Preparation of 1-Propenyl Ether Functional Siloxanes by Chemoselective Hydrosilation and Their Cationic Photopolymerization

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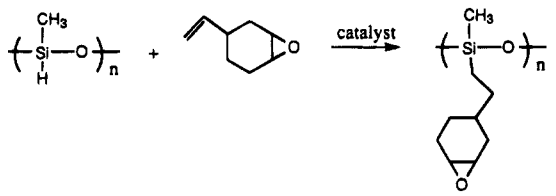
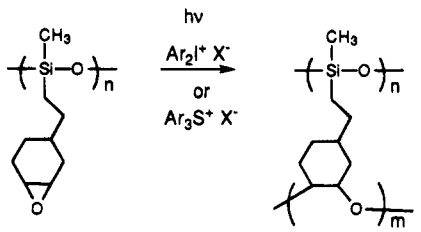
ABSTRACT: Using model compounds, it was shown that the hydrosilation of (1-propenoxy)norborn-5-enes takes place chemoselectively only at the norbornene double bond. Accordingly, a variety of mono-, di-, and multifunctional 1-propenyl ether substituted siloxanes were readily prepared in high yields by the hydrosilation of (1-propenoxy)norborn-5-enes with various linear and cyclic hydrogen functional siloxanes. These new monomers and oligomers undergo rapid photoinduced cationic polymerization in the presence of onium salt photoinitiators. To study these very fast photopolymerizations, extensive use of Fourier transform real-time infrared spectroscopy was made. Employing this technique, the effects of monomer and photoinitiator structure on the rates of polymerization were studied.

Introduction

In recent years, a major effort in this laboratory has been directed toward the design and synthesis of specially tailored multifunctional monomers and oligomers which can be rapidly and efficiently cationically photopolymerized. Of particular interest are reactive monomers and oligomers containing silicon. Previous publications from this laboratory[1–4] and others[5,6] have described the preparation and cationic photopolymerization of epoxy functional siloxanes. An example of the preparation of siloxane oligomers bearing pendant epoxycyclohexane rings is given in eq 1.



(1)



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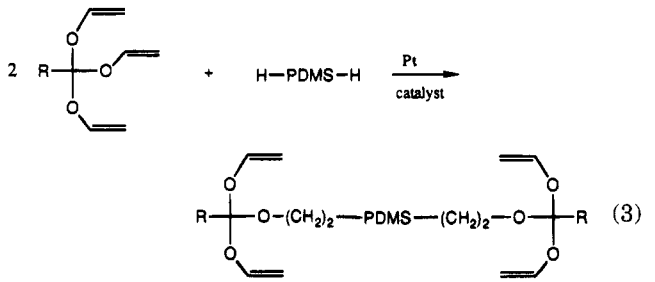
Siloxane monomers bearing epoxycyclohexyl groups display extraordinarily high reactivity in photoinitiated cationic polymerization (eq 2), which makes them especially attractive for applications as electronic and decorative coatings, adhesives and inks, and composites. One current commercial application for epoxy functional siloxane oligomers is as photocurable adhesive release coatings. The high rates of photopolymerization and low surface energy are the key attractive properties of these materials for adhesive release coating applications.

While epoxy functional siloxane monomers and oligomers exhibit excellent reactivity in photoinitiated cationic polymerization, there is a continual search for alternative materials with even higher reactivities. One class of monomers which exhibits even higher reactivity than epoxy monomers in cationic photopolymerizations are vinyl ethers.[7] For this reason, attempts have been made to incorporate a vinyl ether functional group into siloxane monomers and oligomers. Herzig and his coworkers[8] have prepared poly(dimethylsiloxanes) bearing pendant and terminal vinyl ether groups. An example of the route which was employed for their synthesis is depicted in eq 3.



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The reaction shown in eq 3 shows the product to be a tetrafunctional poly(dimethylsiloxane) (PDMS) oligomer. However, since the hydrosilation reaction occurs equally and without selectivity at all three of the vinyl ether groups, a variety of higher functional oligomers are also simultaneously produced. When the synthesis of poly(dimethylsiloxane) oligomers bearing many pendant vinyl ether groups is attempted using this method, uncharacterizable gels result. The objective of this investigation was to develop alternative chemistry which would allow the synthesis of well characterized siloxanes bearing functional groups with reactivities similar to vinyl ethers.

Experimental Section

General Procedures. 1,1,3,3-Tetramethyldisiloxane, phenyldimethylsilane, methyltris(dimethylsiloxy)silane, phenyltris(dimethylsiloxy)silane, and 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H) were used as purchased from Hüls America, Inc. Poly(dimethylsiloxane-*co*-methylhydrosiloxane) random copolymer (average structure $M^HD_{60}D_5^HM^H$; i.e., Si–H terminated, 60:5 mol ratio dimethylsiloxy:methylhydrogensiloxy repeat units; M_n = 4874), an epoxycyclohexyl functional poly(dimethylsiloxane) (GE-9500), the Karstedt catalyst,[9] and UV-9380C (45% bis(4-dodecylphenyl)iodonium hexafluoroantimonate in a 47% solution of C_{12-14} alkyl glycidyl ethers

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containing 2% 2-isopropylthioxanthone) were obtained as gifts from General Electric Silicones. Allyl bromide, tetra-*n*-butylammonium bromide, 5-norbornene-2-methanol (**I**), *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride, furan, ethyl acrylate, and tris(triphenylphosphine)ruthenium (II) dichloride [$(Ph_3P)_3RuCl_2$] were purchased from Aldrich Chemical Co. and used without further purification. Toluene used for hydrosilations was dried over metallic sodium. The cationic photoinitiator, (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate was prepared as described previously.[10]

Routine 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% phenylmethylsilicone) column and a flame ionization detector. ^{1}H-NMR spectra were obtained using a Varian XL 500 MHz spectrometer at room temperature in $CDCl_3$. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

Synthesis of (1-Propenoxy)norborn-5-enes. The following experimental procedures are typical of those used for the preparation of (1-propenoxy)norborn-5-enes.

Preparation of 5-Norbornene-1,2-dimethanol (1,2-Bis(hydroxymethyl)bicyclo[2.2.1]hept-5-ene) (II). Into a 100 mL round-bottom flask fitted with an overhead mechanical stirrer, addition funnel, reflux condenser, and nitrogen inlet was dispersed 12.48 g (0.33 mol) of lithium aluminum hydride in 400 mL of dry THF. To this mixture was slowly added 50 g (0.274 mol) of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride at such a rate that the THF boiled gently. After complete addition, the mixture was refluxed for an additional 3 h and then allowed to stand overnight at room temperature. To the reaction mixture was slowly added 100 mL of a saturated NaCl solution. The solution was filtered to remove the precipitated salts, and the filtrate and the salts were extracted with ethyl acetate and combined. After removal of the solvents on a rotary evaporator, the residue was recrystallized from toluene. The desired product, **II**, was obtained in 87% yield (41.0 g) as colorless needles with a melting point of 84 °C.

^{1}H-NMR ($CDCl_3$): δ 1.37 ppm (s, 2H), 2.50 (m, 2H), 2.75 (s, 2H), 3.32 (m, 2H), 3.62 (m, 2H), 4.1–4.7 (2H, OH), 6.01 (s, 2H).

Preparation of Ethyl 7-Oxanorborn-5-ene-2-carboxylate (Ethyl 7-Oxabicyclo[2.2.1]hept-5-ene-2-carboxylate). Weighed into a 50 mL Fisher–Porter reactor were 9.53 g (0.14 mol) of furan, 10.06 g (0.1 mol) of ethyl acrylate and 12.5 g of zinc chloride. The reaction vessel was sealed and the zinc chloride was dissolved by stirring and heating at 70 °C. Heating was continued at 60 °C for 18 h. After cooling, the reaction mixture was diluted with 100 mL of ethyl acetate, and washed first with 20 mL of a saturated sodium thiosulfate solution and then with distilled water, and finally dried over anhydrous sodium sulfate. The solution was concentrated in vacuo and then distilled under reduced pressure to give 6.60 g (39% yield) of the desired unsaturated bicyclic ester with a bp of 60 °C/0.1 mmHg. The isolated product was a 1:4.5 mixture of *endo*:*exo* isomers.

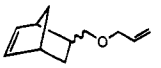
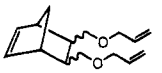
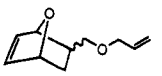
^{1}H-NMR ($CDCl_3$): δ 1.29 (m, 3H), 1.53 (m, 1H), 2.13 (m, 1H), 2.41 (quart, 1H, *exo*), 3.09 (quint, 1H, *endo*), 4.15 (m, 2H), 5.05 (m, 1H), 5.17 (s, 1H), 6.17–6.44 (m, 2H).

Synthesis of 7-Oxanorborn-5-ene-2-methanol (2-(Hydroxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene) (III). In a manner similar to the above procedure, 35 g (0.208 mol) of ethyl 7-oxanorborn-5-ene-2-carboxylate was reduced in 300 mL of dry THF using 4.74 g (0.125 mol) of lithium aluminum hydride. Employing an identical workup procedure, 22.3 g (85% yield) of the desired 7-oxanorbornene-2-methanol with a bp of 50 °C/0.01 mmHg were obtained.

^{1}H-NMR ($CDCl_3$): δ 0.70 (quart, 1H), 1.1–1.47 (m, 2H), 1.7–2.05 (m, 2H), 2.45 (m, 1H), 3.20 (t, 1H), 3.39–3.82 (m, 2H), 4.82–5.07 (m, 2H), 6.20–6.40 (m, 2H).

General Synthesis of the Allyl Ethers of 5-Norbornene-2-methanol, 5-Norbornene-2,3-dimethanol, and 7-Oxanorborn-5-ene-2-methanol (2-(Allyloxy)bicylco[2.2.1]hept-5-ene, 2,3-Bis(allyloxy)bicyclo[2.2.1]hept-5-ene, and 2-(Allyloxy)-7-oxabicyclo[2.2.1]hept-5-ene, IA, IIA, and IIIA).

Table 1. Structure and Properties of (Allyloxy)norborn-5-enes

Structure	Notation	Yield (%)	Boiling Point (°C/mm)
	IA	93	45/0.8
	IIA	67	89/0.15
	IIIA	84	47/0.05

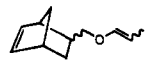
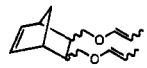
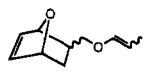
To 0.5 mol of the appropriate alcohol (0.25 mol of 5-norbornene-2,3-dimethanol) were added 78.64 g (0.65 mol) of allyl bromide, 26 g (0.65 mol) of sodium hydroxide, and 200 mL of toluene in a three-necked flask equipped with a thermometer, overhead stirrer, and a reflux condenser. The reaction mixture was stirred under nitrogen for 15 min and then heated by means of a heating mantle to 45 °C. At this point, 10 g of tetra-*n*-butylammonium bromide was added and the temperature raised to 90 °C. The reaction mixture was maintained at this temperature for 18 h, cooled to room temperature, and poured into 300 mL of water. The organic layer was separated and washed twice with water to remove the phase transfer catalyst. After evaporation of the solvent on a rotary evaporator, the residue was distilled under reduced pressure and then further purified by flash column chromatography on silica gel using a 1:9 mixture of ethyl acetate and hexane. After this procedure, the products were free of the starting alcohols and displayed the complete absence of an OH band in the infrared. Table 1 gives the structures, yields, and boiling points of the (allyloxy)-norborn-5-enes.

General Procedure for the Isomerization of (Allyloxy)norborn-5-enes to (1-Propenoxy)norborn-5-enes (2-(1-Propenoxy)bicylco[2.2.1]hept-5-ene, 2,3-Bis(1-Propenoxy)-bicyclo[2.2.1]hept-5-ene, and 2-(1-Propenoxy)-7-oxabicyclo[2.2.1]hept-5-ene, IP, IIP, and IIIP). Into a 50 mL three-necked flask fitted with a nitrogen inlet, a reflux condenser, magnetic stirrer, and an addition funnel was dissolved under nitrogen at 120 °C 1.22 g (10 mmol) of potassium *tert*-butoxide in 10 mL of DMSO. To this solution maintained between 115 and 120°C was added 0.1 mol of the allyl ether via the addition funnel. After the addition had been completed, the dark reaction mixture was stirred for 15 min, cooled to room temperature, and poured into 100 mL of water. To this mixture was added 30 mL of ethyl acetate and the organic phase was separated and washed three times with 50 mL of distilled water. The organic solvent was removed on a rotary evaporator and the residue distilled under reduced pressure to give the desired 1-propenyl ethers. Table 2 presents the data for the three (1-propenoxy)norborn-5-enes produced according to the above procedure.

Hydrosilations of (1-Propenoxy)norborn-5-enes. All the hydrosilations of the (1-propenoxy)norborn-5-enes using a variety of Si–H functional silanes and siloxanes were carried out in a similar manner. The following procedure is typical for the preparation of the 1-propenyl ether functional siloxanes.

To 2.69 g (20 mmol) of 1,1,3,3-tetramethyldisiloxane and 6.73 g (41 mmol) of 5-norbornene-2-methyl 1-propenyl ether (**IP**) in a 50 mL round-bottom, two-necked flask was added 10 mL of dry toluene. To this solution was added 1 μL of the Karstedt catalyst (3% Pt complex solution in xylene). The reaction mixture was stirred under nitrogen initially at 50 °C. The resulting reaction exotherm carries the temperature to approximately 100 °C. After 1 h the reaction was complete as indicated by the disappearance of the Si–H infrared band at 2160 cm^{-1}, and the reaction mixture was cooled and the

Table 2. Structure and Properties of (1-Propenoxy)norborn-5-enes

Structure	Notation	Yield (%)	Boiling Point (°C/mm)	Elemental Analysis	%C	%H
	IP	97	38/0.1	Calc: Found:	80.44 80.15	9.82 9.82
	IIP	98	89/0.15	Calc: Found:	76.88 76.81	9.46 9.52
	IIIP	98	52/0.025	Calc: Found:	72.26 72.23	8.49 8.55

solvent removed on a rotary evaporator. In this case, the product was further purified by distillation under reduced pressure (0.1 mm) at 210 °C in a microdistillation apparatus. A 97% yield (8.95 g) of the difunctional siloxane monomer **IP2** was obtined.

Nonvolatile monomers were purified by first removing the solvent from the reaction mixture. Then the residue was poured into methanol, the lower (siloxane containing) phase was recovered, and the solvent and unreacted starting materials removed in vacuo at 180 °C.

Table 3 gives the structures, yields, and notations for the silicon-containing monomers prepared during this work.

Photopolymerization of 1-Propenyl Ether Functional Siloxanes. Thin-Film Photopolymerizations. 1-Propenyl ether functional monomers and oligomers containing 0.5 mol % (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate were spread as thin (approximately 25 μm) films onto glass plates and then irradiated using a Fusion Systems Inc. laboratory UV cure processor fitted with a microwave-activated 300 W UV lamp aligned perpendicular to the travel of the conveyor belt and mounted at a distance of 10 cm from the belt. The monomers and oligomers exhibited very high rates of polymerization and required less than 1 s of irradiation to produce a tack-free film.

Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR). More definitive photopolymerization data were obtained using Fourier transform real-time infrared analysis (FT-RTIR). This method involves the monitoring of an appropriate IR band due to the polymerizing group while simultaneously irradiating the thin-film sample with UV light. Measurements were performed on a Midac Series M Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled MCD detector. The instrument was fitted with a UVEXS Co SCU 110 UV lamp equipped with a flexible liquid optic cable directed at a 45° angle onto the sample window. All studies were conducted using broad band, unfiltered UV light at an intensity of 18–19 mW/cm^2. Samples were prepared by placing the liquid monomer containing 0.25 mol % per 1-propenyl ether equivalent of either (4-(*n*-decyloxy)-phenyl)phenyliodonium hexafluoroantimonate or 2 wt % commercial bis(dodecylphenyl)iodonium hexafluoroantimonate solution (UV-9380C) between two poly(vinylidene chloride) films and then mounting the sandwich in 5 cm × 5 cm slide frames. The progress of the polymerizations of the 1-propenyl ether functional silanes and siloxanes were determined quantitatively by monitoring the decrease of the 1-propenyl ether double bond peaks at 1660–1670 cm^{-1}. Similarly, the polymerization of an epoxy functional silane (GE-9500) was monitored by following the 3000 cm^{-1} bond due to the epoxy C–H bond. The data were collected on a Bit-Wise Co. 486 PC computer, reduced, and plotted as conversion versus time curves with the aid of a Galactic Industries Corp. Grams 386, Version 3.0 software package. Light intensity measurements were made with the aid of an International Light Co. Control-Cure radiometer.

The kinetic parameter $R_p/[M_0]$ was determined from the slopes of the irradiation time–conversion curves according to eq 4.

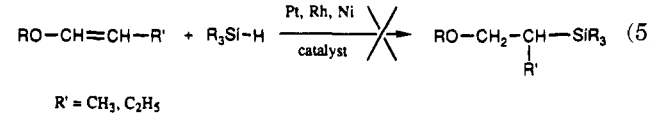
$$R_p/[M_0] = ([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1})/(t_2 - t_1) \quad (4)$$

where R_p and $[M_0]$ are respectively the rate of polymerization and the initial monomer concentration and the conversions are as determined from the curves at irradiation times t_1 and t_2.

Results and Discussion

Monomer Synthesis and Characterization. One of the most widely utilized reactions in silicon chemistry is the hydrosilation reaction in which the Si–H group is added to an unsaturated carbon–carbon double bond in the presence of a catalyst or light. Typically, hydrosilation reactions proceed under mild conditions to high conversions of the desired organosilicon compound. We decided to employ this reaction for the preparation of monomeric and oligomeric siloxanes bearing cationically polymerizable functional groups. To accomplish this objective, we therefore required a series of intermediates with two functional groups, an unsaturated group which undergoes facile hydrosilation and an additional functional group which is highly reactive toward cationic polymerization but does not itself hydrosilate nor inhibit the hydrosilation of the first functional group.

Several key observations suggested that it might be possible to meet these criteria. Recent investigations in this laboratory showed that 1-propenyl ethers are a class of highly electron-rich monomers which undergo facile photoinitiated cationic polymerization in the presence of onium salt photoinitiators.[11,12] The rates of photopolymerization of 1-propenyl ethers are comparable to those of vinyl ethers. An additional key observation which has been made in this laboratory[13] is that despite their close structural and electronic similarity to vinyl ethers, 1-propenyl ethers fail to undergo hydrosilation reactions to any appreciable extent (eq 5).



(5)

It has also been observed that while cyclohexene or substituted cyclohexenes are usually quite unreactive toward hydrosilation, norbornene and its derivatives are very reactive in hydrosilation reactions, giving the corresponding alkylsilanes in high yields.[14–16] A further important characteristic of the norbornene system is that migration of the norbornene double bond cannot take place since placing the double bond at the bridgehead position would violate Bredt's rule. Such bond migrations sometimes complicate transition metal catalyzed hydrosilations.

The above observations suggested that a molecule incorporating both a norbornene double bond and a 1-propenyl ether group would undergo chemoselective hydrosilation only at the norbornene double bond. The resulting 1-propenyl ether functional silanes or siloxanes should then undergo facile photoinduced cationic polymerization. To test this hypothesis, the synthesis of three representative (1-propenoxy)norborn-5-enes was undertaken employing straightforward synthetic procedures.

5-Norbornene-2-methanol[17] (**I**), was allylated as shown in eq 6 to give the corresponding allyl ether, (**IA**), under

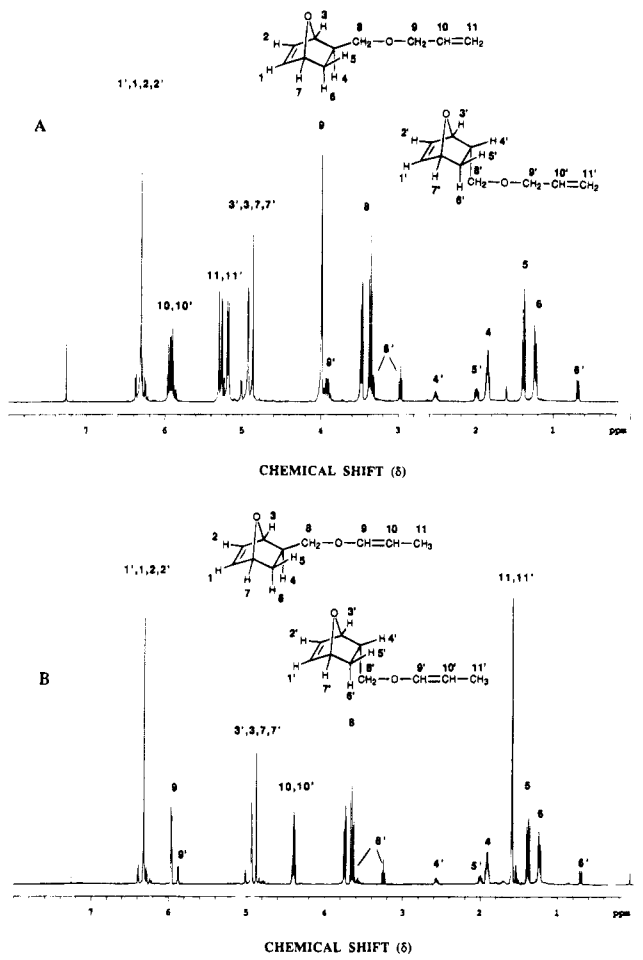
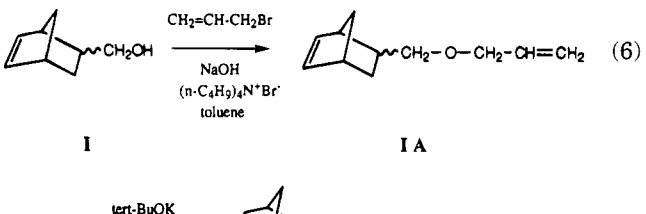


Figure 1. 500 MHz ^{1}H-NMR spectra for (A), **IIIA** and (B), **IIIP** in $CDCl_3$.

phase transfer catalysis conditions. **IA** was then treated with potassium *tert*-butoxide in DMSO at 130 °C to isomerize the allyl ether group to produce **IP** containing the cationically polymerizable 1-propenyl ether group (eq 7).



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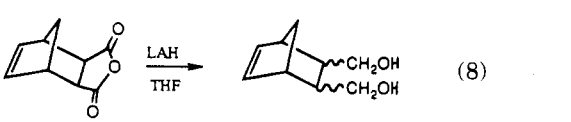
The bis(1-propenyl) ether **IIP** was synthesized by first reducing bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride with LAH (eq 8). Then the dialcohol, **II**, was allylated to give the bisallyl ether, **IIA**, and finally isomerized to afford **IIP** (a mixture of *endo* and *exo* and *cis* and *trans* isomers) using potassium *tert*-butoxide in DMSO in a manner similar to that given in eqs 6 and 7.

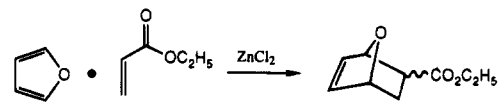


(8)

Table 3. Synthesis of 1-Propenyl Ether Functional Siloxanes by the Hydrosilation of (1-Propenoxy)norborn-5-enes

Silane	Reactant	Notation	Yield (%)	Elemental Analysis	%C	%H
$Ph(CH_3)_2SiH$	IP	IP1	78	Found:	75.75	9.45
				Calc:	75.94	9.39
$[H(CH_3)_2Si]_2O$	IP	IP2	97	Found:	66.89	10.12
				Calc:	67.47	10.02
$PhSi[OSi(CH_3)_2H]_3$	IP	IP3	81	Found:	65.69	9.01
				Calc:	65.64	9.06
$[Si(CH_3)H\text{-}O]_4$ (D_4^H)	IP	IP4	67	Found:	63.67	8.79
				Calc:	64.24	8.98
	IIP	IPM	94	Found:		
				Calc:	--	--
$Ph(CH_3)_2SiH$	IIP	IIP1	91	Found:	74.23	9.41
				Calc:	74.54	9.25
$[H(CH_3)_2Si]_2O$	IIP	IIP2	78	Found:	67.12	9.71
				Calc:	67.72	9.69
$PhSi[OSi(CH_3)_2H]_3$	IIP	IIP3	87	Found:	66.68	9.12
				Calc:	66.23	8.97
$[Si(CH_3)H\text{-}O]_4$ (D_4^H)	IIP	IIP4	89	Found:	64.83	9.01
				Calc:	65.26	8.90
	IIP	IIPM	91	Found:		
				Calc:	--	--
$Ph(CH_3)_2SiH$	IIIP	IIIP1	98	Found:	71.47	8.66
				Calc:	71.53	8.62
$[H(CH_3)_2Si]_2O$	IIIP	IIIP2	97	Found:	60.99	9.13
				Calc:	61.76	9.07
$PhSi[OSi(CH_3)_2H]_3$	IIIP	IIIP3	95	Found:	60.83	8.26
				Calc:	60.70	8.29
$[Si(CH_3)H\text{-}O]_4$ (D_4^H)	IIIP	IIIP4	98	Found:	58.37	8.02
				Calc:	58.39	8.11
	IIIP	IIIPM	99	Found:		
				Calc:	--	--

The last intermediate, **IIIP** was prepared from alcohol **III** which was synthesized according to eqs 9 and 10.



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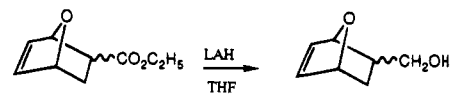

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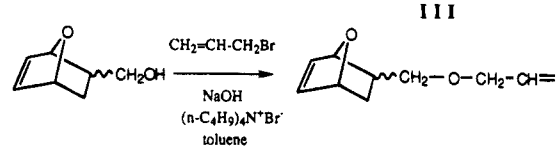
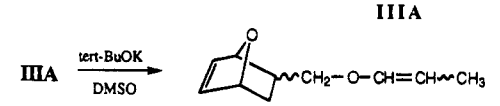
III



(11)

IIIA



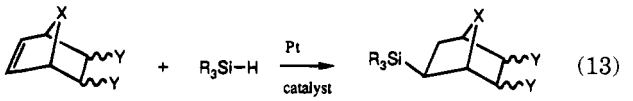
(12)

IIIP

First, ethyl 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylate was prepared by the zinc chloride catalyzed Diels–Alder reaction of furan with ethyl acrylate (eq 9). The ester was subsequently reduced with LAH to give the alcohol, **III** (eq 10), and this latter compound allylated (eq 11, **IIIA**) and the double bond isomerized as before to give **IIIP** (eq 12). Tables 1 and 2, respectively, show the structures, yields, and boiling points of the (allyloxy)-norborn-5-ene and (1-propenoxy)norborn-5-ene intermediates prepared during the course of this investigation. It should be mentioned that, as indicated in Tables 1 and 2, these compounds are mixtures of isomers due to the *endo* and *exo* substitution at the norbornene ring and the *cis* and *trans* isomerism of the 1-propenyl ether

double bond. Shown in Figure 1 are the ^{1}H-NMR spectra for **IIIA** and **IIIP**. In this case, **IIIP** consists only of the *endo–cis* and *exo–cis* isomers, which are present in a ratio of 8:2. The ^{1}H-NMR spectra of **IP** and **IIP** are more complicated due to the additional presence of the corresponding *endo–trans* and *exo–trans* isomers.

(1-Propenoxy)norborn-5-enes **IP**, **IIP**, and **IIIP** undergo facile and exclusive chemoselective hydrosilation reaction at the norbornene double bond. A general reaction depicting this is shown in eq 13.

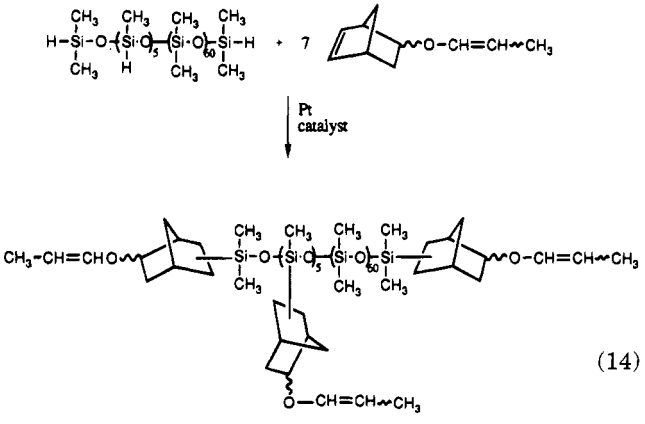


(13)

X = CH_2 or O

Y = H or -O-CH_2-CH=CH_2

When polyfunctional siloxanes are employed in this reaction, multifunctional 1-propenyl ether substituted siloxanes are readily produced. The structures of a series of 1-propenyl ether functional monomers prepared during the course of this investigation are given in Table 3. The hydrosilation reactions were carried out in toluene solution in the presence of the Karstedt catalyst,[9] which is a platinum complex with 1,1,3,3-tetramethyl-1,3-divinyldisiloxane. In no case was there any indication that competitive hydrosilation at the 1-propenyl group occurred. This was particularly evident by the absence of cross-linking in the hydrosilation of the Si–H functional siloxane oligomers to produce soluble, liquid copolymers **1PM**, **IIPM,** and **IIIPM** bearing pendant 1-propenyl ether groups (eq 14).



(14)

IPM

Hydrosilations of **IIIP** were especially rapid and proceeded to high conversions with stoichiometric amounts of reagents. This may be attributed to the higher polarity of this monomer and to its coordinating effect with the platinum catalyst. **IP** and **IIP** were less reactive and a 10% excess of these reagents was required to drive the reactions to completion. The hydrosilation of **IIP** bearing two 1-propenyl ether groups is especially attractive since it yields very highly functional monomers such as the octafunctional cyclic monomer **IIP4**. This hydrosilation method is very versatile and mono-, di-, and multifunctional monomers and oligomers can be readily prepared under mild conditions. The structures, yields, and elemental analyses of the monomers and oligomers prepared during this investigation are included in Table 3. All the 1-propenyl

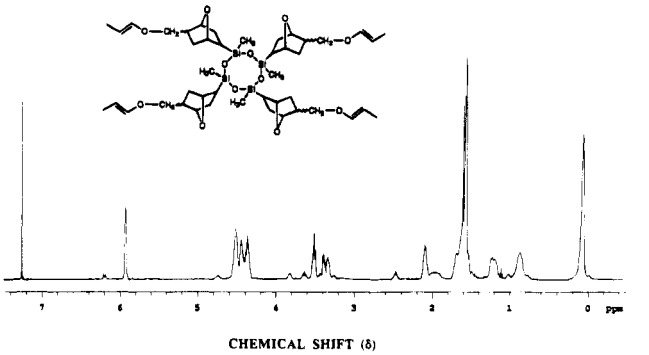
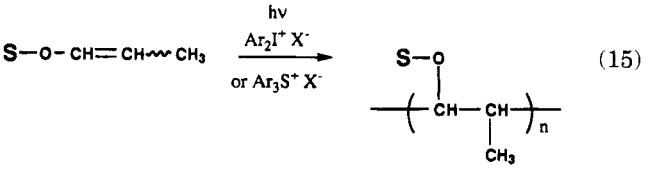


Figure 2. 500 MHz ^{1}H-NMR spectrum of **IIIP4** in $CDCl_3$.

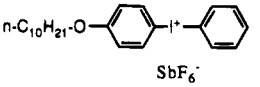
ether functional siloxane monomers and oligomers prepared during this investigation were transparent, colorless, and odorless slightly viscous to highly viscous oils. The structures of the monomers and oligomers were definitively established by means of ^{1}H-NMR spectroscopy. For example, Figure 2 gives the ^{1}H-NMR spectrum of monomer **IIIP4**. Further confirmation of the structure of these materials was provided by elemental analysis. The high purity of these materials was indicated by the observation that photoinduced cationic polymerization proceeds without a substantial induction period and in many cases to high conversions.

Evaluation of the Photoinitiated Cationic Polymerization of 1-Propenyl Ether Functional Siloxanes. The 1-propenyl ether functional siloxane monomers are very rapidly photopolymerized by exposure to UV irradiation in the presence of a variety of diaryliodonium salt cationic photoinitiators. This is depicted in a general fashion in eq 15, where S represents a siloxane containing group and X^- is a nonnucleophilic anion.

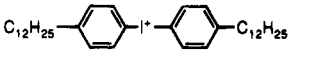


(15)

Critical to the success of these photopolymerizations is the solubility of the onium salt photoinitiator in these nonpolar monomers. It has been found that diaryliodonium salts bearing long alkoxy or alkyl side chains are particularly well suited for the polymerization of these materials because of their enhanced solubility in the monomers. For this study, we have employed as photoinitiators the diaryliodonium salts (4-(*n*-decyloxyphenyl)phenyl)iodonium hexafluoroantimonate (IOC10), and the commercially available bis(4-dodecylphenyl)iodonium hexafluoroantimonate (UV-9380C) with the structures shown below.



IOC10



UV-9380C

Initially, the various monomers shown in Table 3 were evaluated by conducting photopolymerizations in thin films. Accordingly, 25 μm (1 mil) films of the monomers containing 0.5 mol % (4-*n*-decyloxyphenyl)-phenyl)iodonium hexafluoroantimonate were drawn onto glass plates and irradiated with broad-band UV light using a Fusion Systems 300 W microwave-actuated

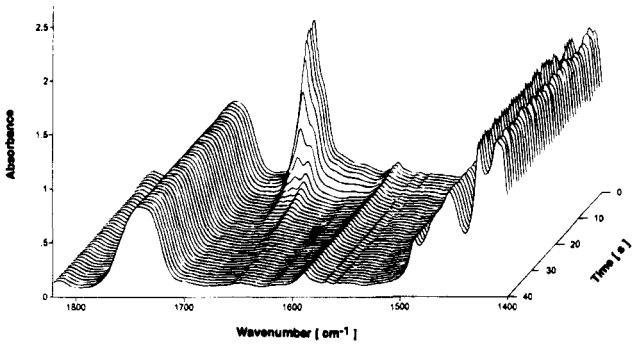


Figure 3. FT-IR spectra for the photopolymerization of monomer **IP1** using 0.25 mol % IOC10 as photoinitiator.

medium-pressure mercury arc lamp. The apparatus was fitted with a conveyor which can be adjusted to pass samples under the lamp at controlled speeds to provide different exposure doses. It was observed that with the exception of the two monofunctional monomers, **IP1** and **IIIP1**, all the di- and multifunctional monomers and oligomers were converted to cross-linked tack-free films at the highest speed of the conveyor (97.5 cm/s, 3.2 ft/s). This means that a UV dose of less than 78 mJ/cm^2 was required in all cases. Polymers derived from **IP1** and **IIIP1** were completely soluble in common solvents.

The rapid photopolymerization of these novel monomers can be monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). The decrease in the IR bands in the 1660−1670 cm^{-1} region assigned to the *cis*- and *trans*- 1-propenyl ether double bonds was followed continuously as a function of time while the sample was simultaneously irradiated with UV light. Thus, this method directly monitors the disappearance of the reactive 1-propenyl ether groups as the polymerization proceeds. The polymerization studies described here were conducted at a low light intensity of 18−19 mW/cm^2 and at a photoinitiator concentration of 0.25 mol % IOC10 per 1-propenyl ether group to slow them sufficiently to allow kinetic analysis. In the case of the oligomeric 1-propenyl ether functional poly(siloxane)s, a photoinitiator (UV-9380C) concentration of 2 wt % was employed.

It should be noted that these and the previous thin-film polymerizations do not obey the reciprocity law. This is due to the less than ideal conditions under which these experiments were necessarily run. During sample preparation and prior to photopolymerization, the liquid monomer films were briefly exposed to the atmospheric moisture and other adventitious laboratory contaminants. The results show a typical induction or threshold period in which these inhibitors are removed from the monomer by reaction with the photogenerated acid. This is followed by rapid cationic polymerization.

Figure 3 shows the evolution of the FT-IR spectra obtained in the photoinduced cationic polymerization of monomer **IP1** at a repetition rate of approximately 1 scan/s. In this figure, the absorptions for the *trans* (1650 cm^{-1}) and *cis* (1670 cm^{-1}) 1-propenyl ether groups present in the monomer can be clearly delineated. As polymerization proceeds over the course of 40 s, both bands markedly decrease nearly to zero, with the major decrease occurring within the first 5−10 s. By inspection of this figure, it can also be noted that the *cis*-1-propenyl ether is more reactive than the *trans* isomer. This observation has been noted previously.[18,19]

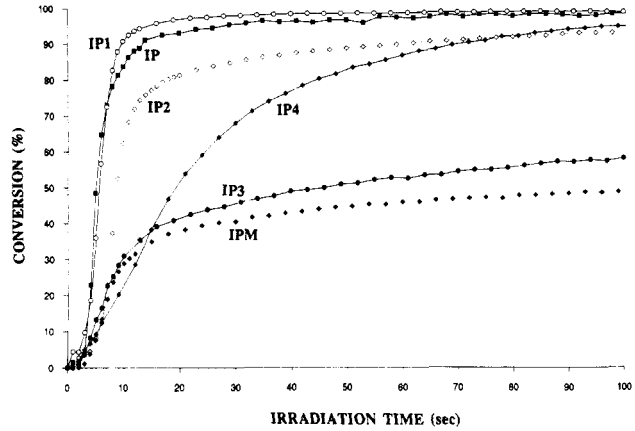


Figure 4. FT-RTIR curves for the photopolymerization of monomers based on the hydrosilation of **IP** with various silanes using IOC10 as photoinitiator.

Table 4. Photopolymerization of 1-Propenyl Ether Functional Monomers and Oligomers

monomer	photoinitiator conc (mol %)[a]	$Rp/[M_0]$ (s^{-1})	conv (%)[b]
IP	0.25	0.24	100
IP1	0.25	0.17	100
IP2	0.5	0.15	98
IP3	0.75	0.05	69
IP4	1.0	0.05	51
IPM	0.5[a]	0.03	100
IIP	0.5	0.06	78
IIP1	0.5	0.15	97
IIP2	1.0	0.04	68
IIP3	1.5	0.04	46
IIP4	2.0	0.01	23
IIPM	0.5[c]	0.01	49
IIIP	0.25	0.02	84
IIIP1	0.25	0.13	99
IIIP2	0.5	0.06	97
IIIP3	0.75	0.05	72
IIIP4	1.0	0.01	44
IIIPM	0.5[c]	0.04	100

[a] IOC10. [b] After 300 s. [c] Weight % UV-9380.

In Figure 4 are plotted the FT-RTIR conversion versus irradiation time curves for the six silicon-containing monomers in which **IP** was used as the derivatizing (1-propenoxy)norborn-5-ene. Also included for comparison in this figure is a curve for the photopolymerization of **IP** itself. Table 4 presents rate and conversion data extracted from these curves. Monofunctional monomers **IP** and **IP1** undergo very rapid photoinduced cationic polymerization and proceed to essentially complete conversion. Both monomers yield soluble, un-cross-linked polymers. A similar high rate of photoinduced cationic polymerization was observed for the difunctional propenyl ether **IP2**, which also proceeds to a surprisingly high degree of polymerization (98%). However, the conversions of the higher functional silicon-containing monomers, **IP3** and **IP4** show lower rates of polymerization and also proceed to lower extents of conversion due to the higher cross-link density and earlier vitrification of the cross-linked polymers which are formed. **IPM** shows the lowest rate of polymerization, and this was attributed to a lower photoinitiator concentration in this case due to the high molecular weight of this oligomer. Thus, the poly(dimethylsiloxane) chain acts like a diluent reducing the probability of the reactive chain end to find and react with the 1-propenyl ether groups. Despite the slow reaction rate, the polymerization proceeds to eventually (after 300 s) complete consumption of the 1-propenyl

Table 5. Photopolymerization of 1-Propenyl Ether Functional Poly(dimethylsiloxane) Oligomers

monomer	photoinitiator conc (wt %)[a]	$R_p/[M_0]$ (s^{-1})	conv (%)[b]
IPM	2.0	0.25	100
IPM	1.0	0.15	100
IPM	0.5	0.02	100
IPM	0.25	0.01	98
IIPM	1.0	0.01	78
IIIPM	1.0	0.05	100
UV-9100	2.0	0.03	87

[a] UV-9380C. [b] After 300 s.

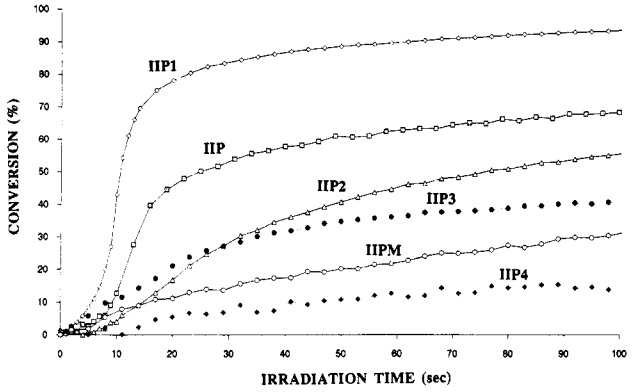


Figure 5. FT-RTIR curves for the photopolymerization of monomers based on the hydrosilation of **IIP** with various silanes using IOC10 as photoinitiator.

ether groups. In this case, the low T_g (−125 °C) of the poly(dimethylsiloxane) chain provides sufficient mobility for all the 1-propenyl ether groups to react. The ability of the oligomers to polymerize to high conversions is especially desirable for coating applications, since the initially obtained properties would not be expected to change with time. To provide a comparison for the rate data given in Tables 4 and 5, the photopolymerization of diethyleneglycol divinyl ether containing 0.5 mol % IOC 10 was measured under identical conditions. The $R_p/[M_0]$ value was found to be 0.23 s^{-1}, and an ultimate conversion of 90% for this difunctional monomer was determined. Thus, the reactivities of the many of simple 1-propenyl ether monomers described in the present paper compare favorably with this divinyl ether.

Shown in Figure 5 and in Table 4 are, respectively, the FT-RTIR curves and the data determined from them for the photopolymerization of a series of monomers and oligomer based on difunctional intermediate **IIP**. Here, in order to maintain the same molar ratio of photoinitiator to 1-propenyl ether groups as with the other monomers (0.25 mol %) in Table 4, the concentration of the photoinitiator was doubled. In all cases, the rates of polymerization and extents of conversion are lower than for the previous series of compounds. These results are attributed to the corresponding higher functionality of this series of monomers and oligomers, which leads to a high degree of vitrification in the polymer even at low extents of conversion.[21] In addition, it has been noted that monomers such as the octafunctional monomer **IIP4** are very viscous at room temperature. It is interesting to compare the difunctional monomers **IIP** and **IIP1**. The rate of conversion of **IIP1** is at least double that of **IIP** and the extent of conversion is also significantly higher. At this moment, we do not have an explanation for this observation.

FT-RTIR curves for the photoinitiated cationic polymerization of monomers and the oligomer based on

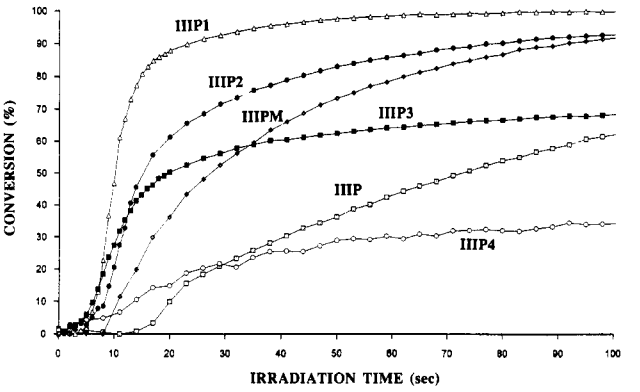
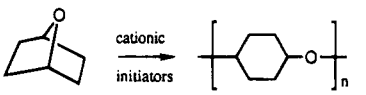


Figure 6. FT-RTIR curves for the photopolymerization of monomers based on the hydrosilation of **IIIP** with various silanes using IOC10 as photoinitiator.

IIIP are shown in Figure 6, and the data derived from the curves are presented in Table 4. In these compounds there is the added complication of the presence of an ether oxygen in the bicyclic ring. First, the oxygen in these compounds is basic and can reduce the rate of polymerization by competing with the 1-propenyl ether group for initiating protons or chain ends. Second, it is known that 7-oxabicyclo[2.2.1]heptane undergoes cationic ring-opening polymerization as depicted in eq 16.[20]



(16)

The introduction of a double bond into this bicyclic system might be predicted to increase its ring strain and to further favor ring-opening polymerization. On the basis of the above considerations, monomer **IIIP** would be expected to be difunctional. Indeed, while **IP** gives soluble, linear polymers on photopolymerization, under the same conditions, **IIIP** yields cross-linked network polymers. Comparing the FT-RTIR curves, it can be seen that the rate of polymerization for **IIIP** is slower than for **IIIP1** and that the extent of conversion is also significantly lower, suggesting that due to the more efficient ring-opening reaction of **IIIP**, a more highly cross-linked matrix is formed. On the other hand, since hydrosilation removes the ring strain and increases the steric hindrance, **IIIP1** undergoes only polymerization at the 1-propenyl ether group without competing ring-opening polymerization. Consequently, soluble linear polymers are produced from the cationic polymerization of this monomer. The tetrafunctional monomer, **IIIP4**, exhibits rather sluggish polymerization behavior which appears to be a consequence of the highly viscous nature of this monomer. The oligomer, **IIIPM**, shows the highest rate of polymerization when compared with the analogous materials, **IPM** and **IIPM**. This can be attributed to the greater solubility of the photoinitiator, IOC10, in the more polar **IIIPM** due to the presence of the pendant oxygen-bridged bicyclic groups present in this oligomer.

To eliminate the problem of photoinitiator solubility in the 1-propenyl ether functional oligomers, **1PM**, **IIPM**, and **IIIPM**, FT-RTIR studies were conducted using the commercially available photoinitiator UV-9380C. This initiator contains approximately 45% of bis(4-dodecylphenyl)iodonium hexafluoroantimonate in

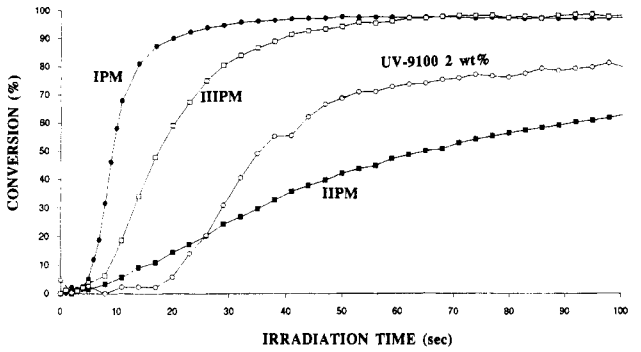


Figure 7. FT-RTIR study of the photopolymerization of 1-propenyl ether and epoxy functional poly(dimethylsiloxane) oligomers using UV-9380C as photoinitiator.

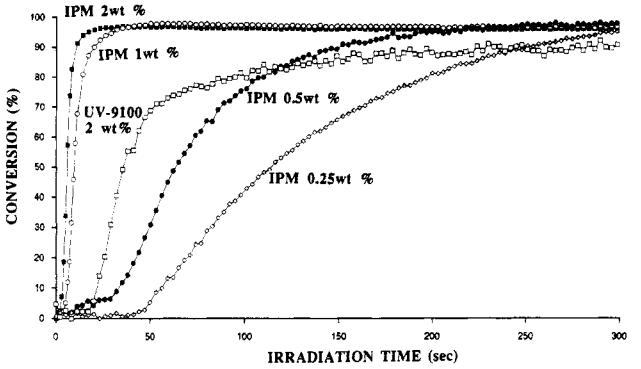


Figure 8. Study of the effect of concentration of UV-9380 photoinitiator on the photopolymerization of 1-propenyl ether and epoxy functional poly(dimethylsiloxane) oligomers.

a mixture of C_{12-14} alkyl glycidyl ethers. The solubility of this photoinitiator is quite good in all five oligomers. For comparison, the analogous commercially available epoxycyclohexyl functional poly(dimethylsiloxane) oligomer UV-9100[5,6] was included in the study. Figure 7 and Table 5 give a direct comparison of these functionalized silicone oligomers. As the data clearly indicate, the photopolymerization of the 1-propenyl ether functional poly(dimethylsiloxane) oligomers **IPM** and **IIIPM** proceed much faster than UV-9100. The conversions of the 1-propenyl ether groups measured at 300 s for these former oligomers are also quantitative while for the latter epoxycyclohexyl functional oligomer, the epoxide conversion is 87%. It should also be noted that to achieve comparable rates, 2 wt % of the photoinitiator solution (0.95 wt % of diaryliodonium salt) had to be added to UV-9100. Among the 1-propenyl ether oligomers, **IIPM** gives the slowest rate and the lowest conversion of functional groups, again attesting to the higher functionality and consequent higher cross-link density produced on polymerization.

In Figure 8 is shown the effect of the photoinitiator (UV-9380C) concentration on the photopolymerization of **IPM**. Also included for comparison in this figure is the epoxy functional siloxane oligomer UV-9100. There is a marked increase in the rate of polymerization of **IPM** as the photoinitiator concentration is increased up to 1 wt %. Further increase in the photoinitiator concentration produces only a marginal increase in the polymerization rate. Inspection of Figure 8 may give some insight into why there is a rapid increase in the rate of polymerization as the concentration of the photoinitiator is increased from 0.5 to 1.0%. The curves at the lower concentrations (0.25 and 0.5%) display appreciable induction periods suggestive of the presence of inhibiting basic agents. These starting oligomers were commercial products and could not be rigorously purified prior to functionalization. Using a photoinitiator concentration of 1% and greater results in the formation of sufficient Brønsted acid early in the polymerization to completely overwhelm the impurities. In these cases, the induction period is very short or absent. On the other hand, at lower photoinitiator concentrations less acid is generated and because of the lower optical density also more slowly during the initial phases of the polymerization. The acid is consumed by the impurities until they are exhausted and then polymerization begins.

Conclusions

A novel series of cationically photopolymerizable siloxane monomers and oligomers has been prepared by the chemoselective hydrosilation of several different (1-propenyl)norborn-5-enes with various Si−H-containing precursors. Chemoselective hydrosilation of these bifunctional compounds takes place exclusively at the norbornene double bonds, thereby affording 1-propenyl ether functional siloxanes in high yields. These novel monomers and oligomers exhibit very high reactivity in cationic photopolymerization. The novel monomers and oligomers may have interesting applications as photocurable coatings, inks, and adhesives.

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(17) The IUPAC nomenclature for these compounds becomes rather complex and cumbersome. For example, the IUPAC name for **IIIP** is 2-(2-oxapent-3-enyl)-7-oxabicyclo[2.2.1]hept-5-ene. For this reason, we have elected to name these compounds as derivatives of norbornene as per the common nomenclature.
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