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Communications

Synthesis and Photopolymerization of Vinyl Ether and Epoxy-Functionalized Silicones

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Abstract: The reactive precursors, vinyl ethers, and epoxy-silicones, were synthesized. The vinyl ether monomers were prepared from primary alcohol and ethyl vinyl ether with mercury (II) acetate. The epoxy-functionalized silicones have been achieved by the controlled, rhodium-catalyzed, chemoselective hydrosilation of vinyl ether with siloxanes or silane. It was shown that the hydrosilation proceeds exclusively at the vinyl ether group of alkenyl vinyl ether without participation at the alkenyl group. The photoinduced cationic polymerization of these monomers was studied and found to be all highly reactive.

Keywords: cationic polymerization, siloxane, silicone, uv-curing, vinyl ether, epoxy, hydrosilation.

Introduction

Functionalized siloxane and silane monomers and oligomers that undergo rapid photoinitiated cationic crosslinking reactions are technologically important materials. These siloxane network polymers possess interesting properties, such as high thermal stability, oxidative stability, low surface energy, water repellency, good dielectric properties, high gas permeability, and bioinertness.[1-3] Photoinitiated cationic polymerization using onium salts as efficient photoinitiators have the advantages of oxygen insensitivity and the ability to polymerize by vinyl ether, propenyl ether, and epoxy functional groups.[4-8] Besides the high rates of polymerization that can be achieved using photoinduced polymerization, such materials are attractive in that they also require inherently low energy consumption and produce no air or water pollution.[2,3]

For most practical application, it is especially important to develop monomers with high reactivity and low cost. There is an ever-increasing demand for silicone monomer systems that undergo even more rapid photopolymerization. It would also be of considerable interest if means could be devised to find the simple synthetic method. Several approaches to the synthesis of photopolymerizable siloxane monomers and oligomers have been taken.[9-12] Typically, epoxy-modified siloxanes and silanes can be prepared by the hydrosilation of vinyl or vinyl ether-containing molecules using various Si-H functional materials.[14-17]

In this study, we describe the synthesis of a new vinyl ether monomers and epoxy modified silicone monomers. Results of the cationic photopolymerization of a number of novel vinyl ether and epoxy silicone monomers are also reported.

Experimental

Materials. 1,1,3,3-Tetramethyldisiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane, methyldiphenylsilane, crotyl alcohol, 3-cyclohexene-1-methanol, 2,4-hexadien-1-ol, oleyl alcohol, ethyl vinyl ether, mercury (II) acetate, *m*-chloroperbenzoic acid, and $Rh(PPh_3)_3Cl$ were purchased from Aldrich Chemical Co. and used without further purification. Common reagents such as sodium bicarbonate, sodium carbonate, sodium hydrogen sulfate, and methylenechloride were used without further purification. The cationic photoinitiator, (4-decyloxyphenyl) phenyliodonium hexafluoroantimonate, was prepared as described previously.[18] The ^1H NMR spectra were recorded on a Brucker DRX (300 MHz) spectrometer. $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) was used as internal standard. Routine infrared spectra and real-time infrared spectra were recoded on a Midac M-2000 Fourier transform spectrometer.

Preparation of 3-Cyclohexene-1-methyl Vinyl Ether

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(VE1). The reaction was carried out by following the literature procedure.[19] To a 1 L round bottom flask equipped with a reflux condenser and a nitrogen inlet were added ethyl vinyl ether (300 g, 4.6 mol), 3-cyclohexene-1-methanol (25 g, 0.023 mol), and mercury (II) acetate (2.2 g, 0.007 mol), is stirred at room temperature for 18 h while is monitored periodically by GC and TLC. The mixture was poured into 500 mL water and organic layer was separated. The separated solution was evaporated on rotary evaporator; 89% yield; IR (KBr); 1210, 1320 cm^{-1} (vinyl ether C-O-C), 1630 cm^{-1} (vinyl ether double bond), 1655 cm^{-1} (cycloaliphatic double bond). ^1H NMR ($CDCl_3$) 0.88-2.08 (m, aliphatic CH), 3.56 (d, C$\underline{H}_2$-O, J=3.7 Hz), 3.96-3.98 (d, O-CH=C$\underline{H}_2$, J_{cis}=8.5 Hz), 4 15-4.19 (d, O-CH=C$\underline{H}_2$, J_{cis}=13.7 Hz), 5.65-5.69 (m, cyclohexene C$\underline{H}$=C$\underline{H}$), 6.46-6.51 (q, O-C$\underline{H}$=CH_2).

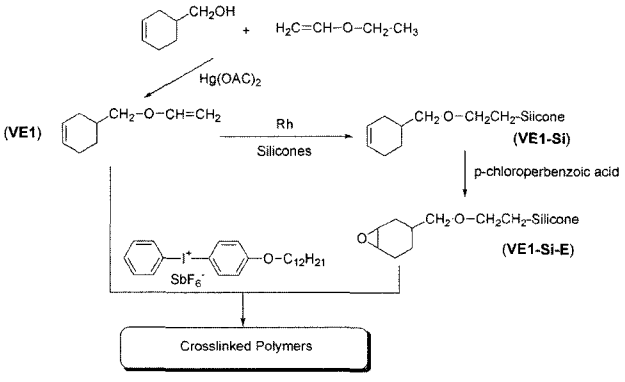
Preparation of a Siloxane-Containing 3-Cyclohexene-1-Methyl Ether (VE1-Si1). In a 50 mL three-necked flask fitted with a condenser, a thermometer, and a magnetic stirrer was placed vinyl ether (**VE1**) (5.14 g, 37.2 mmol) under a nitrogen atmosphere. 1,1,3,3-Tetramethyldisiloxane (2.5 g, 18.6 mmol) and $Rh(PPh_3)_3Cl$ (0.05 g, 0.055 mmol) were added to the solution. The reaction mixture was heated and stirred at 40 °C for 2 h. During that reaction, the initial reaction mixture became a light yellow solution. The mixture was washed with water and chloroform (1 : 1) and organic layer was separated. The organic layer dried with magnesium sulfate and evaporated on rotary evaporator; 95 yield; IR (KBr); 1655 cm^{-1} (cycloaliphatic double bond). ^1H NMR ($CDCl_3$) δ 0.06-0.13(m, Si-CH_3), δ 0.96(t, -CH_2-Si, J=7.4 Hz), δ 3.26(t, -C$\underline{H}_2$- CH_2-Si, J=3.2 Hz), δ 3.50(t, C$\underline{H}_2$-O, J =3.6 Hz), δ 5.65-5.69 (m, cyclohexene C$\underline{H}$=C$\underline{H}$).

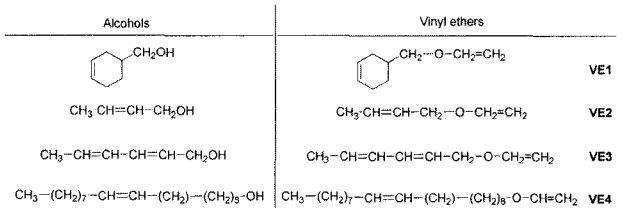
Epoxidation of VE1-Si1 (VE1-Si1-E). To a 100 mL round bottom flask fitted with condenser, and a thermometer were placed **VE1-Si1** (5 g, 0.012 mol) in 60 mL of dichloromethane. Sodium bicarbonate (2.23g, 0.021 mol) was added and the reaction mixture cooled to 0 °C in an ice bath. A solution of 9.0 g of 85% *m*-chloroperbenzoic acid in 80 mL dichloromethane was added to the reaction mixture and allowed to stir for 2 h. The reaction mixture was filtered, and the filtrate diluted with ether and extracted first, with a saturated aqueous solution of sodium carbonate, then a 10% solution of sodium hydrogen sulfate and finally, a saturated solution of sodium bicarbonate. The ether layer was separated and dried over anhydrous magnesium sulfate. **VE1-Si1-E** was obtained as a colorless liquid after removal of the solvents on a rotary evaporator; 65% yield; IR (KBr); 785, 810 cm^{-1} (epoxy group). ^1H NMR ($CDCl_3$) δ 0.06-0.13 (m, Si-CH_3), δ 0.96 (t, -CH_2-Si, J = 7.3 Hz), δ 3.13-3.22 (m, O-C$\underline{H}_2$- C$\underline{H}_2$-Si and epoxy-$\underline{H}$), δ 3.46 (t, C$\underline{H}_2$-O, J = 3.5 Hz).

Real-Time Infrared Spectroscopy (RTIR). The photoinitiated cationic polymerizations of the monomers were studied by RTIR.[16] Measurements were performed on a Midac M2000 FTIR and equipped with a Dr. Honle UV lamp fitted with a fiber optic cable. Samples were prepared by placing the liquid monomer containing 0.5 mol% of (4-decyloxyphenyl)phenyliodonium hexafluoroantinonate per vinyl or epoxy equivalent between two 13.5 μm polyethylene films.

Results and Discussion

Vinyl ether synthesis was accomplished by the treatment of primary alcohols with a large excess (20 eq.) of ethyl vinyl ether in the presence of a catalytic amount (2.5 mole%) of mercury (II) acetate. The mixture compounds were separated by flash column. The silane compounds have been prepared by selective hydrosilation of silane (Si-H) vinyl ether monomers using an Rh catalyst without participation on double bond of alkenyl group (Scheme I). A series of multifunctional siloxane monomers were prepared by using Wilkinson's catalyst ($RhCl[(C_6H_5)_3P]_3$) for the hydrosilation reaction.[6,17] The hydrosilation reaction may be conveniently monitored by following the decrease of the bands at δ 3.97 ppm, 4.17 ppm, and 6.48 ppm due to the attachment at the carbon of double bond of the vinyl ether group or the appearance and increase of the band at δ 0.97 ppm due to the Si-CH_2 groups which are newly formed. The ^1H NMR spectrum is complicated by the peaks in the area of aliphatic groups as expected.(Figure 1) The siloxane and silane compounds were listed in Table I. The epoxy silicone precursor was prepared by epoxidation on double bond of alkenyl group. (Scheme I) The silicon monomers were listed in Table I. Among them, epoxidation of **VE2-Si** and **VE3-Si** was successfully carried out under same condition, but they





Scheme I. Synthetic scheme for vinyl ether and epoxy functionalized silicones.

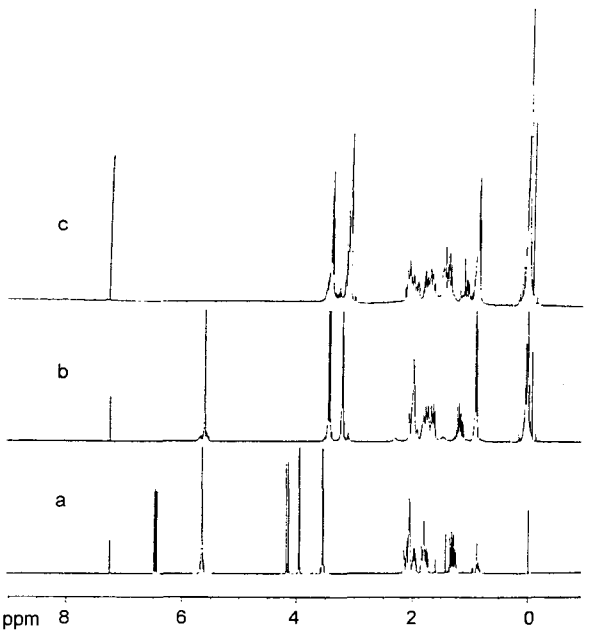
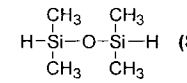
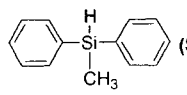
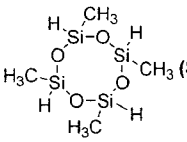


Figure 1. ^{1}H-NMR spectra of (a) **VE1**, (b) **VE1-Si1**, and (c) **VE1-Si1-E** in $CDCl_3$.

could not be isolated. It may be occurred to ring-opening reaction itself because of instability in air atmosphere. The analysis of these compounds is now under way.

The prepared vinyl ether and epoxy siloxane monomers are readily and rapidly photopolymerized by exposure to UV in the presence of decyloxy-diarylidonium salts as cationic photoinitiators.[18] In most cases, 0.5 mol% of this photoinitiator per vinyl or epoxy equivalent was employed. The reactivity of the novel monomers was obtained using real-time infrared spectroscopy (RTIR).[20] In these studies, the decrease in IR bands at 1210 cm^{-1} (vinyl ether C-O-C), 1630 cm^{-1} (vinyl ether double bond), and 810 cm^{-1} (epoxy) assigned to monomers were followed continuously as a function of time. Because many of the monomers were found to be highly reactive, it was found necessary to adjust the light intensity to a low level (1100 $mJ/cm^2 \cdot min$) to slow the polymerization sufficiently to allow data collection and to facilitate direct comparison of their rates. The results are shown in Figures 2 and 3. As is usually observed, the short chain vinyl ether monomers (**VE1**, **VE2,** and **VE3**) proceeded to the highest conversion (~95%) than **VE4** containing long chain (80%) (Figure 2). This result can be explained based on the following speculation; the long chain alkyl chain provides for efficient intermolecular reaction of epoxy groups due to unhindered and conformationally free to rotate. Mono- and di-epoxy silicone monomers (**VE1-Si1-E, VE1-Si2-E**) proceeded to the highest conversion, while increasingly higher functional monomer (**VE1-Si2-E**) proceed to lower overall conversions due to the decreasing mobility of functional groups as increasingly higher cross-linked networks are formed. The epoxy-silicone monomer (**VE4-Si1-E**) containing long chain alkyl group shows a lower conversion rate than the short chain monomers. Tetra-epoxy monomers (**VE1-Si4-E**) exhibit higher polymerization rates than mono-and di-epoxy monomers (**VE1-Si1-E, VE1-Si2-E, VE4-Si1-E**) at an early stage. The kinetic parameter $R_p/[M_o]$ for selected kinetics runs was determined from the initial slopes of the irradiation time-conversion curves according to equation: $R_p/[M_o] = ([\text{conversion}]_{t2} - ([\text{conversion}]_{t1})/(t_2 - t_1)$ where R_p and $[M_o]$ are the rate of polymerization and the initial monomer concentration, respectively, and the conversions are as determined from the curves at irradiation time t_1 and t_2.[4] The slopes of the curves indicate that the cat-

Table I. Structure and Notation of Alkenyl Silicones and Epoxy Functionalized Silicones

Silane or siloxysilane compounds	Vinyl-Si	Epoxy-Si
 (Si1)	VE1-Si1, VE4-Si1	VE1-Si1-E, VE4-Si1-E
 (Si2)	VE1-Si2	VE1-Si2-E
 (Si3)	VE1-Si3	VE1-Si3-E

VE-Si : R—O—CH_2·CH_2·Si, VE-Si-E : Epoxy—O—CH_2·CH_2·Si

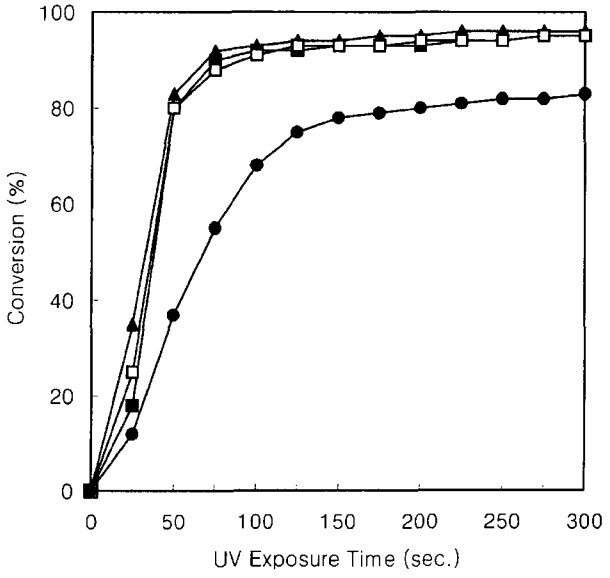


Figure 2. RTIR study of the cationic photopolymerization of **VE1** (▲), **VE2** (□), **VE3** (■), and **VE4** (●).

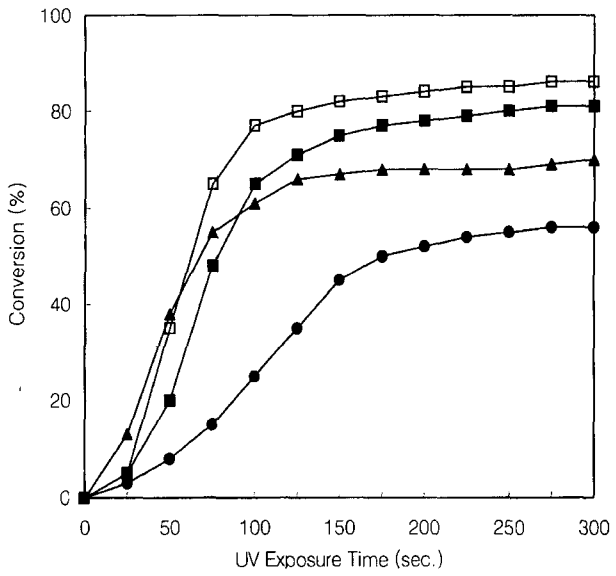


Figure 3. RTIR study of the cationic photopolymerization of **VE1-Si1-E** (▲), **VE1-Si2-E** (□), **VE1-Si3-E** (■), and **VE4-Si1-E** (●).

ionic polymerizations of **VE**, **VE2,** and **VE3** take place at the highest rate ($R_p/[M_o]$ = 1.1-1.2 s^{-1}), whereas the corresponding polymerization of **VE4** proceeds slowly ($R_p/[M_o]$ = 0.6 s^{-1}). Di-epoxy silicone monomer (**VE1-Si1-E**) proceeds to the highest rate ($R_p/[M_o]$ = 0.89 s^{-1}), while **VE1-Si2-E**, **VE1-Si3-E**, and **VE4-Si1-E** undergo at the rate of 0.83, 0.74, and 0.29 s^{-1} respectively. In general, the rate of polymerization of vinyl ether is more rapid than the epoxide ring opening polymerization reaction.[4,5] Similar effect was observed and the conversions of vinyl ethers were higher than those of epoxy ones in this study. From these results, it would appear that such monomers possess the requisite reactivity necessary to be useful in such high curing speed applications as paper and plastic coatings.

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