# An Examination of a Styrenic Thermoset Formed by an α,ω 4-Vinylphenyl Functional Diphenylsiloxane Oligomer

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To overcome the difficulties associated with processing polydiphenylsiloxane, a method for generating a regular three-dimensional network from easily processable and curable diphenylsiloxane oligomers has been examined. This has involved the successful tethering of various groups at the terminal positions of the three unit oligomer, hexaphenyltrisiloxanediol. A curable composition was obtained by end functionalization with 4-vinylphenyldimethylsilyl units. The derived material can be cured thermally at temperatures above 200 °C or at lower temperatures by adding a radical initiator. The composition, cured under nitrogen as films or monoliths, was transparent, hard, and amorphous. The thermal stability of the cured composition was good but failed to reach the stability observed for pure polydiphenylsiloxane. Mechanical analysis has revealed a slight reduction in the modulus of the cured material below 100 °C that might be attributable to the onset of diphenylsiloxane segmental motion; otherwise, the material is rigid to a temperature above 300 °C. The thermal expansion coefficient of 168 ppm/°C was rather high compared to other highly cross-linked thermosetting resins. The electrical properties of the cured material were good and similar to those of polydiphenylsiloxane, with a low dielectric constant, good resistivity, and moisture resistance.

## Introduction

Polydiphenylsiloxane is a highly crystalline polymer that displays high thermal stability but poor processability, requiring the use high-boiling solvents at temperatures above 150 °C for dissolution.[1−8] Processing from the bulk is also difficult due to a high melting temperature of 260 °C and a higher temperature mesomorphic phase throughout which the polymer continues to exhibit many of the properties of a crystalline solid.[9] A number of methods for improving the processability of polydiphenylsiloxane have been examined and these include modifications of the side group phenyl substituents,[1,8,10] the incorporation of dimethylsiloxane substituents into the polymer chain,[2,4] or a reduction in the polymer molecular weight.[11,12] All of these methods contribute to a reduction in the degree of crystallinity of the material. It has recently been demonstrated that a reduction of the molecular weight of polydiphenylsiloxane, particularly to a degree of polymerization of 20 or less, functions to greatly reduce the isotropic melting point and improves the solubility of the material.[12] The biggest disadvantages of this strategy are that the mechanical properties and chemical resistance of the material are compromised. To recover the mechanical properties and chemical resistance, cross-linkable groups can be attached to the terminal positions of the diphenylsiloxane oligomer such that after processing the material can be cured to its final form. This approach has already been utilized to aid the processing of polyimide films,[13] but this is the first time it has been examined for diphenylsiloxane segments.

There are many potential candidates for the cross-linking unit; however, to preserve the thermal stability of the cured product, it is necessary to choose a functional unit that also shows good thermally stability. Recently it has been reported that vinyl functional dimethylsiloxanes, with terminal benzocyclobutene functionalities, form thermally stable resins when heated.[14,15] The mechanism of cure is the thermal transformation of the benzocyclobutene to the reactive *o*-quinodimeth-

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ylene species that then proceeds to rearrange with the vinyl group. To utilize this cure mechanism it is essential to incorporate both vinyl and benzocyclobutene functionalities into the oligomer. A simpler approach is to end functionalize the oligomer with 4-vinylphenyl units. It is known that the 4-vinylphenyl group undergoes spontaneous radical polymerization at temperatures above 150 °C, thus allowing for cure in the absence of catalysts.[16] Alternatively, cure can be promoted by radical initiators if a lower cure temperature is desired. The 4-vinylphenyl functional group has previously been utilized to prepare thermosetting resins on the basis of a 2,2-bis(4-vinylphenyloxyphenyl)hexafluoropropane[17] repeat unit or from 4-vinylphenyl substituted multifunctional polyphenols.[18] These approaches have been reported to yield high-temperature stable resins with low thermal expansion coefficients[18] and low dielectric constants after cure.

In this report the preparation of 1,9-bis(4-vinylphenyl)-1,1,9,9-tetramethyl-3,3,5,5,7,7-hexaphenylpentasiloxane from 1,1,3,3,5,5-hexaphenyltrisiloxane-1,5-diol and 4-vinylphenyldimethylchlorosilane is described. The processes for curing of the oligomer to a hard resin and the properties of the resin as compared to those of pure polydiphenylsiloxane are discussed.

## Experimental Section

**1,1,3,3,5,5-Hexaphenyltrisiloxane-1,5-diol**. In a 500 mL Erlenmeyer flask, 55 g of hexaphenylcyclotrisiloxane was dissolved in approximately 400 mL of tetrahydrofuran. To this solution were then added 40 g of water and 3 mL of *n*-hexylamine. The reaction was stirred at room temperature for 30 min (with the degree of conversion to diol being monitored by TLC with toluene as the solvent). The mixture was then poured into 500 mL of water. Dilute hydrochloric acid was added to the solution until the pH became neutral, and the diol product was then extracted with 600 mL of toluene. The toluene layer was washed several times with water, dried over sodium sulfate, and filtered. The volume of toluene was reduced to 150 mL by rotary evaporation, following which hexane was slowly added to induce crystallization of the diol. After cooling of the solution to 0 °C, the crystals were isolated by filtration and dried to yield 51 g (92% yield) of the diol; mp110−111 °C. The $^{29}$Si NMR spectrum of the product dissolved in chloroform-*d* displayed peaks at −36 and −44 ppm with an integral ratio of 2:1, respectively.

**1,1,9,9-Tetramethyl-3,3,5,5,7,7-hexaphenylpentasiloxane.** Hexaphenyltrisiloxanediol (5 g) was dissolved in approximately 20 mL of toluene in a 100 mL round-bottom flask. To this was added a mixture of 0.8 g of dimethylchlorosilane and 1.1 g of tetramethyldisilazane. The addition was rapidly followed by a rise in the solution temperature and the appearance of a white precipitate. The reaction was stirred for 1 h at 40 °C and then poured into 150 mL of water. An additional 100 mL of toluene was added and the organic layer isolated. The organic layer was washed several times with deionized water and dried over anhydrous sodium sulfate. The solution was filtered and the solvent removed by rotary evaporation and vacuum to yield 6 g of a colorless oil. GPC indicated a product purity of 94%. IR analysis of the oligomer revealed a medium-intensity Si−H stretching band at 2131 cm$^{-1}$ but no silanol bands. The $^1$H NMR solution spectrum for the product in chloroform-*d* was consistent with the oligomer structure, with methyl protons as a singlet at 0 ppm, the Si−H protons as a singlet at 4.7 ppm, and the aromatic protons as a group of signals from 7.1 to 7.5 ppm.

**1,9-Divinyl-1,1,9,9-tetramethyl-3,3,5,5,7,7-hexaphenylpentasiloxane**. Hexaphenyltrisiloxanediol (20 g) was dissolved in approximately 100 mL of toluene in a 250 mL round-bottom flask. To the stirring solution was then added a mixture of 10 g of vinyldimethylchlorosilane and 10 g of triethylamine. Immediately upon addition the solution temperature increased and a white precipitate slowly appeared. The reaction was stirred for 1 h at 40 °C and then poured into 150 mL of water. An additional 100 mL of water was added and the organic layer isolated. The organic phase was washed several times with deionized water and dried over anhydrous sodium sulfate. The solution was filtered and the organic solvent removed by rotary evaporation to yield 24.4 g of a colorless oil. GPC analysis indicated a purity of approximately 94%. IR analysis confirmed the loss of the silanol band. The $^1$H NMR solution spectrum for the product dissolved in chloroform was consistent with the proposed structure, with the methyl protons appearing as a singlet at 0 ppm, the vinyl groups as multiplets between 5.5 and 6 ppm, and the aromatic protons as multiplets between 7.1 and 7.5 ppm.

**1,1,1,9,9,9-Hexaethyl-3,3,5,5,7,7-hexaphenylpentasiloxane**. An attempt to prepare this oligomer according to the above route but using a mixture of triethylchlorosilane and triethylamine was unsuccessful. A successful preparation was achieved using the method described below for the 4-vinylphenyl functional oligomer.

**Preparation of 4-Vinylphenyldimethylchlorosilane**. In a 500 mL four-necked round-bottom flask equipped with a mechanical stirrer, 12.16 g of magnesium turnings was vigorously stirred under a nitrogen atmosphere. Anhydrous ether (25 mL) was initially added to the flask followed by a few drops of dibromoethane. A few minutes later, 5 mL of a 50 vol % tetrahydrofuran solution of *p*-chlorostyrene was added to the flask. The solution was brought to reflux by heating and to the refluxing solution was added 55.6 g of *p*-chlorostyrene in 50 mL tetrahydrofuran dropwise. The solution then assumed a dark brown color. This solution was then added to a mixture consisting of 40 mL of ether and 83.1 g of dimethyldichlorosilane over a period of 1 h. After an additional 30 min of stirring, a vacuum was applied (without heating) to remove low boiling materials. To the resultant slurry was then added 300 mL of dry pentane and this stirred for 30 min. The slurry was then filtered and the solid washed with an additional 100 mL of dry pentane. The combined filtrate was fractionally distilled under reduced pressure to give 50 g of product containing 97% (4-vinylphenyl)dimethylchlorosilane and 3% *p*-chlorostyrene according to GLC analysis. The $^1$H NMR spectrum of the product in chloroform-*d* was consistent with the proposed structure: 0.72 (s, 6H), 5.35 (dd, 1H), 5.86 (dd, 1H), 6.76 (dd, 1H), 7.48 (m, 2H), 7.63 (m, 2H).

**1,9-Bis(4-vinylphenyl)-1,1,9,9-tetramethyl-3,3,5,5,7,7-hexaphenylpentasiloxane**. Into a three-necked 200 mL round-bottom flask equipped with a stirrer and condenser were added 20 g of hexaphenyltrisiloxanediol and 45 mL of dry tetrahydrofuran. Under an argon atmosphere, 38.5 mL of *n*-butyllithium in hexanes (1.87 M) was slowly added to the stirring solution (the solution became quite hot upon addition; hence, the flask was placed into an ice−water bath). Approximately 30 s after the addition, 4-vinylphenyldimethylchlorosilane (15 mL) was added to the solution. The mixture was heated to 65 °C and stirred for 1.5 h. To the flask was then added 1 mL of trimethylchlorosilane and 1 mL of triethylamine to ensure complete end blocking of the oligomer. After 10 min, the solution was poured into 200 mL of water and the product extracted with 300 mL of toluene. The organic phase was washed several times with deionized water and the toluene removed by rotary evaporation. The oily product was again dissolved in a small amount of toluene, filtered through silica gel to remove residual silanol containing impurities, and dried to yield 26 g of the 4-vinylphenyldimethylsilyl end-blocked oligomer. The low-melting solid was examined by GPC and found to have a purity of 95%. The absence of a hydroxyl stretching band in the IR spectrum indicated that all of the

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silanol functionalities were completely blocked. The $^1$H NMR spectrum of the product was consistent with the proposed structure with the methyl protons appearing as a singlet at −0.1 ppm and the vinyl protons at 5.2 (doublet), 5.7 (doublet), and 6.7 ppm (quartet). The aromatic protons appear as a group of signals between 7.1 and 7.5 ppm.

**Thin Film and Monolith Preparation**. Films were prepared by dissolving the oligomer in toluene at concentrations of between 15 and 30 wt % and casting the solutions onto clean glass slides, silicon wafers, or aluminum panels. The samples were thoroughly dried prior to being cured. Films prepared with a radical initiator used the same route, with the exception that the initiator was dissolved into the solution prior to casting. Thermal curing of the films was performed with a Mettler Hotstage FP98 attached to a Mettler FP90 central processor. To cure samples under an inert atmosphere, the Mettler hot stage was placed into a large plastic bag with a nitrogen purge. Monoliths were prepared by placing the oligomer into a suitable mold and heating to 300 °C under air or nitrogen in a glass tube furnace.

**General Procedures**. The purity of the oligomers was measured with a TOSOH HLC-8020 gel permeation chromatograph with toluene as the eluting solvent. Infrared spectra were recorded with a Jasco FT/IR-5300 spectrometer in the transmission mode. The IR transmission spectra were recorded for samples coated on silicon wafers or as KBr pellets. $^1$H and $^{29}$Si NMR were recorded with a Brüker APC300 NMR spectrometer at frequencies of 300 and 59.6 MHz, respectively, for samples dissolved in chloroform-*d*. DSC, TG, and linear expansion measurements were performed with Rigaku TAS 200-DSC830D, TG81201D, and TMS 8140C thermal analysis systems. The DSC scans were conducted under nitrogen with a heating/cooling rate of 10 °C/min. TG−DTA determinations were conducted in air or nitrogen with a heating rate of 10 °C/min. The linear expansion coefficient was measured in air with a heating rate of 5 °C/min. UV−visible spectra of the films were recorded with a Hitachi U-3210 spectrometer. The X-ray diffraction pattern was recorded with a JEOL JDX-3530 X-ray diffractometer system. Dynamic mechanical analysis was performed with an Orientec Rheovibron DDV-II-EP attached to an Orientec Rheovibron Dynamic Viscoelastometer Model 2000 and a process controller Model 4301. The flexural properties were measured with an Instron Model 4301. Water absorbency was determined by drying a cured sample under vacuum at 120 °C for 3 days, weighing the sample, and then placing it above a boiling water bath for 3 days. The moisture absorbed was determined from the weight gain on exposure.

## Results and Discussion

**Oligomer Preparation**. Reported methods for the preparation of diphenylsiloxane oligomers include the condensation polymerization of diphenylsilanediol,[19] careful hydrolysis of diphenyldichlorosilane,[20] and ring-opening polymerization of hexaphenylcyclotrisiloxane.[12] Problems associated with these methods include high polydispersity and difficulties in recovering the oligomeric product from the residual cyclic siloxanes. To generate a monodisperse diphenylsiloxane core it was decided to start with pure $\alpha,\omega$-hexaphenyltrisiloxanediol and end block the silanol functionalities with the 4-vinylphenyldimethylsilyl group. Hexaphenyltrisiloxanediol was prepared by hydrolysis of hexaphenylcyclotrisiloxane in a mixture of water and tetrahydrofuran, with a small amount of *n*-hexylamine as catalyst. Under these conditions the cyclic trimer is smoothly converted into the diol in only a few minutes. A problem encountered in recovery of the oligomer was that

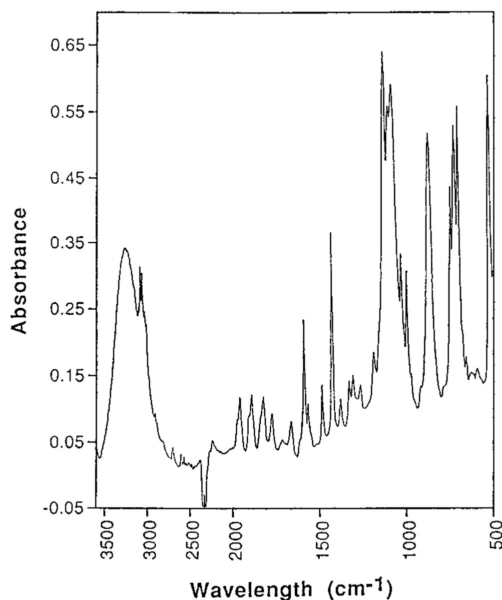


**Figure 1.** IR spectrum for hexaphenyltrisiloxanediol.

removal of water during the purification steps shifted the equilibrium of the mixture toward the formation of the cyclic trimer. This reverse process is also base-catalyzed and proceeds by condensation of the terminal silanol groups when water becomes scarce. Neutralization of the amine catalyst with a dilute acid prior to oligomer purification and isolation prevented the reverse process and allowed the isolation of high-purity hexaphenyltrisiloxanediol, with a melting point of 110−111 °C, in yields greater than 85%. The IR spectrum of the purified oligomer is shown in Figure 1 and clearly shows the strong silanol stretching band centered about 3240 cm$^{-1}$. The $^{29}$Si NMR spectrum was also consistent with the product, having two peaks at −36 and −44 ppm and an integral ratio of 2:1, respectively.

The next step in the synthetic sequence was to end block the free silanol terminal groups to generate a cross-linkable oligomer. Prior to reaction with 4-vinylphenyldimethylchlorosilane, it was decided to examine the viability of the end-blocking process with readily available reactive silanes. With toluene as solvent, hexaphenyltrisiloxanediol was reacted with an excess of a mixture of tetramethyldisilazane and dimethylchlorosilane. Under the same conditions, hexaphenyltrisiloxanediol was also reacted with vinyldimethylchlorosilane and triethylamine as acid acceptor. In both of the above reactions, silylation occurred quite rapidly, as evidenced by the rapid appearance of the salt byproduct. IR and NMR spectra of the products were consistent with dimethylsilyl and vinyldimethylsilyl end-terminated hexaphenyltrisiloxane oligomers, respectively. The reaction of hexaphenyltrisiloxanediol with a mixture of triethylchlorosilane and triethylamine failed to generate the clean disubstituted product but instead yielded the cyclic trimer, hexaphenylcyclotrisiloxane, as the major product and the monosubstituted and disubstituted oligomers as minor products. The final product ratios indicated that cyclization of the diol, catalyzed by triethylamine, was more rapid than reaction of the silanol with the chlorosilane. It was assumed that this results from steric repulsion between the two bulky reactants. To generate the disubstituted trieth-

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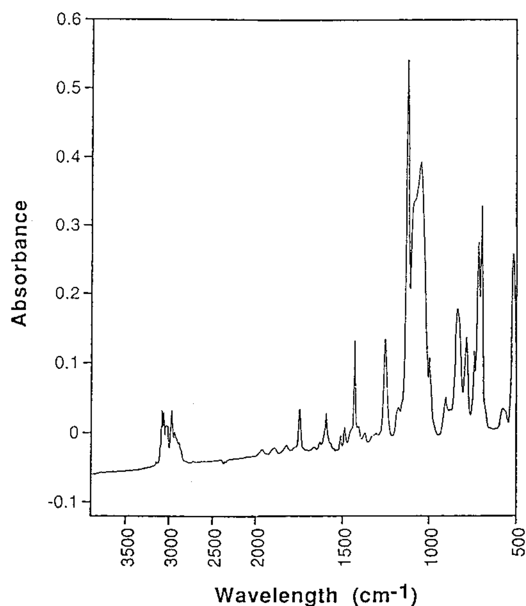
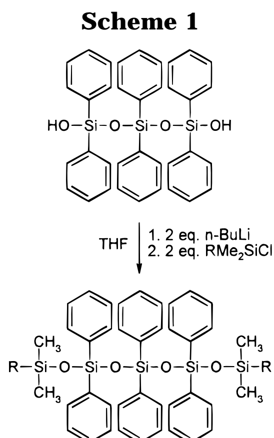



**Figure 2.** IR spectrum for the 4-vinylphenyl end-blocked oligomer.

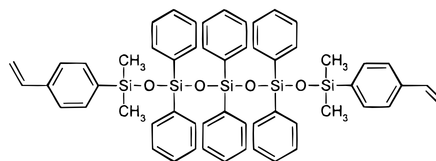
**Scheme 1**




ylsilyl-terminated oligomer, it was first necessary to convert the hexaphenyltrisiloxanediol to the dilithium silanolate by reaction with *n*-butyllithium in tetrahydrofuran and then add triethylchlorosilane to the reactor (Scheme 1). Under these conditions, the disubstituted oligomer became the major product, constituting 88% of the mixture as measured by GPC. The remaining components were the monosubstituted oligomer and a small amount of hexaphenylcyclotrisiloxane.

To prepare the target 4-vinylphenyl-terminated oligomer (structure I), hexaphenyltrisiloxanediol dissolved in tetrahydrofuran was converted to the dilithium silanolate and then reacted with slightly more than 2 equiv of 4-vinylphenyldimethylchlorosilane. The reaction products were isolated and the oligomer purified by column chromatography to remove the excess end blocker and other impurities, yielding a low-melting solid as the product. The IR spectrum for the 4-vinylphenyldimethylsilyl end-terminated oligomer is shown in Figure 2. The almost complete absence of a silanol stretching band confirms the high degree of substitution. The $^1$H NMR spectrum was also consistent with the oligomer structure.

**Cure of the 4-Vinylphenyl Substituted Oligomer.** As discussed earlier, the 4-vinylphenyl functional group




is capable of undergoing thermal polymerization at elevated temperature or can be polymerized at lower temperatures using a radical initiator. Styrene is known to undergo a self-initiated polymerization process when heated to temperatures of 150 °C or higher.[16] In the absence of catalytic impurities, heating styrene to 180 °C for 40 min results in 80% conversion to polymer. It is reasonable to assume that this process will also take place upon heating of the 4-vinylphenyl-substituted oligomer. Figure 3 shows the DSC trace for a sample of the oligomer heated at a rate of 10 °C/min under a nitrogen atmosphere. An exothermic event begins at 145 °C, reaching a maximum at 190 °C before completion at 240 °C. According to these data, cure is essentially complete at 240 °C.

The 4-vinylphenyl functional oligomer was found to be soluble in a wide range of organic solvents. To form thin films on glass substrates a solution of the oligomer at a concentration of 20 wt % in toluene was used. Typically the films were cast and dried on glass microscope slides and thermally cured in a Mettler hot stage that had been preheated to the desired temperature. The extent of cure in air as a function of curing time was monitored by measuring the pencil hardness according to ASTM D3363. Films of the oligomer on glass with thicknesses in the range of 75–150 $\mu$m were cured in air at temperatures of 220, 260, and 300 °C. Samples were removed from the oven at a given time interval, and the hardness was measured. Fresh samples were utilized for each time interval at a fixed temperature to generate the cure profiles shown in Figure 4. The results show that the maximum attainable pencil hardness for this cured system is 3H. At a temperature of 220 °C, cure is slow, requiring approximately 35 min; however, increasing the temperature to 260 or 300 °C resulted in a pencil hardness of 3H in less than 3 min. A disadvantage of high-temperature curing in air was the development of a distinct yellow color in the films. If the same films are heated to 300 °C under a nitrogen atmosphere, cure is again very rapid but yields a colorless film with a hardness of 3H. Attempts to cure similar films under these conditions but at temperatures above 300 °C resulted in cracking. Monoliths could be obtained by heating the oligomer to 300 °C under an inert atmosphere in a mold. Cured, crack-free, transparent, and colorless resin blocks could thus be obtained with thicknesses in the range of millimeters and a Shore D hardness of 80.

To reduce the cure temperature a radical initiator was incorporated into the resin at a concentration of 1 wt % or less. These were then dissolved into toluene and cast as films on glass slides. After drying, the films were purged with nitrogen for 2 min and heated to 150 °C at a rate of 20 °C/min. After 5 min the films were removed and examined. The results confirmed that radical initiators such as benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, dicumyl peroxide, and 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane were effective for ini-

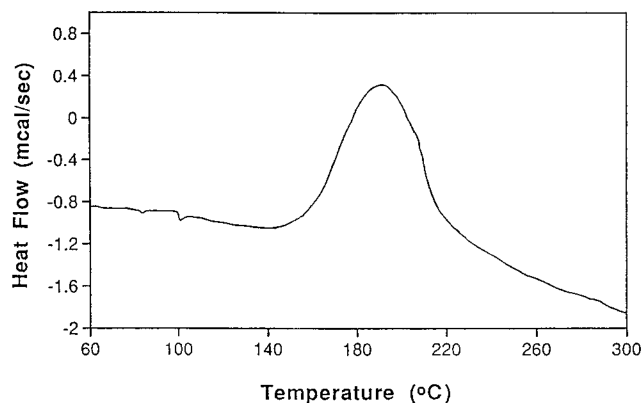



**Figure 3.** DSC trace for the 4-vinylphenyl end-blocked oligomer heated at a rate of 10 °C/min under nitrogen.

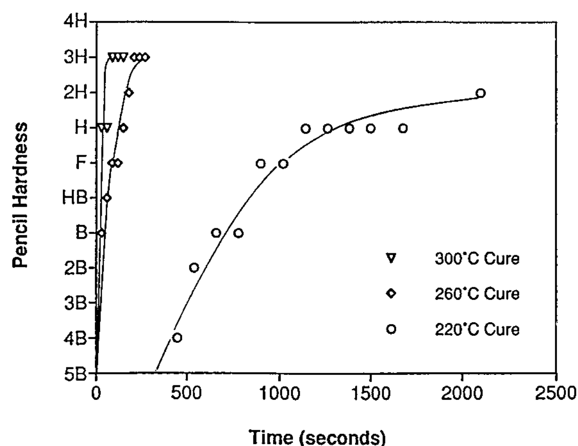



**Figure 4.** Thermal cure profile for the 4-vinylphenyl end-blocked oligomer.

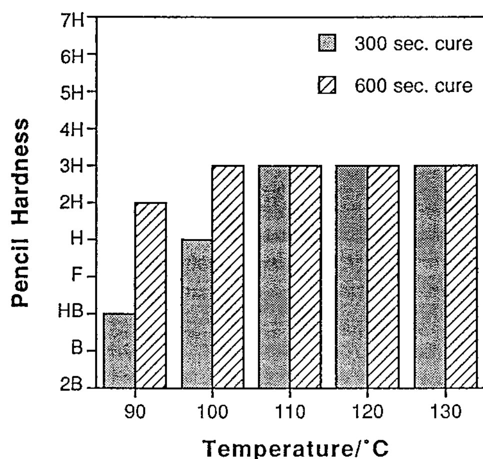



**Figure 5.** Thermal cure profile for the 4-vinylphenyl end-blocked oligomer containing 0.85 wt % benzoyl peroxide.

tiating radical cure of the oligomers. Figure 5 shows the cure profile for an oligomer containing 0.85 wt % benzoyl peroxide. At temperatures as low as 110 °C, cure is complete in under 300 s. Complete cure can be attained at lower temperatures; however, this requires longer cure times. With 0.35 wt % benzoyl peroxide, a pencil hardness of 3H was attained within 300 s of heating at a temperature of 130 °C.

**Properties of the Cured Resin.** *Thermal Stability.* It has been established that polydiphenylsiloxane is a very thermally stable material with a decomposition onset temperature in the vicinity of 400 °C and a 10% weight loss temperature of 510 °C.[9] In the case of the 4-vinylphenyldiphenylsiloxane oligomer, the diphenylsiloxane segment is expected to show good thermal stability, but there is some question concerning the thermal stability of the 4-vinylphenyl end groups. It is known that polystyrene undergoes chain cleavage and depolymerization processes at temperatures above 300 °C with the release of gaseous volatiles.[21] Figure 6 shows the weight loss profiles for the cured oligomer on heating under atmospheres of air or nitrogen. The onset of weight loss in air occurs at a slightly lower temperature (350 °C) than under a nitrogen atmosphere when the rate of heating is 10 °C/min. The temperatures for a 10% weight loss were 440 and 460 °C under nitrogen and air atmospheres, respectively. The thermal stability under prolonged heat exposure in an air atmosphere was evaluated for 80 $\mu$m thick films cured under nitrogen on a silicon wafer. After curing, the films were placed into the air oven at constant temperatures of 300 and 350 °C, and the weights of the samples were recorded as a function of time. The results are shown graphically in Figure 7. At a baking temperature of 300 °C there was a slow but steady weight loss of approximately 2%/h. At 350 °C there was an initial rapid loss weight loss within the first 2 h (10%/h) but this rate slowed considerably with time. The films subjected to the above thermal treatments were intact with no evidence of cracking; however, a distinct yellowing of the samples had occurred.

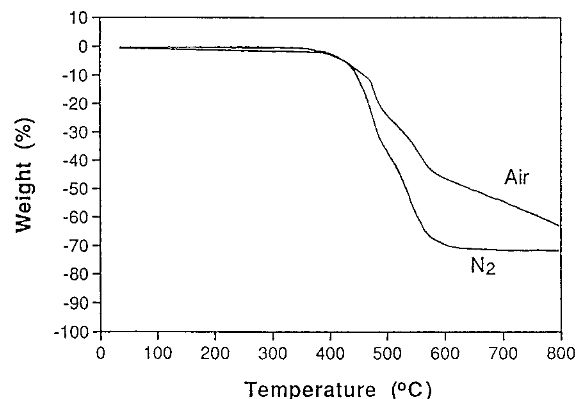



**Figure 6.** Weight loss profiles for the cured oligomer recorded under nitrogen and air atmospheres at a rate of 10 °C/min.

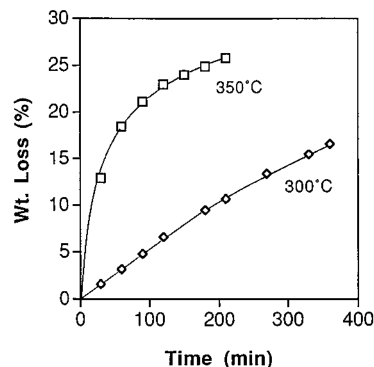



**Figure 7.** Isothermal decomposition curves for cured oligomer films heated in air at temperatures of 300 and 350 °C.

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**Table 1. Physical Properties of the Cured 4-Vinylphenyl Functional Oligomer and Polydiphenylsiloxane**

| property | 4-vinylphenyl oligomer | polydiphenyl-siloxane[9] |
|---|---|---|
| specific gravity (25 °C) | 1.13 | 1.25 |
| refractive index (25 °C) | 1.59[a] | |
| flexural strength, kg/mm$^2$ | 6.0 | 2.4 |
| flexural modulus, kg/mm$^2$ | 168 | 440 |
| $E'$ (25 °C), dyn/cm$^2$ | $1 \times 10^{10}$ | $1.5 \times 10^{10}$ |
| coeff thermal expansion, ppm/°C | 168 | 84 ($T$ < 200 °C) |
| volume resistivity, Ω·cm | $1.6 \times 10^{16}$ | $1.2 \times 10^{17}$ |
| dielectric constant | 2.87 | 2.7 |
| dissipation factor | $2 \times 10^{-4}$ | $1.2 \times 10^{-4}$ |
| water absorbency | 0.2 | 0.15 |

[a] Measured for the uncured oligomer.

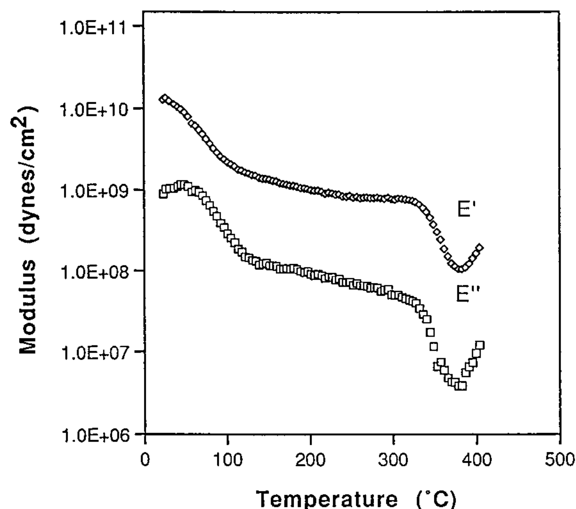


**Figure 8.** Storage and loss moduli ($E'$ and $E''$) for the cured oligomer measured at 11 Hz on heating at a rate of 2 °C/min.

*Mechanical Properties.* Films and monoliths of the diphenylsiloxane oligomer cured under nitrogen at 300 °C were hard but had a degree of flexibility. Cured samples were obtained by placing the oligomer in glass tubes sealed at one end and heating to 300 °C for 5 min (due to thermal contraction, the cylindrical monoliths were easily removed from the tubes on cooling). The flexural properties were measured for several samples and averaged to give a flexural modulus of 1.7 ± 0.4 GPa and a flexural strength of 6 ± 1 kg/mm$^2$. Compared to pure polydiphenylsiloxane, the flexural modulus was reduced by 60%, but the flexural strength increased by 150% (see Table 1).

An examination of the cured resin by DSC showed no evidence for a glass transition or crystallite melting. The absence of sample crystallinity was confirmed by X-ray diffraction analysis, which revealed only two broad amorphous halos with $d$ spacings at the peak maxima of 4.7 and 9.3 Å. This pattern is very similar to that reported earlier for amorphous diphenylsiloxane oligomers.[11] Dynamic mechanical testing of the cured oligomer was performed by first casting and curing thin films followed by evaluation in a Rheovibron mechanical analyzer. As a result of the brittleness of the films, individual samples with suitable dimensions for analysis had to be prepared. The storage and loss moduli ($E'$ and $E''$) as a function of temperature at a frequency of 11 Hz are recorded in Figure 8. The first event on heating appears between 20 and 100 °C, where a drop in the storage modulus by a factor of 10 can be observed. This coincides with a maximum in tan $\delta$ at 71 °C and a maximum in the loss modulus and is likely attributable to the onset of molecular motion of the diphenylsiloxane segment. This transition coincides well with the glass transition temperature of polydiphenylsiloxane, which is in the range of 55−60 °C.[9] Increases in temperature above 100 °C result in a slow gradual drop in the storage modulus. At 320 °C, a further rapid drop in modulus was recorded. This second transition appears to be the softening point of the resin; however, this is interrupted by a rise in the modulus at 375 °C. The close proximity of this rise to the onset of resin thermal degradation is indicative of a high-temperature cross-linking process.

Cylindrical monoliths of the cured oligomer were used to measure the thermal expansion coefficient, which was found to range from a minimum of 141 to a maximum of 168 ppm/°C on heating from 26 to 320 °C. The thermal expansion of polydiphenylsiloxane is more complicated than the cured oligomer. It has an initial expansion coefficient of 84 ppm/°C that increases significantly through the crystal to mesophase transition above 200 °C but then decreases again to 112 ppm/°C above 280 °C.

*Electrical Properties.* Electrical properties of a 1.95 mm thick disk of the oligomer cured under nitrogen at 300 °C were measured after equilibration in a 50% relative humidity environment at a temperature of 21 °C. Under these conditions, a dielectric constant of 2.88 was recorded at a frequency of 100 kHz, with a dissipation factor of $2 \times 10^{-4}$. A volume resistivity of $1.6 \times 10^{16}$ was recorded for the equilibrated sample. Exposure of the thoroughly dried cured resin to hot steam for 3 days resulted in water uptake amounting to 0.2% of the sample weight. The electrical properties of the cured oligomer are similar to those obtained for pure polydiphenylsiloxane (Table 1).

## Conclusions

To avoid the difficulties associated with processing polydiphenylsiloxane, a method for generating a regular network of easily processable and curable diphenylsiloxane oligomers has been developed. This has involved the successful tethering of various groups at the terminal positions of a three unit oligomer, hexaphenyltrisiloxanediol. Smooth conversion to the end-blocked product was obtained by the reaction of simple chlorosilanes in the presence of base. In the case of sterically bulky functionalities it was necessary to convert the oligomer to the lithium silanolate prior to reaction with the chlorosilane in order to avoid the formation of hexaphenylcyclotrisiloxane. A curable composition was obtained by end functionalization of hexaphenyltrisiloxanediol with 4-vinylphenyldimethylsilyl units. The resultant material can be cured thermally at temperatures above 200 °C or at lower temperatures by adding a radical initiator. The composition cured under nitrogen as films or monoliths was colorless, transparent, hard, and amorphous. The thermal stability of the cured composition was good but failed to reach the stability observed for pure polydiphenylsiloxane and can likely be attributed to the lower thermal stability of the polymerized 4-vinylphenyl units. Mechanical analysis has revealed a slight softening of

the cured material below 100 °C that might be attributable to the onset of diphenylsiloxane segmental motion; otherwise, the material is rigid to a temperature above 300 °C. The thermal expansion coefficient was rather high compared to other thermosetting resins,[14,18] which may also be related to a high degree of diphenylsiloxane segment mobility and a lower overall cross-link density. The electrical properties of the cured material were good, and like pure polydiphenylsiloxane, the material showed a low dielectric constant, good electrical resistivity, and moisture resistance. A summary of the properties of the cured oligomer compared to polydiphenylsiloxane appear in Table 1.

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