max}: 247 nm)



SOC

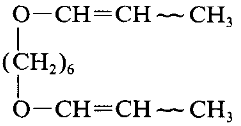
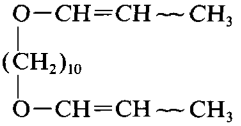
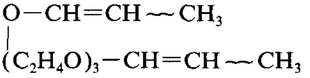
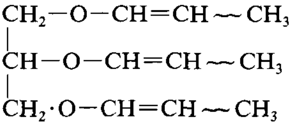
(λ_{max}: 262 nm)

Photoinitiators were dissolved in the monomers at 50°C. The concentration of the above initiators in all formulations (unless specifically noted) was 0.25 mol% per olefinic equivalent.

Photogel Point Measurements

The Gel Pointe GP-101 instrument was equipped with a UVEXS Co. SCU 110 UV mercury arc lamp fitted with a fiber optic cable. A detailed description of this apparatus appeared in previous papers [11, 12]. The samples were irradiated by UV light with an intensity of 5 mW/cm^2 (probe distance 5 cm). The curable material

TABLE 1. Structure and Properties of Propenyl Ether Monomers

Monomer	Structure	Notation	MW	OE[a]
1-Propenoxydodecane	$C_{12}H_{25}{-}O{-}CH{=}CH{-}CH_3$	C12M	226	226
1,6-Di(1-propenoxy)hexane	 $\begin{array}{l} O{-}CH{=}CH{-}CH_3 \\ \vert \\ (CH_2)_6 \\ \vert \\ O{-}CH{=}CH{-}CH_3 \end{array}$	C6D	198	99
1,10-Di(1-propenoxy)decane	 $\begin{array}{l} O{-}CH{=}CH{-}CH_3 \\ \vert \\ (CH_2)_{10} \\ \vert \\ O{-}CH{=}CH{-}CH_3 \end{array}$	C10D	254	127
Triethyleneglycol di(1-propenyl) ether	 $\begin{array}{l} O{-}CH{=}CH{-}CH_3 \\ \vert \\ (C_2H_4O)_3{-}CH{=}CH{-}CH_3 \end{array}$	TEG	230	115
1,2,3-Tris(1-propenoxy)propane	 $\begin{array}{l} CH_2{-}O{-}CH{=}CH{-}CH_3 \\ \vert \\ CH{-}O{-}CH{=}CH{-}CH_3 \\ \vert \\ CH_2{\cdot}O{-}CH{=}CH{-}CH_3 \end{array}$	GTPE[b]	212	71

[a] OE = olefinic equivalent.

[b] Glycerol tripropenyl ether; trivial name.

under examination was placed in a 40-μL micropipet tube and then sealed at one end. The opposite end of the tube was placed in the instrument and made to oscillate back and forth by means of a pumping system. As the sample is irradiated and photopolymerization takes place, the amplitude of the oscillation decays and reaches zero when the photogel point is reached. The irradiation time required to reach a zero oscillation amplitude is called the photogel time [10]. All of the photogel time measurements were carried out at room temperature.

Thin-Film Photopolymerizations

Thin films (1-4 mils) were drawn onto glass slides or steel plates with a drawknife. The formulations were photopolymerized using a Fusion Systems, Inc. Laboratory UV Cure Processor, equipped with a 300-W mercury arc lamp mounted at a distance of 10 cm from a conveyor. The conveyor speed was varied between 12 and 175 ft/min (4 and 53 m/min). Some experiments were performed with a General Electric 200 W medium pressure mercury arc lamp mounted at 12 cm from a stationary sample. In both cases the irradiation dose was measured using a UV Process Supply Inc. Control Cure Radiometer.

The dose or the tack-free cure rate required to obtain a tack-free coating was determined, as well as the gel fraction, hardness, adhesion, and impact of the cured polymer. The maximum tack-free cure rate was determined by varying the speed of the conveyor belt of the processor until any further increase in the belt speed produced a tacky film when tested immediately after irradiation.

Gel fractions were measured by immersing preweighed 3 mil films of the photocured polymer (obtained under different irradiation doses) in a Soxhlet extractor with acetone for 3 hours, followed by drying for 24 hours at 60°C under vacuum and then reweighing.

Coating characterization methods for the determination of impact, pencil hardness, and adhesion were conducted in accordance with ASTM Methods D-2794-84, D-3363-84, and D-3359-87, respectively.

RESULTS AND DISCUSSION

Propenyl Ether Monomers

Using the general synthetic methods depicted in Scheme 1, a wide variety of monomers bearing the highly reactive propenyl ether group may be prepared. Of particular interest in this research has been the application of these methods to the preparation of multifunctional monomers derived from biorenewable sources [7–9, 13]. Shown in Table 1 are the structures of a number of multifunctional monomers prepared and used during the course of this investigation. Both natural and synthetic polyols were employed as substrates for these monomers. It should be noted that in all cases, while the monomers were purified, no attempt was made to separate the *E* and *Z* isomers. Rather, the monomers employed during these studies were mixtures of monomers with the indicated structures containing the isomeric double bonds.

The monomers shown in Table 1 were intended to represent typical examples of mono-, di, and trifunctional propenyl ethers in this study with respect to reactivity and to the properties which can be obtained. Specifically, it was of interest to determine the properties of some thin-layer homopolymers and copolymers prepared by photoinitiated cationic polymerization for potential use in a large number of coating and, adhesive applications. Among these novel monomers, the 1,2,3-tris(1-propenoxy)propane (trivial name: glycerol tripropenyl ether, GTPE) appeared to be very attractive for these applications because of its high functionality and due to the fact that it is potentially inexpensive and can be derived from natural sources. Using GTPE as a base monomer, one can readily modify the reactivity, the viscosity of the photopolymerizable mixture, and the mechanical properties of the photocrosslinked films by copolymerization with the other monomers shown in Table 1. For example, while the homopolymerization of GTPE gives hard, very brittle, transparent films, the incorporation of the dipropenyl ether of triethylene glycol (TEG) should impart flexibility due to the presence of the polyethylene oxide chain and the lower resulting crosslink density.

Accordingly, a comparative analysis was carried out to determine the influence of the structure and functionality of propenyl ethers on the process of cationic photopolymerization and the properties of photocrosslinked films.

Thin-Layer Photopolymerization of GTPE

To determine a baseline for the reactivity and the properties of GTPE, a detailed photopolymerization study was carried out using this monomer. A 10-second UV irradiation of a 1-mil (25 μm) liquid film of GTPE containing 0.5 mol%

SOC as the photoinitiator in air using a 200-W UV lamp (dose, 180 mJ/cm^2) leads to a hard, brittle, colorless, tack-free film. Figure 1 shows a series of infrared spectra taken before, immediately after irradiation, and after standing for 15, 45, and 60 minutes following the cessation of irradiation.

Immediately after irradiation (Spectrum 2), one can see a marked decrease of the propenyl ether double bond peak at 1673 cm^{-1} and in the C—O—C peak (ether groups attached to the double bonds) at 1245 cm^{-1}. At the same time, the formation of aldehyde carbonyl groups is indicated by the appearance of a strong band at 1730 cm^{-1}. There is also an increase in the intensity of the C—H bands near 3000 cm^{-1} and 1450 cm^{-1} as well as of the C—O—C band at 1000-1200 cm^{-1}. After a 10-second irradiation, the infrared spectrum indicates that there is only a very small amount of OH groups (3450 cm^{-1}) in the film. However, the spectrum taken 15 minutes after termination of the irradiation (Spectrum 3) shows an increase in the conversion (from 42 to 56%) of the double bonds (bands at 1673 cm^{-1}) due to continued dark polymerization. This is accompanied by an increase in the OH-band intensity (3450 cm^{-1}). The spectra taken after 45 minutes and 1 hour (Spectra 4 and 5) show that these processes continue, with the conversion of double bonds reaching 70%.

Based on an analysis of these data, several conclusions may be reached. First, there is considerable dark polymerization or postcure which takes place after irradi-

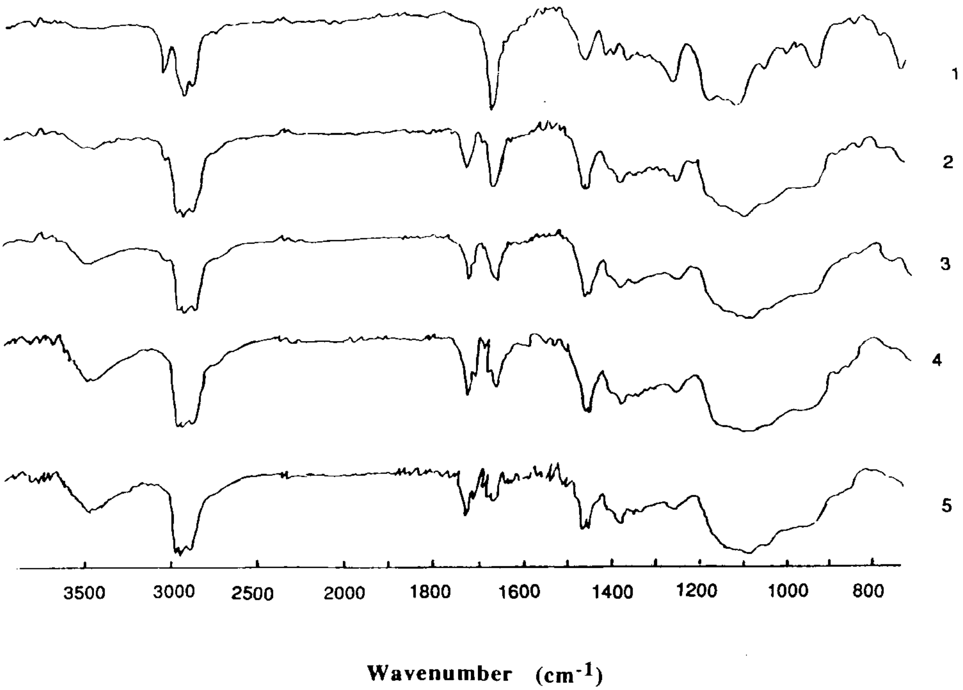
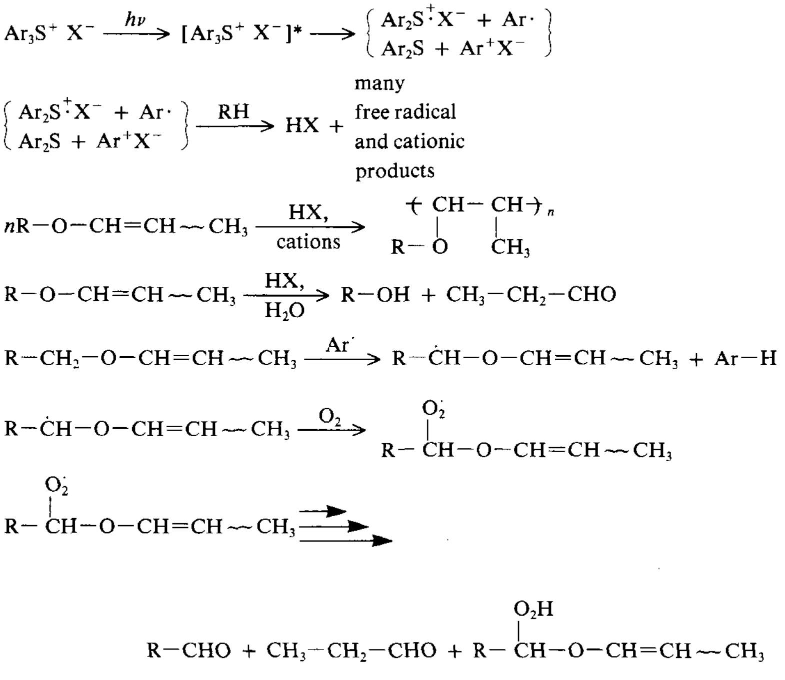


FIG. 1. IR spectra of GTPE in the presence of 0.5 mol% SOC. (1) before irradiation, (2) after irradiation, (3) 15 minutes after irradiation, (4) 45 minutes after irradiation, and (5) 60 minutes after irradiation.

ation has ceased and which leads to an increased conversion of the propenyl ether double bonds. After a considerable time (1 hour), the conversion is high (70%) but not complete. This is due to the fact that an appreciable number of unreacted double bonds are entrapped and immobilized within the rigid, comparatively high T_g, three-dimensional polymer network which cannot be further polymerized without substantially raising the temperature. Second, several side reactions involving the propenyl ether double bonds also compete with polymerization. As shown in Scheme 2, irradiation of the photoinitiator releases several types of reactive species which can interact with the propenyl ether monomers in various ways.

The acid generated during photolysis of the onium salt photoinitiator (Eqs. 4 and 5) initiates the facile polymerization of the propenyl ether groups of GTPE (Eq. 6) leading to the formation of a highly crosslinked network. During and subsequent to the polymerization, the propenyl ether groups may undergo acid-catalyzed hydrolysis in the presence of atmospheric moisture to give alcohols and propionaldehyde (Eq. 7). Propenyl ethers are enol ethers which are known to undergo facile hydrolysis under acidic conditions [14]. The hydrolysis can continue for long periods after the network is formed by slow diffusion of water into the polymer matrix, resulting in the consumption of the unreacted propenyl groups remaining from the photopolymerization. Propionaldehyde is a volatile substance and is easily lost by diffusion from the polymer film. Thus, while the intensity of the alcohol band in the infrared tends to steadily increase with time, the aldehyde carbonyl band appears to reach a maximum and even to decrease slightly. In addition to hydrolysis, an oxidative processes can also take place during and after



$$Ar_3S^+X^- \xrightarrow{h\nu} [Ar_3S^+X^-]^* \longrightarrow \left\{\begin{array}{l} Ar_2S^{\dot{+}}X^- + Ar\cdot \\ Ar_2S + Ar^+X^- \end{array}\right\} \qquad (4)$$

$$\left\{\begin{array}{l} Ar_2S^{\dot{+}}X^- + Ar\cdot \\ Ar_2S + Ar^+X^- \end{array}\right\} \xrightarrow{RH} HX + \begin{array}{l}\text{many} \\ \text{free radical} \\ \text{and cationic} \\ \text{products}\end{array} \qquad (5)$$

$$nR{-}O{-}CH{=}CH{\sim}CH_3 \xrightarrow[\text{cations}]{HX,} \left(\underset{R-O}{\underset{|}{CH}} - \underset{CH_3}{\underset{|}{CH}} \right)_n \qquad (6)$$

$$R{-}O{-}CH{=}CH{\sim}CH_3 \xrightarrow[H_2O]{HX,} R{-}OH + CH_3{-}CH_2{-}CHO \qquad (7)$$

$$R{-}CH_2{-}O{-}CH{=}CH{\sim}CH_3 \xrightarrow{Ar^{\cdot}} R{-}\dot{C}H{-}O{-}CH{=}CH{\sim}CH_3 + Ar{-}H \qquad (8)$$

$$R{-}\dot{C}H{-}O{-}CH{=}CH{\sim}CH_3 \xrightarrow{O_2} R{-}\overset{O_2^{\cdot}}{\overset{|}{C}H}{-}O{-}CH{=}CH{\sim}CH_3 \qquad (9)$$

$$R{-}\overset{O_2^{\cdot}}{\overset{|}{C}H}{-}O{-}CH{=}CH{\sim}CH_3 \longrightarrow R{-}CHO + CH_3{-}CH_2{-}CHO + R{-}\overset{O_2H}{\overset{|}{C}H}{-}O{-}CH{=}CH{\sim}CH_3 \qquad (10)$$

SCHEME 2.

irradiation, and this is depicted in Eqs. (8)-(10) of Scheme 2. Free radicals, such as the aryl free radical formed on photolysis of the photoinitiator, can abstract hydrogen atoms from the α-ether carbons which can react further with atmospheric oxygen to yield peroxy radicals (Eqs. 8 and 9). A similar mechanism has been proposed by Hult and his coworkers [15] for the free-radical-induced autoxidation of vinyl ether monomers during their cationic photopolymerization. Further reactions, as shown in Eq. (10), lead to the formation of hydroperoxides and propionaldehyde as well as other aldehydes by cleavage of the ether bond [16].

The consequences of these observations are that photopolymerized films of propenyl ether monomers are likely to possess a considerable number of hydroxyl groups which may tend to increase slowly over time due both to the hydrolysis of residual unreacted propenyl ether groups and to the oxidative cleavage of these and other ether groups within the matrix. Figure 2 shows the infrared spectrum of a photopolymerized film of GTPE after removal of unreacted monomer and hydrolysis or oxidation products by solvent extraction. The spectrum shows a broad OH peak, indicating that the hydroxyl groups are bound to the polymer chain. Thus, the above results imply that the level of hydroxyl groups ultimately present in the resin may depend on the relative humidity present during photopolymerization. The effects of humidity on the rate and extent of polymerization of these monomers has not been studied in detail. However, the effect of the presence of hydroxyl groups in the polymerized films may be considered either an advantage or a disadvantage. For example, the presence of hydroxyl groups may make the crosslinked polymer films more sensitive toward swelling by polar solvents. On the other hand, these same groups may provide better adhesion of the photopolymerized films to various substrates when used as coatings or adhesives.

The efficiency of the cationic photopolymerization of GTPE was studied in the presence of various levels of the photoinitiators SOC and IOC. Irradiations were conducted using a Fusion System Laboratory UV Cure Apparatus equipped with a 300-W medium pressure mercury arc lamp. When GTPE was exposed as thin films (1-4 mil, 25-100 μm) using this apparatus, polymerization took place within a few

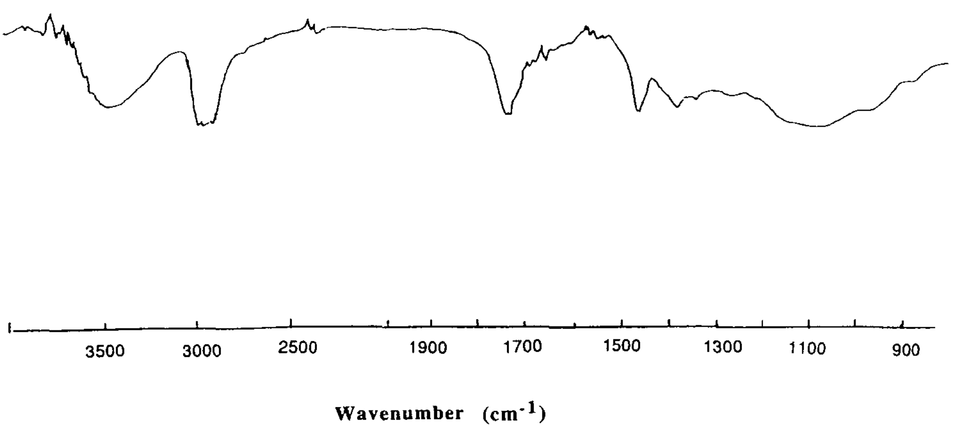


FIG. 2. IR spectrum of photopolymerized GTPE after extraction for 3 hours in acetone.

seconds of irradiation. After photopolymerization, the polymers were found to be insoluble in acetone, thus indicating that an extensive crosslinking process had taken place. The gel fractions of the films were then determined by exhaustively extracting them with acetone. Then, the gel fractions of the films were related to the irradiation dose and also correlated with the photoinitiator type and concentration. The data obtained in this study are shown plotted in Fig. 3. In all but the case in which a very low concentration (0.1 mol%) of SOC was used, there appears to be a minimum dose required to achieve saturation of the gel fraction. Thus, a dose of 130 mJ/cm^2 is necessary which is essentially independent of the structure or the amount of photoinitiator used. At the lowest SOC concentration, there is a marked change of slope in the curve at a radiation intensity of 130 mJ/cm^2. However, high gel fractions (i.e., greater than 83%) are not obtained below an irradiation dose of 450–500 mJ/cm^2. Similar results were obtained by determining the dose required to give tack-free films of the four monomer-photoinitiator samples. The dose required to produce tack-free films of 0.5–1.0 mol% IOC or SOC containing mixtures was 65–70 mJ/cm^2, whereas with 0.1 mol% SOC this dose was insufficient to obtain a tack-free film. It is interesting to note in Fig. 3 that all four of the curves appear to converge at a limiting gel fraction of approximately 83–85% independent of the photoinitiator or its concentration. This would tend to suggest that the ultimate conversion of the propenyl ether double bonds is dependent on a parameter which is a function of the network which is formed. As the crosslink density of the network increases during the photopolymerization, the T_g also rises, resulting in an increasing immobility with a consequent slowing of the polymerization rate as the material changes from a liquid to a glassy solid.

Several properties of films obtained by photopolymerization of GTPE are shown in Table 2. GTPE is a very reactive multifunctional monomer, and high, nearly identical tack-free speeds are observed for both photoinitiators IOC and SOC

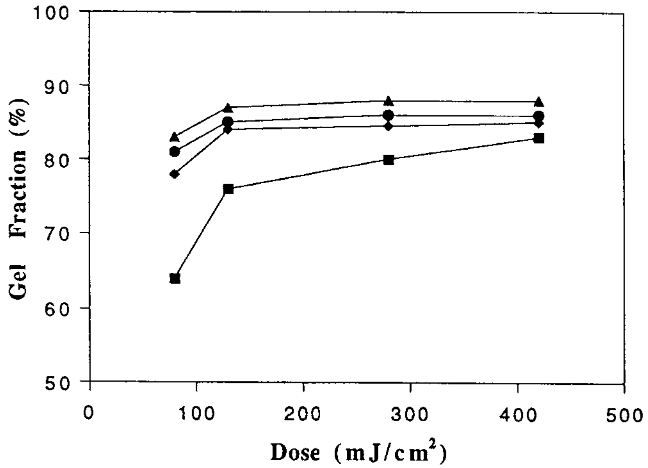


FIG. 3. Dependence of the gel fraction of photopolymerized GTPE on the type and concentration of the photoinitiator: (▲) 0.5 mol% IOC, and (●) 1.0, (◆) 0.5, and (■) 0.1 mol% SOC.

TABLE 2. Properties of Photopolymerized Films of GTPE[a]

Property	IOC, 0.5 mol%	SOC 0.5 mol%	SOC 1.0 mol%
Maximum tack-free speed, ft/min	171	145	175
Pencil hardness	2B	2B	HB
Adhesion	2B	2B	3B
Gardner impact, ft-lb	<2	<2	10–12
Gel fraction, %	88	84	85

[a] Film thickness = 4 mils (100 μm); properties determined 1 hour after an irradiation dose of 130 mJ/cm^2.

at the same concentrations. The limiting factor in determining the speed of the photopolymerization in these cases appears once again related to the crosslink density and the T_g of the resin matrix which is formed. Similarly, there are not substantial differences in the properties of coatings containing 0.5 mol% IOC or SOC, although the gel fraction with IOC is slightly higher. Some increase of adhesion and impact is observed by increasing the photoinitiator concentration from 0.5 to 1.0 mol% SOC. The exact reason is not known for certain, but it might be speculated that the greater amount of acid which is generated in this case increases the hydroxyl group content by promoting the hydrolysis of unreacted propenyl ether groups. The presence of the polar hydroxyl groups would be expected to contribute to increased adhesion and impact. One can see also some improvement in the pencil hardness at the higher concentration of SOC. It was subsequently shown that the hardness can be further increased from 2B to H when the irradiation dose is increased from 130 to 530 mJ/cm^2.

Taking into consideration all the data which have been presented thus far for the photopolymerization of GTPE, it may be concluded that the photoinitiator concentration should be in the 0.5 to 1.0 mol% range to obtain the best properties. Since it was observed that mixtures of GTPE and IOC had a tendency to undergo polymerization on standing, while the mixtures containing SOC as the photoinitiator were indefinitely shelf stable, the latter photoinitiator was used in most of the subsequent studies. Irradiation doses >130 mJ/cm^2 should be employed since better film properties and more rapid polymerizations are observed at higher doses. Photopolymerized GTPE is a very brittle, friable material; the brittleness can probably be decreased by copolymerization with propenyl ether monomers which contain long aliphatic chains.

Copolymerization of GTPE with Other Monomers

The copolymerizations of 1,6-di(1-propenoxy)hexane (C6D) and triethylene glycol di(1-propenyl) ether (TEG) with GTPE were studied. In both cases a 50:50 weight ratio of monomers containing 0.25 mol% per olefinic equivalent of SOC as the photoinitiator were used. In Table 3 are shown the photogel time results of these mixtures in direct comparison with the pure monomers. The photogel-time studies

TABLE 3. Polymerization and Properties of Propenyl Ether Films

Monomer(s)	Gel time,[b] seconds	Film character[c] 70 mJ/cm^2	Film character[c] 90 mJ/cm^2
C6D	35	Tack-free	Mar-free
TEG	50	Tacky	Tacky
GTPE	71	Tack-free	Mar-free
C6D/GTPE[a]	60	Tack-free	Mar-free
TGE/GTPE[a]	71	Oil	Viscous oil

[a] 50:50 weight ratio.
[b] UV intensity = 5 mW/cm^2.
[c] 300-W lamp.

were conducted using a Gel Pointe Instrument at a UV intensity of 5 mW/cm^2 [11, 12]. Photogel time measurements indicate the rapidity with which a polymer network is formed. The data indicate that the difunctional monomers undergo the most rapid network formation while GTPE and the mixtures of GTPE with TEG and C6D are all considerably slower.

Photopolymerizations were also carried out by irradiating thin films of the pure monomers and their mixtures with GTPE. These data are also displayed in Table 3. The minimum dose required to cure a 3-mil (75-μm) liquid film of monomer C6D, GTPE, or their 50:50 mixture on a glass substrate in air to a tack-free state was found to be 65–70 mJ/cm^2. A higher dose of 85–90 mJ/cm^2 was needed to produce a film which could not be scratched with a fingernail (i.e., mar-free). In contrast, both homopolymer and copolymer films which contain TEG remain soft and tacky up to a dose of 450 mJ/cm^2. This may be due to the inherently low T_g of this monomer which contains a polyether chain. One can also speculate that such polyether-containing monomers are more prone to hydrolysis than other more hydrophobic monomers. Lastly, the polyether chain of TEG is much more sensitive to photoinduced free-radical oxidation and autoxidation processes which may occur as chain cleavage side reactions during polymerization.

When these compositions are photopolymerized as thin films in air using an irradiation dose of 400 mJ/cm^2, as shown in Fig. 4 and Table 4, the gel fraction decreases in the order: C6D > C6D + GTPE > GTPE > GTPE + TEG > TEG. These data collected on thin films do not agree with the order of reactivity as indicated by the gel time data shown in Table 3. The photogel time data would indicate that TEG is considerably more reactive than indicated by the thin film results. The differences may be rationalized as due to the aforementioned hydrolytic and oxidative processes which are much more prevalent in the case of thin films cured in air (gel fraction studies) than when the monomer is photopolymerized in a closed capillary tube in which there is both limited air and moisture.

As may be noted in Table 5, the hardness of homopolymers is higher than that of the copolymers. An increase in hardness of the films can be observed on prolonged standing after irradiation, again indicating continued dark polymerization

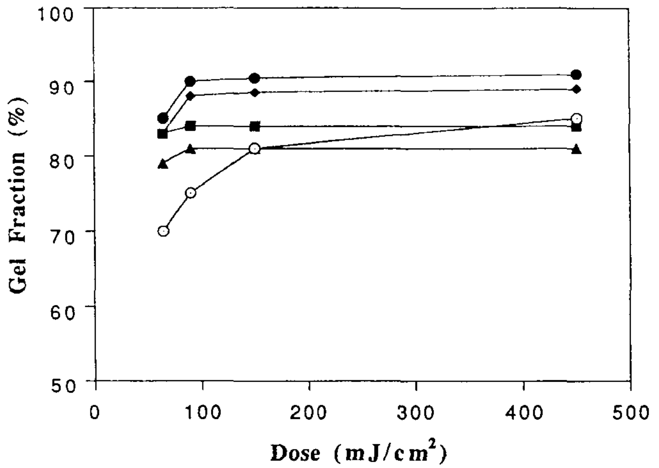


FIG. 4. Dependence of the gel fraction on the irradiation dose for various propenyl ether monomers: (●) C6D, (◆) 50:50 C6D/GTPE, (■) GTPE, (▲) TEG, (○) 50:50 GTPE/TEG.

of the unreacted propenyl ether groups. Similarly, the increase of hardness on standing is accompanied by a decrease in the impact and oftentimes adhesion. As expected, the poor photopolymerization response of the GTPE/TGE mixture also leads to very poor mechanical properties of the films.

The copolymerizations of GTPE with long-chain mono- and difunctional propenyl ethers, specifically 1-propenoxydodecane (C12M) and 1,10-(di-1-propenoxy)decane (C10D), were also carried out. The results of those studies are similar to those described above. Addition of 50 wt% of the monofunctional propenyl ether raises the tack-free dose to more than 480 mJ/cm^2. Consequently, the highest tack-free speed which could be obtained was only 12 ft/min. Analogous results were

TABLE 4. Polymerization and Properties of Propenyl Ether Films[a]

Monomer(s)	Gel fraction,[b] %	Pencil hardness 1h[b]	Pencil hardness 2w[c]	Impact, ft-lb 1h[b]	Impact, ft-lb 2w[c]	Adhesion 1h[b]	Adhesion 2w[c]
C6D	91	HB		<1		5B	
TEG	80	HB		4		1B	0B
GTPE	84	HB	H	2	<1	5B	5B
C6D/GTPE[d]	89	2B		<1		5B	
TGE/GTPE[d]	86	F	3H			5B	5B

[a] 300-W lamp; UV dose = 400 mJ/cm^2.
[b] 1h = 1 hour after irradiation.
[c] 1w = 1 week after irradiation.
[d] 50:50 weight ratio.

TABLE 5. Weight Loss during the Photopolymerization of Propenyl Ether Monomers[a]

	Dose, mJ/cm^2 [b]					
	800[c]	70	140	280	500	800
Composition	Weight loss, %					
TEG	2-4	1.5	2.7	3.2	4.7	4.8
GTPE	3-5	1.3	1.7	2.1	3.6	3.8
TEG/GTPE[d]	2-3				1.5	4.4

[a] Samples cured as 3 mil films on glass using a 300-W mercury arc lamp with 0.25 mol% SOC per olefinic equivalent as a photoinitiator.

[b] Relative humidity ~ 60%.

[c] Control, no photoinitiator present.

[d] 50:50 weight ratio.

obtained for mixtures of GTPE with C10D. Free standing films derived from the above mixtures of monomers were typically soft and had poor integrity. Decreasing the amount of either C12M or C10D to 25 wt% had the effect of substantially lowering the tack-free dose to 200 and 140 mJ/cm^2, respectively. Films obtained from these mixtures remained soft with poor mechanical properties.

Photodegradation Studies

Previously, as was described in Scheme 2, it had been speculated that hydrolytic and oxidative processes may occur during photopolymerization of propenyl ether monomers. The appearance of a C=O peak in the IR spectra of polymer films together with the detection of a characteristic odor during the photopolymerizations suggested that propionaldehyde was being produced during polymerization of the monomers. Accordingly, a brief investigation of the weight loss taking place during photopolymerization of GTPE, TEG, and their 50:50 mixture was conducted. The results are shown in Table 5. Small weight losses which increase with increasing irradiation dose are observed, suggesting that the side reactions increase in direct relationship to the quantity of photolysis products generated from the photoinitiator.

The results shown in Table 5 were obtained at a relative humidity of 60%. Figure 5 shows a similar study conducted when the relative humidity was very nearly 100%. The weight loss at low irradiation doses is very similar for all three photocrosslinked films. However, as the dose is further increased, considerable differences are observed. While the weight losses of GTPE and C6D appear to stabilize at approximately 5 and 8%, respectively, and are further insensitive to increases in dose, TGE loses 18% of its weight at an irradiation dose of 560 mJ/cm^2. There is also a noticeable increase in the yellowing of the TGE-containing films with increasing dose. GTPE and C6D remain colorless and transparent even at the highest doses investigated. On the basis of these experiments, it may be concluded that acid-catalyzed hydrolysis is the major process taking place which

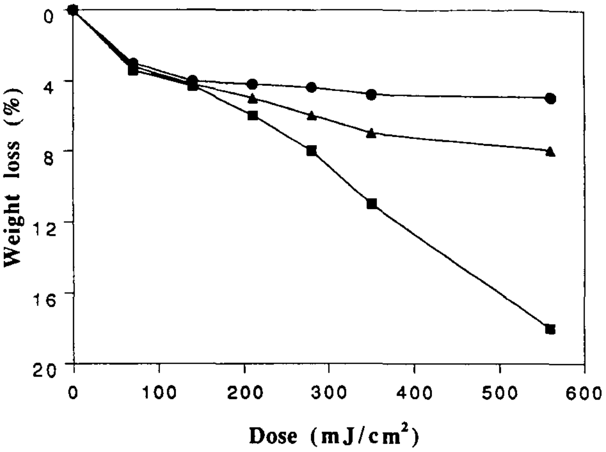


FIG. 5. Weight loss as a function of irradiation dose for three propenyl ether monomers at a relative humidity of ~100%: (●) GTPE, (▲) C6D, (■) TEG.

contributes to the weight loss in these materials. However, in the case of TGE, free-radical oxidation and autoxidation processes probably also play a significant role.

CONCLUSIONS

GTPE is a novel, highly reactive trifunctional monomer derived from renewable sources. It is very attractive for use in photopolymerizable coatings, inks, and adhesives as well as for many other potential applications. While the photoinitiated cationic homopolymerization of GTPE gives hard, brittle films on exposure to UV light, these properties can be readily modified by copolymerization with other mono- and difunctional monomers. Through formulation, the viscosity and photopolymerization rate can also be modified. It was also observed that such properties as hardness, impact, and gel fraction are affected by the conditions under which cationic photopolymerization is carried out. When propenyl ether monomers are irradiated in the presence of diaryliodonium and triarylsulfonium salt photoinitiators, some of the propenyl ether groups undergo hydrolysis, leading to the formation of propionaldehyde and introducing hydroxyl groups into the crosslinked resin matrix. The degree to which this hydrolysis reaction takes place depends greatly on the structure of the monomer, the irradiation dose used, and probably also on the relative humidity present during photopolymerization. The presence of hydroxyl groups in the cured films appears to improve their adhesion to glass and metal substrates.

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