Synthesis and Photoinitiated Cationic Polymerization of Organic−Inorganic Hybrid Resins

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A streamlined synthetic scheme was developed for the preparation of a novel series of cationically polymerizable epoxy-functional organic−inorganic hybrid resins. The reaction sequence consists, first, of the regioselective rhodium-catalyzed monoaddition of an α,ω-Si−H difunctional siloxane to a vinyl epoxide. The second step involves the addition of the remaining Si−H bond of the latter adduct to vinyl trimethoxysilane. Finally, an ion-exchange-catalyzed sol−gel hydrolysis of the resulting trialkoxysilane-functional epoxide yields the desired silicone−epoxy resins bearing pendant epoxy groups. These resins undergo facile UV and thermally induced cationic photopolymerization in the presence of onium salt photoinitiators to give cross-linked organic−inorganic hybrid glassy matrixes. The mechanical and thermal properties of the polymerized resins were determined and were correlated with the structures of the resins.

Introduction

In recent years, organic−inorganic hybrid resins have received much attention in the literature because of their unique electrical, optoelectronic, and mechanical properties.[1] Much work is currently focused on the synthesis of cross-linked glasslike matrixes composed of Si−O−Si linkages employing sol−gel techniques that involve the hydrolysis and subsequent condensation of tri- or tetraalkoxysilanes.[2−4] Once hydrolysis has taken place to form a cross-linked network, the gel can be further processed, for example, by various combinations of drying and sintering techniques, to form porous or nonporous products.[5] An alternative approach is to employ the sol−gel process to produce relatively low-molecular-weight liquid siloxane oligomers having organic groups that bear polymerizable functional groups. The polymerization of these functional groups leads to the formation of the solid cross-linked organic−inorganic hybrid resin. In recent years, there has been considerable interest in epoxy-functional resins based on the sol−gel hydrolysis condensation of 3-glycidoxypropyltrimethoxysilane (GPTMS).[6−12] In the absence of a catalyst, the hydrolysis of GPTMS is very slow. However, it has been found that a wide variety of amines, protonic and Lewis acids, and transition metal complexes catalyze the hydrolysis of GPTMS. Matejka et al.[13] have shown that cyclization of GPTMS to form a high content of polyhedral siloxane cages prevents gelation, so that low-molecular-weight oligomers are formed. However, when a GPTMS sample stands at room temperature in the presence of the above hydrolysis catalysts, epoxide ring-opening has a tendency to take place and cause the gelation of these oligomers.

We were interested in the possibility of using sol−gel chemistry to produce epoxy-functional oligomers that could be very rapidly cationically photopolymerized to produce organic−inorganic hybrid resins. Such resins are of particular interest as abrasion-resistant coatings and optical adhesives. The previously described oligomers based on GPTMS were not of interest because the glycidyl ether groups of these materials undergo very sluggish cationic photopolymerizations. Instead, we wished to apply sol−gel methodology to the related compound, 2(3,4-epoxycyclohexyl)ethyltrimethoxysilane (**I**) because the resulting resins would bear very highly reactive epoxycyclohexyl groups. It was observed that, when the above-mentioned catalysts employed for the hydrolysis of GPTMS were applied to **I**, gelation of the products always occurred either during the sol−gel reaction or after the sample was allowed to stand for a short time. This problem was solved by employing the two-step methodology depicted in Scheme 1, which afforded the desired resins in high yields.[14]

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(1) Andrews, M. P.; Najafi, S. I. *Sol−Gel and Polymer Photonic Devices*; SPIE Optical Engineering Press: Bellingham, WA, 1997.

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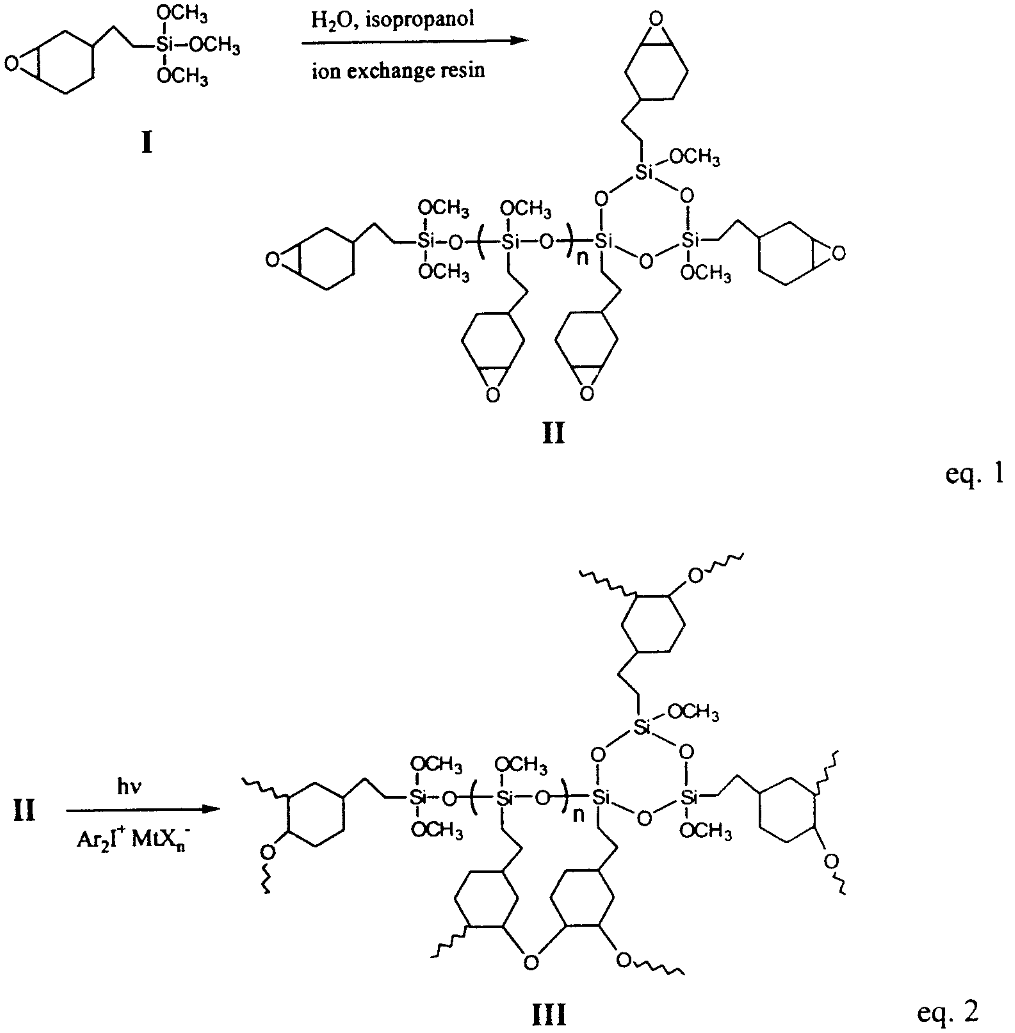
Scheme 1



First, the sol–gel condensation of **I** (eq 1) was carried out using a weakly acidic ion-exchange resin as a catalyst. The resulting product (**II**) is an oligomer with a backbone composed of both cyclic and linear siloxane groups and bearing pendant epoxy groups. The structure of the resin, **II**, shown in eq 1 is idealized. Typically, oligomers with up to 12–15 repeat units can be prepared in which greater than 85% hydrolysis of the alkoxy groups has taken place. Despite the fact that a trialkoxysilane is employed in this reaction, the simultaneous hydrolysis and condensation reactions can be carried out in a controlled manner such that no cross-linking or gel formation takes place. Termination of the reaction can be achieved by removing the catalyst by simple filtration. In a subsequent step, these oligomers can be polymerized via a ring-opening polymerization of the pendant epoxy groups. For example, as shown in eq 2, the oligomers undergo very rapid cross-linking, with formation of organic–inorganic hybrid networks (**III**) when irradiated with UV light in the presence of a diaryliodonium salt photoinitiator.

The present paper describes the development of a new, generally applicable synthetic approach that can be employed to prepare a related family of silicone–epoxy resins using simple, readily available precursors. These resins undergo facile cationic photopolymerization to yield organic–inorganic hybrid resins with a wide range of properties.

Experimental Section

Materials and Analytical Procedures. 2-(3,4-Epoxycyclohexylethyl)trimethoxysilane (**I**) was purchased from United Chemical Technologies, Inc. (Bristol, PA). Amberlite IRA-400 ion exchange resin was obtained from Rohm and Hass Co. (Philadelphia, PA) and washed several times with a large volume of hot toluene. 3-Vinyl-7-oxabicyclo[4.1.0]heptane (VCMX) was supplied by Union Carbide Corporation (Bound Brook, NJ). The α,ω-hydrogen-functional siloxanes and vinyltrimethoxysilane were purchased from Gelest (Tullytown, PA). Chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst) was used as purchased from the Aldrich Chemical Co. (Milwauke, WI). The photoinitiator, (4-*n*-decyloxyphenyl)-phenyliodonium hexafluoroantimonate (**IOC10**), was prepared by procedures described previously.[15] CD1012, (4(2-hydroxydodecyloxy)phenyl)phenyliodonium hexafluoroantimonate, was supplied by the Polyset Company, Mechanicville, NY.

Gel permeation chromatographic (GPC) analyses were carried out using a Hewlett-Packard HP-1090 HPLC equipped with a PLgel 5μ mixed-c column and an HP-1047A refractive index detector. THF was used as the eluent at a flow rate of 1.0 mL/min. All molecular weights are reported relative to polystyrene standards. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5890 Series-II gas chromatograph equipped with a 15 m × 0.53 mm × 1.5 μm film thickness cross-linked methylsilicone gum column and a flame ionization detector. ^{1}H NMR spectra were obtained using a

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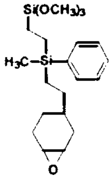
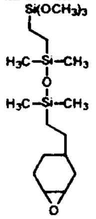
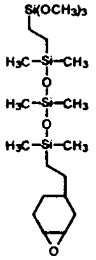
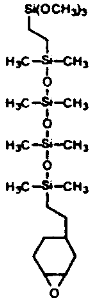
[15] Crivello, J.; Lee, J. L. *J. Polym. Sci. A: Polym. Chem.* **1989**, *73*, 3951.

Table 1. Sol–Gel Precursors

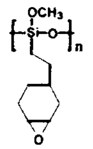
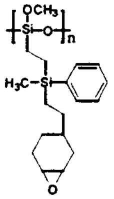
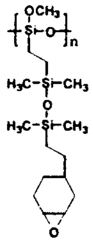
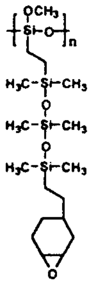
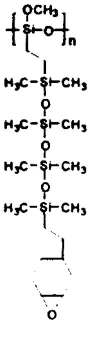
Notation	Structure	Yield (%)	Elemental Analysis			
			Calc.		Fnd.	
			%C	%H	%C	%H
VIIa		72	60.91	8.62	61.31	8.54
VIIIa		90	50.24	9.35	50.65	9.35
IXa		89	47.49	9.16	47.53	9.21
Xa		86	45.47	9.01	45.67	9.05

Varian INOVA-300 MHz spectrometer at room temperature in $CDCl_3$ solvent. Infrared spectra were recorded on a Perkin-Elmer (Stamford, CT) Paragon-1000 Infrared Spectrometer. Bulk viscosities of the epoxy–silicone resins were measured on a Brookfield model DV-II+ cone and plate viscometer (Brookfield Co., Stoughton, MA). Thermogravimetric analyses (TGA) were run on a Perkin-Elmer TGA 7 thermal analyzer at a heating rate of 20 °C/min in nitrogen. The same instrument equipped with a DSC-7 differential scanning calorimeter module was used to obtain DSC measurements. The DSC scans of thermally induced polymerizations and determinations of the glass transition temperatures were carried out in air at a heating rate of 10 °C/min. Dynamic mechanical analyses (DMA) were carried out on the same instrument equipped with a DMA 7 module in a three-point bend mode at a heating rate of 10 °C/min in nitrogen. Samples for DMA testing were prepared by heating 5-g samples of the silicone–epoxy oligomers containing 1 wt % of CD1012 photoinitiator (dissolved in a 50% solution in Union Carbide bicycloaliphatic epoxy resin ERL-4221) in an aluminum dish at room temperature and heating at 5 °C/min to 165 °C in a forced-air oven. Bars (15 mm × 5.5 mm × 1.5 mm) were cut from the pale yellow, solid cross-linked disks that were obtained. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

General Synthesis of α-Epoxy-ω-trialkoxysilanes and Siloxanes. The synthetic procedures given below are typical of those used for the preparation all of the α-epoxy-ω-trialkoxysilanes and siloxanes shown in Table 1.

*Preparation of 1-[2-(3{7-Oxabicyclo[4.1.0]heptyl}ethyl]-3-[2-trimethoxysilylethyl]-1,1,3,3-tetramethyldisiloxane (**VIIIa**).* A mixture of 20.0 g (0.15 mol) of distilled 1,1,3,3-tetramethyldisiloxane, 18.5 g (0.15 mol) of 3-vinyl-7-oxabicyclo[4.1.0]-heptane, and 20 mL of dry toluene was charged into a 250-mL round-bottom flask fitted with a reflux condenser and thermometer. Then, 30 mg of Wilkinson's catalyst was added, and the reaction mixture was heated at 60 °C for 4 h in an oil bath. After this time, the ^1H NMR spectrum showed that the vinyl peaks at 5.5 ppm had disappeared. Next, 22.2 g (0.15 mol) of distilled vinyltrimethoxysilane was added. After 6 h at 90 °C, the infrared absorption at 2160 cm^{-1} (Si–H group) had completely disappeared. Removal of the solvent under reduced pressure gave the desired product (54,6 g, 90% yield)

Table 2. Epoxy-Functional Silicone Resins

Notation	Structure	Reaction Conditions	Yield (%)	Viscosity (cP)	Mw (g/mol)	MWD	DP
Ib		IPA,* 82°C, 6 h	100	2506	2430	1.3	9
VIIb		NPA,[#] 91°C, 24 h	92	33260	2381	1.1	6
VIIIb		IPA, 150°C, 12 h[†]	98	2929	4186	1.3	9
IXb		IPA, 150°C, 12 h[†]	95	648	6440	1.4	11
Xb		IPA, 150°C, 12 h[†]	93	249	8135	1.7	9

* Isopropyl alcohol. [#] *n*-Propyl alcohol. [†] Under pressure.

as a colorless oil, which was characterized by ^{1}H NMR spectroscopy and confirmed to be monomer **VIIIa**.

Preparation of Epoxy-Functional Oligomers. The synthetic procedures given below are typical of those used for the preparation all of the silicone−epoxy oligomers shown in Table 2.

Sol−Gel Condensation of 2-(3,4-Epoxycyclohexylethyl)trimethoxysilane. A mixture of 20 g (0.081mol) of **Ia**, 4.4 g (0.24 mol) of deionized water, 0.8 g of Amberlite IRA-400 ion-exchange resin, and 10 g of 2-propanol was placed into a 100-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The condensation reaction was carried out at the reflux temperature, 82 °C, for 6 h. Thereafter, the solution was cooled, filtered, and passed though a silica gel column using ethyl acetate as the eluent. The solvent was removed under vacuum, and a viscous liquid oligomer (16.3 g) **Ib** was obtained.

^{1}H NMR (CDCl$_3$) δ (ppm): 0.5 (CH$_2$−Si), 1.2−2.2 (aliphatic protons), 3.1 (epoxy CH), 3.48 (OCH$_3$).

Sol−Gel Condensation of 2-(3{7-Oxabicyclo[4.1.0]heptyl}-ethyl-[2-trimethoxysilylethyl]methylphenylsilane. A mixture of 6.0 g (0.015mol) of **VIIa**, 0.82 g (0.0456 mol) of deionized water, 0.24 g of Amberlite IRA-400 ion-exchange resin, and 3.0 g of 1-propanol was placed in a 100-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The hydrolysis−condensation reaction was carried out at the reflux temperature, 97 °C, for 24 h. Then, the solution was filtered and passed though a silica gel column using ethyl acetate as the eluent. The ethyl acetate was removed in a vacuum, and a viscous liquid oligomer (4.9 g) **VIIb** was obtained

^{1}H NMR (CDCl$_3$) δ (ppm): 0.2−2.2 (CH$_2$−Si, CH$_3$−Si, and aliphatic protons), 3.1 (epoxy CH), 3.48 (OCH$_3$), 7.4 (aromatic protons).

Sol−Gel Condensation of 1-[2-(3{7-Oxabicyclo[4.1.0]heptyl}-ethyl]-3-[2-trimethoxy-silylethyl]-1,1,3,3-tetramethyldisiloxane. To a 75-mL pressure vessel fitted with a magnetic stirrer were charged 10 g (24.6 mmol) of **VIIIa**, 1.33 g (73.8 mmol) of deionized water, 0.4 g of Amberlite IRA-400 ion-exchange resin, and 5.0 g of 2-propanol. The reaction mixture was stirred and heated at 150 °C for 12 h under pressure. After the solution was filtered and passed though a silica gel column using ethyl acetate as the eluent, the solvent was removed in a vacuum to give a viscous liquid oligomer **VIIIb** (8.4 g).

^{1}H NMR (CDCl$_3$) δ (ppm): 0−0.1 (CH$_3$−Si), 0.5 (CH$_2$−Si), 1.2−2.2 (aliphatic protons), 3.1 (epoxy CH), 3.4−3.8 (OCH$_3$).

Sol−Gel Condensation of 1-[2-(3{7-Oxabicyclo[4.1.0]heptyl}-ethyl]-5-[2-trimethoxy-silylethyl]-1,1,3,3,5,5-hexamethyltrisiloxane. In a fashion similar to that described above, 10 g (20.1 mmol) of **IXa**, 1.12 g (62.2 mmol) of deionized water, 0.4 g of Amberlite IRA-400 ion-exchange resin, and 5.0 g of 2-propanol were heated together at 150 °C for 12 h in a pressure vessel. After workup as before, 8.6 g of the desired oligomer was isolated as a viscous, colorless liquid **IXb**.

^{1}H NMR (CDCl$_3$) δ (ppm): 0−0.1 (CH$_3$−Si), 0.5 (CH$_2$−Si), 1.2−2.2 (aliphatic protons), 3.1 (epoxy CH), 3.4−3.8 (OCH$_3$).

Sol−Gel Condensation of 1-[2-(3{7-Oxabicyclo[4.1.0]heptyl}-ethyl]-7-[2-trimethoxysilylethyl]-1,1,3,3,5,5,7,7-octamethyltetrasiloxane. In a fashion similar to that described above, 10 g (18.0 mmol) of **Xa**, 0.97 g (54 mmol) of deionized water, 0.4 g of Amberlite IRA-400 ion-exchange resin, and 5.0 g of 2-propanol were heated together at 150 °C for 12 h in a pressure vessel. After workup as before, there were isolated 8.55 g of the desired oligomer **Xb** as a viscous, colorless liquid.

^{1}H NMR (CDCl$_3$) δ (ppm): 0−0.1 (CH$_3$−Si), 0.5 (CH$_2$−Si), 1.2−2.2 (aliphatic protons), 3.1 (epoxy CH), 3.4−3.8 (OCH$_3$).

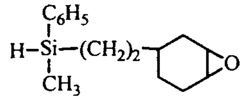
Photopolymerization Studies Using Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR). Photopolymerizations of all of the monomers and oligomers in this work were monitored using Fourier Transform real-time infrared spectroscopy (FT-RTIR). A Midac M-1300 FTIR spectrometer (Midac Corp., Irvine, CA) equipped with a liquid-nitrogen-cooled mercury−cadmium telluride detector was used. The instrument was fitted with a UVEXS Model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a flexible liquid optic wand. The end of this wand was placed at a distance of 5 cm from and directed at an incident angle of 45° onto the sample window. UV light intensities were measured with the aid of a UV Process Supply, Inc. radiometer (Chicago, IL) at the sample window.

Photopolymerizations were carried out at room temperature using broad-band UV light with an intensity of 6.7 mW/cm^2 in solutions of the epoxide monomers containing 2.0 mol % of **IOC10** as the photoinitiator. The monomer/photoinitiator solutions were coated onto a 12-μm oriented and corona-treated polypropylene film (General Electric Capacitor Dept., Hudson Falls, NY), covered with an identical polypropylene film, and then mounted in 5 cm × 5 cm slide frames. The thickness of the liquid monomer films was estimated to be 10−25 μm. Infrared spectra were collected at a rate of 1 spectrum per second using LabCalc, data acquisition software obtained from the Galactic Industries Corp. (Salem, NH) and were processed using GRAMS-386 software from the same company. During irradiation, the decreases in the absorbance band at 886 cm^{-1} due to the epoxy groups of the respective oligomers were simultaneously monitored. Data reduction and subsequent conversion versus time plots were obtained using Excel (Microsoft Corp., Redmond, WA) software. Three to five photopolymerization runs were performed for each kinetic study, and the results were averaged.

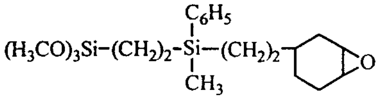
Results and Discussion

Synthesis of Epoxy−Siloxane Oligomers. In Scheme 1 is described the synthesis and photopolymerization of the silicone−epoxide resins that we have previously prepared. This method requires epoxy compounds bearing trialkoxysilane groups as precursors for the sol−gel condensation. There is a dearth of such compounds available from commercial sources, and also few compounds of this type have been reported in the literature. Accordingly, we have been seeking alternative techniques for the synthesis of epoxy-functional sol−gel resins. A novel series of silicon-containing epoxy resins has been prepared by a streamlined three-step process, as depicted in eqs 3−5 of Scheme 2, that makes use of readily available and inexpensive substrates.

The discovery that it is possible to carry out a regioselective monohydrosilation addition of a vinyl epoxide at only one of the two Si−H groups an α,ω-Si−H-terminated poly(dimethylsiloxane) (n = 1, 2, 3) and methylphenylsilane was made in this laboratory.[16,17] This reaction was employed as shown in eq 3 to prepare monoadducts with the general structures **IV** and **V** shown below.



V



VIIa

In the present case, these monoadducts were not isolated but were directly carried forward into the next step of the reaction sequence (eq 4), wherein vinyltrimethoxysilane was added and subjected to further hydrosilation with the remaining Si−H groups to yield **VIa** and **VIIa**.[18] Thus, in a simplified, two-step, one-pot process these and other such compounds bearing both trialkoxysilyl and epoxy groups in the same molecule can be readily prepared in high yields. Given in Table 1 are the structures and elemental analyses of these ambifunctional precursor compounds prepared during the course of this investigation. In Figure 1 is shown a representative ^{1}H NMR spectrum of ambifunctional sol−gel precursor **VIIIa**.

The sol−gel condensations of ambifunctional adducts **Ia** and **VIIa**−**Xa** (eq 5) proceed smoothly in the presence of water and a weakly acidic ion-exchange resin. Typically, the condensations were carried out in solution in

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(16) Crivello, J. V.; Bi, D. *J. Polym. Sci. A: Polym. Chem.* **1993**, *31* (10), 2563.

(17) Crivello, J. V.; Bi, D. *J. Polym. Sci. A: Polym. Chem.* **1993**, *73* (11), 2729.

(18) Crivello, J. V.; Bi, D. *J. Polym. Sci. A: Polym. Chem.* **1993**, *73* (12), 3121.

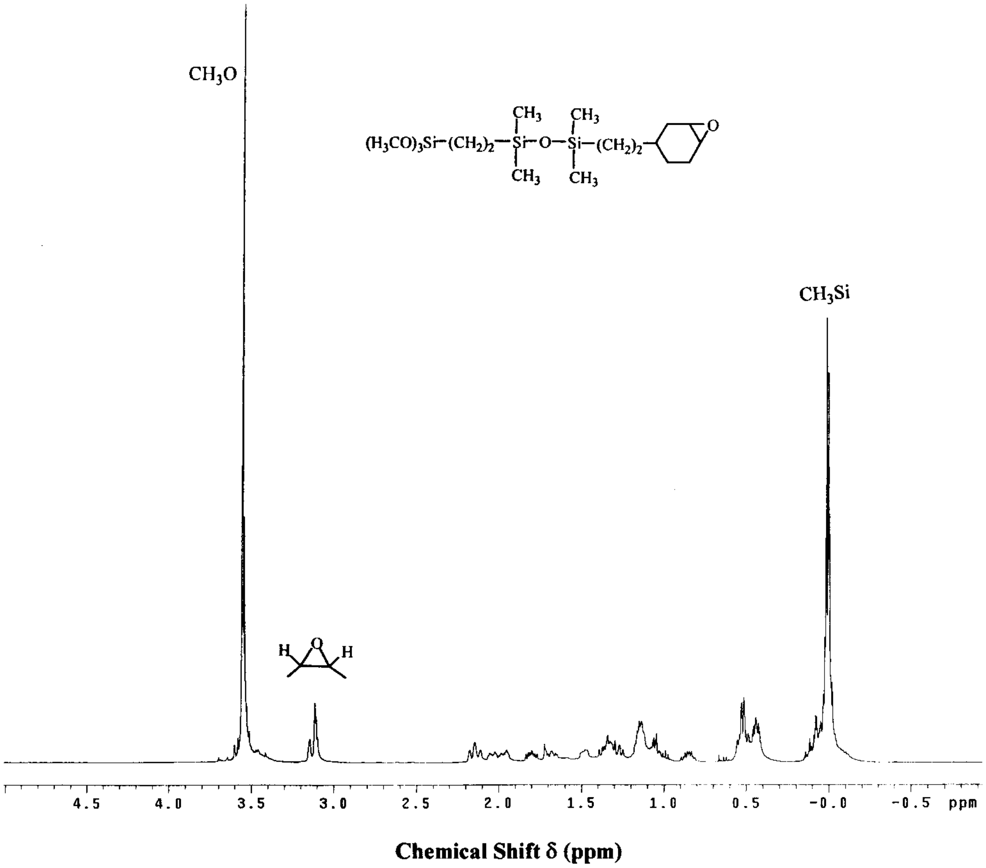
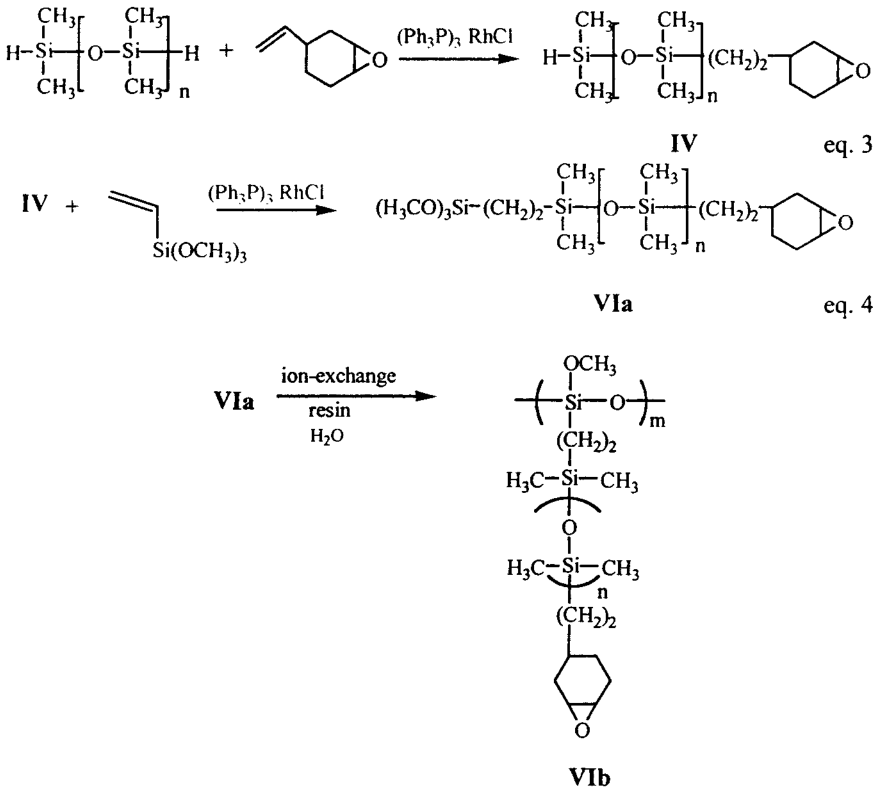


Figure 1. ^{1}H NMR spectrum of ambifunctional sol–gel precursor **VIIIa**.

Scheme 2



either hot 2-propanol or 1-propanol. The reactions were usually terminated when more than 85% of the methoxy groups (3.55 ppm) had undergone reaction as determined by ^{1}H NMR spectroscopy. It was found that, as the siloxane chain of the spacer is lengthened, increasingly more vigorous conditions for the sol–gel reaction were required. Thus, whereas **Ia** undergoes sol–gel condensation in 6 h in 2-propanol at 82 °C, **Xa** requires

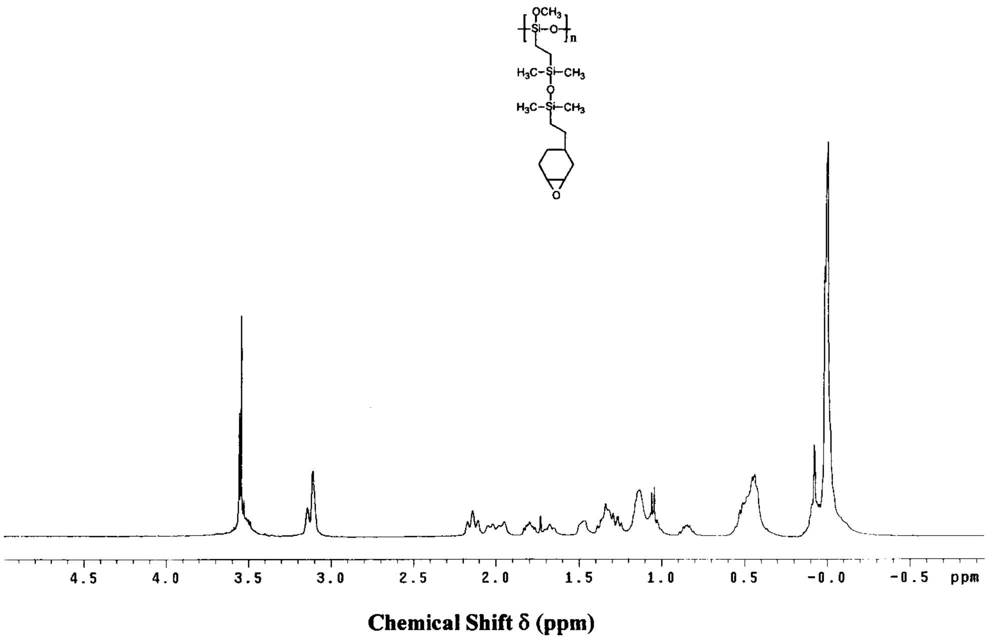


Figure 2. ^{1}H NMR spectrum of silicone–epoxy oligomer **VIIIb**.

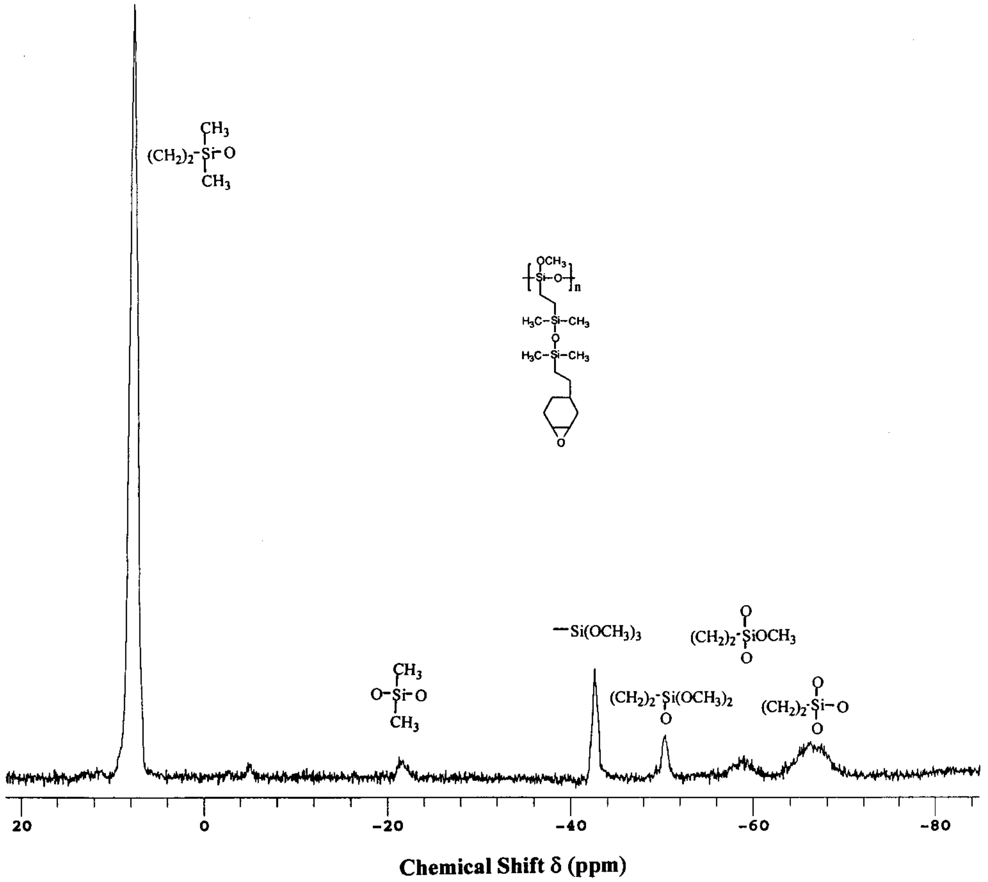


Figure 3. ^{29}Si NMR spectrum of silicone–epoxy oligomer **VIIIb**.

12 h of heating at 150 °C under pressure in a sealed vessel. The desired silicone–epoxy oligomers were obtained as colorless viscous oils by filtering the reaction mixture to remove the ion-exchange resin and then stripping off the solvent under reduced pressure. Under these conditions, ring opening of the epoxy groups was not observed. The resulting silicone–epoxy oligomers were colorless to very pale yellow viscous liquids that displayed high reactivity in photo- and thermally initiated cationic polymerization. In Figure 2 is shown the ^{1}H NMR spectrum of silicone–epoxy oligomer **VIIIa**. The ^{29}Si NMR spectrum for this same oligomer is shown in Figure 3. Resonances corresponding to silicon atoms in six different types of chemical environments are seen in the spectrum and are assigned as noted in Figure 3. Together, these two spectra suggest a structure analogous to the proposed structure for oligomer **II** in which various degrees of hydrolysis of the trialkoxysilyl groups

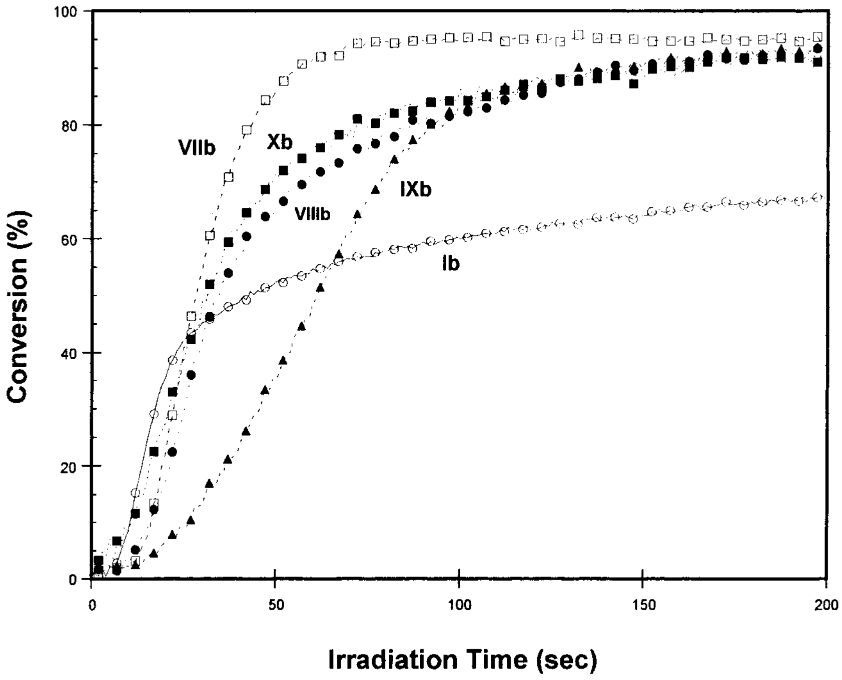
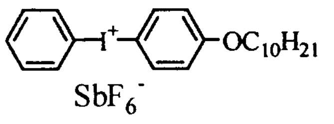


Figure 4. FT-real-time infrared study of the cationic photopolymerization of silicone−epoxy oligomeric resins using 2.0 mol % of IOC10 as photoinitiator. ○, **Ib**; □, **VIIb**; ●, **VIIIb**; ▲, **IXb**; ■, **Xb**.

have taken place. Collected in Table 2 are the structures of the oligomers, together with the conditions of their sol−gel condensations and their molecular weight and viscosity data. Again, it should be noted that the structures of the oligomers shown in Table 2 are idealized and that, in fact, the actual structure is much more complex, with both cyclic and linear siloxane repeat units in the backbone. The approximate degrees of polymerization (DPs) are also given in Table 2. The oligomers range from hexamers to undecamers, implying that they correspondingly possess on the average from 6 to 11 reactive epoxycyclohexyl groups per molecule. It is interesting to note that the viscosity of the oligomers appears to be closely related to the structure of the oligomers. Oligomer **VIIb**, with aromatic groups, has a high viscosity, although its molecular weight is comparatively low because of the increased rigidity caused by the introduction of the phenyl groups into the chain. As the length of the dimethylsiloxane spacer in the resin is increased, the viscosity decreases.

Photo- and Thermally Initiated Cationic Polymerization. In previous papers from this laboratory, it was reported that monomers bearing epoxycyclohexyl groups in general[19] and silicone−epoxy monomers[20] containing these groups in particular display high reactivities in photoinitiated cationic polymerization. The multifunctional sol−gel silicone−epoxy oligomers prepared in this investigation similarly undergo facile photo- and thermally induced cationic ring-opening polymerization in the presence of photosensitive onium salts. In this study, we employed (4-*n*-decyloxyphenyl)-phenyliodonium hexafluoroantimonate (IOC10) as both the thermal initiator and the photoinitiator for the cationic ring-opening polymerization of the epoxide groups. The structure of IOC10 is given below.



IOC10

This compound was selected because of its high solubility in all of the silicone−epoxy oligomeric resins and because it has a high quantum yield (~0.7) and is a very efficient photoinitiator for the cationic ring-opening polymerization of epoxides.[21] Employing the neat resins containing 2.0 mol % of IOC10, the photopolymerizations were monitored using Fourier Transform real-time infrared spectroscopy (FT-RTIR).[22,23] Using this technique, the disappearance of the infrared band at 886 cm^{-1} that is due to the epoxy groups was followed as a function of time. Shown in Figure 4 are the conversion versus time curves obtained from these studies. Included in this figure for comparison is the kinetic curve for the photopolymerization of oligomer **Ib** that was prepared using the process described in Scheme 1. All of the epoxy-functional oligomers display excellent reactivities in cationic epoxide ring-opening photopolymerization. Some structurally dependent trends can be distinguished in this study. **Ib** shows high reactivity as indicated by the initial portion of the kinetic curve; however, the conversion of epoxy groups reached after 200 s of irradiation was only approximately 60%. In contrast, the photopolymerizations of all of the other resins proceed to nearly quantitative conversions. It can be noted that **Ib** has the shortest and stiffest spacer linking the epoxycyclohexyl group with the siloxane main chain of all of the resins. As a

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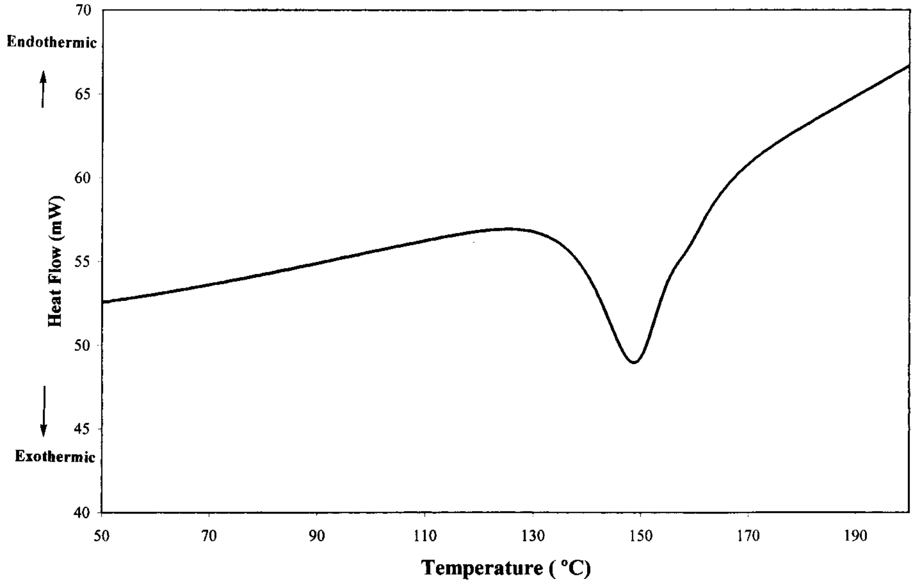

Figure 5. DSC scan of the thermally initiated cationic polymerization of silicone–epoxy oligomer **VIIIb** in the presence of 2.0 mol % IOC10 as initiator.

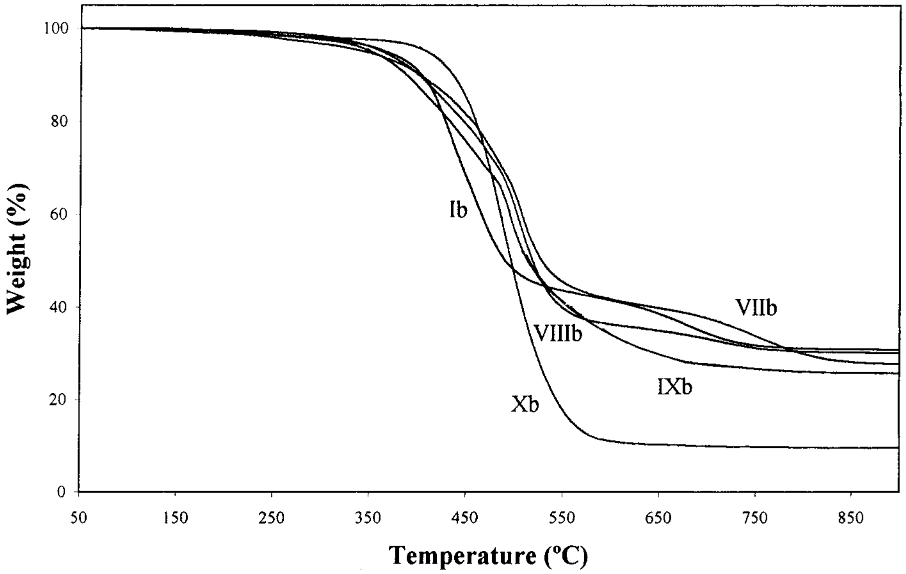

Figure 6. Thermogravimetric analysis study of cross-linked silicone–epoxy resins carried out at a heating rate of 20 °C/min in nitrogen.

consequence, **Ib** is expected to give the most highly cross-linked polymer. Despite several attempts, we were unable to measure a glass transition temperature for this polymer using DSC. This appears to be indicative of a very highly cross-linked nature. The diffusion and mobility of the bulky epoxycyclohexyl groups in such a polymer are expected to be restricted, resulting in vitrification of the polymer at low conversions. **IXb** displays a relatively long induction period prior to polymerization. It is not possible to rigorously purify the oligomers after preparation, and we interpret this induction period as indicating the presence of residual basic impurities that retard the cationic ring-opening polymerization. As with **Ib**, no glass transition temperature was observed by DSC below 225 °C. In contrast, the high mobility of the other resins with flexible siloxane groups in the spacers gives rise to much higher conversions through suppression of the onset of vitrification.

In Figure 5 is shown the differential scanning calorimetric (DSC) curve for the thermal polymerization of oligomer **VIIIb** in the presence of 2.0 mol % of IOC10. The onset of the thermal decomposition of IOC10 takes place at approximately 130 °C. Polymerization of this oligomer is very rapid, as indicated by the sharpness of the exothermic peak in the DSC curve.

Thermal Stability of Epoxy-Functional Organic–Inorganic Hybrid Polymers. The thermogravimetric analysis (TGA) curves for thermally cured samples of the silicone–epoxy oligomers are given in Figure 6. The TGA study was carried out in nitrogen at a heating rate of 20 °C/min. The polymers display excellent stability, with the onset of thermal decomposition at approximately 350–400 °C. Polymer **Xb**, which bears the longest pendant siloxane linker between the main chain and the epoxide group, shows the poorest char yield, probably because of cyclization and subsequent volatil-

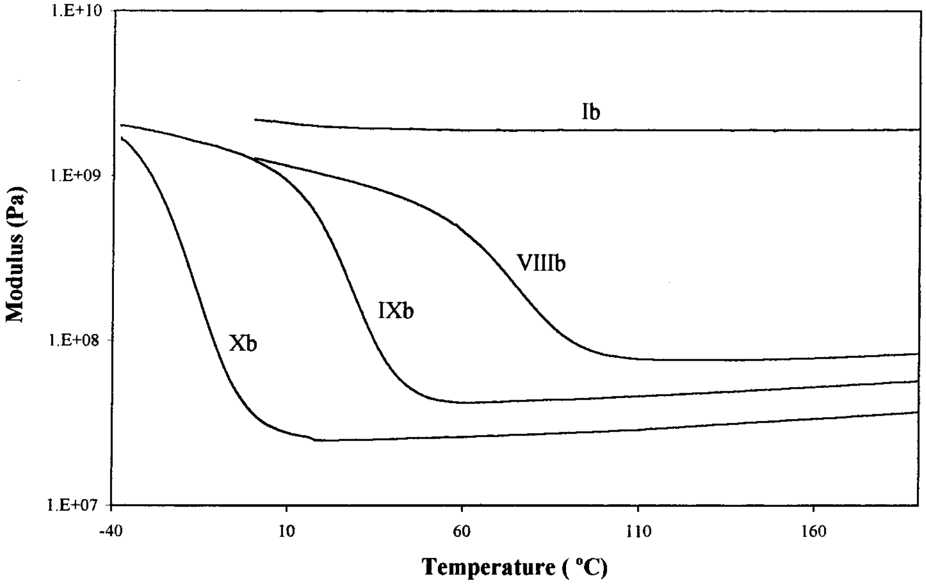

Figure 7. Comparison of the storage moduli as determined by dynamic mechanical testing for thermally cross-linked silicone−epoxy resins Temperature scan rate = 10 °C/min in nitrogen.

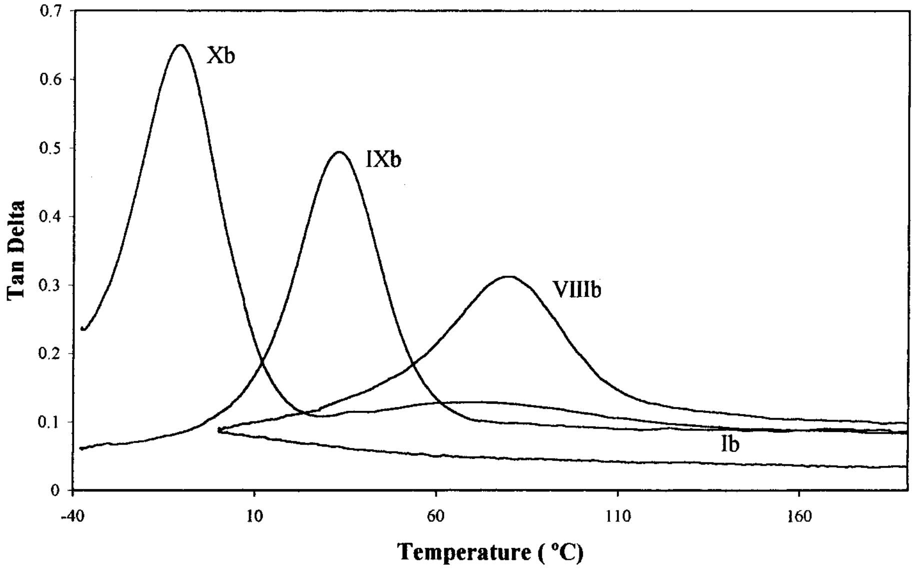

Figure 8. Comparison of the tan delta plots for thermally cross-linked silicone−epoxy resins as determined by dynamic mechanical testing. Temperature scan rate = 10 °C/min in nitrogen.

ization of the cyclic dimethylsiloxanes formed during thermal decomposition.

Mechanical Properties of Epoxy-Functional Organic−Inorganic Hybrid Polymers. The mechanical properties of the organic−inorganic hybrid polymers produced by thermal polymerization of the corresponding epoxy-functional sol−gel oligomers were determined using dynamic mechanical analysis (DMA). The results are shown in Figures 7 and 8. Again, the polymer derived from **Ib** was included in this study for comparison. The mechanical properties of the resins are directly related to the length and type of spacer group separating the epoxycyclohexyl groups from the siloxane main chain. Accordingly, **Ib** is expected to give the stiffest and highest-glass-transition polymer. In Figure 7, it can be seen that this polymer exhibits no decrease in storage modulus up to 180 °C. In fact, there is no decrease in the modulus or evidence of a glass transition at temperatures below 300 °C. As the length of the spacer is increased and flexible siloxane linkages are introduced, one sees a progressive decrease in the temperature of the fall off of the storage modulus, which corresponds to a decrease in the glass transition temperature (Figure 8). Polymer **Xb** displays the lowest glass transition temperature (−6.5 °C), whereas the T_g's for **IXb** and **VIIIb** are, respectively, 33 °C and 80 °C. A similar observation was made for photopolymerized thin films of these oligomers. Whereas the film derived from **Ib** was brittle and could not be handled, the films from **VIIIb**, **IXb**, and **Xb** were increasingly more flexible and tough.

Conclusions

A convenient and high-yield method for the synthesis of novel silicone−epoxy resins has been developed. This method takes advantage of several new reactions discovered in this laboratory. First, the regioselective hydrosilation addition of a vinyl epoxide at only one end of an α,ω-Si−H difunctional siloxane or silane provides an intermediate bearing one epoxy and one Si–H group. Further hydrosilation with vinyltrimethoxysilane leads to ambifunctional molecules bearing both trimethoxysilyl and epoxy groups, which can be employed as substrates in the sol–gel condensation. In this work, we used acidic ion-exchange catalysts to catalyze this latter reaction. The resulting silicone–epoxide oligomers can be readily converted by either photo- or thermally induced cationic ring-opening polymerization to cross-linked organic–inorganic hybrid resins. The properties of the cross-linked resins depend on the length of the spacer group between the siloxane backbone and the pendant epoxy groups. Short spacer groups lead to highly rigid, glasslike matrixes, whereas longer spacer groups produce more flexible materials with considerable elongation. Many new applications for these novel resins are anticipated, including use as composites, optical adhesives and coatings, waveguides, and electronic potting and encapsulating resins.

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