Silacyclobutane-Functionalized Siloxane Thermosets: An Examination of Their Properties and Potential as Copper Metal Site Selective Coatings

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A diphenylsiloxane oligomer with cross-linkable silacyclobutane functionalities at the terminal positions was prepared by the reaction of hexaphenyltrisiloxane diol with 1-chloro-1-methyl-1-silacyclobutane. When coated on inert surfaces, such as glass and plastics, the oligomer cured in air to a hard coating at temperatures above 220 °C, or above 110 °C in the presence of dissolved catalytic species such as platinum or copper complexes. The cured film provided a hard clear coating with a relatively high modulus (810 MPa) and good thermal stability. When coated onto the surface of metallic copper, the oligomer cured rapidly in air when heated to a temperature of 130 °C, without added catalyst. The catalytic species responsible for initiating the ring-opening polymerization of the silacyclobutane groups at the lower temperature are derived from the copper metal surface. Copper plates coated with a photopatterned spin-on-glass film were used to demonstrate the selectivity of the cure process for exposed metallic copper surfaces. This technology offers the potential to specifically apply electrically insulating silacyclobutane functional materials to the surface of copper conductors while deposition on other nonmetallic components is avoided.

Introduction

In recent years there has been considerable interest in the development of thermosetting oligomeric materials for application as high-temperature electrical insulators for electronic devices. The criteria for these applications include high thermal and dimensional stability, good insulating properties combined with a low dielectric constant, and good adhesion and mechanical properties. The general concept in the design of thermosetting oligomeric materials is to attach a thermally polymerizable functionality to a macromolecular core that displays excellent thermal stability. The polymerizable unit must also yield a thermally stable cross-link following the cure process. An advantage of this approach is that high-temperature polymeric materials that are typically difficult to process can be rendered either highly solvent soluble or low-temperature melt processable in the non-crosslinked oligomeric form.

Thermosetting materials of this composition appearing in the literature include 2,2-bis(4-vinylphenyloxyphenyl)hexafluoropropane[1], 4-vinylphenyl end-terminated diphenylsiloxane oligomers,[2] and 4-vinylphenyl functional polyphenols.[3] These three materials undergo autoinitiated polymerization of the 4-vinylphenyl units to yield hard, thermally stable resins with low dielectric constants after cure. They are also amenable to low-temperature cure processes by adding radical initiators

to the compositions. Polyimides are an important class of materials that also have associated processing problems, and this has encouraged the development of cross-linkable imide oligomers containing acetylene functional groups for composite material applications.[4]

Silicon-containing systems have received considerable attention that stems from their enhanced thermal properties and unique cure chemistries. In one example, a thermosetting resin with good thermal stability was derived with bisbenzocyclobutene monomer units linked by a divinylsiloxane bridging unit.[5] This thermosetting material is being promoted as an interlayer dielectric for thin film electronics applications. High-temperature thermosetting resins with polymerizable silacyclobutane groups have recently been described in the literature. It has been shown that 1,1-dimethyl-1-silacyclobutane and other silacyclobutane derivatives can undergo anionic,[6] catalytic,[7,8] and thermal[9] ring-opening polymerization to yield functional polysilabutanes. In one example, a thermosetting resin with a low dielectric constant and high modulus was obtained by heating the oligomer 1,4-bis(1-methyl-1-silacyclobutyl)benzene at 200 °C in the presence of a platinum catalyst.[10]

In this report a method for the preparation of a model diphenylsiloxane trimer unit terminated on both ends

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(1) Hedrick, J. L.; Hilborn, J. G.; Prime, R. B.; Labadie, J. W.; Dawson, D. J.; Russell, T. P.; Wakharker, V. *Polymer* **1994**, *35*, 291.

(2) Harkness, B. R.; Tachikawa, M. *Chem. Mater.* **1998**, *10*, 1706.

(3) Zupanic, J. J.; Zweig, A. M.; Conrad, J. P.; Dinkel, E. A. *Polym. Mater. Sci. Eng.* **1989**, *60*, 610.

(4) Melissaris, A. P.; Morton, H. L. *Macromolecules* **1993**, *26*, 6734.

(5) Johnson, R. W.; Phillips, T. L.; Weidner, W. K.; Hahn, S. F.; Burdeaux, D. C.; Townsend, P. H. *IEEE Trans. Comput., Hybrids, Manuf. Technol.* **1990**, *13*, 347.

(6) Liao, C. X.; Weber, W. P. *Polymer Bull.* **1992**, *28*, 281.

(7) Weyenberg, D. R.; Nelson, L. E. *J. Org. Chem.* **1965**, 30, 2618.

(8) Lu, J.; Weber, W. P. *Bull. Soc. Chim. Fr.* **1995**, *132*, 551.

(9) Nametkin, N. S.; Vdovin, V. M.; Zav'yalov, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1448.

(10) Liao, C. X.; Chen, M.-W.; Sun, L.; Weber, W. P. *J. Inorg. Organomet. Polym.* **1993**, *3*, 231.

with a polymerizable silacyclobutane monomer is described. Methods for curing the thermosetting oligomer using copper metal substrates, inert substrates, and metal complexes, as well as the properties of the cured resin, 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 thin-layer chromatography 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 then was 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, mp 110–111 °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.

Preparation of 1-Chloro-1-methyl-1-silacyclobutane.[11] To a 250 mL, nitrogen purged, three-necked flask equipped with an addition funnel, a water condenser, and a stopper were added 5.3 g of magnesium turnings and 70 mL of dry tetrahydrofuran. Dibromoethane (0.5 mL) was then added to the mixture of magnesium turnings to clean the metal surface. To the flask was then added γ-chloropropylmethyldichlorosilane (15 g) over a period of 1 h. The reaction was allowed to proceed for 1 day at 70 °C. Prior to fractional distillation, the volatiles in the reaction mixture were collected in a dry ice cooled trap by vacuum transfer. Distillation was carried out at ambient pressure. The second fraction, collected within the temperature range of 94–104 °C, contained 96% 1-chloro-1-methyl-1-silacyclobutane and 4% THF. This sample was used for the preparation of the silacyclobutane-functionalized diphenylsiloxane oligomer. The ^{1}H NMR (CDCl$_3$) spectrum of the product was consistent with the proposed structure: δ ∼ 2.17 (1H, m), 1.93 (1H, m), 1.45 (2H, m), 1.38 (2H, m), 0.61 (3H, s).

1,9-Dimethyl-1,1,9,9-bis(trimethylene)-3,3,5,5,7,7-hexaphenylpentasiloxane. A dry 100 mL three-neck round-bottom flask was equipped with a mechanical stirrer, a dropping funnel, a condenser, and an argon inlet system. To the flask was added 8.5 g of hexaphenyltrisiloxane-1,5-diol and 30 mL of tetrahydrofuran. To the solution was then added dropwise 18 mL of *n*-butyllithium (15% in hexane) and the solution was stirred for 1 min (due to heat generation at this step it is advisable to cool the flask in an ice–water bath). To the mixture was then added 4.8 mL of 1-chloro-1-methyl-1-silacyclobutane and the mixture stirred for 2 h. The solvent containing the functionalized oligomer was isolated from the residual salt by filtration and the salt washed three times with a total of 100 mL of hexane. The solvent was removed from the combined extracts by rotary evaporation to yield 8.6 g (85 wt %) of the silacyclobutane oligomer as a colorless oil. IR: 3020–3120, 1591, 1429, 1126, 1047 and 916 cm^{-1}. The ^{1}H NMR (CDCl$_3$) spectrum of the product was consistent with the proposed structure: δ ∼ 0.15 (CH$_3$), 1.1, 1.58, and 2.2 (−CH$_2$−), 7.2–7.7 (C−H, ar). ^{29}Si NMR (CDCl$_3$): δ ∼ −46.2, −46.0, and 7.3 .

Thin Film and Monolith Preparation. Films were prepared by dissolving the oligomer in hexane at concentrations of approximately 20 wt % and casting the solutions, with

Scheme 1. Preparation of the Silacyclobutane Functional Oligomer
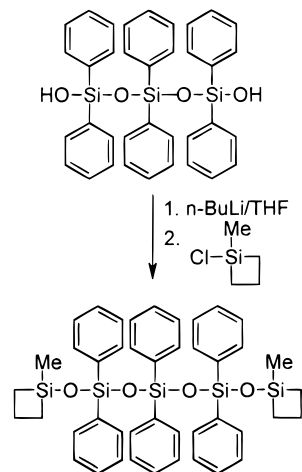
or without added catalyst, onto clean glass slides, silicon wafers, aluminum panels, and copper plates. The samples were thoroughly dried of solvent prior to cure. Thermal curing of the films was performed with a Mettler Hotstage FP98 attached to a Mettler FP90 central processor. The patterned spin-on-glass was prepared from hydrogen silsesquioxane and a photobase generator according to a procedure described in the literature.[12] Following development, the patterned hydrogen silsesquioxane film was heated in air at 200 °C for 5 min, cooled, and thoroughly washed with ethanol and finally toluene. Films of the oligomer were then deposited on the substrate surface by solution casting. Curing processes for the oligomer films are described in the text.

General Experimental. Size exclusion chromatography (SEC) analysis of the oligomer was performed with a TOSOH HLC-8020 gel permeation chromatograph, with toluene as the eluting solvent. Infrared spectra (IR) 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 (nuclear magnetic resonance) spectra were recorded with a Brüker APC300 NMR spectrometer at frequencies of 300 and 59.6 MHz, respectively, for samples dissolved in chloroform-*d*. DSC (differential scanning calorimetry), TGA (thermal gravitational analysis) and linear expansion measurements were performed with Rigaku TAS 200-DSC830D, TG81201D, and TMS 8140C thermal analysis systems. The DSC scan was conducted under air with a heating rate of 5 °C/min. TG−DTA (thermal gravitational analysis−differential thermal analysis) 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. Dynamic mechanical analysis (DMA) was performed with an Orientec Rheovibron DDV−II-EP attached to an Orientec Rheovibron Dynamic Viscoelastometer Model 2000 and a process controller Model 3000. The flexural properties were measured with an Instron Model 4301.

Results and Discussion

Oligomer Preparation. Hexaphenyltrisiloxane-1,5-diol, was utilized as the core for the silacyclobutane-functionalized thermosetting oligomer. End functionalization of the core diol was accomplished, as illustrated in Scheme 1, by initially converting the diol to the lithium silanolate prior to the addition of 1-methyl-1-chloro-1-silacyclobutane.[2] Conversion to the silanolate was necessary to limit reversion of the starting diol to

(11) Damrauer, R.; Davis, R. A.; Burke, M. T.; Karn, R. A.; Goodman, G. T. *J. Organomet. Chem.* **1972**, *43*, 121.

(12) Harkness, B. R.; Takeuchi, K.; Tachikawa, M. *Macromolecules* **1998**, *31*, 4798.

the cyclic trimer, as has been observed when a combination of bulky chlorosilanes and proton acceptors such as triethylamine are utilized in the reaction.[2] Reaction of the lithium silanolate with the chlorosilane proceeded smoothly and completely to yield the bis functional oligomer as a viscous oil, with a recovered yield of 85 wt %. The purity and structure of the oligomer were confirmed by SEC and IR and NMR spectroscopies. The virtual absence of a silanol stretching band in the IR analysis confirmed complete substitution of the silanol functionalities. In the absence of catalytic impurities, the oligomer showed excellent long-term stability in both the bulk and solution phases. This oligomer was utilized without further purification.

Curing of the Silacyclobutane-Substituted Oligomer. The silacyclobutane functional group is capable of undergoing autoinitiated ring-opening polymerization at elevated temperature[9] or at lower temperatures in the presence of a transition metal catalyst.[7,8] The result of the polymerization process is a three-dimensional cured network of the bis functional oligomer. Autoinitiated cure of the oligomer was monitored by heating a portion of the material in an aluminum DSC pan at a rate of 5 °C/min, under an air atmosphere. Under these conditions a broad exotherm, representing the exothermic ring-opening polymerization, appeared with an onset at 160 °C, a peak maximum at 194 °C, and conclusion at approximately 250 °C. If it is assumed that polymerization under these conditions was not influenced by catalytic species (including the sample pan), it can be expected that complete cure will only be attained at temperatures above 200 °C.

To test the cure process on solid substrates, the silacyclobutane-functionalized diphenylsiloxane oligomer was dissolved in hexane at a concentration of 20 wt %. The solution was then cast and dried on surfaces such as glass microscope slides, aluminum panels, or copper plates and subsequently thermally cured in a Mettler Hotstage 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 plates, with coating thicknesses in the range of $75-150$ μm, were cured in air at temperatures of 220, 240, 260, and 300 °C to monitor the autoinitiated cure process. 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 1. On a glass surface under an air atmosphere, cure is very rapid at 300 °C, yielding a transparent colorless film with an ultimate pencil hardness of H within 2 min. Reducing the cure temperature to 260 and 240 °C resulted in the same degree of hardness being achieved in 30 and 50 min, respectively. Temperatures below 240 °C failed to yield a fully cured film. This result corroborates with the DSC result that showed that temperatures above 250 °C are necessary to attain complete cure.

Acceleration of the cure process at lower temperatures was achieved by dispersing part per million quantities of transition metal catalysts such as a platinum–vinylsiloxane complex or copper(II) acetylacetonate into the film. Pencil hardness profiles as a function of time
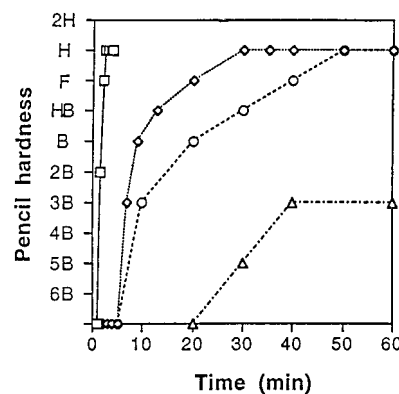

Figure 1. Pencil hardness as a function of temperature and time for the silacyclobutane oligomer cured on glass in the absence of catalyst (squares, 300 °C; diamonds, 260 °C; circles, 240 °C; triangles, 220 °C).
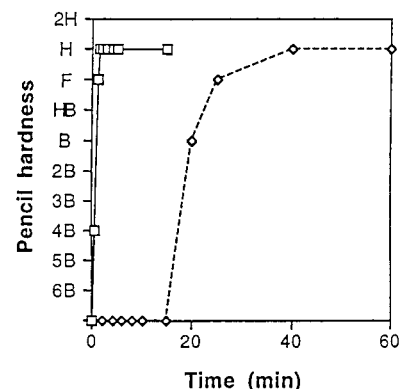

Figure 2. Pencil hardness as a function of temperature and time for the silacyclobutane oligomer cured on glass with 100 ppm copper(II) acetylacetonate as catalyst (squares, 150 °C; diamonds, 110 °C).

and temperature for an oligomer film, containing 100 ppm of the copper(II) acetylacetonate complex, as cured on a glass plate, are shown in Figure 2. At a temperature of 150 °C, cure was rapid, with an ultimate pencil hardness of H achieved in 2 min. Reducing the cure temperature to 110 °C slowed the cure process such that the same degree of hardness was attained only after 40 min. The cured films exhibited a slight yellow color that can be attributed to the catalyst residue. A significant acceleration of the cure rate was attained by using a platinum–vinylsiloxane complex as catalyst.[13] At a concentration of 10 ppm of catalyst, a pencil hardness of H could be achieved in approximately 3 min at a temperature of 110 °C; however, lower temperatures failed to yield a similar hardness level after extended curing times.

To test the possibility of cure on copper metal, hardness profiles were recorded as a function of time and temperature for thin films of the oligomer coated onto the surface of polished copper plates (Figure 3). At temperatures of 150 and 130 °C the cure process was rapid, yielding films with a pencil hardness of H within 3 min. Reducing the temperature to 110 °C failed to yield a hardened film. The mechanism for cure on the surface of copper metal has not been investigated, although it is evident that copper or copper oxide on

(13) Hitchcock, P. B.; Lappert, M. F.; Warhurst, N. J. W. *Angew Chem.* **1991**, *103*, 439.
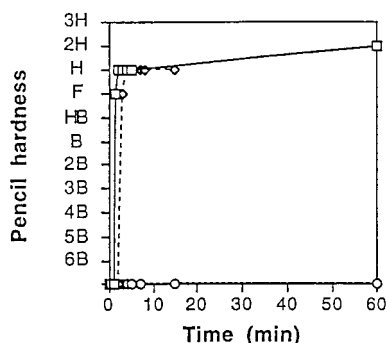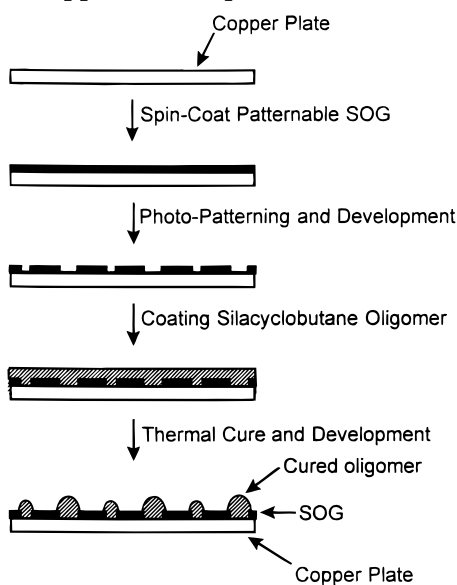
Figure 3. Pencil hardness as a function of temperature and time for the silacyclobutane oligomer cured on a copper plate with no added catalyst (squares, 150 °C; diamonds, 130 °C; circles, 110 °C).

Scheme 2. Process for Testing the Specificity of the Copper Metal Specific Cure Process

the metal surface is functioning as a heterogeneous catalyst. In the literature there are few reports of metallic copper as a heterogeneous polymerization catalyst, with most examples describing heterogeneous solution phase[14,15] or a combination of metal plasma and organic vapor phase processes.[16]

Copper Metal Selective Cure Process. To test the selectivity of the copper metal cure process, a thin film of the oligomer was coated onto the surface of a metal plate that had been previously patterned with a directly photopatternable spin-on-glass composition (the photo-patternable spin-on-glass was a mixture of hydrogen silsesquioxane and a photobase generator and has been described in the literature elsewhere[12]). A simple line and space pattern consisting of 170 and 680 μm wide trenches was fabricated that allowed portions of the underlying copper metal surface to be exposed. The remaining surface was covered with a thin film of hydrogen silsesquioxane which was not capable of catalyzing the silacyclobutane cure process. After coating
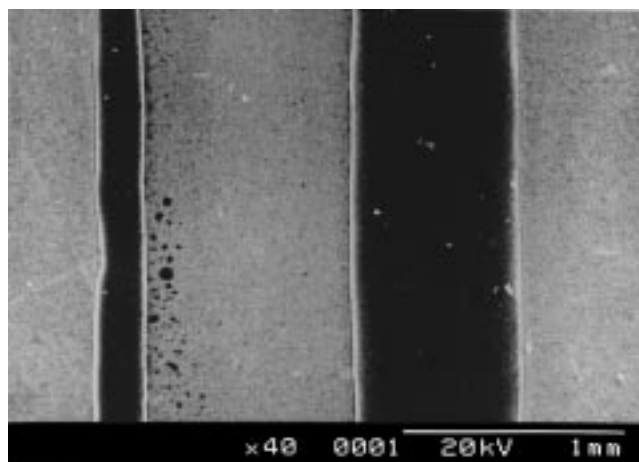
(14) Mitra, B. C.; Ghosh, P.; Palit, S. R. *Makromol. Chem.* **1966**, *98*, 285.
(15) Muramatsu, Y.; Yamamoto, T. *Chem. Lett.* **1997**, *7*, 581.
(16) Wijekoon, W. M. K. P.; Stry, J. J.; Prasad, P. H.; Garvey, J. F. *Langmuir* **1996**, *12*, 4929.

Figure 4. Scanning electron micrograph of a cured patterned film of the silacyclobutane oligomer formed on a patterned spin-on-glass-coated copper plate.

of the patterned surface with the oligomer, the copper plate was placed into an oven at 160 °C and cured in air for 5 min. The plate was then cooled and washed with hexane to remove the non-cross-linked portions of the film. After washing, an approximately 150 μm thick film of the cured oligomer was found to have deposited exclusively on the exposed copper metal surface, with no deposition on the hydrogen silsesquioxane coated areas. The entire process described above is illustrated in Scheme 2. Figure 4 shows a scanning electron micrograph of the surface of the film, with the two dark bands corresponding to the cured oligomer and the light areas corresponding to the areas where the copper surface was selectively coated with the hydrogen silsesquioxane resin. The widths of the cured line patterns are approximately 200 and 750 μm with a film thickness of approximately 150 μm. The above results indicate the selective nature of the coating material; however, the ultimate resolution limit for the coating process remains to be examined. A problem encountered in the metal-selective coating process for the oligomer model described above was its low viscosity, which presented difficulties in obtaining quality coatings, particularly at high temperatures. A solution to this might be to use higher molecular weight silacyclobutane-functionalized thermosetting materials or to extend the silacyclobutane functionality to solid organic resins and polymers.

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.[17] The thermal properties for cured 1,9-bis(4-vinylphenyl)-1,1,9,9-tetramethyl-3,3,5,5,7,7-hexaphenylpentasiloxane has been recently examined.[2] This material showed an onset of weight loss at 350 °C and temperatures for 10% weight loss of 440 and 460 °C under nitrogen and air atmospheres, respectively. The weight loss profiles for the corresponding silacyclobutane oligomer, cured with 10 ppm platinum catalyst at 250 °C, are shown in Figure 5. In air at a heating rate of 10 °C/min, the onset of weight loss was observed at a temperature of approximately 300 °C with 10% weight loss recorded at a

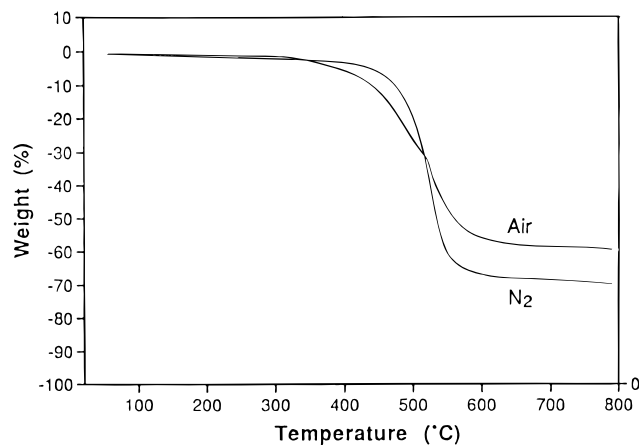(17) Harkness, B. R.; Tachikawa, M. *Chem. Mater.* **1998**, *10*, 1700.

Figure 5. Weight loss profiles for the silacyclobutane oligomer, cured with 10 ppm platinum catalyst at 250 °C, measured under air and nitrogen atmospheres at a rate of 10 °C/min.
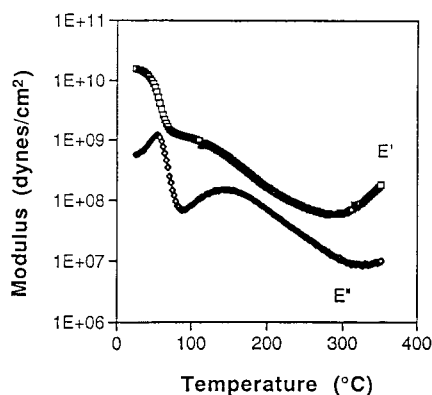

Figure 6. Storage modulus, E', and the loss modulus, E'', at 11 Hz, recorded as a function of temperature for the oligomer containing 10 ppm platinum catalyst cured in air at 250 °C.

temperature of 440 °C. Under a nitrogen atmosphere, the onset of weight loss was observed at approximately 360 °C with 10% weight loss recorded at 470 °C.

Mechanical Properties. A thin film of the silacyclobutane oligomer was partially cured on a glass plate in air at a temperature of 80 °C in the presence of 10 ppm platinum catalyst. The film was then removed from the glass plate and cut to thin strips for analysis. The strips were then heated to a temperature of 250 °C in air to complete the cure process. The storage modulus, E', and the loss modulus, E'', recorded as a function of temperature for the cured oligomer, at a frequency 11 Hz, are shown in Figure 6. There is an initial decrease in E' by approximately 1 order of magnitude between 25 and 75 °C with a corresponding maximum in tan δ at 62 °C. This corroborates well with the mechanical properties observed for the 4-vinylphenyl-functionalized oligomer[2] and appears at the same temperature as the glass transition recorded for polydiphenylsiloxane. This suggests that segmental motion of the diphenylsiloxane trimer in the cured silacyclobutane oligomer may be responsible for this mechanical behavior. Increasing the temperature above 70 °C results in a steady decrease in the storage modulus; however, above 300 °C an upturn in E' is observed. This temperature-induced increase in the modulus corresponds with the onset of decomposition in air, as indicated by DSC, and suggests that thermally induced cross-linking at elevated temperatures is part of the decomposition process.

Films and monoliths of the cured oligomer were hard but had a degree of flexibility. Samples obtained by curing the oligomer in glass tubes, sealed at one end and heated to 150 °C for 2 h in the presence of 20 ppm platinum catalyst (due to thermal contraction, the cylindrical monoliths were easily removed from the tubes on cooling), exhibited a flexural modulus of 810 MPa and a flexural strength of 24 MPa. The cured samples showed a linear thermal expansion over the temperature range of 20 to 200 °C, with a coefficient of thermal expansion of 205 ppm/°C.

Conclusions

A model diphenylsiloxane oligomer with cross-linkable silacyclobutane functionalities at the terminal positions was prepared by the reaction of hexaphenyltrisiloxanediol with 1-chloro-1-methyl-1-silacyclobutane and characterized. When coated on inert surfaces such as glass and plastics, the oligomer was found to cure spontaneously above 220 °C in air or above 110 °C in the presence of dissolved platinum or copper complexes. The platinum catalyst was the most effective, attaining complete cure in minutes at 110 °C, with only 10 ppm of catalyst. The model oligomer upon cure was found to yield a hard clear coating with a high modulus (810 MPa) and good thermal stability. Thin films of the oligomer (<150 μm) when coated onto the surface of metallic copper would cure spontaneously in air at temperatures of 130 °C and above without added catalyst. The catalytic species responsible for initiating the low-temperature ring-opening polymerization of the silacyclobutane groups is derived from the copper metal surface, although this remains to be investigated in detail. Copper plates coated with a photopatterned spin-on-glass film were used to demonstrate the specificity of the cure process for exposed copper surfaces. This technology offers the potential to specifically apply electrically insulating silacyclobutane functional materials to the surface of metallic copper conductors and avoid deposition on nonmetallic components.