The Synthesis, Characterization, and Photoinitiated Cationic Polymerizaton of Difunctional Oxetanes

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THE SYNTHESIS, CHARACTERIZATION, AND PHOTOINITIATED CATIONIC POLYMERIZATION OF DIFUNCTIONAL OXETANES

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ABSTRACT

Seven novel difunctional oxetane monomers have been prepared and characterized using standard spectroscopic techniques. The photoinitiated cationic polymerization of these seven monomers was carried out and their reactivity compared to a typical diepoxide monomer. In these studies the reactivities of the various oxetane monomers were evaluated and compared by three different techniques: gel time measurements, differential scanning photocalorimetry, and real time infrared spectroscopy. It was observed that the difunctional oxetanes are generally more reactive than their structurally similar epoxide counterparts in photoinitiated cationic polymerization.

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915

INTRODUCTION

In recent years, photoinitiated cationic polymerization, also called cationic UV curing, has become an important technique for the application and cure of coatings and adhesives because of its high throughputs, low energies required, and the lack of the need for polluting solvents. Many different types of monomers and oligomers, including vinyl ethers and epoxide compounds, have been used in the photoinitiated cationic polymerization [1, 2]. In particular, the photopolymerization of epoxy compounds gives coatings with high thermal capability, excellent adhesion, and good chemical resistance. Although photopolymerized epoxy coatings are known for their high performance, commercially available epoxy monomers undergo photoinitiated cationic polymerization at rather slow rates. In some industrial applications, the low reactivity of these epoxy monomers has proved to be a considerable drawback to their use [3]. Thus, it has been a long-range goal in this laboratory to evaluate monomers which have the same performance capabilities as epoxy monomers while at the same time have higher reactivities.

Three major factors contribute to the reactivity of heterocyclic monomers in cationic ring-opening polymerization [4]. These are: 1) the nature of the heteroatom, its electronegativity and bond strength with the neighboring carbon atoms; 2) the ring strain; and 3) steric factors. It is interesting and informative to compare these factors for two classes of cyclic ethers; oxetanes and epoxides. For example, the ring strain of ethylene oxide has been calculated [5] to be 27.3 kcal/mol while that for oxetane is 25.5 kcal/mol. At the same time, the pK_b's for these two ethers are, respectively, 7.4 and 3.1 [6–10]. Since the mechanism of the cationic ring-opening polymerization of cyclic ethers involves an S_N2 displacement by attack of the ether oxygen of a cyclic ether upon the carbon adjacent to the oxonium center of the growing chain as shown below, the steric requirements of these two monomer types are nearly identical.
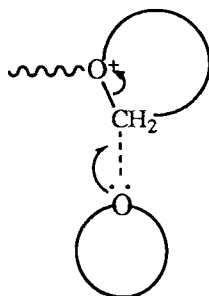
Thus, while both cyclic ethers have similar steric requirements and ring strains, the basicity of oxetane is considerably greater than for ethylene oxide. This latter parameter should, therefore, dominate making the oxetanes more reactive than epoxides in photoinitiated cationic ring-opening polymerizations. These conclusions have not been tested experimentally.

While many simple, monofunctional oxetane compounds have been photopolymerized using onium salt photoinitiators [11, 12], the polymerization of multifunctional oxetane monomers using this method has not been reported. Accordingly, the preparation of several representative difunctional monomers has been

undertaken, and in this communication we report the preliminary results of an investigation of their reactivity in photoinitiated cationic polymerization.

EXPERIMENTAL

General

Trimethylopropane (2,2-dihydroxymethyl-1,3-propanediol), 1,4-dibromobu-tane, 1,4-dibromoxylene, and methallyldichloride (1,1-dichloromethylethylene) were used as purchased from the Aldrich Chemical Co. Ditrimethylolpropane (bis[(2,2-dihydroxymethyl)butyl] ether, structure shown in Eq. 1) was a gift of the Perstorp Company. 1,4-Butanediol diglycidyl ether (E) was purchased from the Ciba-Geigy Co. All other starting materials and solvents were reagent quality and were used as received. (4-Pentadecyloxyphenyl)phenyliodonium hexafluoroantimo-nate [13] and diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate [14] used as photoiniators in these investigations were prepared by procedures which have been described previously.

Routine infrared spectra were obtained on a Buck Scientific Model 500 Spec-trometer. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5840A Gas Chromatograph equipped with 6 ft × 1/8 in. OV-17 phenylsilicone columns and a flame ionization detector. ^{1}H-NMR spectra were obtained using a Varian XL-200 MHz Spectrometer at room temperature in $CDCl_3$ solvent. UV irradiation intensity measurements were made with the aid of a UVPS Con-Trol-Cure radiometer at 365 nm.

Preparation of Monomers

The synthetic procedures given below are typical for those used for all of the difunctional oxetane monomers shown in Table 1.

Preparation of 3-Ethyl-3-hydroxymethyloxetane

Into a 150-mL round-bottom flask fitted with a magnetic stirrer, thermometer, condenser, distillation head, and receiver were placed a mixture of 67.0 g (0.5 mol) trimethylolpropane, 59.0 g (0.5 mol) diethyl carbonate, and 0.05 g potassium hydroxide dissolved in 2 mL absolute alcohol. The mixture was refluxed until the pot temperature fell below 105°C and then ethanol was removed by distillation while keeping the head temperature at 76–78°C. Distillation was continued until the pot temperature rose to 145°C. Then the pressure was reduced gradually to 15 mmHg while maintaining the pot temperature at 140–150°C. Upon heating above 180°C, carbon dioxide evolution was rapid and most of the product distilled at 100–160°C. Fractional distillation of the product gave 43.9 g of pure 3-ethyl-3-hydroxyethyloxetane (yield, 76%; bp, 114–115°C at 16 mmHg).

^{1}H NMR $(CDCl_3)$ δ (ppm) = 0.85–0.95 (t, 3H, $C\underline{H}_3$—CH_2); 1.65–1.80 (q, 2H, CH_3—$C\underline{H}_2$); 2.5 (s, 1H,—$O\underline{H}$); 3.7 (s, 2H, —$C\underline{H}_2OH$); 4.4–4.5 (dd, 4H, —O—$C\underline{H}_2$—*oxetane ring*).

Analysis. Calculated for $C_6H_{12}O_2$: C, 62.04; H, 10.41%. Found: C, 62.01; H, 10.48%.

TABLE 1.   The Structure and Molecular Weights of Oxetane Monomers

Monomer (notation)	Structure	MW	Yield, %
C0		214	42
C4		286	69
C8		342	48
C10		370	49
C12		398	48
MA		284	62
XY		334	92
E		202	—

Preparation of 3,7-Bis(3-oxetanyl)-5-oxa-nonane (Monomer C0)

Employing the same apparatus as described in the first example, a mixture of 25.0 g (0.1 mol) ditrimethylolpropane, 23.6 g (0.2 mol) diethylcarbonate, and 5.0 g potassium carbonate was refluxed until the pot temperature was below 120°C. The mixture was distilled while keeping the head temperature at 76–78°C. Distillation was continued until the pot temperature was 180°C, during which time the mixture became viscous as a polymer formed. Upon heating above 220°C, the viscous polymer melt reverted to a mobile liquid and carbon dioxide evolution was rapid. Then the pressure was reduced gradually to 15 mmHg, and most of the material distilled at 120–170°C. Fractional distillation gave 8.9 g of pure 3,7-bis(3-oxetanyl)-5-oxa-nonane (yield; 42%; bp, 165–170°C at 16 mmHg).

^{1}H NMR (CDCl$_3$) δ (ppm) = 0.85–0.95 (t, 6H, C$\underline{H}_3$—CH$_2$); 1.7–1.8 (q, 4H, CH$_3$—C$\underline{H}_2$); 3.6 (s, 4H,—C$\underline{H}_2$—O—C$\underline{H}_2$—); 4.4–4.5(dd, 8H, —O—C$\underline{H}_2$—*oxetane ring*).

Analysis. Calculated for C$_{12}$H$_{22}$O$_3$: C, 67.26; H, 10.35%. Found: C, 66.83; H, 10.54%.

Preparation of 3,3′-(1,10-Decanediylbis(oxymethlene))bis(3-ethyloxetane) (Monomer C10)

To a solution of 34.8 g (0.3 mol) 3-ethyl-3-hydroxymethyloxetane in 30.0 g (0.1 mol) 1,4-dibromodecane and 50 g of a 50 wt% aqueous solution of potassium hydroxide was added 1.0 g tetra-*n*-butylammonium bromide with vigorous stirring at 0°C. After 24 h, 100 mL ether and 100 mL water were added to the reaction mixture. The organic phase was washed with water twice, dried over magnesium sulfate, filtered, and the solvent removed on a rotary evaporator. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 1:1), giving 19.8 g 3,3′-(1,10-decanediylbis(oxymethlene))bis-(3-ethyloxetane) (yield: 49%).

^{1}H NMR (CDCl$_3$) δ (ppm) = 0.85–0.95 (t, 6H, C$\underline{H}_3$—CH$_2$); 1.6–1.65 (m, 4H, —OCH$_2$—(C$\underline{H}_2$)$_8$—CH$_2$O—); 1.65–1.80 (q, 4H, CH$_3$—C$\underline{H}_2$); 3.4–3.5 (t, 4H, —OC$\underline{H}_2$CH$_2$C$\underline{H}_2$CH$_2$O—); 3.6 (s, 4$\underline{H}$, —CH$_2$O—); 4.4–4.5 (dd, 8H, —O—C$\underline{H}_2$—*oxetane ring*).

Analysis. Calculated for C$_{22}$H$_{42}$O$_4$: C, 71.31; H, 11.42%. Found: C, 70.98; H, 11.58%.

The method given above for C10 was employed for the synthesis of monomers C4, C8, and C12 without substantial variation.

Preparation of 3,3′-(1,3-(2-Methylenyl)propanediylbis(oxymethylene))bis-(3-ethyl Oxetane) (Monomer MA)

The previous reaction was repeated using 3-ethyl-3-hydroxymethyloxetane (12.8 g; 0.11 mol) and methallyldichloride (1,1-dichloromethylethylene) (6.25 g; 0.05 mol). A colorless oil was obtained on purification by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 1:1); yield, 8.8 g (62%).

^{1}H NMR (CDCl$_3$) δ (ppm) = 0.85–0.95 (t, 6H, C$\underline{H}_3$—CH$_2$); 1.65–1.80 (q, 4H, CH$_3$—C$\underline{H}_2$); 3.6 (s, 4H, —CH$_2$O—); 4.0 (s, 4H, —OC$\underline{H}_2$—C(=CH$_2$)—C$\underline{H}_2$O—); 4.4–4.5 (dd, 8H, —O—C$\underline{H}_2$—*oxetane ring*); 5.2 (s, 2H, C=C$\underline{H}_2$).

Analysis. Calculated for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92%. Found: C, 67.22; H, 10.10%.

Preparation of 3,3'-(1,4-Xylenediylbis(oxymethlene))bis(3-ethyloxetane) (Monomer XY)

The previous reaction was repeated using 3-ethyl-3-hydroxymethyloxetane (12.8 g; 0.11 mol) and 1,4-dibromoxylene (13.2 g; 0.05 mol). A colorless oil was obtained on purification by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 2:3); yield, 15.4 g (92%).

^{1}H NMR (CDCl$_3$) δ (ppm) = 0.85–0.95 (t, 6H, C$\underline{H}_3$—CH$_2$); 1.65–1.80 (q, 4H, —CH$_3$—C$\underline{H}_2$); 3.6 (s, 4H, —C$\underline{H}_2$O—); 4.4–4.5 (dd, 8H, —O—C$\underline{H}_2$—*oxetane ring*); 4.55 (s, 4H, —OC$\underline{H}_2$—Ph—C$\underline{H}_2$O—); 7.3 (s, 4H, aromatic protons).

Analysis. Calculated for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04%. Found: C, 71.86; H, 9.11%.

Photopolymerization of Difunctional Oxetane Monomers

The monomers prepared during this work are listed in Table 1. Photopolymerizations were carried out with bulk monomers containing 0.5 mol% of onium salts as photoinitiators.

Gel Time Measurements

The rates of polymerization of the various monomers were measured by recording their gel times using a Gel Pointe instrument (shown in Fig. 1). This apparatus is equipped with a UVEXs Co. SCU 110 UV lamp fitted with a fiber optic cable. Samples of the monomers containing 0.5 mol% of the indicated photoinitiator were drawn into 40 mL borosilicate micropipet tubes, and one end was sealed with a plastic tube and pinch clamp. The time from when the lamp is turned on until the oscillation of the meniscus ceases in the capillary tube is recorded as the gel time. The shorter the gel time, the more reactive the monomer is in cationic UV curing.

Real Time Infrared Measurements

The conversions of the monomers to polymer were measured using real time infrared spectroscopy employing the method of Decker [15]. The apparatus used for these measurements consisted of a Buck Scientific Model 500 Infrared Spectrometer which was equipped with a UVEXS Co. SCU 110 UV lamp fitted with a fiber optic cable. The probe of the fiber optic cable was positioned so that the UV irradiation was directed onto the sample window of the spectrometer. The intensity of the irradiation could be varied by fixing the probe at various distances from the sample.

Polymerizations were carried out at room temperature on samples of the monomers coated onto 1 mil polyethylene films. The samples were irradiated at UV intensities of 20 mW/cm^2 (probe distance, 5 cm) or 79 mW/cm^2 (probe distance, 2.5 cm). During the irradiation, the absorbance decrease of oxetane band at 980 cm^{-1} was monitored. After the absorbance decrease had ceased, the conversions of the samples were calculated by comparing the initial and final absorbances. The equation $R_p/[M_0] = ([conversion]t_2 - [conversion]t_1)(t_2 - t_1)$ was used to calculate the $R_p/[M_0]$ values used in Table 3.
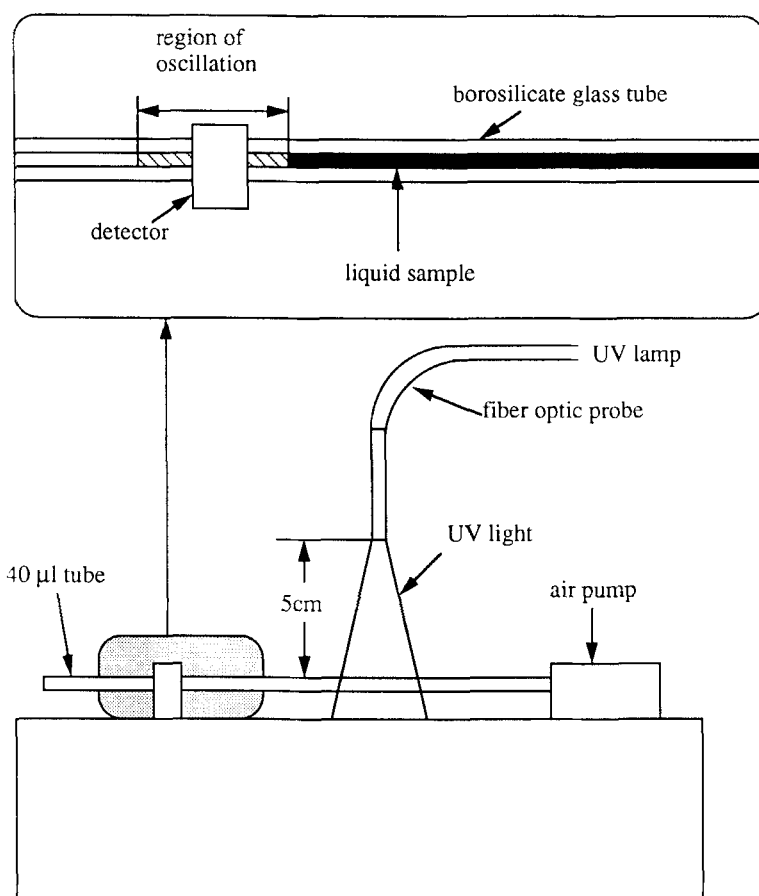
FIG. 1.   Schematic drawing of the Gel Pointe instrument.

## Differential Scanning Photocalorimetric Determinations

The photoinitiated polymerization of the difunctional oxetane monomers was carried out using a Perkin-Elmer DSC-7 Differential Scanning Calorimeter equipped with a Photocalorimeter Module fitted with a 100-W lamp. Polymerizations were conducted isothermally at 30°C on 0.2 to 0.5 mg samples of the monomer-photoinitiator solutions. Heats of polymerization were determined from the areas under the exothermic curves, and the cumulative heats of polymerization were calculated from the integrated areas as various irradiation times.

RESULTS AND DISCUSSION

Synthesis of Multifunctional Oxetanes

A number of synthetic methods are available for the preparation of oxetanes. In this research the method of Pattison [16] was used extensively because it is a straightforward, convenient procedure which makes use of readily available starting

materials and generally gives good yields of the desired oxetane products. An additional reason for using this method is that oxetanes functionalized in only the 3-position can be readily obtained. 3-Substituted oxetanes are the most reactive in cationic polymerizations because both of the carbon atoms adjacent to the ether oxygen are not sterically hindered by the presence of substituents. An example of this reaction is shown in

$$R_1R_2C(CH_2OH)_2 \quad + \quad (C_2H_5O)_2CO \xrightarrow[-2\,EtOH]{K_2CO_3} \xrightarrow[-CO_2]{\Delta} \quad \text{(1)}$$
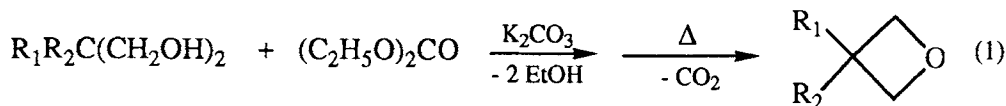
This method involves an ester exchange of a 1,3-diol with diethylcarbonate to give the cyclic carbonate with the elimination of ethanol. On further heating, the cyclic carbonate undergoes loss of carbon dioxide, generating the oxetane. Using this synthetic approach, the hydroxy functional oxetane, 3-ethyl-3-hydroxymethyl-oxetane ($R_1 = C_2H_5$, $R_2 = CH_2OH$), was prepared and used as an intermediate for the synthesis of several difunctional oxetanes. 3-Ethyl-3-hydroxymethyloxetane was condensed with dibromoalkane or dichloroalkanes under phase transfer conditions to give the desired dioxetanes in good yields as shown in

$$2 \quad \xrightarrow[]{OH} + \quad Br\!-\!R\!-\!Br \xrightarrow[(n\text{-}C_4H_9)_4N\,Br]{aq.\,KOH} \quad \text{(2)}$$
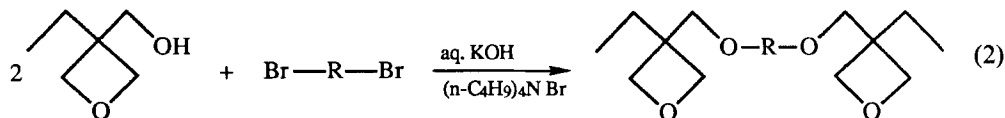
The structures of the various dioxetanes prepared during the course of these investigations are shown in Table 1 along with their yields and calculated molecular weights. As may be noted, monomers with different types of spacer groups, which represent flexible and rigid groups of different lengths, were synthesized between the two oxetane groups. Monomer C0 was prepared by a slightly different method as shown in Eq. (3), starting with ditrimethylolpropane (bis[2,2-dihydroxymethyl)butyl] ether).

$$HO\!-\!\overset{O}{\diamond}\!-\!OH + \quad 2\,(C_2H_5O)_2CO \xrightarrow[-4\,EtOH]{K_2CO_3} \xrightarrow[-2\,CO_2]{\Delta}$$

$$\text{(3)}$$
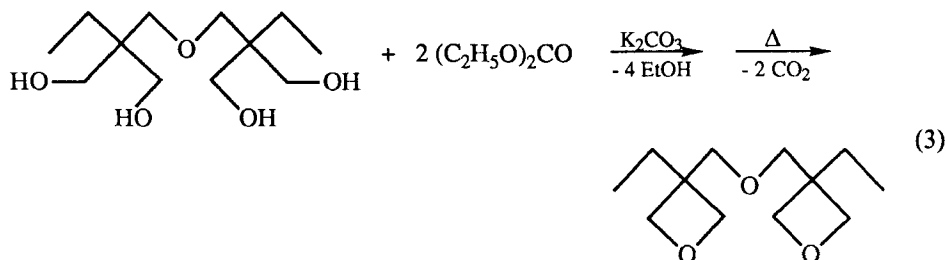
The initial reaction product of ditrimethylolpropane with diethylcarbonate is a polycarbonate which undergoes a smooth loss of carbon dioxide to give monomer C0 in 42% yield.

All the monomers used in this study were carefully purified by distillation or by flash column chromatography. The purity of each of the monomers was checked by thin layer chromatography, and all give elemental analyses which agreed with the calculated values based on the molecular structures shown in Table 1.

Study of the Reactivity of Difunctional Oxetane Monomers

The reactivities of the difunctional oxetane monomers depicted in Table 1 were compared with each other and with a representative structurally analogous difunctional epoxide, 1,4-butanediol diglycidyl ether (E), in bulk photoinitiated cationic polymerizations. In these studies the two onium salt photoinitiators shown below with different UV absorption characteristics were employed depending on the particular measurement technique used.
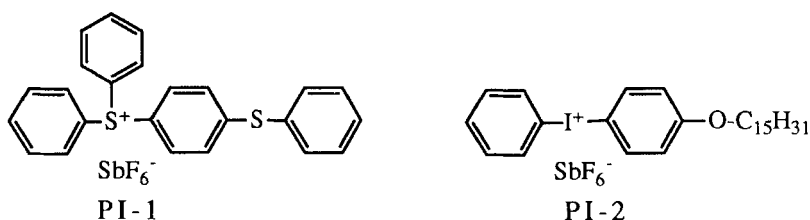
Diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate (PI-1) has two UV absorption bands at 225 nm (ϵ = 23,400) and 300 nm (ϵ = 19,500) and is, therefore, responsive to radiation in the mid and short regions of the UV. (4-Pentdecyloxyphenyl)phenyliodonium hexafluoroantimonate (PI-2) has a λ_{max} at 247 nm (ϵ = 14,900) and is useful only in the short wavelength UV region. At the same time, PI-2, with its long alkoxy chain, is much more soluble in the difunctional oxetane monomers than is PI-1. Thus, while PI-1 was insoluble in monomers C8, C10, and C12, PI-2 readily dissolved and the reactivities of these three monomers were examined using this photoinitiator. In all cases the photoinitiator concentration was 0.5 mol% so that the oxetane monomers and the reference epoxides could be compared directly regardless of the differences in their molecular weights.

Three different techniques were used for the determination of the reactivities of the monomers: gel time measurements, real time infrared analysis, and differential scanning photocalorimetry. Each of these methods is based on a different analytical principle and, thus, the parameters by which the reactivity is determined are also different. In the following sections these three methods will be compared and contrasted with each other.

Gel Time Measurements

A new instrument called a Gel Pointe instrument has recently been developed for the determination of the reactivity of photopolymerizable mixtures by the measurement of their gel times [17]. A schematic diagram of this apparatus is shown in Fig. 1. The sample tube consists of a uniform bore capillary tube or, most conveniently, a micropipet. The sample tube is partially filled with a liquid photopolymerizable monomer or oligomer and the end closed off to provide an air space at the end of the pipet. The capillary is connected via a rubber septum to a reciprocating

air pump which oscillates the meniscus of the liquid sample in and out of the range of an infrared emitter–detector assembly. UV radiation is directed onto the micropipet by means of a fiber optic cable. The oscillation of the sample is continually monitored by means of a strip chart recorder or a timing device. When the photopolymerization reaches the gel point, the oscillation ceases and this is taken to be the gel time. Typically, the reproducibilities of gel time measurements made in this instrument are in the range of ± 5%.

This type of measurement determines the characteristic increase of viscosity of the liquid sample as it changes during photopolymerization from a free-flowing liquid to a monomer swollen network. The gel time is, therefore, related to a number of parameters such as the degree of crosslinking in the network, the flexibility of the spacer units between the crosslinking points in the network, the degree of swelling of the network by the monomer, and the presence or absence of microgel particles during the crosslinking reaction.

The gel times of oxetane monomers C0, C4, MA, XY and 1,4-butanediol diglycidyl ether are compared in Table 2. All the difunctional oxetanes had shorter gel times than the epoxide reference monomer E. Monomers MA and XY had the fastest gel times, and monomer XY, containing the xylylene spacer group, was particularly reactive. One rationale for this result may be that the network formed by the polymerization of this monomer would be expected to be quite stiff even at low conversions as a result of the rather rigid xylylene group in this monomer. More flexible monomers such as C4 give comparatively longer gel times.

It is also interesting to compare the results in Table 2 as a function of the two photoinitiators used. Clearly, PI-1 gives the shortest gel times in all cases. This is due to the cut-off of the short wavelength (< 300 nm) UV irradiation by the borosili-

TABLE 2. Gel Times of Oxetane Monomers

Monomer	Photoinitiator,[a] wt%	Gel time, s[b]
C0	PI-1 (1.41 wt%)	65
C4	PI-1 (1.06 wt%)	60
MA	PI-1 (1.07 wt%)	15
XY	PI-1 (0.91 wt%)	5
E	PI-1 (1.50 wt%)	75[c]
C0	PI-2 (1.53 wt%)	360
C4	PI-2 (1.14 wt%)	280
C8	PI-2 (1.08 wt%)	160
C10	PI-2 (1.00 wt%)	165
C12	PI-2 (0.93 wt%)	240

[a]Concentration of photoinitiators 0.5 mol%, PI-1 = diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate; PI-2 = (4-pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate.

[b]Irradiation intensity; 20 mW/cm².

[c]During irradiation, epoxide E became very viscous but remained a liquid.

cate micropipet sample tubes used. In addition, the fiber optic probe used to transmit the UV irradiation has the same approximate cut-off limitations. Since PI-1 has a long wavelength absorption while PI-2 does not, PI-1 is a much more efficient photoinitiator for these studies. As the chain is lengthened in the series C4, C8, C10, and C12, the gel times first shorten, reach a minimum, and then begin to lengthen. This is expected since the mobility of the functional groups becomes greater as the chain is lengthened. However, beyond a certain chain length, the reactivity begins to fall off as the probability of the oxetane groups finding each other in order to react decreases.

Real Time Infrared Measurements

Real time infrared spectroscopy has been shown by Decker [15] to be an excellent method for determining both the rate and extent of free radical and cationic photopolymerizations. This method involves monitoring the decrease or increase of a distinctive infrared band with time during simultaneous UV irradiation as a monomer is converted to polymer during a photopolymerization. In these studies the decrease of the characteristic cyclic ether band at 980 cm^{-1} was monitored for the oxetane monomers, while the band at 760 cm^{-1} was followed for the epoxide monomer. The 760-cm^{-1} band was not obscured in the infrared spectrum of this compound, while the epoxy band at 915 cm^{-1} was irregular and less well defined. In Figs. 2–6 are shown the conversion to polymer versus time plots for various monomers obtained in these studies using PI-1. Figure 2 compares the conversion as a function of time for monomers C0 and C4 with the epoxide reference monomer E. While epoxide E initially has a steeper slope indicative of a higher reactivity than the oxetane C0, the ultimate conversion of these two monomers is about the same. However, monomer C4 is clearly more reactive than either C0 or E, and the polymerization of this monomer also reaches a higher conversion. Figure 3 compares the three most reactive difunctional oxetane monomers C4, MA, and
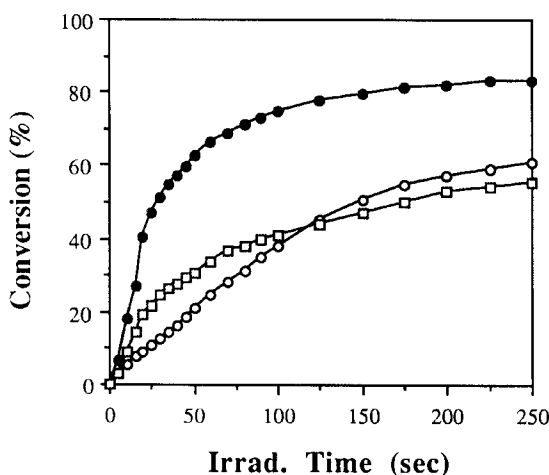

FIG. 2.   Conversion versus irradiation time curves for monomers C0 (○), C4 (●), and E (□) using 0.5 mol% PI-1 at a UV intensity of 20 mW/cm^2.
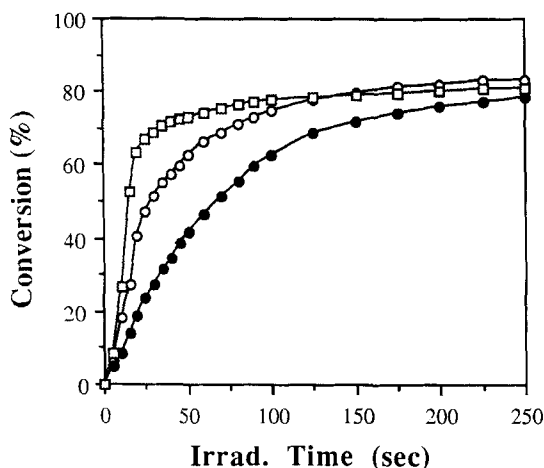
FIG. 3. Conversion versus irradiation time curves for monomers C4 (○), MA (●), and XY (□) using 0.5 mol% PI-1 at a UV intensity of 20 mW/cm².

XY with each other. In good agreement with the gel time studies, monomer XY shows the highest rate of conversion of oxetane to linear polyether groups. However, in contrast to the gel time studies, the reactivity in terms of the rate of disappearance of oxetane groups as determined by real time infrared shows that oxetane monomer C4 is more reactive than monomer MA. In Fig. 4 are compared the irradiation time versus monomer conversion curves for monomers C0 and C4 in which photoinitiator PI-2 was used. First, it should be noted that the overall rates of conversion of the cyclic ether monomers to linear polyethers are very much less
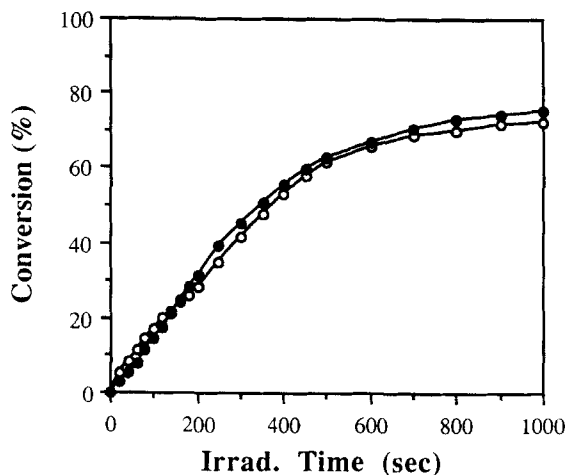

FIG. 4. Conversion versus irradiation time curves for monomers C0 (○) and C4 (●) using 0.5 mol% PI-2 at a UV intensity of 20 mW/cm².

than observed in Fig. 2 for these same monomers. Second, in contrast to the previous studies, both monomers polymerized using this photoinitiator appear to have very nearly the same reactivity. An explanation for this result is as follows. The amount of radiation transmitted via the fiber optic cable at wavelengths below 300 nm where PI-2 absorbs is very small. Thus, in this experiment the overall rate and extent of polymerization is light-intensity limited and independent of the monomer structure. In agreement with this conclusion, Fig. 5 shows an identical plot of study of these two monomers in which the light intensity is quadrupled. Once again, the marked difference in reactivity between these two monomers is clearly apparent.

In Table 3 are given the $R_p/[M_0]$ values calculated from the maximum values of the slopes of the absorbance versus time curves for the four difunctional monomers studied with different photoinitiators and at different radiation intensities. A comparison of the $R_p/[M_0]$ values is another measure of the relative reactivites among the monomers. However, it should be stated that these values are generally representative of only the initial stages of the photopolymerization and are most significant when they are compared among closely related monomers. Thus, the relative order of the $R_p/[M_0]$ for the oxetane monomers are in general agreement with the observations made above by examining the conversion versus photolysis time curves, while the value (1.2 s^{-1}) for the epoxide monomer is anomalously high.

Determination of Reactivities by Differential Scanning Photocalorimetry

Another technique which was used during these investigations to examine the reactivities of the difunctional oxetane monomers was differential scanning photocalorimetry. Two typical photocalorimetry curves are shown in Fig. 6 in which the photopolymerization of monomer C4 is compared to that of the analogous epoxide E. As this figure shows, the polymerization of the oxetane-containing monomer gives a sharp exothermic curve which rapidly returns to the baseline. In
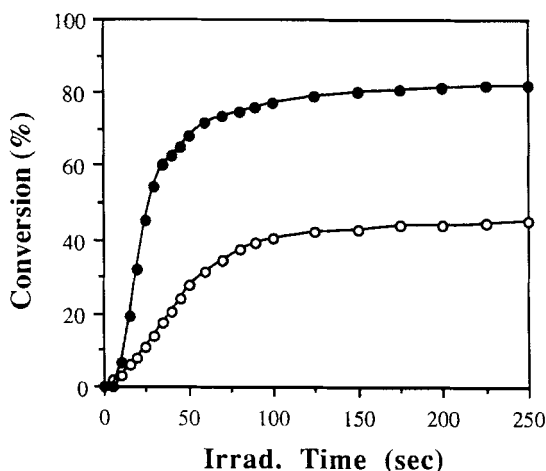

FIG. 5.   Conversion versus irradiation time curves for monomers C0 (○) and C4 (●) using 0.5 mol% PI-2 at a UV intensity of 79 mW/cm².

TABLE 3. Real Time Infrared Studies of the Reactivity of Oxetane Monomers

Monomer	Photoinitiator[a]	Irradiation intensity, mW/cm^2	$R_p/[M]_0$, s^{-1}[b]
C0	PI-1	20	0.44
C4	PI-1	20	2.0
MA	PI-1	20	0.96
XY	PI-1	20	4.4
E	PI-1	20	1.2
C0	PI-2	20	0.13
C4	PI-2	20	0.17
C0	PI-2	79	1.1
C4	PI-2	79	2.5

[a]Concentration of photoinitiators 0.5 mol%, PI-1 = diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate; PI-2 = (4-pentadeclyoxyphenyl)phenyliodonium hexafluoroantimonate.

[b]Calculated from following equation: $R_p/[M_0] = ([conversion]t_2 - [conversion]t_1)/(t_2 - t_1)$.
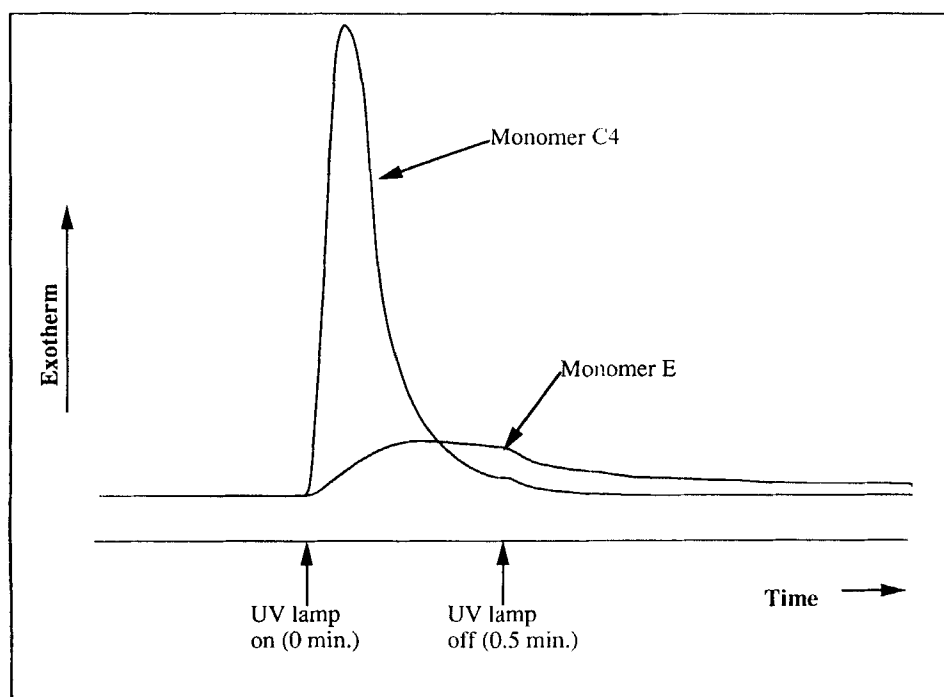

FIG. 6. Differential scanning photocalorimeter curves for the polymerization of monomers C4 and E using 0.5 mol% PI-1.
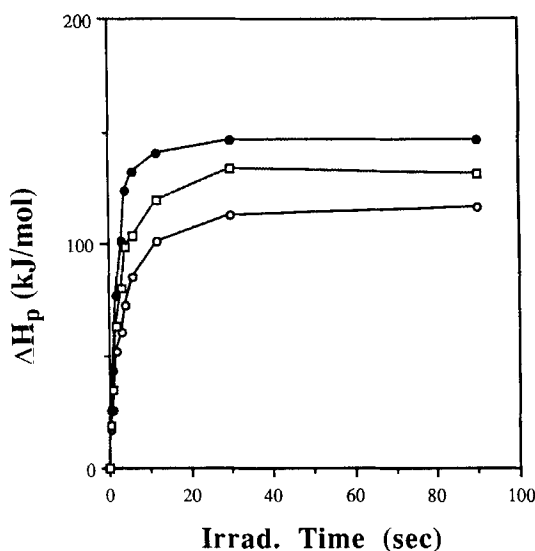
FIG. 7. Differential scanning photocalorimeter plots of the heat of polymerization versus irradiation time for monomers C0 (○), C4 (●), and XY (□) using 0.5 mol% PI-1.

contrast, the exothermic peak due to polymerization of the epoxide is broad and featureless and extends well beyond the irradiation period (0.5 min). In Fig. 7 are given three curves showing the cumulative exothermic heat of polymerization plotted against the irradiation time for the difunctional oxetane monomers C0, C4, and XY. These curves were obtained by integrating the areas under the exothermic differential scanning photocalorimeter traces. The cumulative heats of polymerization are directly proportional to the percent conversion of monomer to polymer at a given irradiation time. The initial rates of all three oxetane monomers are high, and it is difficult to clearly distinguish between them. However, the total amount of heat which is related to the ultimate conversion is different for each case. Hence, it appears from these and the infrared studies that the photopolymerization of monomer XY reaches the highest conversion followed by C4 and then C0.

The precise reasons for the higher reactivity of monomer XY as measured by all three techniques discussed above is not clear. However, preliminary investigations with monomers having similar structures indicate that these monomers also exhibit enhanced reactivity in photoinitiated cationic polymerization. These studies will be the subject of additional communications from this laboratory.

CONCLUSIONS

Difunctional oxetane monomers are a new class of reactive monomers easily prepared by a two-step synthesis. These monomers are more reactive than epoxides with similar structures in photoinitiated cationic polymerization. Among the difunctional oxetane monomers evaluated, monomer XY, containing the xylylene moiety, exhibits the fastest gel time and higher reactivity as judged by real time infrared analysis and photodifferential scanning calorimetry.

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