Oligodimethylsiloxane Linked Cyanate Ester Resins

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ABSTRACT: A series of dimethylsiloxane linked cyanate ester monomers (NCOC₆H₄(CH₂)₃(Si(CH₃)₂O)_nSi-(CH₂)₃C₆H₄OCN, n = 1, 2, 3) have been synthesized and characterized. Monomer melting points range from 5 to -12 °C, and characterization includes ¹H, ¹³C NMR, and IR spectroscopies and DSC. Thermoset formation occurs by a cyclotrimerization of the cyanate group to a cyanurate structure. Cured resins are homogeneous rubbery castings with T_g ranging from 15 to -43 °C. Dielectric constants display little dependence on siloxane chain length but a strong dependence on frequency (2.5/15 GHz; 2.85/1 GHz). The corresponding loss tangent increases with siloxane chain length and displays a small frequency dependence.

Introduction

The incorporation of short lengths of dimethysiloxane chains into rigid thermoset polymer structures is a very effective method for modifying properties associated with the rigid polymer toward those associated with the silicone. Property modifications include reduction of brittleness, depression of the glass transition temperature, diminishment of flammability, enhancement of chemical resistance, more facile processing, etc. A property of particular interest with regard to silicone tailoring of thermosets is that of electromagnetic permittivity. Polysiloxanes are remarkable for their low dielectric loss, low water absorption, high electrical resistivity, temperature stability, and chemical inertness. Depending on chain length, frequency, and temperature, poly(dimethylsiloxane) has a relatively low permittivity (2.3–2.75).¹ Incorporation of dimethylsiloxane, DMS, structural units into a higher dielectric thermoset may have the effect of lowering this property parameter along with other beneficial property changes indicated above. The objective of this work is to determine the contributions of additions of small and systematic increments of the PDMS structural unit. The thermoset selected is the cyanate ester resin, and the PDMS modification of it is depicted in Figure 1. The cyanurate thermoset network structure is generated by cyclotrimerization of the monomer cyanate ester functional group.

The properties of this thermoset are governed by both the cyanurate linkage and the connecting structure of the monomer. The cyanurate linkage, whose symmetry cancels polarity usually associated with heteroatom structures, correlates with a resin low dielectric character.² The monomer connecting structure, which usually consists of one, two, or three phenylene moieties, regulates the cross-link density and correlates with the resin's high glass transition temperature. All current commercial cyanate ester resins are derived from phenolic precursors. The chemistry and stability of the cyanate functional group usually require that it be bonded to an aromatic structure for appropriate utility as a resin monomer.³ Fluoromethylene⁴ and carborane⁵ linked cyanate esters are exceptions. Silicone-containing cyanate ester resins are a relatively recent development with very little research having been done. The cyanate functional group may be bonded directly to silicon, but

alkyl and aryl silicon cyanates are apparently not sufficiently stable to undergo the polycyclotrimerization reaction.^{6,7} A modified approach is to terminate the silicone chain with a phenyl cyanate structure. Such oligomers of molecular weight 1000-10 000 have been reported as phase-separating toughening agents for other cyanate resins.⁸ In this instance no structure or property characterization of the silicone cyanates was presented. A second example reports a seven-step synthesis of phenyl cyanate terminated silicone macromonomers with two and eight dimethylsiloxane units again for evaluation as a toughening agent additive in another cyanate ester resin.9 Ă more practical synthesis is the two-step hydrosilylation-cyanation route from readily available inexpensive starting reagents (Figure 1). This route is the subject of a patent involving hydrosilylation of a variety of allylphenols with hydrosilyl terminated organosilicones followed by cyanation of the phenol.¹⁰ In present work we are using this route to prepare and characterize an homologous series of phenyl cyanate terminated dimethylsiloxane macromonomers with short monodisperse siloxane chain lengths. This route generates a product with trimethylene connecting structures between the phenylcyanate and siloxane units.

The focus of our interest is on the electromagnetic permittivity of the cyanate ester resin family and is related to applications requiring a low dielectric character such as radomes and electronics. Of particular interest are the magnitudes of variation in the storage and loss permittivity and in the glass transition caused by introduction of incremental DMS units to a cyanate ester. The extremes in material composition are represented by the resorcinol dicyanate resin (dielectric constant 3.2,¹¹ tan δ 0.003,¹¹ $T_{\rm g}$ 275 °C¹²) and the oligodimethylsiloxane (dielectric constant 2.3–2.75,¹ power factor 0.0003–0.0006,¹ $T_{\rm g}$ –127 °C¹³).

Experimental Section

General Information. All reagents and solvents were of reagent-grade quality, purchased commercially, and used without further purification unless otherwise noted.

Infrared spectra of monomers were obtained from samples deposited as thin films on NaCl plates and from polymers as fine particulates dispersed in KBr. IR spectra were recorded using a Nicolet Magna FTIR 750.

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Figure 1. Siloxane CyResin synthesis.

¹H and ¹³C NMR spectra of monomers and precursors were recorded using a Bruker AC300. Acetone- d_6 was used as solvent, and the chemical shifts are internally referenced to CD₃COCD₃ (2.04 and 29.8 ppm) for the respective ¹H and ¹³C nuclei.

Differential scanning calorimetry (DSC) data were recorded on a DuPont 2100 thermal analysis system/910 DSC module from 13 to 24 mg samples (prepared by curing in the DSC pan) under a nitrogen atmosphere at 10 °C/min scan rate. Macromonomer melting points were determined at the onset of the melting endothermic transition.

Thermogravimetric analysis (TGA) data were recorded on a DuPont 2100 thermal analysis system/951 TGA module from 17 to 18 mg resin samples in a nitrogen atmosphere at 10 $^{\circ}C/$ min scanning conditions.

Density measurements were made on void-free 0.32-0.50 g resin castings according to the ASTM D 792-66 displacement method at 23 °C.

Electric field permittivity measurements were made over two frequency ranges. An electrode contact method was used for L-band (0.5-1.8 GHz) measurements employing an HP4291A impedance/material analyzer as described in previous work.⁴ Samples were 12 mm diameter disks of uniform thickness (approximately 1.5 mm). The disk is inserted into a spring-loaded parallel electrode arrangement and held in good contact with the electrode by compressive force from the spring. A waveguide transmission line method was used for the K_u -band (12.5–18 GHz) measurements employing an HP8722C network analyzer. Ku-band measurements require rectangular samples (1.6 cm by 0.8 cm by 0.4 cm) which were fabricated as castings and custom fit to sample holders in the waveguide. In this method, the scattering parameters are measured and used to determine the transmission and reflection coefficients which can then be used to calculate the complex permittivity. In general, the error in the calculated results is generated from the measured sample distances such as the thickness, sample holder length, and sample position in the holder as well as the instrument repeatability and sample curvature.¹⁴ Calibration is performed with the sample holder in place and as such is taken out of the calculation. The position is also not an issue as the sample is placed at the plane of calibration for port one. The thickness can be measured to 0.01 mm, and the samples were relatively flat and tightly fit within the waveguide. Several data reduction models were used to determine the material properties. One method described by Nicolson and Ross places equal weighting on the transmission and reflection coefficients which yields both the complex permittivity and complex permeability for the sample.¹⁵ This provides a good check on the measurement and calculation for nonmagnetic samples where the complex

permeability should be "1-j0". In addition, a measurement was made on a control sample with a value close to the test samples. Ultrahigh molecular weight polyethylene was used.

Synthesis of Precursor Trimethylenephenol Terminated Poly(dimethylsiloxane)s (HOC₆H₄(CH₂)₃[Si-(CH₃)₂O]_nSi(CH₃)₂(CH₂)₃C₆H₄OH, n = 1,2,3; Si2–PhOH, Si3–PhOH, Si4–PhOH, Respectively). *General Procedure:* A 0.025 mol quantity of hydride terminated poly(dimethylsiloxane) (H[(CH₃)₂SiO]_nSi(CH₃)₂H, n = 1, 2, 3) was added dropwise to 6.70 g (0.050 mol) of 2-allylphenol containing 3 drops of H₂PtCl₆·6H₂O (5% solution in 2-propanol) at 60 °C. The mixture was stirred for 1 h at this temperature. The product was purified by Kugelrohr vacuum distillation to remove residual of 2-allylphenol (60 °C/20 Torr). The n = 1member of the series was additionally purified by column chromatography on silica (CH₂Cl₂:hexane 1:1 elution).

1,3-Bis(3'-(2-hydroxylphenyl)propyl)-1,1,3,3-tetramethyldisiloxane (Si2–PhOH). Isolated yield: 6.84 g (68%) of oil; n_D 1.5258. ¹H NMR (300 MHz, CD₃COCD₃) δ : 0.04 (br s, 12H, CH₃), 0.60 (m, 4H, CH₂), 1.65 (q, 4H, CH₂), 2.62 (t, 4H, CH₂), 6.70–7.06 (m, 8H, H_{arom}), 8.08 (s, 2H, OH). ¹³C NMR (75 MHz, CD₃COCD₃) δ : 0.500 (CH₃), 19.03, 24.50, and 34.58 (CH₂), 115.7, 120.2, 127.5, 129.6, and 130.9 (C_{arom}), 155.9 (C– OH). IR (NaCl) ν : 3444 (OH), 2953 (C–H), 1595, 1498, and 1466 (C–C), 1253 (Si–CH₃), 1065 (SiOSi), 800 cm⁻¹ (Si–C).

1,5-Bis(3'-(2-hydroxylphenyl)propyl)-1,1,3,3,5,5-hexamethyltrisiloxane (Si3–PhOH). Isolated yield: 8.58 g (72%) oil; n_D 1.4961. ¹H NMR (300 MHz, CD₃COCD₃) δ : 0.03 (s, 6H, CH₃), 0.11 (d, 12H, CH₃), 0.63 (m, 4H, CH₂), 1.67 (q, 4H, CH₂), 2.63 (t, 4H, CH₂), 6.70–7.07 (m, 8H, H_{arom}), 8.17 (s, 2H, OH). ¹³C NMR (75 MHz, CD₃COCD₃) δ : 0.372 and 1.424 (CH₃), 18.88, 24.42, and 34.56 (CH₂), 115.6, 120.1, 127.5, 129.5, and 130.9 (C_{arom}), 155.8 (C–OH). IR (NaCl) ν : 3425 (OH), 2959 (C–H), 1601, 1498, and 1466 (C–C),1259 (Si–CH₃), 1046 (SiOSi), 800 cm⁻¹ (Si–C).

1,7-Bis(3'-(2-hydroxylphenyl)propyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (Si4–PhOH). Isolated yield: 12.39 g (90%) oil; $n_{\rm D}$ 1.4939. ¹H NMR (300 MHz, CD₃COCD₃) δ : 0.04 and 0.06 (2xs, 24H, CH₃), 0.64 (m, 4H, CH₂), 1.65 (m, 4H, CH₂), 2.63 (t, 4H, CH₂), 6.71–7.07 (m, 8H, H_{arom}), 8.11 (s, 2H, OH). ¹³C NMR (75 MHz, CD₃COCD₃) δ : 0.374 and 1.385 (CH₃), 18.79, 24.32, and 34.50 (CH₂), 115.6, 119.9, 127.4, 130.7, and 130.7 (C_{arom}), 155.8 (C–OH). IR (NaCl) ν : 3450 (OH), 2959 (C–H), 1589, 1492, and 1459 (C–C), 1259 (Si–CH₃), 1091 and 1039 (SiOSi), 800 cm⁻¹ (Si–C).

Synthesis of Trimethylenephenylcyanato Terminated Poly(dimethylsiloxane) Monomers (NCOC₆H₄(CH₂)₃-[(CH₃)₂SiO]_nSi(CH₃)₂(CH₂)₃C₆H₄OCN, n = 1, 2, 3; Si2–Cy, Si3–Cy, Si4–Cy, Respectively). *General Procedure:* To a three-neck 25 mL flask fitted with a stirring bar, thermometer, nitrogen inlet, and dropping funnel were added 1.27 g (0.0120 mol) of BrCN and 6 mL of acetone. The mixture was cooled at -30 °C. A solution of 0.00569 mol of the corresponding siloxane phenol, 1.21 g (0.0120 mol) of Et₃N, and 2 mL of acetone was transferred to the dropping funnel and added dropwise to the BrCN solution while a -20 °C reaction temperature was maintained. The resulting suspension was stirred 1 h at -20°C and 1 h while warming to room temperature. The suspension was rapidly filtered and washed with 3 mL of CH₂Cl₂. The filtrate was concentrated under vacuum without heating. The oil obtained was dissolved in 10 mL of CH₂Cl₂ and extracted three times with 10 mL of HCl (1%) and three times with 10 mL of distilled water. The organic phase was dried over anhydrous MgSO₄. Filtering and vacuum rotary evaporation yielded the corresponding dicyanate as amber oil. IR and ¹H NMR of the n = 1 member indicated significant quantities of the diethylcyanamide byproduct present.⁴ It was removed by Kugelrohr vacuum distillation (60 °C/1 Torr).

1,3-Bis(3'-(2-cyanatophenyl)propyl)-1,1,3,3-tetramethyldisiloxane (Si2–Cy). Isolated yield: 1.11 g (41%) oil; $n_{\rm D}$ 1.5097; mp 5.35 °C. ¹H NMR (300 MHz, CD₃COCD₃) δ : 0.049 (s, 12H, CH₃), 0.60 (m, 4H, CH₂), 1.66 (q, 4H, CH₂), 2.71 (t, 4H, CH₂), 7.31–7.49 (m, 8H, H_{arom}). ¹³C NMR (75 MHz, CD₃-COCD₃) δ : 0.412 (CH₃), 18.57, 24.73, and 33.37 (CH₂), 109.6 (OCN), 115.3, 127.8, 128.9, 131.5, 132.4, and 152.2 (C_{arom}). IR (NaCl) ν : 2959 (C–H), 2261 (OCN), 1595, 1492, and 1453 (C–C), 1259 (Si–CH₃), 1168 and 1136 (SiOSi), 1078 cm⁻¹ (Si–C).

1,5-Bis(3'-(2-cyanatophenyl)propyl)-1,1,3,3,5,5-hexamethyltrisiloxane (Si3–Cy). Isolated yield: 1.61 g (51%) oil; $n_{\rm D}$ 1.5086; mp 8.56 °C. ¹H NMR (300 MHz, CD₃COCD₃) δ : 0.008 (s, 6H, CH₃), 0.65 (s, 12H, CH₃), 0.62 (m, 4H, CH₂), 1.70 (q, 4H, CH₂), 2.71 (t, 4H, CH₂), 7.29–7.50 (m, 8H, H-arom). ¹³C NMR (75 MHz, CD₃COCD₃) δ : -0.636 and 0.503 (CH₃), 17.65, 23.88, and 32.54 (CH₂), 109 (OCN), 114.43, 127, 128.14, 130.70, 131.67, and 151.45 (C_{arom}). IR (NaCl) v: 2966 (CH), 2255 (OCN), 1582, 1492, and 1453 (C–C), 1259 (Si–CH₃), 1162 and 1059 (SiOSi), 800 cm⁻¹ (Si–C).

1,7-Bis(3'-(2-cyanatophenyl)propyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (Si4–Cy). Isolated yield: 1.98 g (55%) oil; $n_{\rm D}$ 1.4847; mp –12.23 °C. ¹H NMR (300 MHz, CD₃-COCD₃) δ : 0.019 and 0.072 (2xs, 24H, CH₃), 0.63 (m, 4H, CH₂), 1.69 (q, 4H, CH₂), 2.72 (t, 4H, CH₂), 7.31–7.50 (m, 8H, H_{arom}). ¹³C NMR (75 MHz, CD₃COCD₃) δ : 0.282 and 1.328 (CH₃), 18.51, 24.75, and 33.42 (CH₂), 1100 (OCN), 115.3, 127.9, 129.0, 131.4, 132.5, and 152.3 (C_{arom}). IR (NaCl) v: 2959 (w, CH₂), 2261 (OCN), 1576, 1492, and 1453 (C–C), 1153 (Si–CH₃), 1162 and 1039 (SiOSi), 800 cm⁻¹ (Si–C).

Resin Cure Procedure. The dicyanate monomers (Si2– Cy, Si3–Cy, and Si4–Cy) were cured with a copper naphthenate–nonylphenol catalyst solution.¹⁶ The dicyanate monomers was initially degassed at 100 °C/1 Torr for 10 min followed by addition of 2.3 phr of catalyst solution (0.31 g of copper naphthenate in 3.00 g of nonylphenol) and degassed again a second time (100 °C/1 Torr/10 min). The hot degassed molten resin was transferred to an appropriate mold and cured according to the schedule 175 °C (12 h) \rightarrow 225 °C (2 h). The cured resins are ejected from the mold and cut/polished where necessary for a uniform surface and thickness. All castings are dark amber in appearance.

Results and Discussion

Monomer Synthesis. The sequence of reactions in the synthesis of the oligodimethylsiloxane linked cyanate ester macromonomers is depicted in Figure 1.

The first step is the chloroplatinic acid catalyzed hydrosilylation of 2-allylphenol with the corresponding hydride terminated dimethysiloxane to yield the respective siloxane bisphenols. This reaction has been reported to work remarkably well with an unexpected acceleration in rate correlated with the presence of the phenol functional group.¹⁷ In our hands, this reaction proceeded well but not quite quantitatively, and distillation was necessary to separate residual unreacted phenol. These



Figure 2. IR spectra of allylphenol, tetramethyldisiloxane, Si2–PhOH precursor, Si2–Cy monomer, and cured Si2–CyResin.

intermediates were characterized by IR, ¹H, and ¹³C NMR spectroscopies (see Experimental Section), and the IR spectrum of Si2-bisphenol is included in Figure 2. The corresponding spectra show the disappearance of the Si-H group (2128 cm⁻¹; 4.8 ppm) and conversion of the $-CH_2-CH=CH_2$ group (1615 cm⁻¹; 6.1 and 5.2 ppm) to the $-(CH_2)_3$ - group (2.65, 1.65, 0.60 ppm; 19, 24, 34 ppm).

The second step is the cyanation of the bisphenol intermediates. A modification of the Grigat and Pütter reaction conditions¹⁸ was used as previous experience has shown altering the order of reagent mixing such that the phenol is prereacted with the triethylamine reduced byproduct formation.¹⁹ Also, 5% excesses of the triethylamine and cyanogen bromide are used to ensure that the phenol is completely converted to the cyanate. This causes diethylcyanamide to form as a byproduct, but it is far easier to separate from the product than is unreacted phenol.¹⁹ The three cyanate ester macromonomers (Si2–Cy, Si3–Cy, Si4–Cy) were characterized by IR, ¹H, and ¹³C NMR spectroscopies, and the IR spectrum of Si2-Cy is presented in Figure 2. In addition to the bands associated with the dimethylsiloxane structure (1168 and 1136 cm⁻¹ Si-O-Si stretching; 1078 cm⁻¹ Si-C stretching and CH₃ rocking; 1259 cm⁻² Si-CH₃ deformation), the triple bond stretching of the cyanate group appears as a strong unsplit band at 2261 cm⁻¹. The unsplit character of this cyanate band is a unique feature for this aromatic cyanate ester series. For all other known aromatic cyanate esters the band in this region is split into two or more resolved bands.³ The origin of this splitting is not understood although unsuccessful attempts have been made to correlate it with electronic substituent effects.^{20,21} In this case it may be possible that the ortho substitution of the large trimethylenesiloxane group may have a steric influence. In the NMR diagnostics for the phenol to cyanate



Figure 3. DSC thermograms of siloxane–Cy series depicting the melting points and processing window.

conversion are the disappearance of the phenolic proton (8.1 ppm), a downfield shift and smaller splitting of the aromatic protons and the appearance of the cyanate carbon resonance (110 ppm).

Sufficient macromonomer purity is very important for subsequent processing operations. The cyanation reaction reagents (phenol and triethylamine) and byproducts (diethylcyanamide, triethylammonium bromide) are polymerization catalysts that may de detrimental to monomer storage as well as controlled processing. As a purity diagnostic the width of the processing window (discussed below) correlates with the presence of these reactive impurities.³ For this series of siloxane cyanate macromonomers the window is very wide (~200 °C). This is attributable to both a good level of purity and a low macromonomer melting point.

Thermoset Formation. Cyanate ester monomers polymerize by a cyclotrimerization reaction to form a cyanurate cross-linked structure as illustrated in the final step in the reaction sequence in Figure 1. This reaction occurs thermally at elevated temperatures and with catalysis at lower temperatures. For aromatic cyanate esters, this transformation has been structurally characterized by IR, 13C, and 15N NMR spectroscopies²² and by a model compound study.²³ In Figure 2 the lower spectrum of the cured Si2-CyResin shows the complete disappearance of the 2261 cm⁻¹ OCN band and the emergence of the 1569 and 1379 $\rm cm^{-1}$ cyanurate bands characteristic of this transformation. This conversion is quantitative for all three members of this resin series. For cyanate ester resins with high glass transition the quantitative conversion in not usually observed.

In Figure 3 the DSC thermograms of the siloxane cyanate macromonomer series display a strong exotherm corresponding to the thermal polymerization and a large processing window (temperature range between a melting transition and onset of the polymerization exotherm). For most cyanate ester monomers the maxi-



Figure 4. DSC thermograms of siloxane–CyResin series depicting the glass transition temperature.

Table 1. Siloxane Resin Thermal Characterization

resin	<i>T</i> _g (°C)	<i>T</i> _{10% d} (°C)	char yield
Si2-CyResin	15	445	0.23
Si3-CyResin	-8	438	0.13
Si4-CyResin	-43	410	0.09

Table 2. Siloxane Resin Physical Property Characterization

	ρ		ϵ'	tan δ	ϵ'	tan δ
resin	(g/cm ³)	$\phi_{ m Si}$	(15 GHz)	(15 GHz)	(1 GHz)	(1 GHz)
Si2-	1.102	0.361	2.51	0.0025	2.88	0.0025
CyResin Si3-	1.087	0.467	2.49	0.004	2.82	0.0060
CyResin Si4– CyResin	1.060	0.537	2.47	0.007	2.85	0.013

mum of the exotherm occurs in the 200–300 °C range. The ortho substitution in the system under study may moderately diminish the reactivity and shift the exotherm to the higher end of this temperature range. Such an observation has been made for a di-ortho-methylsubstituted cyanate monomer.3,24 The width of the processing window in Figure 3 is a consequence of a low melting transition (8-14 °C) and a relatively high exotherm temperature (260-305 °C). Impurities, particularly those from the cyanation reaction (reagents such as phenol and triethylamine and byproducts such as diethylcyanamide and triethylammonium bromide), are polymerization catalysts and will broaden and shift the exotherm to lower temperatures.¹⁹ Copper transition metal catalysts dissolved in nonylphenol are much more efficient catalysts^{16,22,24} and were employed in preparing castings from the silicone cyanate macromonomers.

Resin Properties. Tables 1 and 2 summarize thermal and dielectric properties of the cured siloxane cyanate thermoset series.

Thermal analyses includes DSC and TGA. In the DSC thermograms only a single glass transition is observed for each member of the siloxane cyanate resin series (Figure 4). This is consistent with a non-phase-separated system. This transition is a observed as a 5-10 °C step, and the $T_{\rm g}$ is assigned at the midpoint of the step. As summarized in Table 1, the $T_{\rm g}$ of each resin is below room temperature, and the decreasing $T_{\rm g}$ cor-





Figure 6. Effect of increasing dimethylsiloxane chain length on the repeat unit molecular volume.

relates with an increasing length of the dimethylsiloxane chain. The TGA thermograms also display an interesting trend with siloxane chain length (Figure 5). With increasing chain length, the onset of the weight progresses to a lower temperature, and the char yield diminishes. This correlates with a lower cross-link density and may indicate that the siloxane segments are being volatilized presumably by breakage of the trimethylene linkages. This chain length dependence is an interestingly opposite trend to that observed for an oligofluorormethylene cyanate ester resin system⁴ where the cyanurate structure was determined to be the thermally weak link in the thermoset structure.

In Table 2, the density measurement for the siloxane cyanate resin series displays a decrease with increasing silicone chain length. This system is a homologous series with the molecular volume of the repeat unit increasing by an integral number of dimethylsiloxane units. In Figure 6 a plot of the repeat unit molecular volume (calculated from the density) against the number of dimethylsiloxane units in the repeat unit is linear with a slope of 129.7 Å³/Si(CH₃)₂O unit. This Si(CH₃)₂O molecular volume is in good agreement with an analogous value for poly(dimethylsiloxane) of 126.2 Å³/Si-



Figure 7. Dielectric constant dependence on frequency for siloxane–CyResin.

(CH₃)₂O unit calculated from the PDMS repeat unit molecular weight (74.2 g/mol) and density (0.976 g/cm³). From the density measurements and the Si(CH₃)₂O molecular volume, it is possible to calculate the volume fraction of the siloxane component, ϕ_{DMS} , in the cyanate thermoset matirx.²⁵ For the three member series, these values range from 36.1 to 53.7% (Table 2).

Complex electric field permittivity in the L (0.5–1.5 GHz) and K_u (12.5–18 GHz) bands was measured on castings of the siloxane cyanate resin series. Plots of the dielectric constant, ϵ' , and loss tangent, tan δ , as a function of frequency are presented in Figures 7 and 8 along with data for a polyethylene control sample. The ϵ' and tan δ values for the midrange of these bands are also entered in Table 2.

The dependence of ϵ' on frequency is relatively flat in the K_u -band with its value gradually decreasing as the siloxane chain length increases from 2 to 4. In the L-band the dielectric constants are higher and have a much steeper dependence on frequency. This is a consequence of an orientation polarization making a larger contribution to the dielectric constant at lower frequencies. For the polyethylene control sample the effect is smaller, reflecting a smaller dipole and a crystalline morphology. The difference in ϵ' between individual members of the siloxane cyanate resin series is small within each band, and its correlation with siloxane chain length in the L-band data appears to be out of order (i.e., Si2-Cy > Si4-Cy > Si3-Cy) when compared with that in the Ku band (see Table 2). This L-band sequence may be a consequence of opposing physical factors (discussed below) or, possibly, of the ϵ measurement technique in the L-band. The apparatus used for L-band measurements mounts a 1-2 mm thick disk-shaped sample between two parallel plate electrodes under a weak spring-loaded compressive force. If this compressive force causes a slight deformation of the sample, the actual sample thickness may be very slightly less than that measured, particularly for the



Figure 8. Loss tangent dependence on frequency for siloxane-CyResin.

resin	ϕ_{Si}	$\epsilon'_{\rm Si}$ (15 GHz)	$\epsilon'_{\rm Si}$ (1 GHz)
Si2-CyResin	0.361	2.35	2.67
Si3-CyResin	0.467	2.36	2.61
Si4-CyResin	0.537	2.37	2.72
-			

 $^{a}\epsilon'_{Cy}(15 \text{ GHz}) = 2.60; \epsilon'_{Cy}(1 \text{ GHz}) = 3.00.$

most compliant member (Si4–CyResin) of this resin series. This could cause a very small positive deviation from the true measurement.

An interpretation of the data in Figure 7 is that both the magnitude of the dielectric constants and the slope of their dependence on frequency in each band are characteristic of a low- T_g amorphous material embedded with dipoles that can reorient to follow an oscillating electric field at the lower frequency. In the introduction it was hypothesized that the siloxane cyanate ester resin might be viewed as a blend of a low dielectric and soft silicone component diluting a higher dielectric and structurally rigid cyanurate component. This hypothesis may be modeled with a simple but crude rule-ofmixtures calculation using the volume fractions of silicone and cyanate components as weighting factors:

$$\epsilon' = \phi_{\text{DMS}} \epsilon'_{\text{DMS}} + \phi_{\text{Cy}} \epsilon'_{\text{Cy}} \text{ or} \phi_{\text{DMS}} = (\epsilon'_{\text{Cy}} - \epsilon')/(\epsilon'_{\text{Cy}} - \epsilon'_{\text{DMS}})$$

where ϵ' is the observed dielectric constant, ϕ_{DMS} is the silicone volume fraction, ϵ'_{DMS} is the dielectric constant associated with the silicone component, ϕ_{Cy} is the cyanurate volume fraction, and ϵ'_{Cy} is the dielectric constant associated with the cyanurate component. Values of ϵ'_{DMS} for each member of the siloxane cyanate resin series may be calculated by making use of the volume fraction data in Table 2 and reasonable approximations for ϵ'_{Cy} (3.00/1GHz and 2.60/15GHz) from data on a series of hydrocarbon cyanate ester resins.²⁶ The results of this calculation are presented in Table 3. In the 15 and 1 GHz ranges this ϵ'_{DMS} parameter is in reasonable agreement with that reported in the

literature for low molecular weight PDMS oligomers.^{27–31} For a series of poly(dimethylsiloxane) compounds, Dasgupta and Smyth²⁹ reported dielectric constants at 3 GHz of 2.39, 2.45, and 2.54 for a PDMS series of 2, 3, and 5 dimethylsiloxane units, respectively, at 25 °C. These 3 GHz values for short DMS chain structures are intermediate between the 1 and 15 GHz values calculated for the resin substructures in Table 3. The 3 GHz dielectric constants have a larger dependence on PDMS oligomer chain length and progress in a different direction than those for the resin structural analogues. This is reasonable in that the PDMS oligomer is an unconstrained liquid with a much larger free volume per oligomer that decreases with chain length. The dimethylsiloxane substructures of the resin are constrained to a thermoset network, and the cross-link density effects could operate on the dielectric constant in the opposite direction.

In Table 2, the 1 GHz ϵ' data appear to pass through a minimum with increasing DMS chain length. While this could be a consequence of the measurement technique as described above, we think a more probable explanation is that this result is a consequence of opposing physical factors that correlate with increasing DMS chain length; the dilution of the cyanurate structure and the decreasing cross-link density. The dipole associated with the cyanurate structure is most able to reorient at the lowest cross-link density and lowest frequency. Thus, in the siloxane cyanate resin series the high concentration of cyanurate structures is the larger ϵ' contributor for the Si2–CyResin member, and the low cross-link density (high dipole mobility) is the larger ϵ' contributor for the Si4–CyResin member.

The loss tangent dependence on frequency for the siloxane cyanate resin in the L- and K_{u} -bands is displayed in Figure 8. Some of the scatter reflects the 0.001 resolution limit of the apparatus. The polyethylene control is flat across both bands, and the siloxane cyanate resin series exhibits a regular increase with increasing siloxane chain length. This correlates well with an increasing energy loss to molecular relaxation

with decreasing cross-link density. The low magnitude of the loss tangent, especially for Si2-Cy and Si3-Cy, is exceptional for thermoset resins in general³² and relatively good cyanate ester resins in particular.² The low-energy loss associated with PDMS conformational transitions and consequent low dielectric loss factor over a very wide range of frequencies are unique to this structure.^{1,28} For thermoset resins, incorporation of a small amount of this PDMS structure is a unique and useful way of depressing the T_g without significantly elevating the loss factor.

Summary

A series of dimethylsiloxane oligomer linked cyanate ester monomers have been synthesized and characterized. These monomers are transformed into to corresponding to thermoset resins by conversion of cyanate ester functional group to a cyanurate heterocycle linkage. Phase separation does not occur during the curing reaction. The incorporation 2, 3, and 4 DMS units results in a large depression of the glass transition (15 to -43 °C). The dielectric constant of the resin series displays a strong dependence on frequency and small dependence on siloxane chain length which correlates with siloxane composition. The loss tangent of the resin series increases with siloxane chain length, is moderately frequency dependent, and is relatively small for a low- $T_{\rm g}$ thermoset resin.

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