Synthesis of Cycloaliphatic Substituted Silane Monomers and Polysiloxanes for Photocuring

D. P. Dworak and M. D. Soucek*

Department of Polymer Engineering, The University of Akron, 250 S. Forge Street, Akron, Ohio 44325-0301

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ABSTRACT: A synthetic scheme was developed to prepare cationically polymerizable methyl, cyclopentyl, and cyclohexyl substituted polysiloxanes. Initially, the desired cycloalkene and dichlorosilane were reacted at high pressure (approximately 250 psi) and high temperature (120 °C) to yield the desired cycloaliphatic dichlorosilane. The chlorosilane monomers underwent an oligomerization to produce cyclic oligomers of low molecular weight (∼2000 g/mol). Polysiloxanes were produced through the acid-catalyzed ring-opening polymerization of the cyclic oligomers to yield high molecular weight polysiloxanes (∼45 000 g/mol). The polysiloxanes were then functionalized with a cycloaliphatic epoxy and alkoxysilane groups via hydrosilylation. Monomers, oligomers, and polymers were characterized by ^{1}H and ^{29}Si NMR, FT-IR, and electrospray ionization mass spectroscopy. The photoinduced curing kinetics and activation energies were investigated using photodifferential scanning calorimetry. Differential scanning calorimetry was used in order to observe any physical changes in the films that are brought about due to the variation of the pendant groups. The cycloaliphatic substituents raised the glass transition temperature and affected the curing kinetics when compared to a methyl substituted polysiloxane. The activation energies were found to be 144.8 ± 8.1 kJ/mol for the methyl substituted and 111.0 ± 9.2 and 125.7 ± 8.5 kJ/mol for the cyclopentyl and cyclohexyl substituted polysiloxanes.

Introduction

Chlorosilanes are the basic building blocks of silicones and polysiloxanes. Chlorosilanes are utilized in hydrosilylation where the addition of a Si−H compound to a multiple bond, often an alkene or alkyne, is the pathway to synthesize a variety of unique polysiloxane systems. Typically, platinum complexes are used as hydrosilylation catalysts due to activity at relatively low concentrations. The most common platinum catalyst is chloroplatinic acid (Speier's catalyst) which is reduced to a platinum(0) species in the presence of a silane or siloxane. During these reactions an induction period was observed, but this can be reduced by using a platinum(0) complex such as Karstedt's catalyst. Other metal-based catalysts can be used such as the rhodium-based Wilkinson's catalyst, although higher catalyst concentrations are usually required for efficiency.

Processes that involve synthesis of linear siloxane polymers can be divided into two general classifications according to the pathway in which the polymer chain is formed: polymerization of difunctional silanes and ring-opening polymerization of cyclic oligosiloxanes. Hydrolytic polymerization involves the polymerization of halosilanes (mainly chlorosilanes) through the incorporation of water and is often employed for the synthesis of both linear siloxane polymers and cyclic siloxane oligomers, the latter of which can be used further as substrates in ring-opening polymerization. A polysiloxane chain is most often formed as a result of two types of polymerization: homofunctional polymerization of a difunctional silane such as silanediols or dichlorosilanes and heterofunctional polymerization involving a silanol and another functional group. A heterofunctional polymerization approach is useful for a hydrolytic polymerization step. As a result, both steps—hydrolysis and polymerization—usually occur simultaneously during the reaction.

The process of ring-opening polymerization allows greater control over molecular weight; thus, it is often a preferred method for synthesis of high molecular weight polymers. It can be performed via either anionic or cationic routes and may be classified as either thermodynamically or kinetically controlled. Most polymerizations are thermodynamically driven; the siloxane bonds being identical in number and kind both in a chain and in a ring, the net energy change is very small. The increase in entropy that complements the increased molecular freedom of the siloxane segments on going from the cyclic structures to the linear chains drives the polymerization reaction.[1] The molecular weight of the polymer at equilibrium during cyclosiloxane polymerizations is controlled by incorporating an end group, which ensures the closure of the chain with a neutral, nonreactive group.

Polysiloxanes possess a variety of applications, both medical and nonmedical. Polysiloxanes and silsesquioxanes have been functionalized with various reactive (vinyl ethers, epoxy groups[1−6]) and nonreactive groups (1-octene, substituted phenyl groups[7,8]) in order to achieve the desired property. Applications of siloxanes include high-performance elastomers, membranes, electrical insulators, water repellants, antifoaming agents, mold release agents, adhesives, and protective films.[9,10] Furthermore, the ability to synthesize monomers that increase the glass transition temperature could be copolymerized with other polymers such as polyurethanes, polyimides, or other silicone monomers. In previous work it was proposed to prepare poly(dimethylsiloxane-*co*-methylhydrosiloxane) (**1**) functionalized with cycloaliphatic epoxides and alkoxysilanes via hydrosilylation chemistry.[11] The principal silane mono-

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* Corresponding author: Tel 1-330-972-2583; Fax 1-330-258-2339; e-mail msoucek@uakron.edu.

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mers have been methyl and phenyl, and hitherto cycloaliphatic silane monomers have not been reported on account of steric hindrance of the cyclic alkenes.

The synthesis and functionalization of poly(dicyclopentylsiloxane-*co*-cyclopentylhydrosiloxane), hydride terminated (**2**), and poly(dicyclohexylsiloxane-*co*-cyclohexylhydrosiloxane), hydride terminated (**3**), were performed in a method comparable to the methyl and hydrogen substituted polysiloxane. The synthetic route for the cycloaliphatic substituted differs from that of methyl substituted in that the cyclic species needed to be synthesized via hydrolytic polymerization of cycloaliphatic substituted silanes. The monomers were characterized using ^{1}H NMR, ^{29}Si NMR, FT-IR, and mass spectroscopy. From the monomers, oligomers, and polysiloxanes homopolymers were prepared. The synthesis of these monomers makes it possible to examine the unique properties that large bulky pendant groups can induce on high molecular weight polysiloxane chains and to explore the various applications for these polymers.

Experimental Section

Materials. Octamethylcyclotetrasiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane, 1,1,3,3-tetramethyldisiloxane, dichlorosilane, and vinyltriethoxysilane were purchased from Gelest, Inc., and used as supplied. Wilkinson's catalyst (chlorotris(triphenylphosphine)rhodium(I), 99.99%), Karstedt's catalyst (platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, 3% w/w solution in xylenes), cyclopentene, cyclohexene, Amberlyst 15 ion-exchange resin, and 4-vinyl-1-cyclohexene 1,2-epoxide were purchased from Aldrich and used as supplied. Toluene, supplied by Aldrich Chemical Co., was distilled in order to eliminate any impurities. Irgacure 250 was supplied by Ciba Specialty Chemicals and used as received. Air-sensitive materials were transferred and weighed in a drybox under argon.

Instruments. Proton NMR spectra were obtained from a Gemini-300 spectrometer (Varian), while silicon NMR spectra were recorded on a Gemini-400 spectrometer (Varian). All NMR samples were prepared in $CDCl_3$ and recorded at 20 °C. Chemical shifts are given relative to a TMS internal standard. FT-IR spectra were obtained on a Mattson Genesis Series FTIR, and a Waters system was used for GPC analysis. Mass spectroscopy was performed on a Saturn 2200 (Varian) in EI mode with an ion trap readout.

Functional Group Analysis. The Si−H bond is polarized depending to some degree on the substituents of the silicon.[12] The reactivity of the Si−H bond makes it possible to analyze this group with qualitative or quantitative chemical tests. The Si−H was titrated via reduction of a mercury(II) salt:

$$-\mathrm{Si-H} + 2\mathrm{HgCl_2} \rightarrow -\mathrm{Si-Cl} + \mathrm{Hg_2Cl_2} + \mathrm{HCl} \qquad (1)$$

which can be titrated with a base to find the % Si−H in a given sample.[13]

A mercuric chloride solution (4% w/v in 1:1 chloroform−methanol) was pipetted (20 mL) into an Erlenmeyer flask. The sample to be titrated was added and agitated before adding the calcium chloride solution (15 mL, saturated solution in methanol). Phenolphthalein indicator was added (15 drops) after 5−6 min, and the solution was titrated with 0.1 N alcoholic potassium hydroxide. Blanks are titrated in the same manner before and after the analysis. The calculation for % H is shown in eq 2:

$$\%\ \mathrm{H} = [(V_1 - V_2)](N_{\mathrm{KOH}})(1.008/2000)(100)/\text{sample wt (g)} \qquad (2)$$

where V_1 is the end point, V_2 is the averaged blanks, and N is the normality of the basic titrant.

Photopolymerization Procedure. On average, 2−3 mg of sample (polymer and 3% w/w photoinitiator) was placed in an uncovered, hermetic, aluminum DSC pan. An empty pan was used as a reference. The chamber of the DSC was purged with nitrogen before the polymerization and was continued throughout the reaction. The samples were photocured with UV light (150 mW/cm^2) for various exposure times (1, 5, and 15 s) and temperatures (−10, 25, and 60 °C). The heat flux as a function of reaction time was monitored under isothermal conditions, and the rate of polymerization was calculated.[14,15] The heat of reaction (ΔH_R) used for the epoxy group was 23.13 kcal/mol.

The rate of propagation (R_p) is directly proportional to the rate at which heat is released from the reaction. As a result, the height of the DSC exotherm can be used in conjunction with other sample information to quantify the rate of polymerization. The rate formula used in the analysis of the photopolymerization data was

$$R_p = ((Q/s)M)/(n\Delta H_R m) \qquad (3)$$

where (Q/s) is the heat flow per second released during the reaction in J/s, M is the molar mass of the reacting species, n is the average number of epoxy groups per polymer chain, and m is the mass of the sample.

Synthesis of Poly(dimethylsiloxane-*co*-methylhydrosiloxane), Hydride Terminated. To a three-neck round-bottom flask equipped with a reflux condenser and nitrogen inlet/outlet was added octamethylcyclotetrasiloxane (90.00 g, 0.30 mol), 1,3,5,7-tetramethylcyclotetrasiloxane (5.33 g, 22.1 mmol), 1,1,3,3-tetramethyldisiloxane (0.67 g, 5.3 mmol), and Amberlyst 15 (20 wt %) and stirred at 70 °C, under nitrogen, for 15 h. The viscous solution was then filtered to obtain poly(dimethylsiloxane-*co*-methylhydrosiloxane), hydride terminated (**1**), of various molecular weight ranges. Vacuum filtration was performed (<1 mmHg) in order to remove low molecular weight oligomers and unreacted starting materials. Weight-average molecular weight was obtained from gel permeation chromatography (GPC) analysis; M_n = 45 000, PDI = 1.66. Polymer characterization and Si−H functionality were confirmed/analyzed through ^{29}Si NMR, ^{1}H NMR, FT-IR analysis, and titration. Polysiloxanes **2** and **3** were produced in the same manner.

Synthesis of Cycloaliphatic Dichlorosilane. A dry, sealed, and evacuated stainless steel bomb, cooled via a dry ice/acetone bath, was charged with chilled cycloalkene (5 g, ∼30 mmol) and Wilkinson's catalyst (0.15 g, 0.16 mmol) and purged with nitrogen. In a chilled (<−10 °C) calibrated tube dichlorosilane (5 mL, 0.06 mol) was condensed and then distilled into the bomb through the inlet valve via a cannula. The inlet valve was sealed and the bomb was then allowed to warm to room temperature and then heated for 24 h at 120 °C by means of an oil bath. The bomb was then allowed to cool, and the reaction produced a clear, light yellow liquid. After distillation, any unreacted cycloalkene and side products were removed via vacuum (2−3 mmHg) to yield pure cycloaliphatic dichlorosilane (∼88% yield). Product characterization was performed by ^{29}Si NMR, ^{1}H NMR, FT-IR, and mass spectroscopy.

General Synthesis of Cyclic Oligomers of Poly(cycloaliphatic hydrosiloxane). To a three-neck round-bottom flask, equipped with a reflux condenser, nitrogen inlet/outlet, and dropping funnel, was added saturated aqueous sodium bicarbonate (10 mL) and diethyl ether (5 mL). A solution of cycloaliphatic dichlorosilane (4.43 g, ∼0.03 mol) in ethyl ether (5 mL) was then added dropwise via the dropping funnel, and the solution was allowed to stir for several minutes at room temperature. The ether layer was separated and passed through a filter, and any remaining traces of ether were removed via vacuum distillation (3−5 mmHg) to yield a clear, viscous oil. Weight-average molecular weight was obtained for both the cyclopentyl and cyclohexyl substituted cyclic oligomers from gel permeation chromatography. The poly(cyclopentylhydrosiloxane) oligomers had a M_n = 1800 and a PDI = 2.44. The poly(cyclohexylhydrosiloxane) oligomers had a M_n = 2230 and a PDI = 2.53. Oligomer characterization was performed via ^{29}Si NMR, ^{1}H NMR, FT-IR, and mass spectroscopy.

Synthesis of Cyclic Oligomers of Poly(dicycloaliphatic siloxane). To a single-neck round-bottom flask equipped with a reflux condenser was added the cyclic oligomers of the desired poly(cycloaliphatic hydrosiloxane) (5 g), the preferred cycloalkene (15 g), and Karstedt's catalyst (0.1 mL, 0.22 mmol). The reaction was held at 110 °C in an oil bath and magnetically stirred. The disappearance of the Si−H functionality was monitored through FT-IR, and the disappearance of the peak at ~2160 cm^{-1} indicated that the reaction was complete (>48 h). Any unreacted cycloalkenes were removed under vacuum (3−1 mmHg) to yield a clear, viscous oil. Products were characterized by ^{29}Si NMR, ^{1}H NMR, FT-IR, and mass spectroscopy.

Cycloaliphatic Epoxide and Alkoxysilane Functionalization of Prepared Poly(dialkyllsiloxane-*co*-alkylhydrosiloxane), Hydride Terminated Polymers. To a three-neck round-bottom flask, equipped with a reflux condenser and nitrogen inlet/outlet, was added **1**, **2**, or **3** (30 g), 4-vinyl-1-cyclohexene diepoxide (20 g, 0.18 mol), vinyl triethoxysilane (2 g, 0.01 mol), and Wilkinson's catalyst (0.004 g, 4.3 μmol). Dry, distilled toluene (30 g) was added via a cannula. The reaction was held at 75 °C in an oil bath and mechanically stirred under nitrogen. The disappearance of the Si−H functionality was monitored through FT-IR, and the disappearance of the peak at ~2160 cm^{-1} indicated that the reaction was complete. Any solvent and unreacted starting materials were removed under vacuum (3−5 mmHg). Cycloaliphatic epoxide and alkoxysilane functionalization was confirmed/analyzed through ^{1}H NMR, FT-IR analysis, and titration.[16]

Results and Discussion

The objective of this study was to prepare a UV-curable polysiloxane with cyclopentyl and cyclohexyl groups. The route used in the preparation of the cycloaliphatic substitution was taken due the difficulties of reacting the internal alkene with the available silane group. The initial hydrosilylation between dichlorosilane and the cycloalkene was performed in order to control the amount of silane functionality along the polysiloxane backbone. The reaction of the mono- and disubstituted cycloaliphatic substituted cyclic oligomers is similar to that of the methyl substituted polysiloxane (Figure 1). The control over the ratio of mono- and disubstituted cyclic oligomers allows management over the silane functionality present along the polymer backbone. In these experiments, all mono- and disubstituted cyclic oligomer ratios were 1:18.

Attempts at the synthesis of the dicycloaliphatic dichlorosilanes proved exceptionally difficult even under extreme pressure (300 psi) and temperatures (250 °C). Hydrosilylation accelerators, such as benzaldehyde and acetone, and higher catalyst concentrations were employed with no considerable results.

Synthesis and Characterization. A synthetic diagram of the functionalization of poly(dimethylsiloxane-*co*-methylhydrosiloxane), hydride terminated, is presented in Figure 1. The pendant alkoxysilane aids in miscibility during formulation and provides a site for interaction with the metal/silicon oxo cluster, while the cycloaliphatic epoxide provides a cross-linking site for cationic UV induced cure. The overall structure of **1** will be a block copolymer composed of mostly "D" units (R−Si−R) and the desired functionalities.

A diagram of the synthesis of **2** is presented in Figure 2, and functionalization of **2** and **3** is performed in the same manner as for **1**. The cycloaliphatic substitution along the polysiloxane backbone was chosen for raising the glass transition of the polysiloxane, while not contributing to UV absorption and ultimately yellowing.

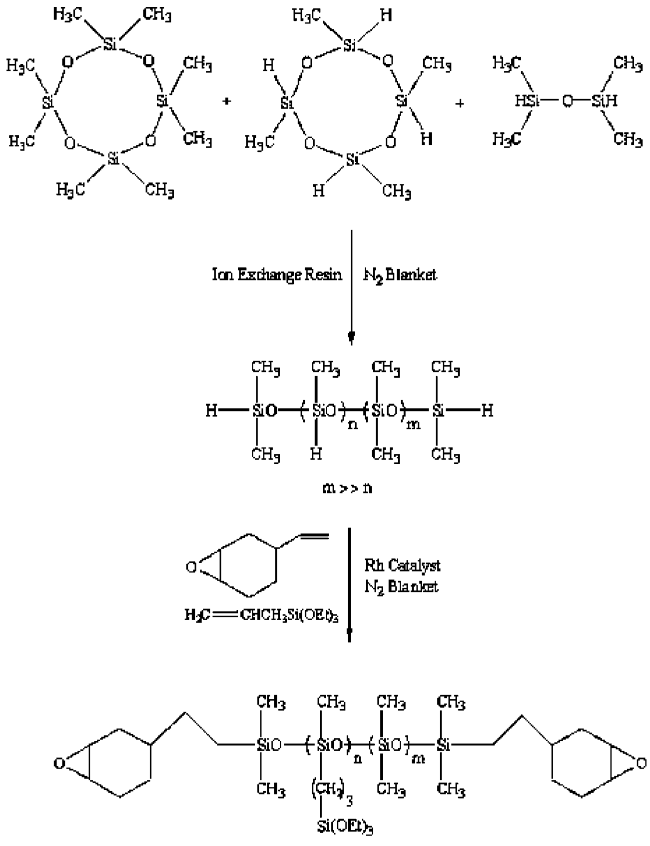

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Figure 1. Synthesis of cycloaliphatic epoxide/alkoxysilane functionalized poly(dimethylsiloxane-*co*-methylhydrosiloxane).

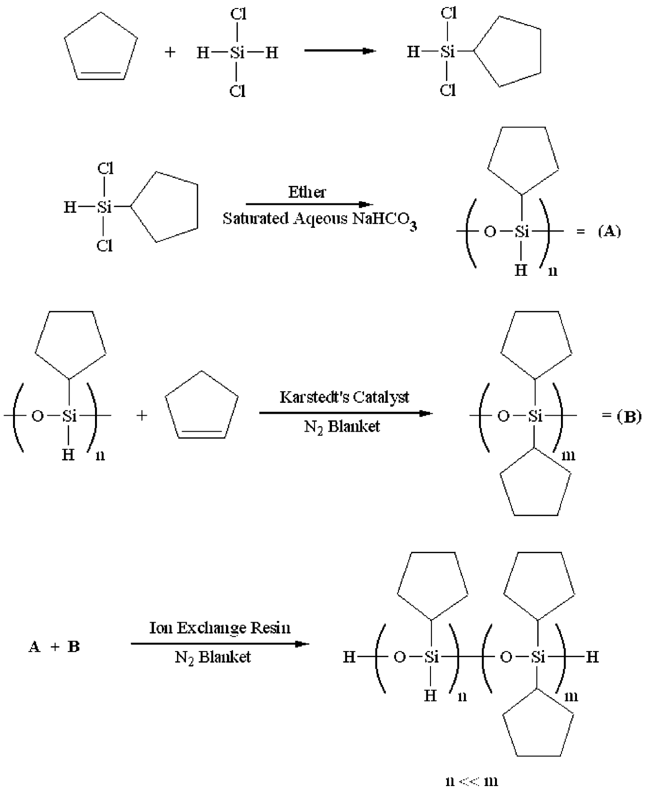

Figure 2. Synthesis of hydride functionalized poly(dicycloaliphatic siloxane-*co*-cycloaliphatic hydrosiloxane).

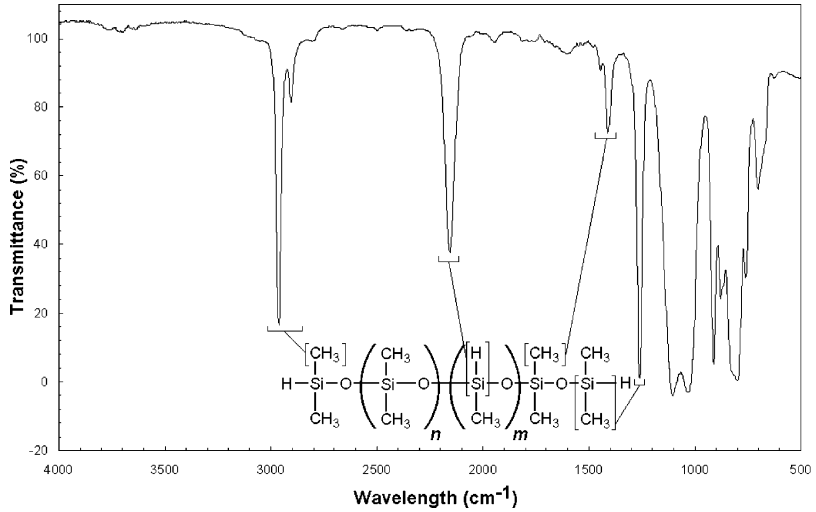

Figure 3. FT-IR spectra of poly(dimethylsiloxane-*co*-methylhydrosiloxane), hydride terminated.

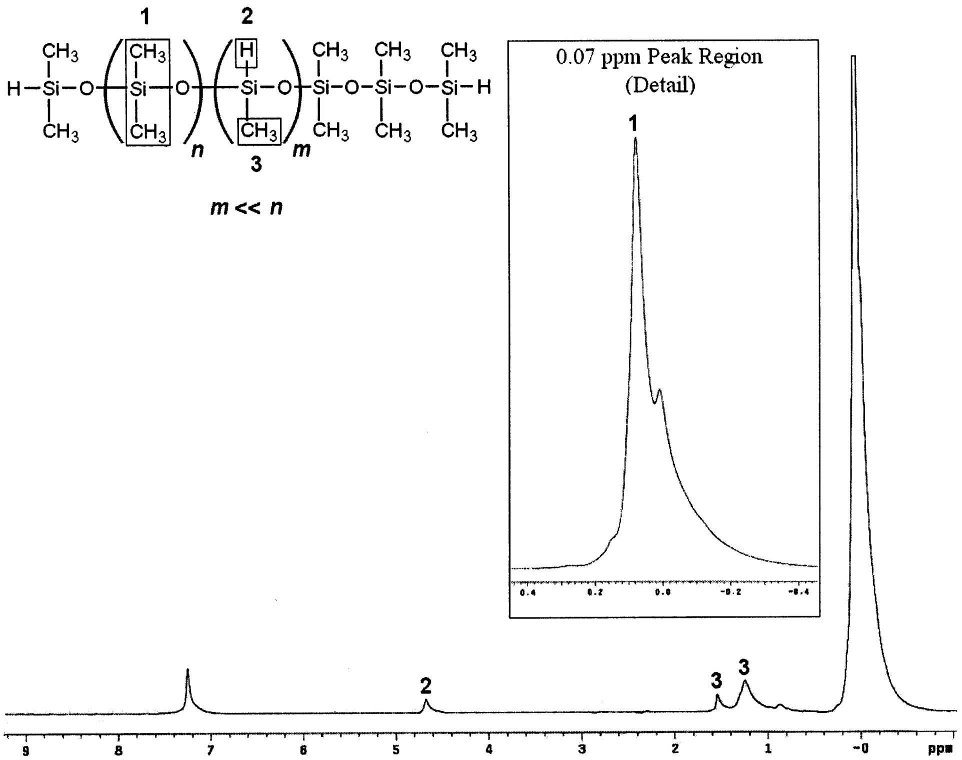

Figure 4. Proton NMR of poly(dimethylsiloxane-*co*-methylhydrosiloxane), hydride terminated.

The synthesis of **1** was verified through FT-IR (Figure 3) and showed that the Si−H functionality is present due to the strong peak at 2160 cm^{-1}, while the two peaks 1090 and 1110 cm^{-1} are indicative of high molecular weight polysiloxanes. The indication of cyclic species would be evident in the region of 1000 cm^{-1} with the band being strong and broad and spanning 50−100 cm^{-1} across. The indication of two bands in this region is strong confirmation of high molecular weight species. However, cyclic species higher than 50 units long can still show similar peaks and present misleading information. As a result, GPC analysis was used to confirm that no traces of cyclic species were present. The GPC chromatogram showed the typical bell curve for high molecular weight polymer, and if cyclic species were present, then two more peaks would have eluted before the main peak, which are evidence of cyclic species. The % Si−H analysis for **1** yielded 15.3 ± 0.8%.

Further analysis via ^{1}H NMR (Figure 4) showed the strong, characteristic peak for Si−Me at δ 0.07 ppm and the Si−H functionality at δ 4.68 ppm. The peak at δ 0.07 ppm is split due to an adjacent Me−Si−H atom. Two smaller peaks were observed at δ 1.22 and δ 1.57 ppm, which are a result of magnetic inequalities due to the different stereoconfigurations of the substituents along the polymer backbone. The magnetic nonequivalence of the CH_3 protons is a result of their different environment due to fact that one methyl group has two other methyl groups as neighbors in the *cis*−*cis* position, whereas these others are surrounded by one methyl and one hydrogen in a *cis*−*trans* position.

The silicon NMR ($J = 200$) of **1** (Figure 5) shows to main groups of signals corresponding to the D and D′ (Me−Si−H) units in the difunctional siloxy unit region. A typical copolymer whose molar ratio is 1:1 and/or have random units show more symmetric peak patterns.

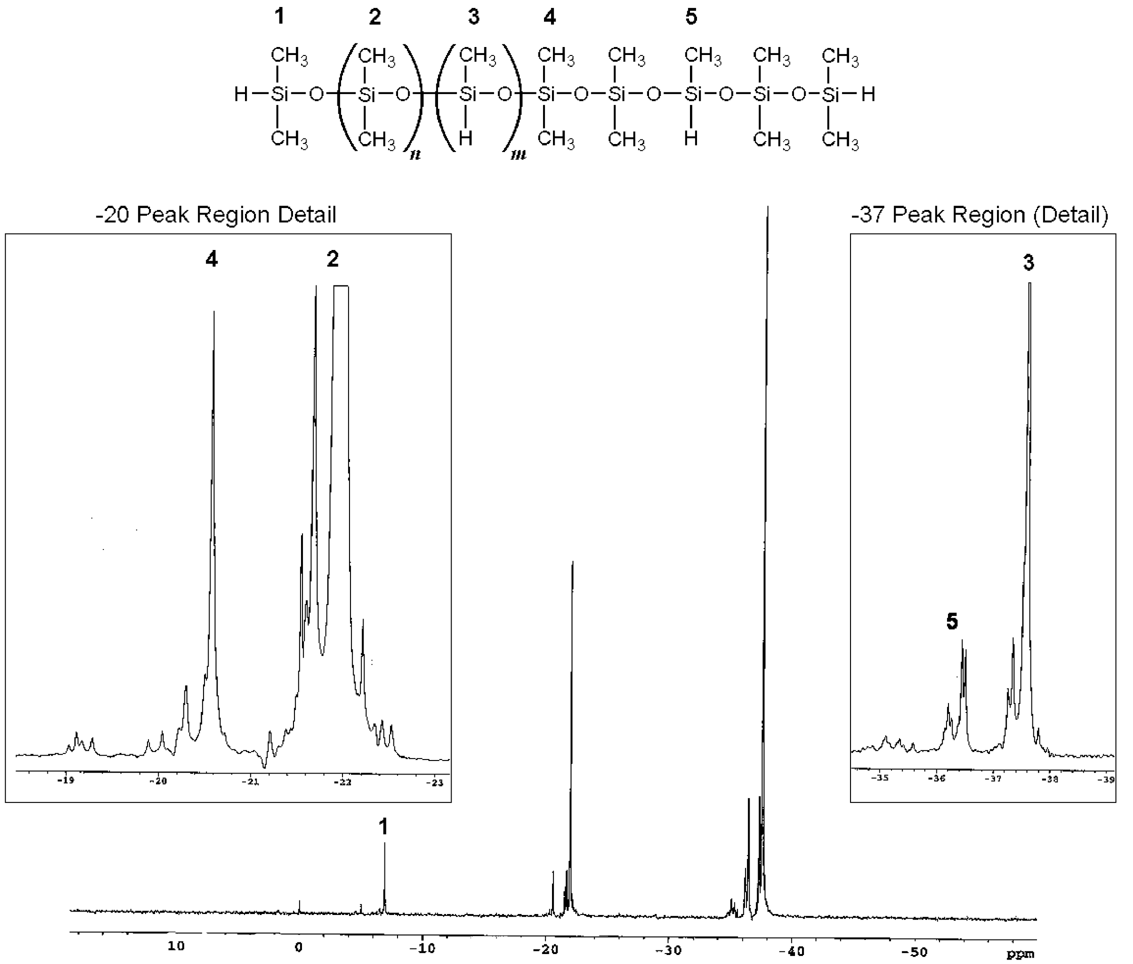

Figure 5. Silicon NMR of poly(dimethylsiloxane-*co*-methylhydrosiloxane), hydride terminated.

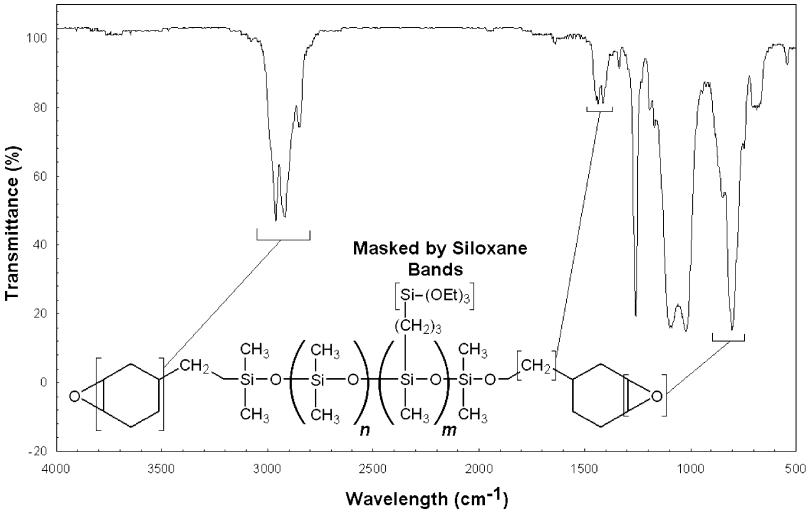

Figure 6. FT-IR spectra of cycloaliphatic epoxide/alkoxysilane functionalization of poly(dimethylsiloxane-*co*-methylhydrosiloxane), hydride terminated.

However, when the molar ratio is no longer equal (14:1 in this case) and/or the copolymer is a blocky microstructure, then the intensities in the NMR patterns deviate from the symmetric case. Furthermore, the observance of a quartet can occur from the nonadditivity of the chemical shifts resulting from different arrangements of the neighboring units.

The small downfield peak at ~δ −8 ppm is representative of a hydrogen substituted “M” (R_3−Si−) unit. Trimethyl substituted M units appear in the δ 5−10 ppm region of the spectra, which is further evidence that the polysiloxane chain is hydrogen terminated. When comparing the D unit silicon atoms to an M unit one, the D unit silicon is bonded to an additional oxygen atom. The downfield shift of the M unit occurs due to the lack of an oxygen atom, which deshields the Si nuclei. The cluster of peaks near δ −21 ppm are representative of various D units. The inset shows peaks between δ −20 and δ −21 ppm, which are representative of D units that are adjacent to a D′ unit. The

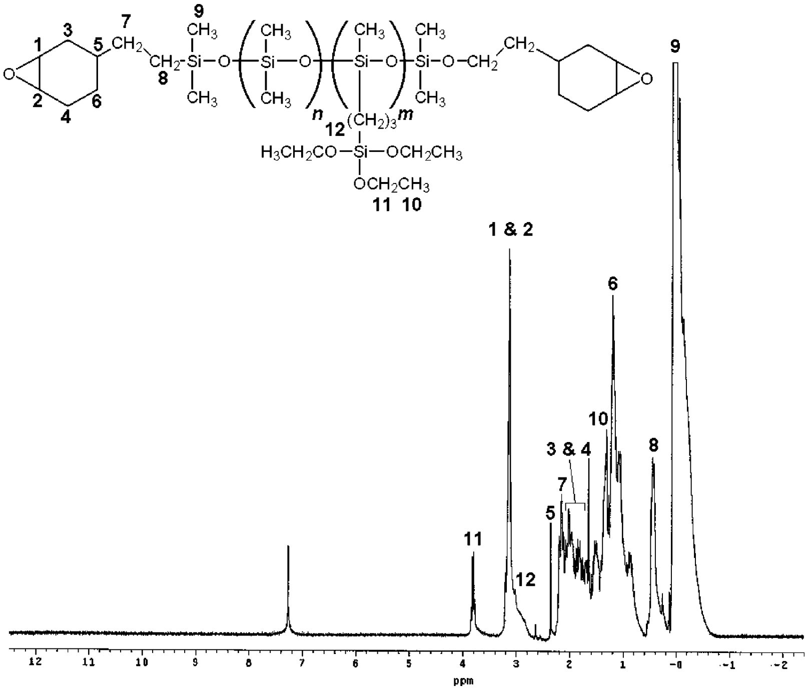

Figure 7. Proton NMR spectra of cycloaliphatic epoxide/alkoxysilane functionalization of poly(dimethylsiloxane-*co*-methylhydrosiloxane), hydride terminated.

nonequivalence of the of the silicon atoms causes a slight downfield shift. The peaks at δ −22 ppm symbolize repeating D units in a linear chain. The various peaks are a result of the different molecular weight chains in the sample. The upfield peaks at ~δ −38 ppm are the D′ units within the polysiloxane chain, and the same trend with the D units is observed with the D′ units, with the repeating units being slightly upfield of the different adjacent silicon atom peaks. In addition, the starting material 1,3,5,7-tetramethylcyclotetrasiloxane has reacted completely due to the fact that it would appear near δ −32 ppm in the spectrum.

Functionalization of **1** with cycloaliphatic epoxides and alkoxysilanes was analyzed with FT-IR (Figure 6) and shows clear evidence of the epoxy ring. However, the Si−O−Si bands at 1000 cm^{-1} take precedence and mask the alkoxysilane functionality. As a result, proton NMR was used for confirmation of the alkoxysilane functionality (Figure 7). The triplet at δ 3.8 ppm represents the −CH$_2$− protons of the alkoxysilane group.

The synthesis of the cycloaliphatic dichlorosilanes was analyzed through FT-IR, proton NMR, and silicon NMR. The FT-IR spectra of the cycloaliphatic dichlorosilanes (Figure 8) show the presence of the Si−H peak at ~2200 cm^{-1} and the existence of the Si−Cl$_2$ functionality at ~500 cm^{-1}. The Si−H transmission peak location can be a good indication of the inductive effects of the other substituents on the silicon atom.[17]

The silane peak position can be predicted accurately if all of the substituents are known. By adding the wavelength values for each of the substituents (−Cl, −Cl, and −C$_5$H$_9$/C$_6$H$_{11}$), the location the Si−H peak value can be found (Table 1).[12]

The proton NMR spectra of the cycloaliphatic dichlorosilanes (Figure 9) show three distinct peaks. The upfield peaks are representative of the cycloaliphatic substituent, while the downfield peak is the Si−H proton. The Si−alkyl groups usually display the expected shift patterns, with the patterns being fairly representative of the substituent due to the shielding effects of the silicon atom.[18] However, this pattern can be affected by the inductive and/or shielding effects of the other substituents on the silicon atom. Closer examination of the Si−H peak reveals a multiplet, which could be the result of the sample reacting with residual water left in the CDCl$_3$ and producing oligomers of 3−6 units long. The presence of the small pair of satellite lines near the main resonance of the Si−H peak is a result of the ^{29}Si isotope. The locations of the Si−H peaks between the cyclopentyl and cyclohexyl group differ by approximately δ 0.1 ppm but show that only subtle changes in the substituents can affect the position of the Si−H peak.

Table 1. Calculated and Actual Values of Si−H Transmittance Peaks

structure	calculated (cm^{-1})	actual (cm^{-1})
cyclopentyldichlorosilane	2206	2202
cyclohexyldichlorosilane	2197	2200

Silicon NMR was also used to analyze the reaction product (Figure 10). Figure 13 shows that several side products are formed in addition to the desired product. The formation of the disilane compounds (tetrachlorodisilane and dicyclopentyltertrachlorosilane) is of particular interest in that the catalyst used is not only selective toward hydrosilylation through alkenes but also can undergo addition reactions to form disilane compounds. Preliminary data show that bulky substituents tend to hinder the formation of disilane compounds, while the smaller groups yield more.

After distillation the silicon NMR (Figure 11) reveals the presence of the desired cycloaliphatic substituted silane. The difference between the two peaks is only 0.276 ppm, showing that one less carbon atom has enough "deshielding" character to cause an upfield shift in the peak signal.

The mechanistic fragmentation of R$_4$Si compounds, where R is alkyl, aryl, hydride, and others (symmetrical or unsymmetrical), has been studied.[19] Figure 12 shows

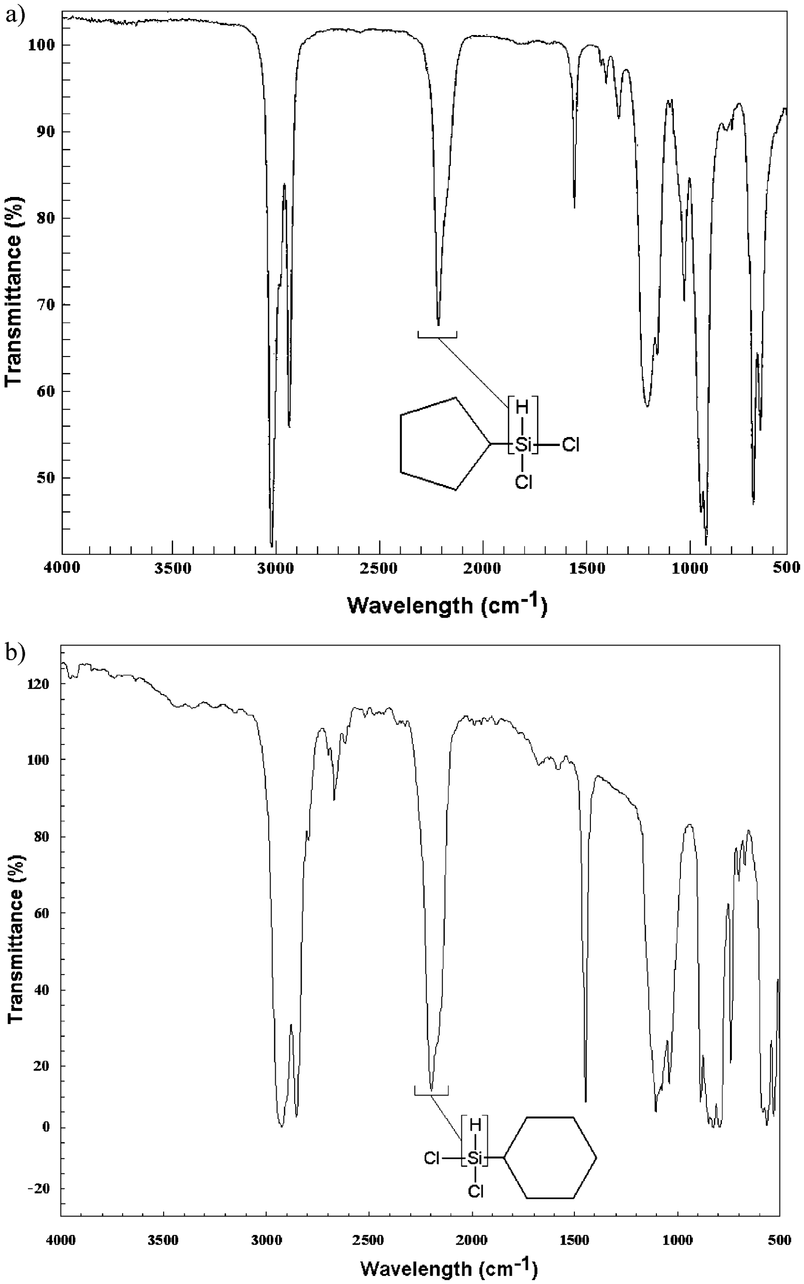

Figure 8. FT-IR spectra of (a) cyclopentyldichlorosilane and (b) cyclohexyldichlorosilane.

the mass spectra for both cyclopentyldichlorosilane and cyclohexyldichlorosilane and shows the radical cleavage of each of the four substitutes. For silanes containing the substituents present on the above samples, the larger alkyl substituents tend to cleave first, which is observed due to the abundance of the cycloaliphatic ring in both of the spectra. In addition, when the breakage of the C−C bond becomes less and less probable, as in the case with cyclohydrocarbons and short alkyl chains, another process competes. The process is the loss of HCl from the molecular ion, leaving another odd electron ion. Figure 12 contains evidence of this loss (*m/z* 133 for cyclopentyldichlorosilane) and (*m/z* 147 for cyclohexyldichlorosilane). The presence of the molecular ion, predictable radical cleavages, and a distribution pattern which allows recognizable isotropic peaks makes the interpretation for this class of compounds straightforward.

The acid liberating polymerization of dichlorosilanes is an equilibrium process; the reverse reaction may seriously affect the molecular weight and overall linearity of the polymerized product unless the acid is neutralized from the system. The substituents are usually resistant toward the HCl that is given off as a byproduct, such as dichlorodimethylsilane. However, if a Si−H group is present, the HCl released will react with it

$$\mathrm{Si{-}H} + \mathrm{HCl} \rightarrow \mathrm{Si{-}Cl} + \mathrm{H_2} \qquad (4)$$

and form an undesired Si−Cl, which can undergo hydrolysis and rather than a linear polysiloxane chain a substituted silsesquioxane is formed. Therefore, a saturated aqueous basic solution is used to neutralize the liberated acid.

The products of the hydrolytic polymerization of the cycloaliphatic dichlorosilanes were analyzed via FT-IR (Figure 13). The strength of the Si−O−Si band indicates that the rings are not of sufficient size (<20) due to the fact that the characteristic antisymmetric stretch of Si−

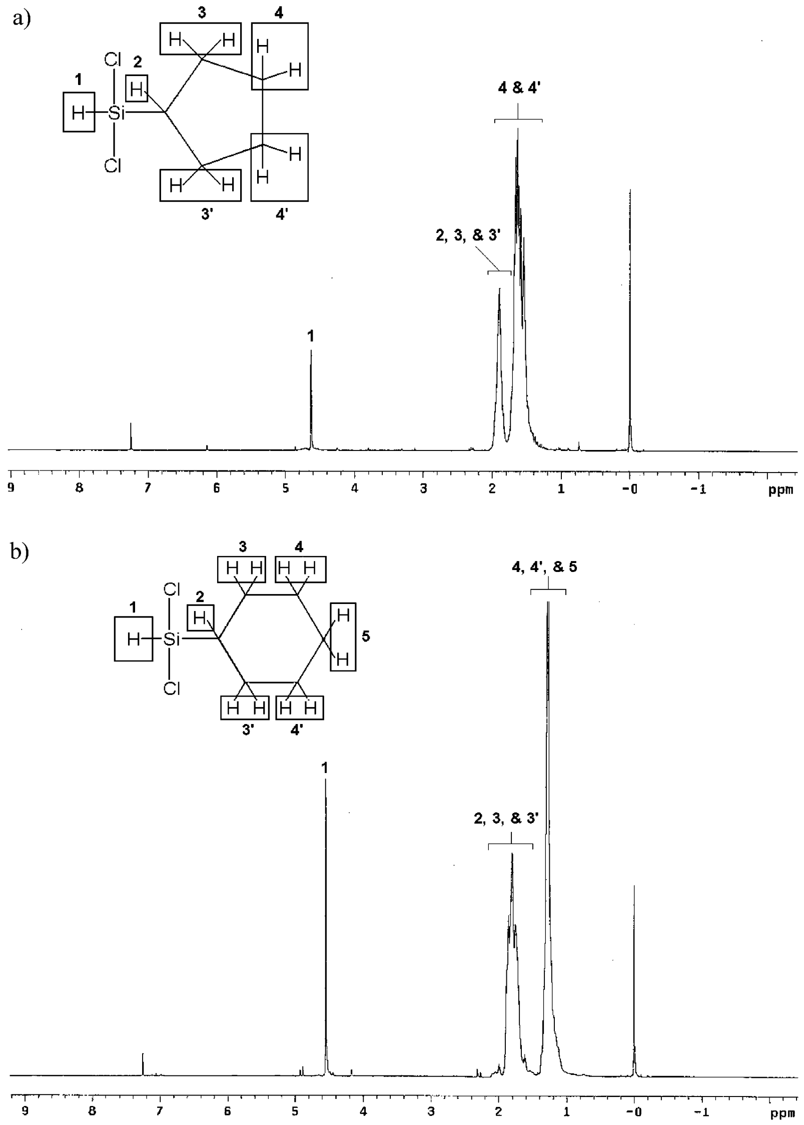

Figure 9. Proton NMR spectra of (a) cyclopentyldichlorosilane and (b) cyclohexyldichlorosilane.

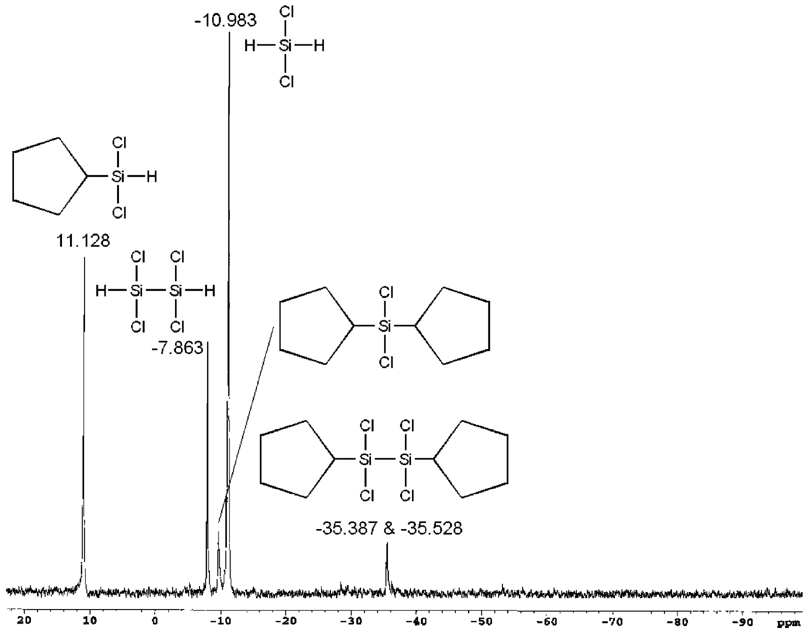

Figure 10. Silicon NMR of dicyclopentyldichlorosilane reaction before distillation.

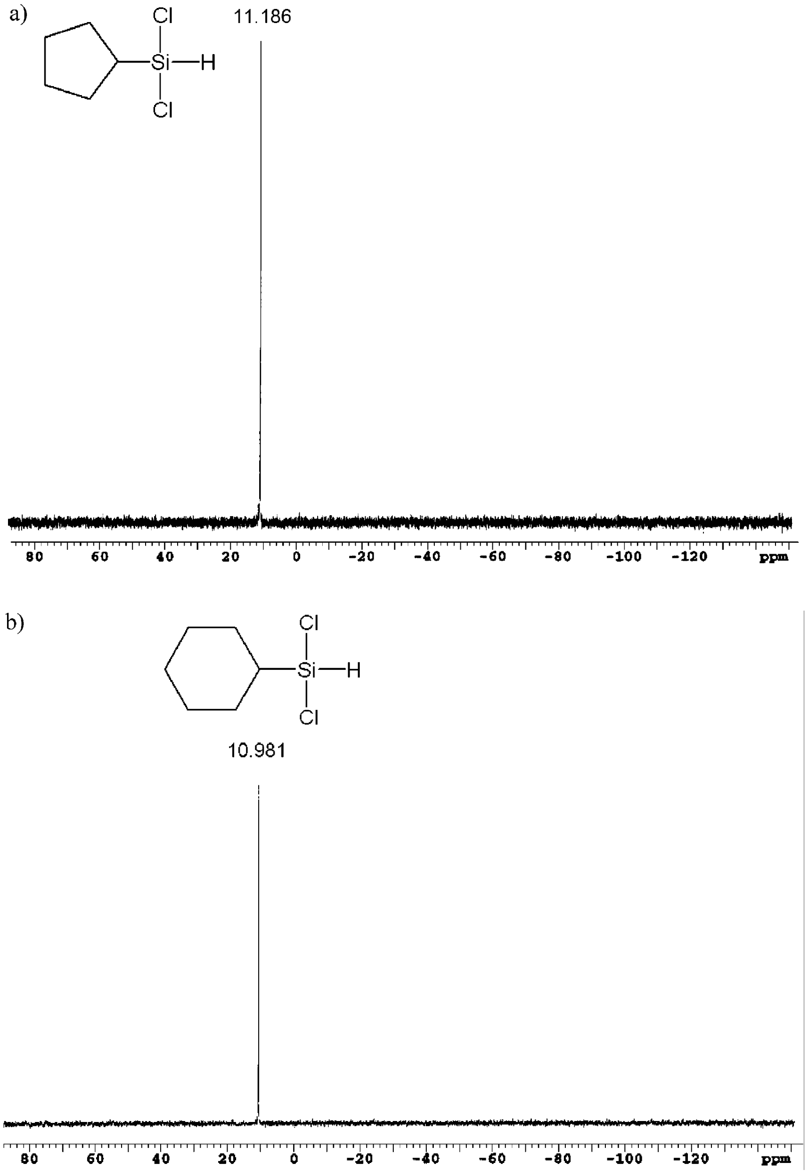

Figure 11. Silicon NMR spectra of (a) cyclopentyldichlorosilane and (b) cyclohexyldichlorosilane.

O–Si at ~1100 cm^{-1} peak is not present, as seen in Figure 8. What is also important to note is the disappearance of the Cl–Si–Cl peaks near the 500 cm^{-1} region, indicating that all of the material had reacted into polysiloxane chains. Another interesting note is the nonexistent Si–OH peak, typically found near the 3700 cm^{-1} region. This lack of this peak is evidence that cyclic species are present and that no linear chains terminated with a terminal Si–OH group were produced. Finally, the Si–H peak was still present, showing that the HCl produced during the reaction was neutralized by the base and did not affect the functionality.

The proton NMR spectra of the cyclic oligomers show the same trend as seen in the NMR spectra of **1** (Figure 4). Since the substituents along the polysiloxane chains are atactic, their environments are different, which causes the protons to possess magnetic nonequivalence. When the spectra in Figure 14 are compared with those in Figure 9, it is apparent that the cis/trans configurations have a dramatic effect on the NMR spectra. When studying the Si–H proton peak at ~δ 4.5 ppm, it is evident that more than one signal is present and the splitting appears to be more predominant in longer chains. This is, again, due to the atactic configurations of the substituents and the hydrogen atom being either surrounded by two hydrogens, one hydrogen and one cycloaliphatic ring, or two cycloaliphatic rings. The same reasoning is behind the multitude of peaks in the region for the cycloaliphatic protons; however, the effect seems to be more prominent with the Si–H protons.

The silicon NMR (J = 200) of the cyclic oligomers (Figure 15) shows evidence of cyclic species. The downfield peaks represent the cyclic D′ units of low molecular weight oligomers, while the upfield peaks are characteristic of larger cyclic D′ units. The peaks present at −30 ppm are indicative of R–Si–H siloxane units, while the peaks near δ −20 ppm represent smaller cyclic siloxane structures.[20,21] The ring strain that the small cyclic siloxanes possess deshields the ^{29}Si nucleus, resulting in shifts to higher frequencies. The multiple peaks, again, come from the number of microenvironments present along the oligomer chain and the various sized cyclic structures. Figure 15 shows that no Si–OH groups exist and also that all the Si–Cl groups have reacted, which would be the possible end groups on linear chains.

Calculations show that the average size of the cyclic structures is 15 units.[13] The small size of the cyclic

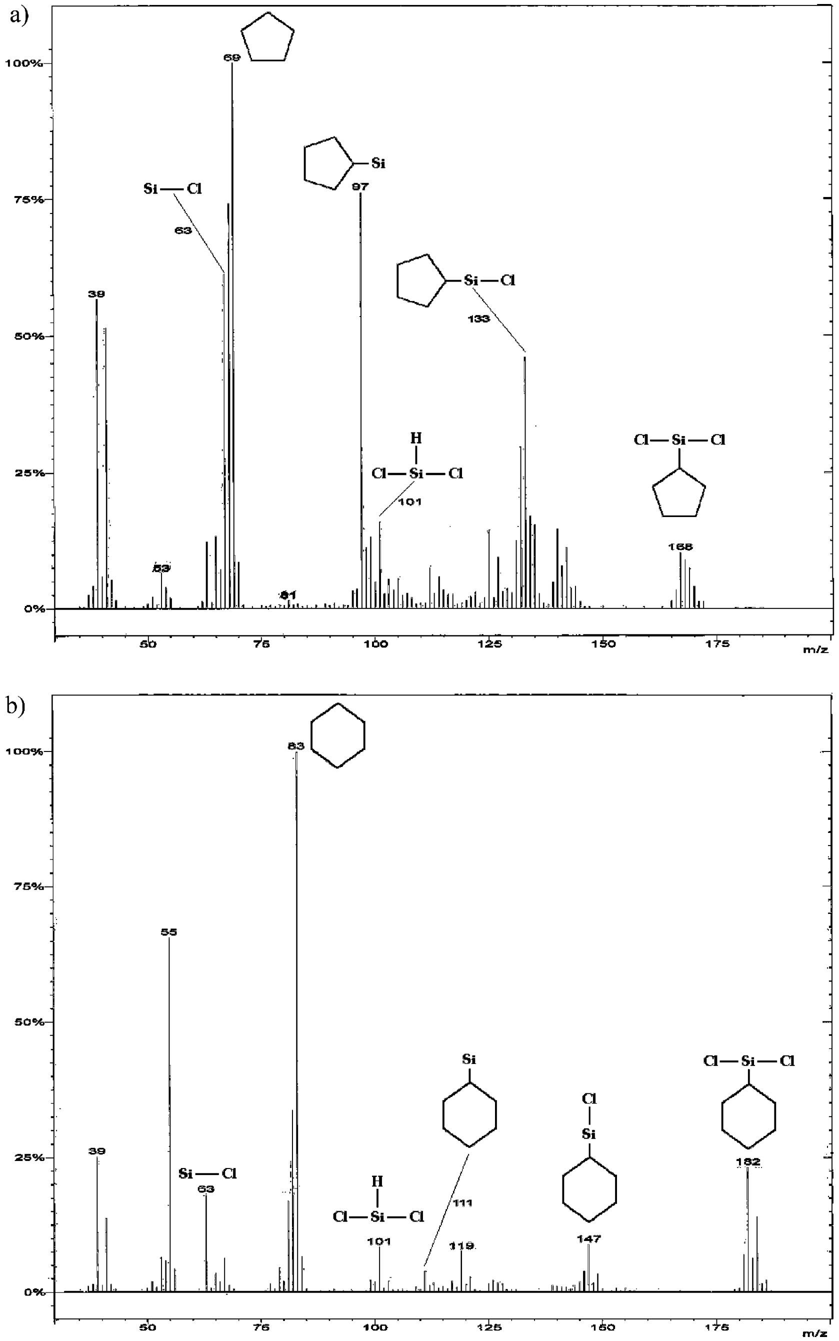

Figure 12. Mass spectroscopy analysis of (a) cyclopentyldichlorosilane and (b) cyclohexyldichlorosilane.

chains could be a result of the dilution of the cycloaliphatic dichlorosilanes along with the dropwise method of adding the dissolved silanes into the organic phase. It is interesting to note that both oligomerization reactions, regardless of the substituent, produced approximately 10% of small cyclic species of about 3−4 siloxane units.

Matrix-assisted laser desorption ionization−time-of-flight mass measurement was attempted to determine the molecular weight and confirm the repeat units. Obtaining this information from the cyclic oligomers proved difficult in that the bulky cyclic groups shield the oxygen atoms from cation attachment. In addition, cyclic species do not readily ionize as a result of cyclic structure hindering coordination of the large sodium ion. A smaller ion (lithium) was used in the likelihood that it was small enough to coordinate with the oxygen atoms, but this attempt also did not yield appreciable results. Quadrupole time-of-flight mass spectroscopy was also attempted but generated the same noisy data. Various ratios of matrix, cation, and sample were tested with no satisfactory results. The highest molecular weight obtained from GPC was ~4000, which would have a ring size of approximately 37 units.

The proton NMR spectra of the results from the hydrosilylation of **2** and **3** with the desired cycloalkene to produce the cyclic oligomers of poly(dicycloaliphatic siloxane) (Figure 16) show the disappearance of the Si−H functionality (~δ 4.5 ppm) and the strong presence of the cycloaliphatic character. The reaction was sluggish due to the bulky substituents and that the alkene functionality undergoing hydrosilylation was an internal alkene as opposed to the faster reacting terminal alkene. The cyclic structure of the polysiloxanes

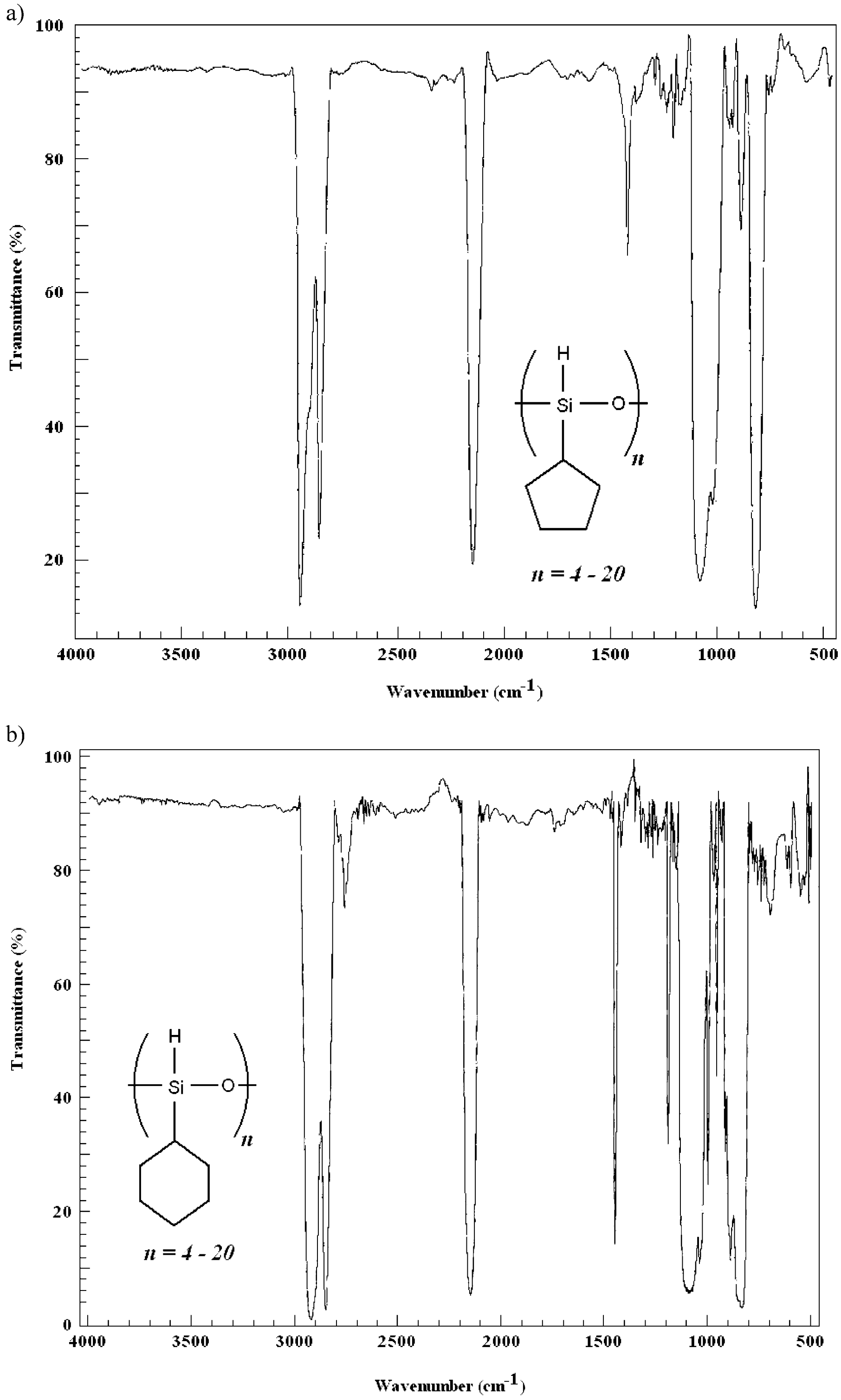

Figure 13. FT-IR spectra of cyclic oligomers: (a) polycyclopentylhydrosiloxane; (b) polycyclohexylhydrosiloxane.

also played a role in the lengthy rate of hydrosilylation. The FT-IR spectra also confirmed the disappearance of the Si−H functionality.

Once the cyclic oligomers of the poly(dicycloaliphatic siloxane)s were prepared, they could be combined with the cyclic oligomers of the poly(cycloaliphatic hydrosiloxane)s to yield poly(dicycloaliphatic siloxane-*co*-cycloaliphatic hydrosiloxane), hydride terminated (**2** and **3**). The procedure to produce **2** and **3** is done in the same matter as it is to produce **1**, which is employing A-15 ion-exchange resin and an end-capper; which is used in order to control the molecular weight. Without the end-capper the chains will terminate by pure chance and will extended the lifetime of the reaction. The % Si−H analyses for **2** and **3** were 11.5 ± 1.1% and 10.8 ± 0.9%. Gel permeation chromatography showed that both **2** and **3** had average molecular weights of ~35 000 g/mol.

Photo and Differential Scanning Calorimetry. Photoinitiated cationic polymerization of functionalized polysiloxanes yields highly cross-linked networks. In addition, it is important to understand the relationship between the polymer structure and reaction conditions with the properties of the networks formed. Photodif-

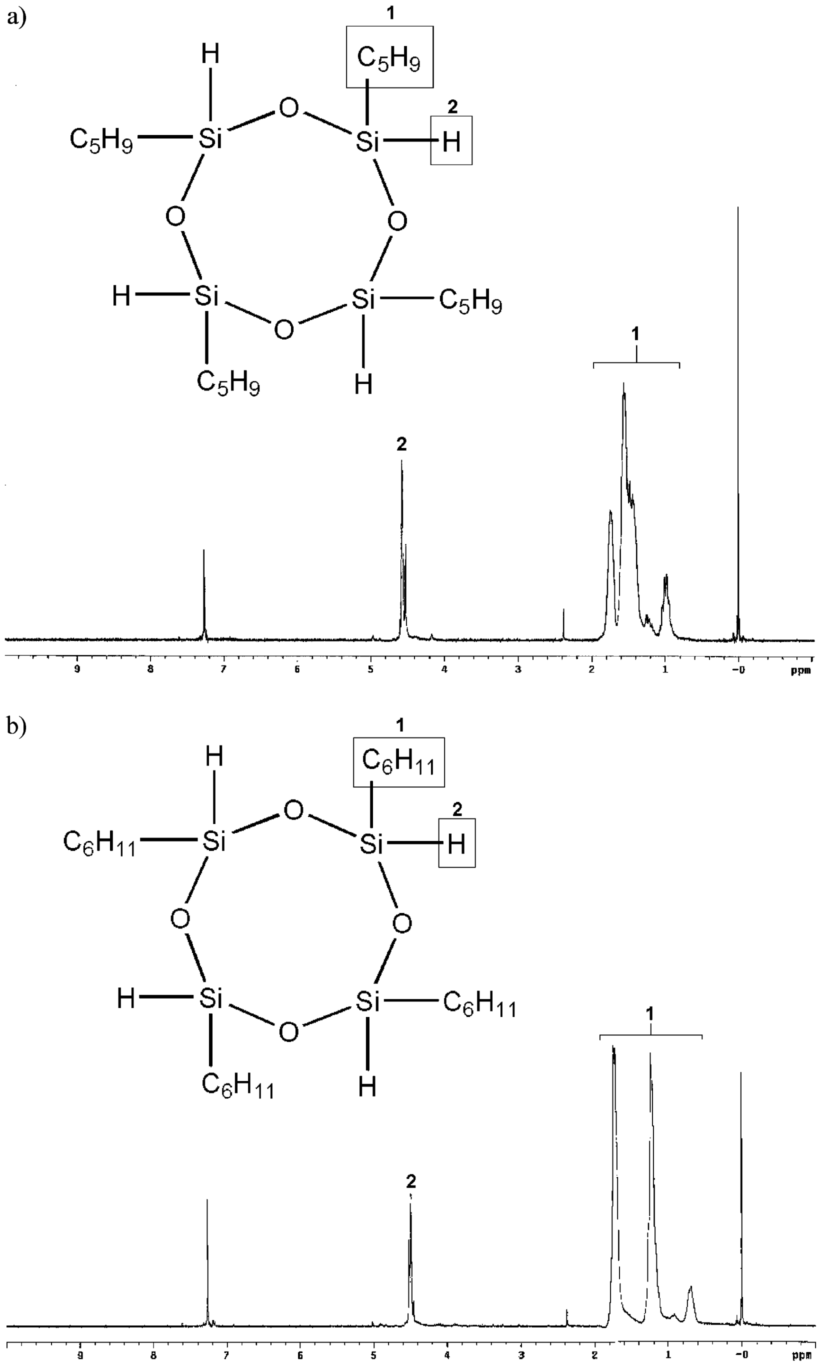

Figure 14. Proton NMR spectra of cyclic oligomers: (a) polycyclopentylhydrosiloxane; (b) polycyclohexylhydrosiloxane.

ferential scanning calorimetry (PDSC) makes it possible to investigate the polymerization behavior, and especially the kinetics of photopolymerization reactions, due to their highly exothermic reaction characteristic upon exposure to UV light. As a result, the reaction rate may be measured by observing the rate at which the heat is released from the sample subject to polymerization. Profiles of reaction heat releases vs time can be utilized to characterize the reaction kinetics.[22−24] The kinetics vary from system to system and are generally complex; therefore, a generalized kinetic expression is not available for cationic polymerizations.[25] This is due to the reactivity of the carbocationic center being heavily dependent on the proximity of the counterion.

In addition, a number of propagating species may be identified during the polymerization such as ion pairs, solvated ions, and/or aggregates.[12] Finally, the pseudo-steady-state approximation is invalid for these types of polymerizations due to the active centers not undergoing combination, as seen in free radical polymerizations. As a result, the rates of initiation and termination are not equal, which require non-steady-state analysis. The understanding of the kinetics of cationic polymerizations is valuable due to the increasing demand for fast curing, low VOC films. The PDSC profiles obtained present significant information about the curing kinetics of cationic photopolymerizations.

Reactions were carried out at various temperatures (−10, 25, and 60 °C) in order to establish an overall activation energy for the polymerization. Reactions were also studied with various exposure times (1, 5, and 15 s) in order to observe any changes in the rate of polymerization. Figure 17 is a typical exotherm obtained from the photoinduced polymerizations.

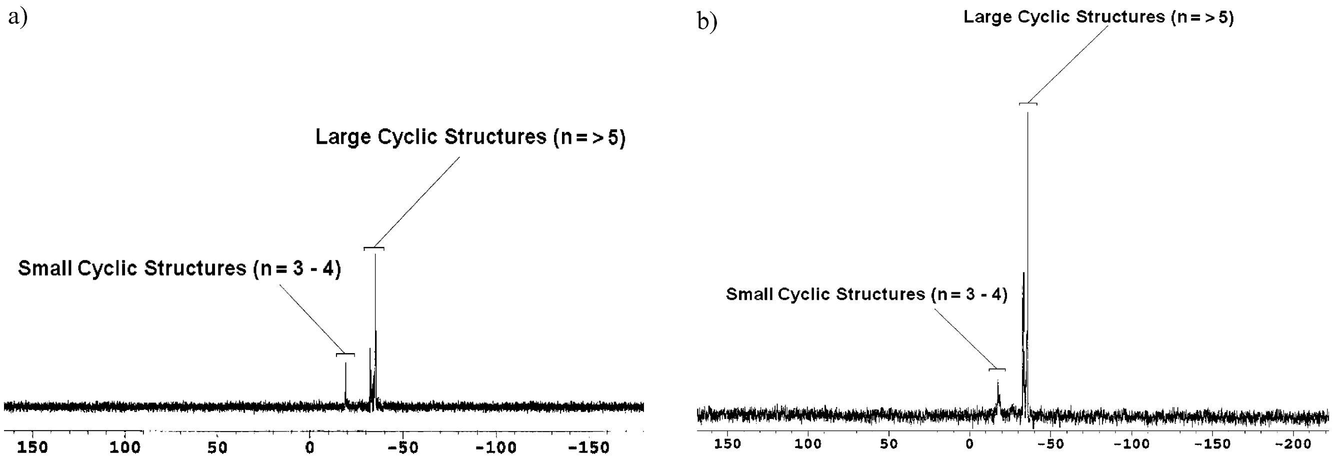

Figure 15. Silicon NMR spectra of cyclic oligomers: (a) polycyclopentylhydrosiloxane; (b) polycyclohexylhydrosiloxane.

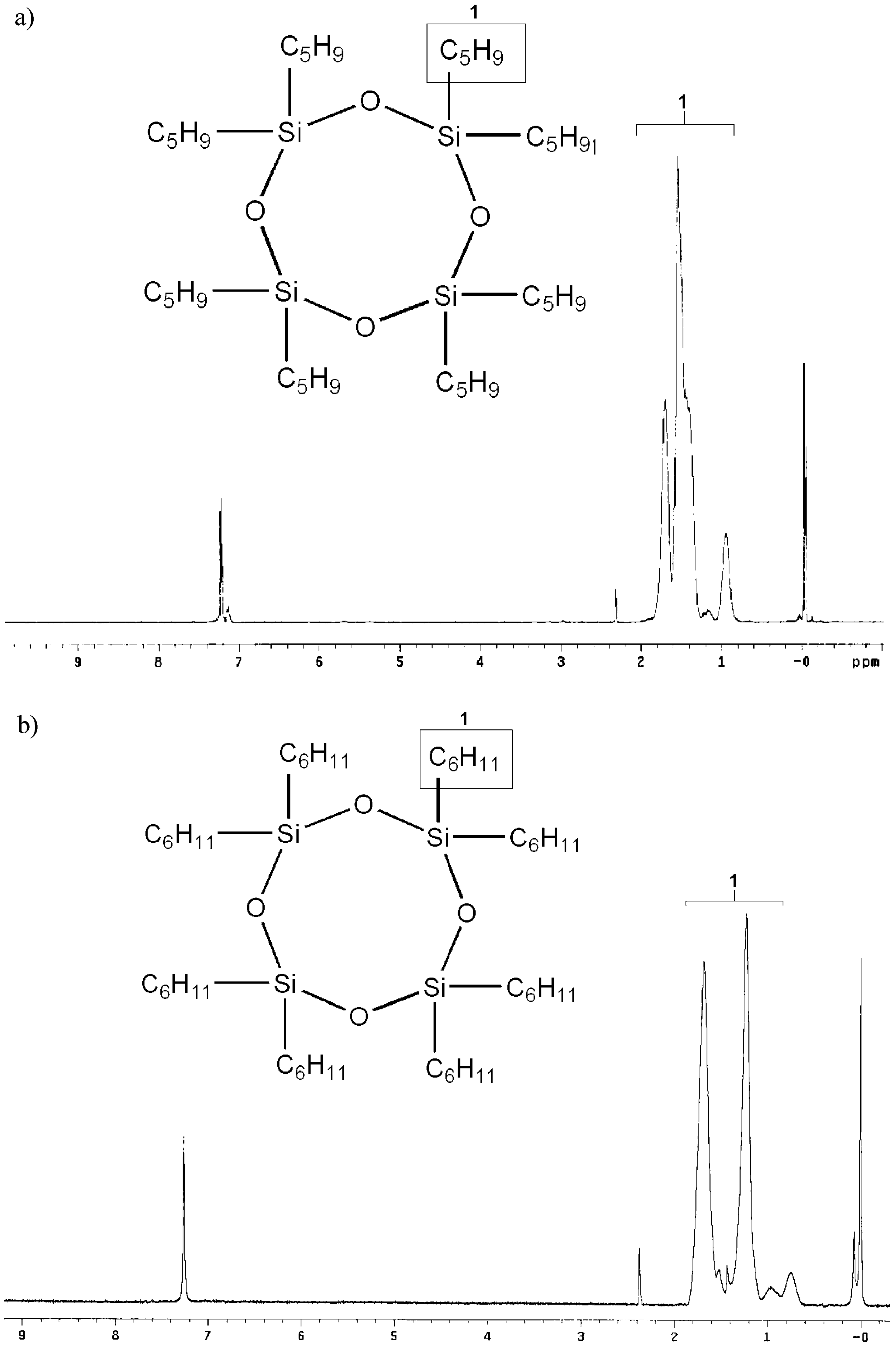

Figure 16. Proton NMR spectra of cyclic oligomers: (a) polydicyclopentylsiloxane; (b) polydicyclohexylsiloxane.

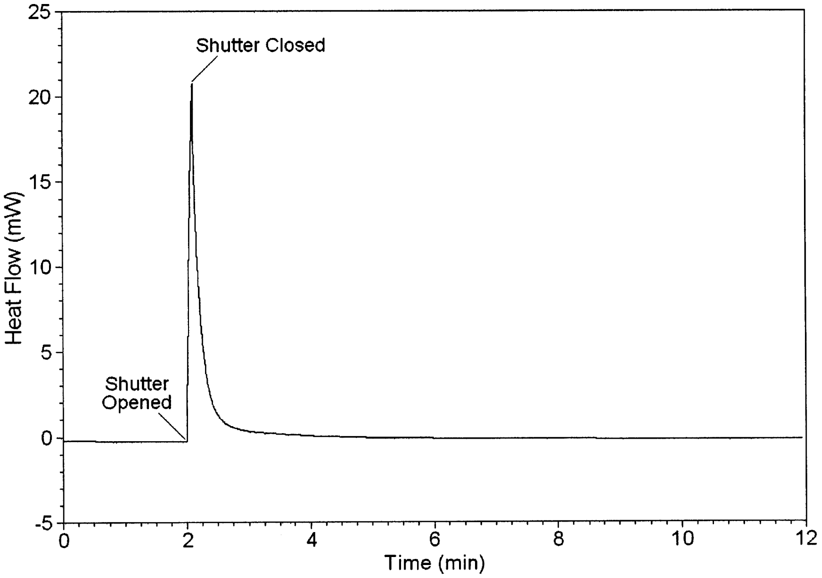

Figure 17. Exotherm of the cationic polymerization of **1** at 25 °C for 15 s.

Table 2. Effect of Substituent and Temperature on the Rate of Polymerization

substituent	av mol wt (M_n) (g/mol)	temp (°C)	exposure time (s)	heat flow per second (J/s)	R_p (s^{-1})	conv (%)	activation energy (kJ/mol)
methyl	45 500	−10	5	9.456	0.0093	99.6	144.8 ± 8.1
		25	5	14.900	0.0110	99.5	
		60	5	19.646	0.0125	99.7	
cyclopentyl	34 530	−10	5	8.223	0.0025	90.4	111.0 ± 9.2
		25	5	5.892	0.0055	97.2	
		60	5	11.723	0.0057	97.4	
cyclohexyl	38 290	−10	5	8.113	0.0054	91.2	125.7 ± 8.5
		25	5	5.932	0.0047	96.7	
		60	5	16.890	0.0068	98.2	

The degree of cure, or conversion, can be estimated from the ratio of the amount of heat evolved from the partial conversion after time t at a specific temperature (H_t) to the total heat evolved from the reaction, ΔH_p:

$$\alpha = H_t/\Delta H_p \tag{5}$$

If eq 5 is a function of conversion, but not temperature, as in photoinduced experiments, the activation energy, E, can be obtained by plotting $\ln[(1/\Delta H_p)(dH_0/dt)]$ vs $(1/T)$, where (dH_0/dt) is the heat of polymerization at the maximum peak of the exotherm. Calculating the slope of this plot will yield the activation energy for the polymerization (Table 2). Photo-DSC experiments record the total heat of polymerization; therefore, the activation energy is representative of an overall activation energy which includes initiation, activation, and termination:

$$E_R = E_P + E_I - E_T \tag{6}$$

In order for the above equation to be valid, the production of active centers must remain throughout the reaction. Previous measurements[26] analyzed the kinetic activity of photosensitizers and showed that the photosensitizers were not completely consumed until after the reaction had progressed. Indicating that the active center concentration had continued to increase after the peak maximum, which was were the reaction rate was measured. As a result, eq 6 can be used to signify the overall activation energy for the photoinduced polymerization reaction. As anticipated, the reaction rate and total conversion increased with an increasing temperature. This is demonstrated from the exotherms exhibiting a larger integrated heat as the temperature was increased.

Increasing the size of the substituent has a dramatic effect on the rate of polymerization and total conversion (Table 2). Figure 18 also shows that as the size of the pendant group is increased, the glass transition temperature increases. The rates of polymerization were decreased by an overall average of 50% when comparing a methyl substituted to a cycloaliphatic substituted polysiloxane. This could be attributed to the large bulky substituents hindering molecular motion during the reaction and preventing the active species from further polymerization. As expected, the longer exposure to UV light yields a higher conversion due to the production of more active species. The percent conversion calculation is taken from the moment the exotherm begins to the when the slope of the thermogram is equal to zero. The effects of "postcure" are not taken into account in the final calculation. The consequence of postcure would undoubtedly increase the final percent conversion value.

The activation energies for the cycloaliphatic substituted polysiloxanes are lower than the methyl substituted polysiloxane value. The higher average molecular weight (M_n) of the methyl substituted polysiloxane reduces the mobility of the epoxy groups, which leads to a higher activation energy.[27,28] The dependence on activation energy with viscosity could also account for the slight difference in activation energy in the cycloaliphatic substituted polysiloxanes.

Figure 18 illustrates that the glass transition temperature can be tailored by being able to add on the

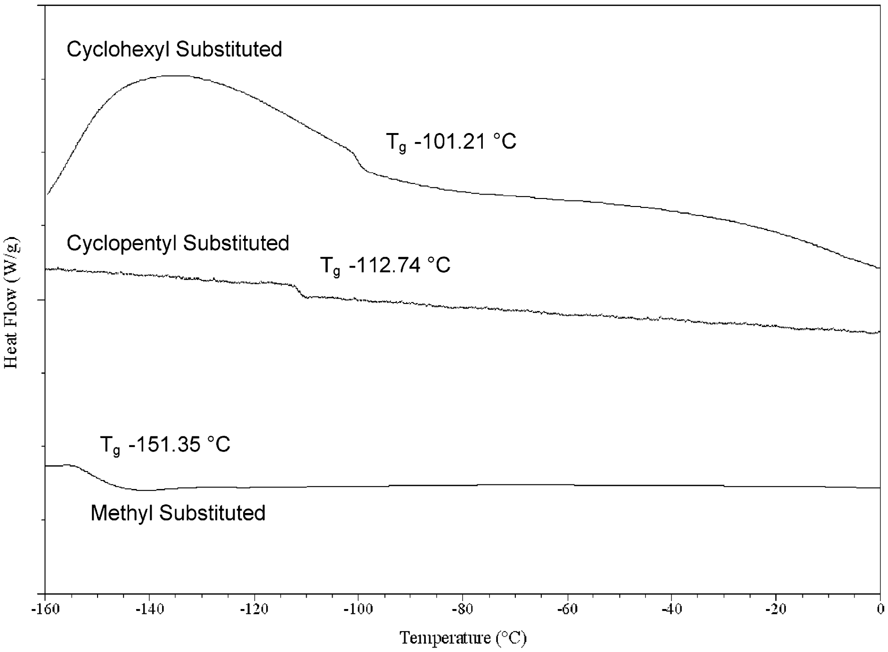

Figure 18. Overlay of T_g analysis of cured coating with 3% photoinitiator.

desired pendant group through hydrosilylation. The pendant group could be chosen from a number of alkene functionalized systems.

The ability to synthesize polysiloxanes with cycloaliphatic pendant groups will be beneficial in that it provides more monomers to be considered for new materials, membranes, films, or other potential applications. The capability to modify and/or tailor the pendant groups could also solve miscibility and grafting issues by making the groups similar in structure and/or polarity to a specific type of solvent. Furthermore, tailoring the polysiloxanes with cycloaliphatic epoxides and alkoxysilane groups to UV curable hybrid films could be used in the application toward membranes or low coefficient of friction coatings.[29−31] The ability to adjust the glass transition temperature through the variation of the pendant groups will also be beneficial for other specialized applications such as lubricants for fibers, wetting agents for polyurethane foams, and temperature-sensitive coagulating agents for latexes.[32]

The need to understand and optimize curing conditions for inorganic/organic materials is critical for the in situ formation of nanocomposite materials.[33] The rise in cationic curing chemistry is increasing due to the unique properties of ring-opening polymerization, which include inhibition of oxygen and the improved adhesion over free-radical UV-cured films. The PDSC experiments were used to determine the rate of polymerization and activation energies for the synthesized polysiloxanes in order to determine what effect the larger substituents have on the kinetics of polymerization in addition to temperature and UV exposure time. The knowledge of cure kinetics and the ability to customize polysiloxanes unlocks new potential in the development of innovative polymers. In a later study, siloxane membranes are studied, and the effect on cycloaliphatic groups on permeability will be reported.

Conclusions

A synthetic route was employed to prepare cationically polymerizable methyl, cyclopentyl, and cyclohexyl substituted polysiloxanes. The hydrosilylation of internal alkenes was possible at high pressure and temperatures but became sluggish when the silane functionality became sterically hindered as seen in the hydrosilylation between the cyclic oligomers and the cycloalkene. In addition, the ability to maintain the silane functionality throughout the hydrolytic polymerization makes it possible for additional hydrosilylation between the polysiloxane chain and desired alkene. Analysis of the hydrolytic polymerization reaction showed the production of a wide range of cyclic oligomers, while the use of the sulfonated ion-exchange resin made the production of high molecular weight polysiloxanes particularly straightforward. Photo-DSC exotherms showed that the bulky pendant groups affect the kinetics by lowering both the rate of polymerization and overall conversion, when compared to the methyl substituted polysiloxane. This is due to the bulky pendant groups interfering with molecular motion. As expected, the increase in UV exposure time and reaction temperature resulted in an increase in the reaction rate for all of the substituted polysiloxanes. This increase yielded higher final conversions as revealed from the total heat of the reaction.

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