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Synthesis and Photopolymerization of Silicon-Containing Multifunctional Oxetane Monomers

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SYNTHESIS AND PHOTOPOLYMERIZATION OF SILICON-CONTAINING MULTIFUNCTIONAL OXETANE MONOMERS

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Key Words: Oxetanes; Photoinitiated cationic polymerization; Multifunctional oxetane monomers; Photopolymerization

ABSTRACT

A series of silicon-containing multifunctional oxetane monomers has been prepared and characterized. These monomers were compared among themselves and with other oxetane monomers with respect to their reactivity in photoinitiated cationic polymerization.

INTRODUCTION

Monomers containing silicon atoms are of considerable interest today. Such monomers can be polymerized to provide a wide diversity of applications including scratch- and abrasion-resistant coatings for wood and plastics, and low surface energy adhesive coatings for paper and metals as well as adhesives for many high performance uses. In addition, the presence of a high level of silicon atoms in crosslinked matrices provides excellent oxygen plasma etch resistance which is important for electronic and space applications [1].

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In the past few years, interest in this laboratory has centered on the development of multifunctional silicon-containing epoxide monomers [2, 3]. These efforts have resulted in the synthesis of a series of highly reactive monomers which not only undergo facile and rapid photopolymerization in the presence of cationic photoinitiators, but also yield polymers with excellent chemical and mechanical properties. Studies of these epoxide monomers showed that they possessed much higher reactivities than structurally related monomers which did not contain silicon.

More recently, in a communication from this laboratory, we reported on the development of general synthetic methodology for the preparation of multifunctional monomers bearing cationically polymerizable oxetane groups [4]. Moreover, these monomers may be prepared in high yields by a simple straightforward synthesis from commercially available precursors. It was observed that the oxetane monomers were as reactive as multifunctional epoxy monomers with related structures in photoinitiated cationic polymerization. Based on these observations, it was decided to prepare a series of silicon-containing oxetane monomers and to evaluate their reactivities.

EXPERIMENTAL

General

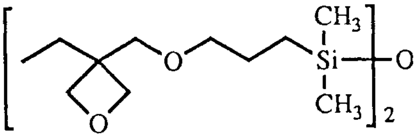
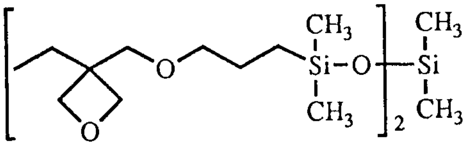
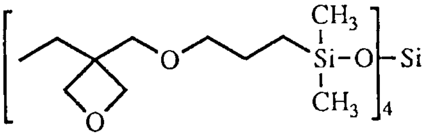
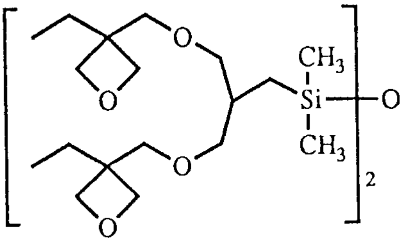
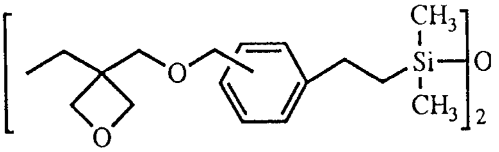
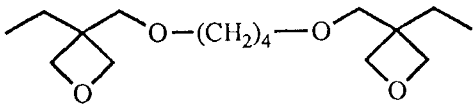
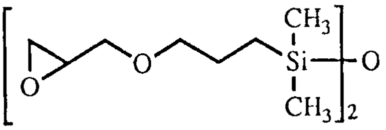
Trimethylolpropane (2,2-dihydroxymethyl-1,3-propanediol) and allyl bromide were used as purchased from the Aldrich Chemical Co. Vinyl benzyl chloride (chloromethylstyrene), a mixture of meta and para isomers, was a gift of the Dow Chemical Co. 1,1,3,3-Tetramethyldisiloxane, 1,1,3,3,5,5-hexamethyltrisiloxane, and tetrakis(dimethylsiloxy)silane were used as purchased from Hüls America. 2-Isopropylthioxanthone was obtained from Polysciences Inc. 1,3-Bis(glycidoxypropyl)-1,1,3,3-tetramethyldisiloxane (monomer SiE) [2] and 3,3′-(1,4-butanediylbis-(oxymethylene))bis(3-ethyloxetane) (monomer C4) were prepared as described previously [4]. All other starting materials and solvents were reagent quality and were used as received. (4-Pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate was synthesized in accordance with a known literature procedure [5].

Routine infrared spectra were obtained on a Buck Scientific Model 500 Spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5840A Gas Chromatograph equipped with 6 ft × ⅛ in. OV-17 phenylsilicone columns equipped with 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. Mass spectra were recorded on a Shimadzu Corporation Model GCMS-QP1000 Mass Spectrometer using chemical ionization techniques with isobutane as the reagent gas.

Preparation of Monomers

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

TABLE 1. The Structure and Characteristics of Oxetane Monomers

Monomer (notation)	Structure	MW	Yield, %
Si2		446.8	67
Si3		520.9	69
Si5		952	48
SMA		679.1	49
ST		599	48
C4		286	–
SiE		362.6	–

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 a head temperature of 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, $-O-C\underline{H}_2-$ *on oxetane ring*).

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

3-Allyloxymethyl-3-ethyloxetane

To a solution of 23.2 g (0.2 mol) 3-ethyl-3-hydroxymethyl-oxetane, 48.4 g (0.4 mol) allyl bromide, 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 hours, 100 mL dichloromethane and 100 mL water were added to the reaction mixture. The organic phase was washed with water twice, dried over magnesium sulfate, filtered, and evaporated. The residue was purified by distillation under vacuum and gave 28.6 g (92% yield) 3-allyloxymethyl-3-ethyloxetane having a boiling point of 55 °C at 1.5 mmHg.

Molecular weight. Calculated for $C_9H_{16}O_2$: 156. Found by CI mass spectroscopy $(M + 1)^+$: 157.

3-((4-Ethenylbenzyl)oxymethylene)-3-ethyloxetane and 3-((2-Ethenylbenzyl)oxymethylene)-3-ethyloxetane (mixture of meta and para isomers)

The previous reaction was repeated using 3-ethyl-3-hydroxymethyloxetane (12.8 g, 0.11 mol) and vinyl benzyl chloride (15.3 g, 0.1 mol). The vinyl benzyl chloride obtained from the Dow Chemical Company was a mixture of meta and para isomers. There was obtained 18.1 g (78% yield) of a colorless oil on purification by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 1:3).

Analysis. Calculated for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%. Found: C, 77.39; H, 8.73%.

Monomer Si2

A mixture of 9.4 g (0.06 mol) 3-ethyl-3-allyloxymethyl-oxetane, 3.4 g (0.025 mol) 1,1,3,3-tetramethyldisiloxane, and 0.01 g tris(triphenylphosphine)rhodium (I) chloride in 15 mL toluene was stirred overnight at 80°C. Then the toluene was removed by using a rotary evaporator. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 1:4) to give 7.5 g (67% yield) monomer Si2.

Analysis. Calculated for $C_{22}H_{46}O_5Si_2$: C, 59.14; H, 10.38; Si, 12.57%. Found: C, 58.58; H, 10.37; Si, 12.27%.

Monomer Si3

Using the previous procedure, 9.4 g (0.06 mol) 3-ethyl-3-allyloxymethyloxetane and 5.2 g (0.025 mol) 1,1,3,3,5,5-tetramethyldisiloxane in the presence of 0.01 g tris(triphenylphosphine)rhodium (I) chloride in 15 mL toluene gave a colorless oil. The pure monomer was obtained in 64% yield (8.3 g) by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 1:4).

Analysis. Calculated for $C_{24}H_{52}O_6Si_2$: C, 55.34; H, 10.06; Si, 16.17%. Found: C, 55.54; H, 10.11; Si, 16.40%.

Monomer Si5

As in the previous example, 7.9 g (0.05 mol) 3-ethyl-3-allyloxymethyloxetane, 3.3 g (0.01 mol) tetrakis(dimethylsilyloxy)silane, and 0.01 g tris(triphenylphosphine)rhodium (I) chloride in 15 mL toluene were combined to give the expected monomer Si5 as a colorless oil. The monomer was purified by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 1:3). There was obtained 7.6 g (80% yield) Si5.

Analysis. Calculated for $C_{44}H_{92}O_{12}Si_5$: C, 55.42; H, 9.72; Si, 14.73%. Found: C, 54.56; H, 9.70; Si, 15.21%.

Molecular weight. CI mass spectroscopy calculated: 952. Found for $(M + 1)^+$: 953.

Monomer ST

The procedure of the previous reaction was repeated using the following reagents: 9.3 g (0.04 mol) 3-((4-ethenylbenzyl)oxymethylene)-3-ethyloxetane, 2.7 g (0.02 mol) 1,1,3,3-tetramethyldisiloxane, and 0.01 g tris(triphenylphosphine)rhodium (I) chloride in 15 mL toluene. Monomer ST was obtained in 5.3 g (41% yield) as a colorless oil on purification by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 35:65). The monomer was a mixture of meta-meta, meta-para, and para-para isomers.

Analysis. Calculated: C, 68.18; H, 9.09; Si, 9.38%. Found: C, 65.97; H, 9.05; Si, 10.34%.

Molecular weight. CI mass spectroscopy calculated for $C_{34}H_{54}O_5Si_2$: 598. Found for $(M + 1)^+$: 599.

Photopolymerization of Difunctional Oxetane Monomers

Photopolymerizations were carried out with bulk monomers containing (4-pentadecyloxyphenyl)phenyldiodonium hexafluoroantimonate (PI-2) as the photoinitiator. In all cases the photoinitiator concentration was kept at 0.5 mol% so that the oxetane monomers and the reference epoxides could be compared directly regardless of the differences in their molecular weights.

Gel Time Measurements

The rates of polymerization of the various monomers were measured by recording their gel times using a Gel Pointe Instrument [6]. 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 μL borosilicate micropipet tubes and one end sealed with a plastic tube and pinch clamp. The time from when the lamp was turned on until oscillation of the meniscus ceased in the capillary tube was recorded as the gel time. The shorter the gel time, the more reactive is the monomer in photoinitiated cationic polymerization.

Real Time Infrared Measurements

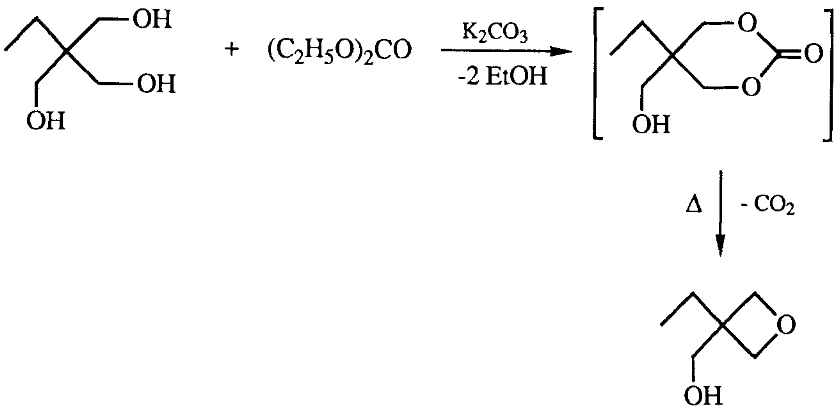
Conversions of the monomers to polymer were measured using real time infrared spectroscopy (RTIR) employing the method of Decker [7]. The apparatus used for these measurements consisted of a Buck Scientific Model 500 Infrared Spectrometer which was equipped with a UVEXS Co. SCU 110 UV Lamp fitted with 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 25 μm thick film samples of the monomers containing 0.5 mol% photoinitiator coated onto 25 μm polyethylene films. Photosensitized polymerizations were conducted with monomer solutions also containing 0.05 mol% 2-isopropylthioxanthone. The samples were irradiated at UV intensities of 20 $\mathrm{mW/cm^2}$ (probe distance: 5 cm) or 79 $\mathrm{mW/cm^2}$ (probe distance; 2.5 cm). During the irradiation, the absorbance decrease of the oxetane band at 980 $\mathrm{cm^{-1}}$ was monitored. After the absorbance decrease had ceased, the conversions of the samples were calculated by comparing the initial and final absorbances. The equation $R_p/[M_0] = ([\text{conversion}]t_2 - [\text{conversion}]t_1)/(t_2 - t_1)$ was used to calculate the $R_p/[M_0]$ values used in Table 3. In the case of the epoxide reference monomer SiE, the decrease in the epoxide band at 760 $\mathrm{cm^{-1}}$ was similarly monitored.

RESULTS AND DISCUSSION

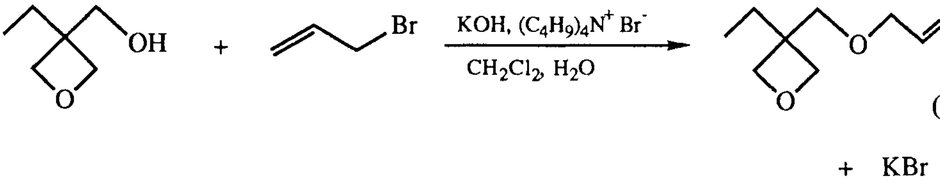
Synthesis of Silicon-Containing Oxetane Monomers

The synthesis of the silicon-containing oxetane monomers used in this research makes use of several common intermediates. The first of these is 3-ethyl-3-hydroxymethyloxetane which was prepared by the method of Pattison [8] and is shown in Eq. (1).

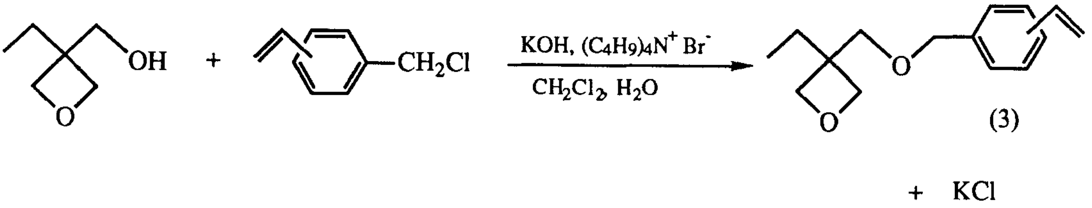


(1)

This method involves an ester exchange of a 1,3-dol with diethylcarbonate to give a six-membered cyclic carbonate with the elimination of ethanol. This cyclic carbonate was not isolated. On further heating, the cyclic carbonate underwent loss of carbon dioxide to generate the desired oxetane. 3-Ethyl-3-hydroxymethyloxetane was condensed, as depicted in Eq. (2), (3), and (4), with allyl bromide and vinyl benzyl chloride to generate oxetanes containing carbon-carbon double bonds.



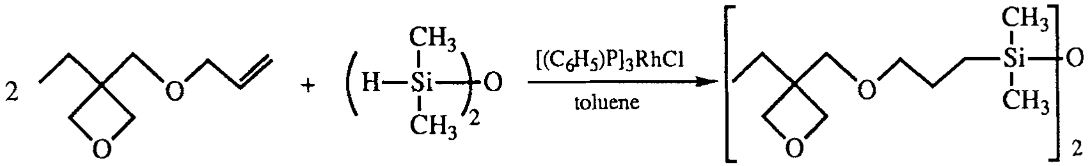
(2)



(3)

The synthetic methods shown in Eqs. (2) and (3) involve the use of phase-transfer catalysis for the nucleophilic displacement of an allylic or benzylic halide. Typically, the yields of these reactions are nearly quantitative. Ethyl-3-hydroxymethyloxetane and 3-allyloxymethyl-3-ethyloxetane were carefully purified by fractional distillation prior to their use in further reactions, while vinylbenzyloxetane was subjected to purification by flash chromatography. A commercially available mixture of isomeric meta and para vinyl benzyl chlorides was used in the reaction shown in Eq. (4). Consequently, a mixture of isomeric vinyl benzyl-substituted oxetanes was obtained as products.

Further condensation of the above two key intermediates with a silane bearing two or four Si—H bonds was carried out using a rhodium-catalyzed hydrosilation reaction. An example of this reaction is given in Eq. (4) for the preparation of monomer Si2.



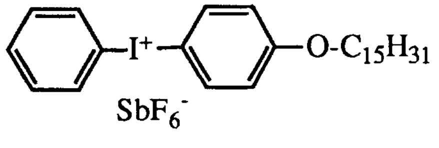
(4)

In the hydrosilation reaction, tris(triphenylphosphine)rhodium (I) chloride (Wilkinson's catalyst) was used as the catalyst. This complex was specifically chosen instead of a conventional platinum-based hydrosilation catalyst to avoid the possibility of competing ring-opening polymerization of the oxetane moieties during synthesis [9].

In general, hydrosilation proceeds smoothly in toluene in the presence of Wilkinson's catalyst to give high yields of the desired silicon-containing multifunctional oxetanes. The monomers were obtained as mobile, colorless liquids after hydrosilation, and they were purified by flash chromatography because of their high boiling points. Displayed in Table 1 are the structures of five different silicon-containing oxetane monomers, along with their calculated molecular weights and yields, that were prepared during the course of these investigations. Each of the monomers was checked for purity by thin layer chromatography and by elemental analysis. Since elemental analyses of silicon-containing compounds is problematic in some cases, the molecular weights and fragmentation patterns of some of the monomers were determined by chemical ionization mass spectroscopy. The yields reported in Table 1 have not been optimized. Monomer ST, prepared from the vinyl benzyl oxetane precursor, was obtained as a mixture of isomers. Also included in Table 1 are the structures of the nonsilicon-containing difunctional oxetane, C4, and the difunctional epoxide, SiE, to which the reactivities of the silicon-containing oxetanes were compared as standards.

Study of the Reactivity of Difunctional Oxetane Monomers

Of primary interest in this work are the reactivities of the silicon-containing multifunctional oxetanes in photoinitiated cationic polymerization. The reactivities of the oxetane monomers shown in Table 1 were compared with each other, with the nonsilicon-containing dioxetane C4, and with the silicon-epoxy monomer SiE in bulk onium salt photoinitiated cationic polymerizations. A number of diaryliodonium and triarylsulfonium salts were screened as cationic photoinitiators for the silicon-containing oxetane monomers. Most simple onium salt photoinitiators were either partially soluble or insoluble in these monomers. However, unsymmetric diaryliodonium salts containing long-chain alkoxy groups substituted at one of the para positions of the two aromatic rings were freely soluble in these monomers [5]. (4-Pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate (PI-2) exhibited very good solubility in all the monomers given in Table 1 and was used in studies of their reactivities.



PI-2

This photoinitiator has a λ_{max} at 247 nm (ϵ = 14,900), and while it has a high quantum yield (~0.7), it is useful only in the short wavelength region of the ultraviolet spectrum. It has been shown, however, that the spectral sensitivity of diaryliodonium salt cationic photosensitizers can be broadened by the use of photosensitizers [10]. Electron-transfer photosensitization is particularly effective for diaryliodonium salts, and the mechanism is depicted in Eqs. (5)-(10).

$$P \xrightarrow{h\nu} P^* \tag{5}$$

$$P^* + Ar_2I^+ X^- \xrightarrow{\text{electron transfer}} P^{+\cdot} X^- + Ar_2I^\cdot \tag{6}$$

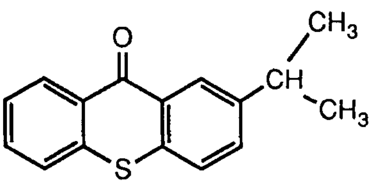
$$Ar_2I^\cdot \longrightarrow ArI + Ar^\cdot \tag{7}$$

$$P^{+\cdot} X^- + Ar^\cdot \longrightarrow Ar{-}P^+ X^- \tag{8}$$

$$Ar{-}P^+ X^- \longrightarrow Ar{-}P + HX \tag{9}$$

$$Ar^\cdot + S{-}H \longrightarrow S^\cdot + Ar{-}H \tag{10}$$

Electron transfer between the excited photosensitizer, P*, and the diaryliodonium salt gives rise to a photosensitizer cation-radical and a diaryliodine free radical (Eq. 6). The diaryliodine free radical (Eq. 7) decomposes to an aryliodide and an aryl radical. Subsequently, the aryl radical can interact both by coupling with the photosensitizer cation-radical (Eq. 8) and by hydrogen abstraction reactions (Eq. 10) with the solvent or monomer, S—H. Most important is the generation of species such as the photosensitizer cation-radical, $P^{+\cdot} X^-$ (Eq. 6), and the acid, HX (Eq. 9), which can initiate cationic polymerization. A large number of different types of photosensitizers for diaryliodonium salts have been investigated. However, in this work we have focused only on one photosensitizer, 2-isopropylthioxanthone [11]:



This compound, with its λ_{max}(MeOH) at 384 nm (ϵ = 6900), has excellent solubility in monomers and exhibits good efficiency in the photosensitization of diaryliodonium salts [12].

Two different techniques were used for the evaluation of the reactivity of the silicon-containing multifunctional oxetane monomers: gel time measurements and real time infrared analysis. It must be noted that each of these methods is based on a different analytical principle, and therefore the reactivities determined by these two methods are also different. In all cases the reactivities of the new monomers were determined by using either the dioxetane C4 or the silicon-containing diepoxide SiE as a reference.

TABLE 2. Gel Times of Oxetane Monomers

Monomer	Photoinitiator,[a] wt%	Gel time,[b] s
Si2	0.82	170
Si3	0.70	190
Si5	0.77	60
ST	0.61	>300
SiE	1.0	270

[a] Concentration of photoinitiator (PI-2) 0.5 mol% excepting monomer Si5: 1.0 mol%. PI-2 = (4-pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate.

[b] Irradiation intensity: 13 mW/cm^2.

Gel Time Measurements

Gel time determinations were made by using a Gel Pointe instrument [7]. This instrument, which was described in a previous communication [4] on oxetane monomers, provides a convenient and reliable measure of the reactivity of photopolymerizable monomers and oligomers. As the monomer containing a photoinitiator is irradiated in a capillary, the oscillation of the meniscus at the air–liquid interface is continually monitored. The oscillation ceases at the gel point, and the total time of irradiation is recorded as the gel time.

This type of measurement is used to monitor 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 crosslinks 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 monomers Si2, Si3, Si5, and ST were determined and compared with the reference compound SiE. The results are given in Table 2. All the oxetane-containing monomers, with the exception of ST, had shorter gel times than the diepoxide reference monomer SiE, indicating that they are more reactive. The tetrafunctional oxetane monomer Si5 shows outstanding reactivity as determined by gel time measurements. Monomer ST appeared to be very sluggish in cationic polymerization (gel time > 300 seconds). We suggest that the reason for the apparent poor reactivity of this monomer could be the presence of aromatic groups in this monomer. These aromatic groups absorb at nearly the same ultraviolet wavelengths as the diaryliodonium salt photoinitiator, and therefore they screen the photoinitiator. Further investigations using real time infrared measurements appear to confirm this conclusion.

Real Time Infrared Measurements

Real time infrared spectroscopy (RTIR) has been shown by Decker [8] to be an excellent method for determining both the rate and extent of free radical and

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

Monomer	Photoinitiator[a]/ photosensitizer[b]	Irradiation intensity, mW/cm^2	$R_p/[M_0]$, s^{-1} [c]
C4	PI-2	13	0.38
Si2	PI-2	13	0.36
Si3	PI-2	13	0.29
Si5	PI-2	13	0.29
ST	PI-2	13	0.23
SiE	PI-2	13	0.14
Si2	PI-2/IPT[c]	13	0.43
ST	PI-2/IPT[c]	13	0.52
C4	PI-2	51	2.5
Si2	PI-2	51	1.1
Si3	PI-2	51	0.81
Si5	PI-2	51	1.4
ST	PI-2	51	1.7
SiE	PI-2	51	0.32

[a] Concentration of photoinitiator (PI-2), 0.5 mol%. PI-2 = (4-pentadecyloxyphenyl) phenyliodonium hexafluoroantimonate.

[b] IPT: 2-Isopropylthioxanthone (0.05 mol%).

[c] Calculated from $R_p/[M_0] = ([\text{conversion}]t_2 - [\text{conversion}]t_1)/(t_2 - t_1)$.

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 SiE. Figures 1-3 show conversion to polymer versus time plots for various monomers obtained in these studies using PI-2 as the photoinitiator. Gathered in Table 3 are the calculated $R_p/[M_0]$ values calculated at the point of maximum change of slope of the absorbance versus time curves for each of the monomers. A comparison of the $R_p/[M_0]$ values is another measure of the relative reactivities among monomers. It should be pointed out, however, that these values are generally representative for only the initial stages of the polymerization prior to the gel point. They are also best applied when comparing a series of closely related monomers.

Figure 1 compares the conversion as a function of time for monomers Si2, Si3, and Si5 with the oxetane (C4) and epoxide (SiE) reference monomers. It is striking that all of the oxetane-containing monomers undergo rapid polymerization to polyethers at approximately the same rates. At the same time the epoxide monomer SiE, which contains glycidyl ether groups, displays considerably poorer reactiv-

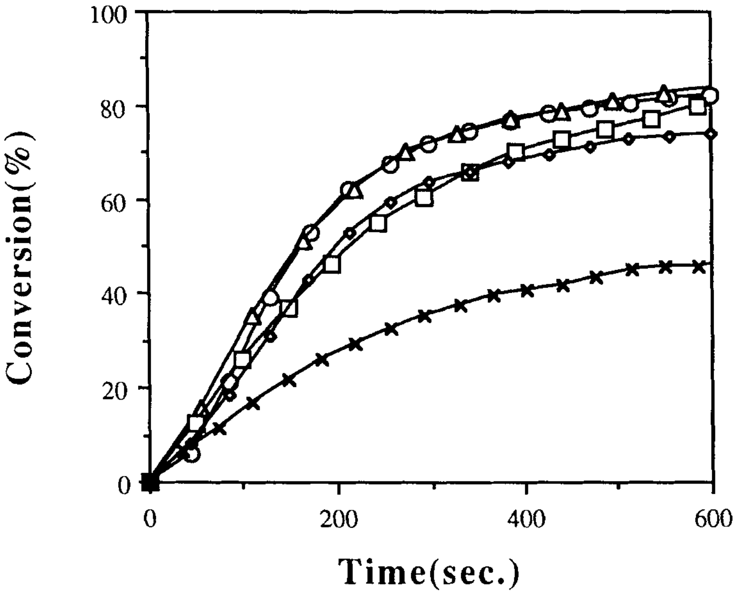


FIG. 1. RTIR conversion versus irradiation time curves for monomers C4 (○), Si2 (△), Si3 (□), Si5 (◇), and SiE (×) using 0.5 mol% PI-2 at a UV intensity of 13 mW/cm^2.

ity. It is also interesting to observe that the polymerizations of the oxetane monomers, independent of their structure, appear to converge at approximately the same degree of conversion. The $R_p/[M_0]$ values from Table 3 generally support the conclusions drawn from an inspection of the conversion versus time curves.

In Fig. 2 the results of the direct and the 2-isopropylthioxanthone photosensitized polymerization of two silicon-containing monomers, Si2 and ST, are compared. When the photosensitizer is employed together with PI-2 to carry out the polymerization of Si2, there is a slight enhancement of the rate of polymerization. This is because Si2 is essentially transparent in the short wavelength region in which the photoinitiator absorbs. Thus, the overall rate enhancement in this case is due to an additive effect of a small incremental amount of photosensitized polymerization to the dominant direct photopolymerization. At the same time, the effect of the presence of 2-isopropylthioxanthone on the polymerization of monomer ST containing aromatic groups is marked. The direct photolysis, which is suppressed due to competitive absorption effects at short wavelengths, can be offset by the addition of the photosensitizer which essentially extends the spectral sensitivity to the mid-UV spectral region in which competitive absorption by the monomer no longer takes place. Thus, the addition of 10 mol% 2-isopropylthioxanthone, based on the diaryliodonium photoinitiator, produces a large increase in rate over direct irradiation. Inspection of the curves shown in Fig. 2 shows that the photosensitized polymerization of ST takes place even faster than that of Si2. This suggests that the reactivity of monomer ST is intrinsically higher than that of Si2.

Data given in Table 3 and the curves shown in Fig. 3 support the above conclusion. In these studies the conversion versus time curves were obtained by using a light intensity of 51 mW/cm^2 as compared to those measured in Fig. 1 at

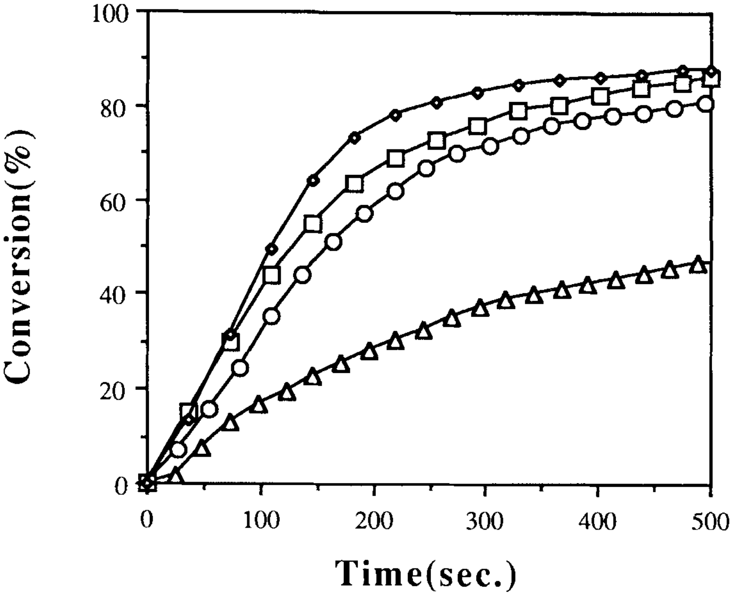


FIG. 2. RTIR conversion versus irradiation time curves for monomers Si2 (○), ST (△), Si2/IPT (□), and ST/IPT (◇) using 0.5 mol% PI-2 at a UV intensity of 13 mW/cm^2.

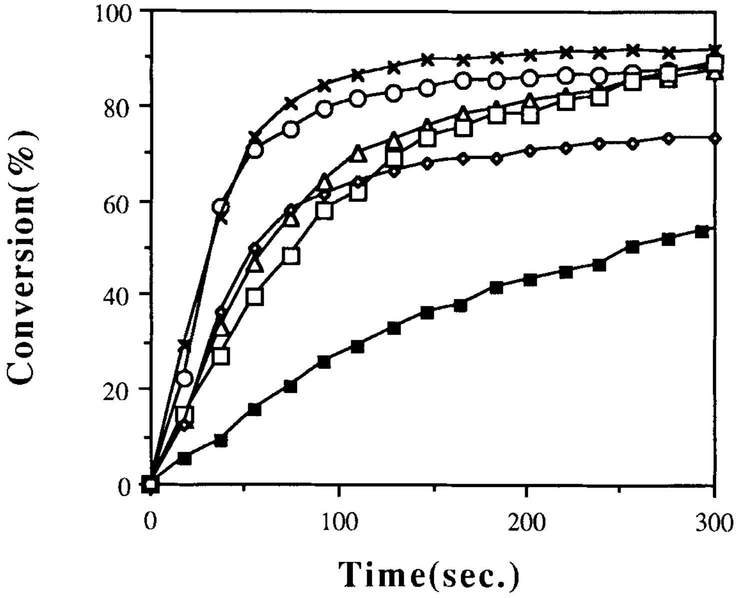


FIG. 3. RTIR conversion versus irradiation time curves for monomers C4 (○), Si2 (△), Si3 (□), Si5 (◇), ST (×), and SiE (■) using 0.5 mol% PI-2 at a UV intensity of 51 mW/cm^2.

13 mW/cm^2. When the light intensity is increased nearly fourfold, the rate of polymerization of monomer ST surpasses all the other monomers except C4. Under these conditions, the competitive absorption by the monomer is overcome by the intensity of the radiation. Silicon-containing oxetane monomers Si2 and Si3 have approximately the same reactivity when irradiated at 13 or 51 mW/cm^2. Since both of these monomers have essentially no absorption in the 240–250 nm region, the photolysis rate of the iodonium salt photoinitiator is already saturated at an intensity of 12 mW/cm^2. However, while the $R_p/[M_0]$ value for the tetrafunctional monomer Si5 indicates an initial high rate, its conversion versus time curve in Fig. 3 shows that the conversion reaches a maximum of only 74%. A considerable number of isolated oxetane groups remain in the polymer film due to the immobility of these groups in the crosslinked matrix. In contrast, the relative reactivity of the difunctional silicon-containing epoxide SiE remains low despite the increase of the light intensity.

CONCLUSIONS

Multifunctional silicon-containing oxetanes can be prepared by simple, straightforward synthetic methods. Gel time and real time infrared analysis are convenient techniques with which to characterize the reactivities of these monomers. The oxetane monomers prepared during this investigation display reactivities in photoinitiated cationic polymerization which are greater than those of structurally related epoxides. However, these novel oxetane monomers containing silicon do not display enhanced reactivity as compared to their nonsilicon-containing analogues. The polymerization of oxetane monomers may be photosensitized by using 2-isopropylthioxanthone, and higher rates of polymerization result due to spectral broadening of the photosensitivity of such systems.

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