

# Polyimides Synthesized from Siloxane-Equilibrated 1,3-Bis(3,4-Dicarboxyphenyl)-1,1,3,3-Tetramethyldisiloxane Dianhydride

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## SYNOPSIS

Silicone polyimides were made with siloxane-equilibrated 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldisiloxane dianhydride (PADS) as the soft portion and [(1-methylethylidene)bis(4,1-phenyleneoxy)]bis-1,3-isobenzofurandione (BPADA) as the hard portion in combination with either *para* or *meta*-phenylene diamine. The silicone polyimides were made with varying siloxane chain lengths and with varying overall weight percent silicone. There were linear correlations between these variables and flexural modulus, percent elongation at break, and cut-through temperature. Glass transition temperatures were evaluated by dynamic mechanical analysis and the thermal stabilities were determined to be greater than 400°C by thermal gravimetric analysis. Melt viscosities were determined on the various copolymers and demonstrated a correlation between type of amine used, siloxane chain length, and overall weight percent silicone.

## INTRODUCTION

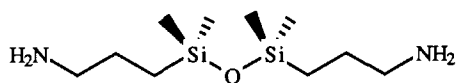
Since the first written report of a silicone polyimide synthesis two decades ago,<sup>1</sup> this class of polymers has been thoroughly investigated. This combination of silicones and polyimides provides properties frequently required for applications in adhesives, wire coating, encapsulants, packaging films, biocompatible devices, etc. Polyimides furnish high-temperature capabilities as well as solvent resistance, strength, and hardness. Silicones impart a degree of flexibility and elasticity and improve the processing conditions.

Originally, workers incorporated the siloxanes into the polyimide by employing siloxane-containing diamines. The most popular of these was 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (Fig. 1). Polymers were made by reacting this monomer with a variety of aromatic dianhydrides.<sup>2</sup>

Extensions of this study included the synthesis of copolymers, both random<sup>3</sup> and block,<sup>4</sup> and the

use of siloxane-containing dianhydrides as the source of the silicone. Greber first reported this by the use of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane as the flexible unit in silicone polyimides.<sup>5</sup> Babu reported on the synthesis of 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldisiloxane dianhydride (Fig. 2;  $x = 1$ ), known as PADS for Phthalic Anhydride DiSiloxane, and 1,5-bis(3,4-dicarboxyphenyl)-1,1,3,3,5,5-hexamethyltrisiloxane dianhydride (Fig. 2;  $x = 2$ ), and the polymers made therefrom with 3,3'- and 4,4'-bis(aminophenyl)methane.<sup>6</sup> Recently, Rich described a novel method for the synthesis of PADS via the palladium-catalyzed silylative decarbonylation reaction of trimellitic acid anhydride chloride and 1,2-dichloro-1,1,2,2-tetramethyldisilane.<sup>7</sup> New polymers synthesized from PADS and various aromatic diamines have been described.<sup>8</sup>

The silicone polyimide copolymers made from siloxane-equilibrated PADS (average  $x \geq 10$ ), [(1-methylethylidene)bis(4,1-phenyleneoxy)]bis-1,3-isobenzofurandione (BPADA), and diamminobenzene (*meta*, mPD and *para*, pPD) are described in this report. These polymers display a wide range of flexibility, elasticity, solvent resistance, and thermal



**Figure 1** 1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyl-disiloxane.

properties depending on the value of  $x$ , the mole ratio of BPADA to PADS, and the type of diamine used.

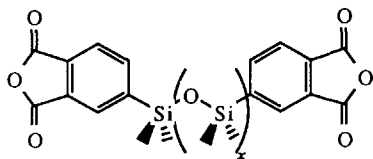
## EXPERIMENTAL

### Materials

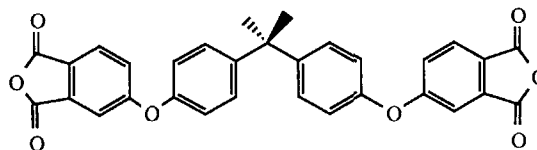
PADS was obtained from Jonathan Rich of GE, Corp. Res. & Dev. Center and had been made as described.<sup>7</sup> It was recrystallized from toluene (mp = 134.5–136.5°C). 1,1,3,3,5,5,7,7-Octamethylcyclotetrasiloxane (OMCTS) was obtained from GE Silicone Products, Waterford, NY, and was distilled from CaH<sub>2</sub> before use. BPADA (mp = 189–190°C) and phthalic anhydride (mp = 131–134°C) were obtained from GE, Plastics Business Group, Mt. Vernon, IN, and were used as received. *Meta*- (mPD) and *para*- (pPD) phenylene diamine were obtained from Dupont Corp. and used as received. Trifluoromethanesulfonic acid and 4-dimethylaminopyridine (DMAP) were acquired from Aldrich Chemical Co. and used without purification. *ortho*-Dichlorobenzene (oDCB) was purchased from EM Science and used without purification.

### Characterization

Molecular weights of the polymers were determined on a Waters Associates Liquid Chromatograph equipped with a Model 440 UV detector (254 nm) with CHCl<sub>3</sub> as the mobile phase. Varian TSK Mixed Bed gel permeation columns were used, and the molecular weights were compared to polystyrene stan-



**Figure 2** PADS.



**Figure 3** BPADA.

dards. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-2C and on a Perkin-Elmer DSC-7. Dynamic mechanical analysis was performed on a Rheometrics, Inc. 7700 Dynamic Spectrometer in the forced torsional mode. Rheological measurements were made using a Rheometrics Dynamic Spectrometer. Thermal gravimetric analysis was performed on a Dupont Instrument 950. Percent elongation and tensile strength determinations were performed on an Instron using 0.08- to 0.11-in diameter circular strands. One-in extensometers were used at a crosshead speed of 1 in/min. Flexural moduli were also measured on the Instron using compression molded bars (5.5 × 0.5 × 0.125 in.). A three-point flexure method in the tension mode was used at a crosshead speed of 0.57 in/min. The cut-through analyses were performed on films on a device modeled after those used in the wire and cable industry.

The silicone polyimide powders (~3 g) were preheated (260–320°C) in the barrel of the Tinius-Olsen Extrusion Plastometer for 10 min and then extruded by the application of a weight (6.6 or 16.6 kg). The melt index was determined by weighing samples collected over a known period of time. The strands were also used for determination of mechanical properties on the Instron.

For compression molding, the silicone polyimide powders (~0.5 g) were predried *in vacuo* at 150°C and placed between two Teflon-coated aluminum sheets and heated at 290°C in a Carver Press with platens touching for 1 min. Pressure was then applied (5,000 psi) for 1 min.

The silicone polyimide powders were placed either in an open mold or a closed mold of proper dimensions (5.5 × 0.5 × 0.125 in.) for flexural modulus or UL-94 and 6 × 6 × 0.625 in. for smoke density by OSU. (Teflon-coated aluminum sheets were always used with the open mold). They were then heated at 290–315°C in a Pasadena Hydraulic Instrument for 2 min with platens touching, then at 2 tons of pressure for 2 min, and finally at 10 tons of pressure for 6 min. This process was followed by 10 tons of pressure on a Pasadena Hydraulic Instrument cold press for 6 min or until comfortable to the touch.

**Table I Weight and Mole Ratios Needed to Obtain  $D$  Values**

$D_x$ Value	PADS	OMCTS	Triflic Acid	MgO
10	213.26 g	367.0 g	75 $\mu$ L	0.34 g
	0.50 mol	1.24 mol	0.484 mmol	8.48 mmol
16	213.26 g	592.2 g	75 $\mu$ L	0.34 g
	0.50 mol	2.00 mol	0.848 mmol	8.48 mmol
22	213.26 g	864.3 g	75 $\mu$ L	0.34 g
	0.50 mol	2.92 mol	0.848 mmol	8.48 mmol

### Monomer Synthesis

#### Equilibration of PADS with OMCTS

PADS was added in 10 aliquots to a mixture of octamethylcyclotetrasiloxane (OMCTS) and trifluoromethanesulfonic acid preheated to 140°C under nitrogen. After the additions were complete, the reaction mixture was stirred at 130–140°C for 3 h. Before cooling, MgO was added to neutralize the acid and the reaction mixture was allowed to cool to room temperature. The insolubles were removed with hardened filter paper, aided by the addition of dichloromethane. The dichloromethane was removed *in vacuo* at room temperature and the excess OMCTS and other cyclics were removed *in vacuo* at 140°C. Phthalic anhydride by-product (from protodesilylation) was removed simultaneously by sublimation into the condenser. The viscous product was cooled to ~70°C to avoid solidification of the lower homologs in the mixture and held there until use. A titration was performed to determine the anhydride equivalence per gram of equilibrate for use in the polymerization.<sup>9</sup> An FTIR analysis of the product revealed absorbances at 2,965, 1,855 (anhydride), 1,783 (anhydride), 1,261 (siloxane), 1,092, 1,023 and 800  $\text{cm}^{-1}$ . In fact, the ratio of absorbances

at 1,261/1,783  $\text{cm}^{-1}$  could be used to corroborate the results of the titration. (See Table I.)

### Polymer Synthesis

#### BPADA and Equilibrated PADS with Phenylene Diamines

*Para*- and/or *meta*-phenylene diamine (43.2 g, 0.3993 mol) and oDCB (500 mL) were combined in a 3-L three-necked flask equipped with a nitrogen bubbler, a Dean-Stark trap with a condenser, and a mechanical stirrer. The flask and contents were heated to 100°C when the solution was homogeneous.  $D_{16}$  equilibrated PADS (219.1 g, 0.1426 mol) was added with oDCB (500 mL) and heating was increased. After the reaction became homogeneous, BPADA (137.8 g, 0.2648 mol), phthalic anhydride (PA) (2.4 g, 0.016 mol), and dimethylaminopyridine (DMAP) (2.0 g, 0.017 mol) were added with oDCB (650 mL). Water began collecting in the Dean-Stark trap along with some oDCB at this temperature (pot 120–130°C; oil bath 145°C). The stoichiometric quantity of water was never collected in the trap but additional water was always seen in the apparatus. The oil bath was heated to 210°C, and over the next hour oDCB was collected in the trap until reaching a total removal of 690 mL. The purpose of this removal of oDCB was to both allow for complete drying and to increase the reaction concentration from ~24–~40% (wt/vol).

The oil bath temperature was reduced to 190°C and the reaction mixture stirred for 6–8 h. After the mixture cooled to 80°C,  $\text{CHCl}_3$  (700 mL) was added slowly. The solution was further cooled to room temperature and the polymer was precipitated into a blender of methanol (3,000 mL), filtered, washed with fresh methanol, and redissolved in  $\text{CHCl}_3$  (2,000 mL). The precipitation process was repeated. The off-white polymer was dried in a baking dish lined with Teflon-coated foil *in vacuo* at 150°C for

**Table II Sample Formulations**

Wt % Silicone	$D$ Value	EqPADS	BPADA	pPD or mPD	PA	DMAP
40	10	219.1 g	118.9 g	47.7 g	3.6 g	2.0 g
		200.5 mmol	228.4 mmol	441.0 mmol	24.2 mmol	17 mmol
45	16	219.1 g	137.8 g	43.2 g	2.4 g	2.0 g
		142.6 mmol	264.8 mmol	399.3 mmol	16.2 mmol	17 mmol
60	22	219.1 g	61.7 g	24.3 g	1.5 g	1.0 g
		110.6 mmol	118.5 mmol	224.7 mmol	10.2 mmol	9 mmol

6–15 h and then at 180°C for 2–3 h. FTIR analysis of the polymer as a solvent-cast film showed absorbances at 2,976, 1,786, 1,734, 1,367, 1,271, 1,099, 1,032, and 808  $\text{cm}^{-1}$ . (See Table II.)

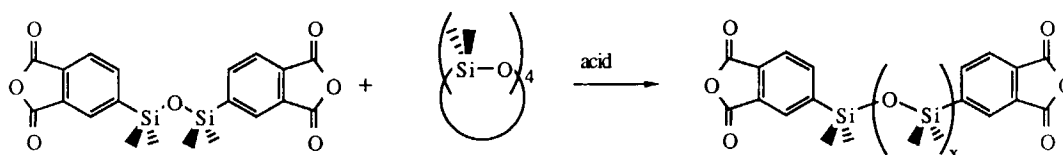
## RESULTS AND DISCUSSION

One purpose of this study was to determine the effect of the amount of silicone in the polymer on the physical and mechanical properties. Two ways of changing this value were used: Modify the number of siloxane units in the equilibrated PADS ( $D_x$  value) and vary the ratio of equilibrated PADS to

BPADA. Polymers were systematically made using the combinations of these two factors that would determine trends in this class of polymers.

### Monomer Synthesis

The acid-catalyzed ring-opening equilibration of OMCTS with PADS was utilized to furnish siloxane-equilibrated PADS of various siloxane lengths. After quenching the reaction, excess unreacted cyclics were removed by distillation. The molecular weights of these equilibrates were determined by anhydride titration.<sup>9</sup> For simplicity, these monomers were denoted as  $D_x$ -PADS, with  $x$  being the average number of siloxane groups in the monomer.

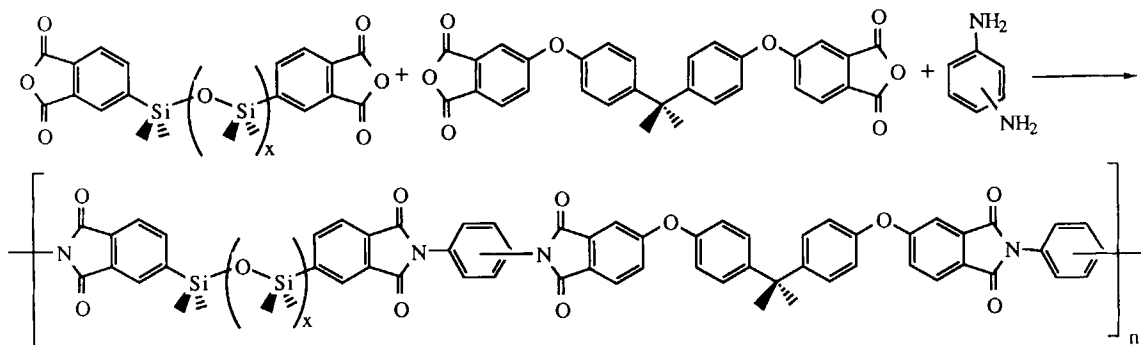


Scheme 1

### Polymer Synthesis

The polymerizations were performed in *ortho*-dichlorobenzene solutions with constant removal of water. The monomers were used in varying ratios with BPADA to provide copolymers with mPD or

pPD. In addition, terpolymers were made using both diamines at various ratios. Different levels of phthalic anhydride, a chain stopper, were used to furnish polymers of different molecular weights. The results of these polymerizations are compiled in Tables III–V.



Scheme 2

### Polymer Properties

#### Mechanical Properties

1. *Flexural modulus.* Figure 4 and 5 indicate that the flexibility was increased with higher weight % silicone and decreased with a decrease in the length of the siloxane chains. Thus, the silicone polyimides made with

$D_{20}$ PADS (polymers 10–13) were quite flexible regardless of the amount of silicone, but for  $D_{10}$ PADS (polymers 1–5) the material became stiff below 50 wt % silicone. The replacement of pPD with mPD had little effect on the flexibility.

2. *Percent elongation and tensile strength.* All the silicone polyimides were analyzed for their elasticity. They all exhibited plastic de-

**Table III Silicone Copolyimides Containing Equilibrated PADS, BPADA, and pPD**

Polymer	$D_x$	Mol % EqPADS	Wt % SiO <sup>a</sup>	$[\eta]^b$	Flexural Modulus <sup>c</sup>	Tensile Strength <sup>c</sup>	% Elongation at Break	Solubility <sup>d</sup>	CTT <sup>e</sup>
1	10	47	40	0.68	123,100	3,516	111		
2	10	51	44			1,684	198	Fully	137
3	10	70	50	1.24	48,000	1,550	200	Fully	110
4	10	89	60			846	377		68
5	11	59	50	0.65		2,206	274	Fully	90
6	16	35	44	0.67	65,500	3,063	90	Partially	147
7	16	39	46	0.60	47,122	2,227	100	Partially	123
8	16	45	50	0.66	29,800	1,640	107	Partially	141
9	16	63	60	0.62		1,850	442	Fully	85
10	22	24	40	0.37	53,000	2,600	37	Slightly	
11	22	33	50	0.62	20,500	1,171	50	Slightly	
12	22	48	60	0.46	4,100	1,250	140	Fully	83
13	22	68	70	0.66	360	443	218	Fully	

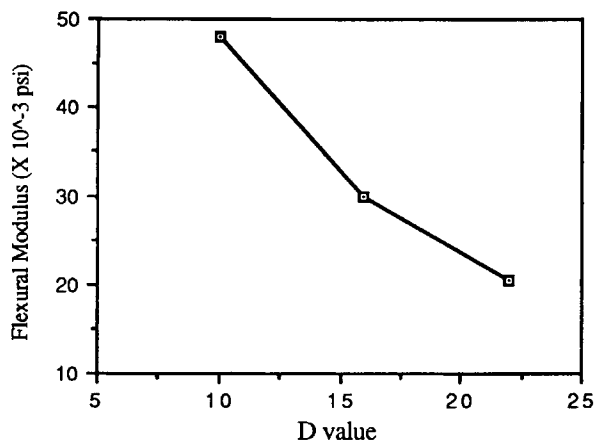
<sup>a</sup> Overall weight percent silicone in the polymer.<sup>b</sup> dL/g, measured as a 1% solution in CHCl<sub>3</sub>.<sup>c</sup> Psi.<sup>d</sup> Solubility in CHCl<sub>3</sub> (fully > partially > slightly) at 1% conc.<sup>e</sup> (°C) Cut-through temperature (median of 5-7 values).**Table IV Silicone Copolyimides Containing Equilibrated PADS, BPADA, and mPD**

Polymer	$D_x$	Mol % EqPADS	Wt % SiO <sup>a</sup>	$[\eta]^b$	Flexural Modulus <sup>c</sup>	Tensile Strength <sup>c</sup>	% Elongation at Break	CTT <sup>d</sup>
14	10	51	44	0.49		3,181	154	128
15	16	12	20	0.50		6,260	6	> 210
16	16	35	44	0.52	65,500	3,427	138	146
17	20	29	44	0.62		2,964	107	157

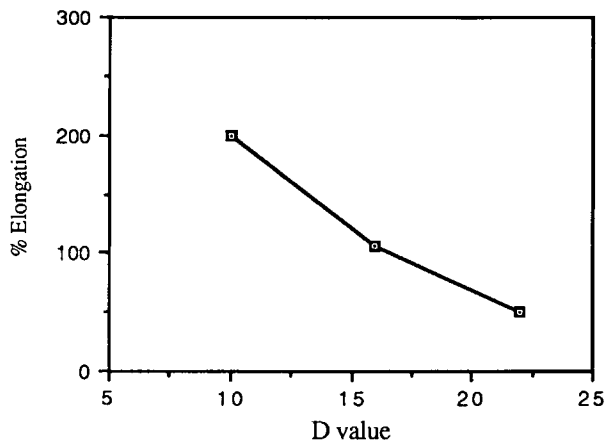
<sup>a</sup> Overall weight percent silicone in the polymer.<sup>b</sup> dL/g, measured as a 1% solution in CHCl<sub>3</sub>.<sup>c</sup> Psi.<sup>d</sup> (°C) Cut-through temperature (median of 5-7 values).**Table V Silicone Terpolyimides Containing Equilibrated PADS, BPADA, pPD, and mPD**

Polymer	$D_x$	Mol % EqPADS	Wt % SiO <sup>a</sup>	pPD/mPD	$[\eta]^b$	Tensile Strength <sup>c</sup>	% Elongation at Break	CTT <sup>d</sup>
18	16	35	44	25/75	0.49	3,389	125	141
19	16	35	44	35/65	0.45	3,322	134	157
20	16	35	44	50/50	0.55	3,323	134	155

<sup>a</sup> Overall weight percent silicone in the polymer.<sup>b</sup> dL/g, measured as a 1% solution in CHCl<sub>3</sub>.<sup>c</sup> Psi.<sup>d</sup> (°C) Cut-through temperature (median of 5-7 values).



**Figure 4** Flexural modulus versus  $D$  value at a constant wt % silicone.



**Figure 6** Percentage elongation versus  $D$  value at a constant wt % silicone.

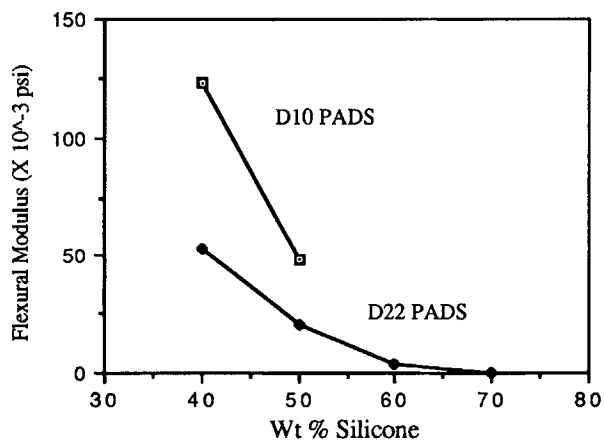
formation; the values are listed in the Tables III-V. As shown in Figures 6 and 7, percent elongation at break increased proportionally with weight percent silicone at a constant  $D$ -value and inversely with  $D$  length at a constant weight percent silicone. For example, 200% elongation could be achieved with lower mole percent of EqPADS if a lower  $D_x$  was used (i.e., polymer 3 vs. 13). Replacement of the pPD with mPD did not affect the elasticity to any extent. The tensile strengths of all the polymers were greater than 2,000 psi, and this property increased inversely with weight percent silicone. As anticipated, the polymers were stronger with a higher mole percent of the more rigid monomer (BPADA).

### Solubility

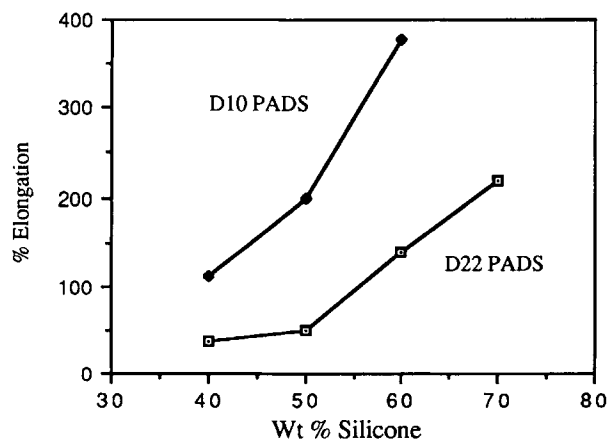
These silicone polyimides were insoluble in most common organic solvents, although chlorinated hydrocarbons, particularly chloroform, were especially aggressive toward these resins. The solubility study consisted primarily of testing the material in a one percent solution in chloroform and determining whether it was fully, partially, or slightly soluble. At a given  $D_x$ , polymers with lower amount of silicone were the least soluble. The materials containing mPD were all totally soluble in  $\text{CHCl}_3$ .

### Thermal Properties

1. *Thermal gravimetric analysis.* Isothermal analysis of polymer 3 at 300°C showed only



**Figure 5** Flexural modulus versus wt % silicone at a constant  $D$  value.



**Figure 7** Percentage elongation versus wt % silicone at a constant  $D$  value.

**Table VI Thermogravimetric Analysis**

Polymer	$D_x$	Wt % Sil	Amine	N <sub>2</sub> <sup>a</sup>		Air <sup>a</sup>	
				5/10/50 <sup>b</sup>	5/10/50 <sup>b</sup>	5/10/50 <sup>b</sup>	5/10/50 <sup>b</sup>
2	10	44	100% pPD	465/495/625		440/460/640	
6	16	44	100% pPD	460/480/540		440/460/615	
9	16	60	100% pPD	450/480/535		430/450/620	
15	16	20	100% mPD	500/520/700		470/510/615	
16	16	44	100% mPD	495/510/550		470/495/590	
19	16	44	65% mPD/35% pPD	450/485/550		440/460/625	

<sup>a</sup> 20°C/min heating rate.

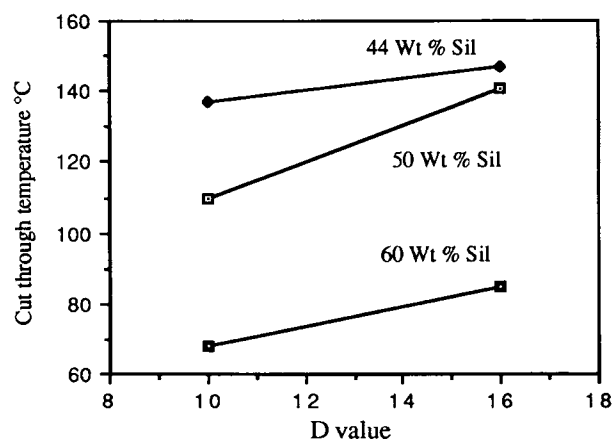
<sup>b</sup> Temperature at which 5, 10, and 50% weight losses occurred.

1.9 and 5.1% weight loss after 4 and 16 h, respectively. Table VI shows the results of the dynamic TGAs for various samples when heated at 20°C/min. Most of the samples lost 5 and 10% of their weight at approximately the same temperatures—460 and 490°C (nitrogen) and 440 and 460°C (air), respectively. Polymer 15 displayed a slightly higher thermal stability, probably due to the lower amount of silicone in the polymer. For the same reason, polymer 9, with 60 wt % silicone, lost weight at slightly lower temperatures than the others.

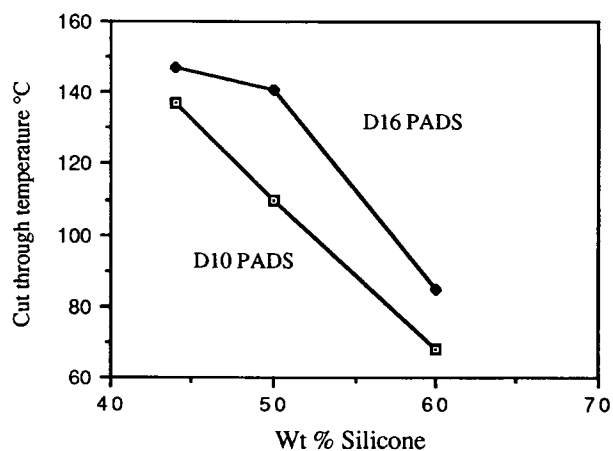
2. *Cut-through temperatures (CTT)*. Designed after a test used in the wire and cable business,<sup>10</sup> this test was used to determine the temperature at which polymer films placed between two stainless steel wires under a 1-kg load softened enough to form an electrical connection between the two wires. This test was more reliable for these polymers than the traditional methods of thermal transition

analysis and seemed to correlate well with the DMA data. The results of this analysis are compiled in Tables III–V and depicted in Figure 8 and 9. It was determined from these data that for a given weight percent silicone the CTT increased as the number of siloxane units increased, and at a constant  $D$  value the CTT varied inversely with the weight percent silicone. Replacement of the pPD with mPD did not have a major effect on the CTT.

3. *Glass transition temperatures*. The polymers were analyzed by differential scanning calorimetry. There were no apparent melting transitions, and it was also difficult to assign glass transition temperatures. The usefulness of thermal mechanical analysis was also never realized. However, when analyzed by dynamic mechanical analysis (DMA) in the torsional mode at a heating rate of 2°C/min, polymer 8 exhibited transitions consistent with  $T_g$ s at -114 and 146°C. Polymers 6 and 9 had glass



**Figure 8** CTT versus  $D$  value at a constant wt % silicone.



**Figure 9** CTT versus wt % silicone at a constant  $D$  value.

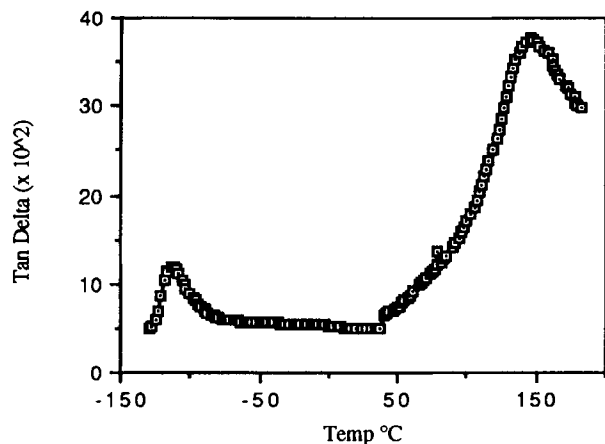


Figure 10 Dynamic mechanical analysis of Polymer 8.

transition temperatures by DMA of 149 and 82°C, respectively. A plot of  $\tan \delta$  vs. temperature for polymer 8 is shown in Figure 10.

### Melt Properties

Two melt flow properties of these polymers were evaluated. The melt flow was determined by measuring the rate at which the molten polymer extruded through a die at a given temperature and pressure. The melt viscosity was measured using a dynamic spectrometer with the parallel plate method and the rate sweep mode. The results are reported in poise.

1. *Molecular weight.* Polymers were made with varying levels of phthalic anhydride as a chain stopper to show the effect on melt properties. Table VII displays the results of this study. It was obvious from this experiment that lowering the molecular weight had a profound effect on both melt flow and viscosity. The flow data indicated that polymers

of higher molecular weight did not extrude as well as those with shorter chains, even at higher temperatures. Melt viscosity measurements showed a dramatic difference in viscosity between the material with high IV (19a) and the polymers of lower molecular weights (19b and 19c).

2. *Type of diamine,  $D_x$ , and weight percent silicone.* Comparing polymers having similar intrinsic viscosities, it was found that melt viscosity decreased by increasing the amount of mPD (polymers 6, 19c, and 16c) in the polymer. At a constant  $D_x$ , increasing the level of silicone (polymers 15 and 16b) lowered the viscosity, and at a constant weight percent silicone a smaller  $D_x$  value (polymers 2 and 16b) had a lower viscosity. (See Table VIII.)

### CONCLUSIONS

High molecular weight silicone-imide copolymers are obtained from BPADA and equilibrated PADS with *para*- and/or *meta*-phenylene diamine. A diverse series of polymers can be made depending on the ratio of equilibrated PADS to BPADA and the  $D$ -value. The overall weight % silicone in the polymer has a profound effect on the mechanical, thermal, and processing properties of these polymers and, therefore, polymers with a desired combination of properties can be obtained.

Flexural moduli range from 360–123,000 psi, and percent elongation from 37–442%. The polymers are thermally stable and have a variety of upper use temperatures. The polymers are insoluble in most common organic solvents and the processing conditions are quite good.

Table VII Effect of Molecular Weight on Melt Flow and Melt Viscosity

Polymer	%CS <sup>a</sup>	$[\eta]^b$	$M_w/M_n^c$	Melt Flow (temp) <sup>d</sup>	Melt Viscosity (temp) <sup>e</sup>
19a	2.0	0.67	77060/29500	0.75 (290°C)	42,900 (270°C)
19b	3.0	0.48	54600/20700	1.24 (270°C)	26,300 (270°C)
19c	3.5	0.43	40950/17700	1.38 (260°C)	22,200 (270°C)

<sup>a</sup> % chain stopper (phthalic anhydride).

<sup>b</sup> dL/g, measured as a 1% solution in CHCl<sub>3</sub>.

<sup>c</sup> Molecular weights as measured by GPC in CHCl<sub>3</sub>.

<sup>d</sup> Measured with 16.6 kg weight (g/min).

<sup>e</sup> Values are in poise.



**Table VIII Effect of Type of Diamine,  $D_x$ , and Weight % Silicone on Melt Viscosity**

Polymer	Wt % SiO <sup>a</sup>	$D_x$	$[\eta]^b$	Amine <sup>c</sup>	Melt Viscosity <sup>d</sup>
6	44	16	0.44	100% pPD	32,000 poise
19c	44	16	0.43	65% mPD/35% pPD	22,200 poise
16a	44	16	0.44	100% mPD	17,100 poise
2	44	10	0.49	100% mPD	9,800 poise
15	20	16	0.50	100% mPD	98,300 poise
16b	44	16	0.52	100% mPD	36,600 poise
18	44	16	0.49	75% mPD/25% pPD	31,600 poise
19b	44	16	0.48	65% mPD/35% pPD	26,300 poise

<sup>a</sup> Overall weight percent silicone.

<sup>b</sup> dL/g, measured as a 1% solution in CHCl<sub>3</sub>.

<sup>c</sup> mPD, meta-phenylene diamine; pPD, para-phenylene diamine.

<sup>d</sup> Viscosities measured at 270°C.

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