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Formulation/Cure Technology for Ultra-High Molecular Weight Silphenylene-Siloxane Polymers

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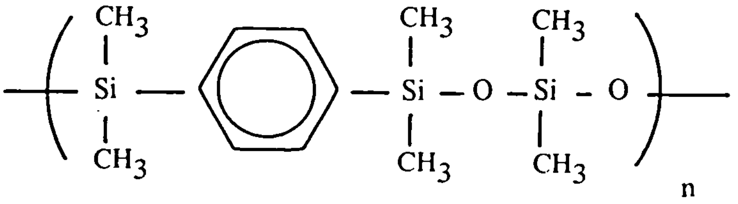
TECHNICAL PAPER

FORMULATION/CURE TECHNOLOGY FOR ULTRA-HIGH MOLECULAR WEIGHT SILPHENYLENE-SILOXANE POLYMERS

I. INTRODUCTION

In the aerospace community a critical need exists for elastomers capable of performing in extreme thermal/oxidative environments. Desirable characteristics for these elastomers include long-term thermal, hydrolytic and oxidative stability, coupled with retention of mechanical properties. A group of elastomers which exhibit some promise in this area are silicone polymers, with their inherent thermal/oxidative stability. One class of silicone polymers, aryl-modified siloxane polymers, designated as silphenylene-siloxane (SPS) polymers, have been the subject of extensive research in this laboratory [1-4]:



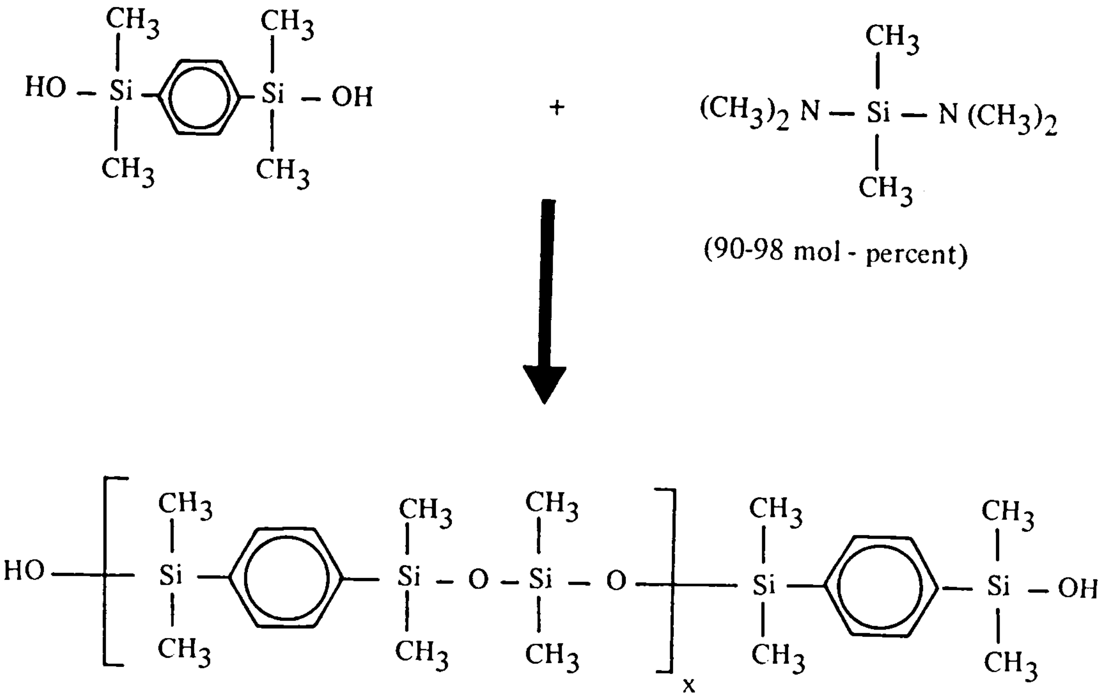
(Polysilphenylene-siloxane)

This class of polymers has historically been characterized by poor mechanical properties but recent studies [5] with an analogous carborane-siloxane system indicated that, at molecular weights approaching 10^6, improvements were obtained in mechanical properties and thermal stability. These improvements were attributed to increased entanglement of the polymer chains occurring at the very high molecular weights. Subsequent research in this laboratory, utilizing a modification of Stewart's multistep polymerization technique [5], produced SPS polymers with molecular weights above 10^6 [4]. These polymers exhibited good thermal stability but could not be easily vulcanized.

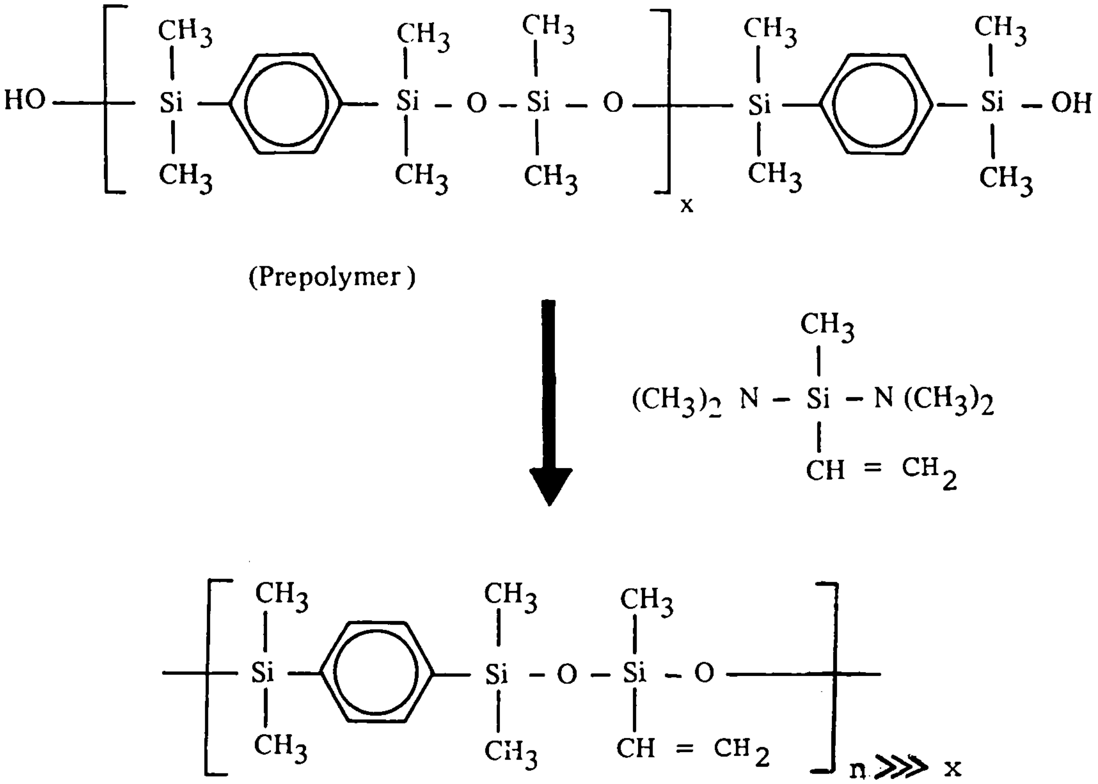
As a continuation of that effort, the current research had three objectives: first, to synthesize a terpolymer with a vinyl moiety which would be more amenable to conventional silicone processing technology yet would still possess the improved molecular weight; second, to produce the terpolymer in lots exceeding 100 grams while retaining molecular weights above 10^6; and third, to investigate the formulation/cure characteristics of this material.

II. POLYMER DEVELOPMENT

Previous research had shown that Stewart's multi-stage polymerization technique could be utilized to produce SPS polymers with molecular weights in excess of 10^6. This technique involved the initial formation of a silanol-terminated prepolymer, using 90 to 98 percent of the aminosilane stoichiometric equivalence, by the following reaction scheme:



In the current research, this prepolymer was isolated and purified by precipitation, then chain-extended to higher molecular weights by incremental addition of aminosilane utilizing the following scheme:



Incorporation of the vinyl group randomly along the polymer chain provided cure sites for subsequent conversion to a crosslinked elastomer.

III. EXPERIMENTAL

A. Materials

Toluene (Fisher Scientific) was distilled from calcium hydride under a nitrogen atmosphere and stored over molecular sieves until used. Tetrahydrofuran (Burdick and Jackson), methanol and methylene chloride (Fisher Scientific) were used without further purification. Nuclear Magnetic Resonance (NMR) spectra were obtained on a Varian 360L. The purity of 1,4-bis(hydroxydimethylsilyl)benzene (Polysciences and Silar Laboratories) was checked by gel permeation chromatography on 100 Å ultraStyragel columns, with tetrahydrofuran as the mobile phase. The white crystals melted at 135 to 136°C and exhibited the following NMR spectrum: 0.067 (s, 12, Si-CH_3); 3.41 (s, 2, Si-OH); 7.36 (s, 4, phenyl ring hydrogens) in deuterated acetonitrile (Aldrich Chemical) with methylene chloride as reference. A gas chromatographic column packed with 3 percent OV17 on 80/100 Chromosorb W was used to check the purity of bis(dimethylamino)dimethylsilane (Silar Laboratories) and bis(dimethylamino)methylvinylsilane (Silar) which were used without further purification. The bis(dimethyl-amino)dimethylsilane produced the following NMR spectrum: 0.08 (s, 1, Si-CH_3); 2.38 (s, 2, N-CH_3) in deuterated acetonitrile with methylene chloride as reference.

B. Prepolymers

For the large scale prepolymer synthesis, 1,4-bis(hydroxydimethylsilyl)benzene (195.95 g, 0.861 mol) was placed in a weighed three-necked, 2-L round botton flask and dried overnight in a vacuum oven at 50°C. The flask was reweighed, fitted with a thermomenter, a mechanical stirrer, and a two-outlet adapter supporting a reflux condenser and a septum-sealed opening. After the system had been purged with nitrogen, dry toluene (600 mL) was added, a positive nitrogen pressure was established and the reaction mixture was slowly heated to a gentle reflux (95 to 105°C). Under a nitrogen atmosphere, approximately 15 grams of bis(dimethylamino)dimethylsilane was withdrawn into a dried, preweighed, air-tight syringe and injected through the septum into the reaction mixture. This addition was repeated eight times over a 46 hr period until 92.5 mol percent of aminosilane (116.58 g, 0.797 mol) had been added. The reaction mixture was allowed to reflux for an additional 22 hr, then was precipitated dropwise with rapid stirring in 4 L of methanol. After decanting the methanol, the product, a low viscosity gum, was dried overnight in a vacuum oven at 50°C. A yield of 210.6 g (80.6 percent based on the amount of silane used) was obtained. This product had an intrinsic viscosity of 0.572 dL/g (THF, 30.1 ± 0.1°C).

C. Polymers

In the large-scale polymer synthesis, prepolymer (204.8 g, 78.4 percent theoretical yield) was added to a 5 L three-necked flask and dried overnight in a vacuum oven at 50°C. The system was assembled as for the prepolymer synthesis and 1.7 L of dry toluene was added. Bis(dimethylamino)-methylvinylsilane (12.89 g, 0.0814 mol), an amount 1.6 times the 7.5 mol percent deficiency existing from the prepolymer synthesis, was added by the following scheme: After reflux (95 to 105°C) was established, three additions of aminosilane (2 g each) were made over a 4 hr period. The reaction mix was allowed to reflux overnight (17 hr), then three more additions of 2 grams each were made over a 7 hr period, and the mixture again refluxed overnight (17 hr). The last addition of aminosilane was then made and the reaction mixture was refluxed for a final 6 hr. Samples (0.1 mL) were withdrawn before each addition of silane, dissolved in THF and analyzed by gel permeation chromatography. When the reaction was complete, the hot solution was dripped, with rapid stirring, into 4.5 L of methanol, the methanol was decanted and the product, a rubbery gum, was dried in a vacuum oven at 50°C for two days. The yield was 195.7 g (95.5 percent of the amount of prepolymer used). This product had an intrinsic viscosity of 1.56 dL/g (THF, 30.1 ± 0.1°C).

D. Polymer Characterization

Intrinsic viscosities of both prepolymers and polymers were determined in tetrahydrofuran at 30.1 ± 0.1°C using a Cannon-Ubbelohde viscometer. Stock solutions were diluted three times.

Molecular weights and polydispersities were determined on a Waters Associates liquid chromatograph with a bank of 10^4 Å and 10^6 Å ultraSytragel columns, using tetrahydrofuran as the mobile phase and a flow rate of 1.0 mL/min. A Perkin-Elmer Sigma 15 with GPC 2S software was used for data collection as well as molecular weight and polydispersity calculations. The calibration curve was determined from the product of each standard's peak M and intrinsic viscosity. Experimental molecular weights were derived by dividing out the intrinsic viscosity. Low polydispersity polystyrene standards (Waters Associates, 3.45 x 10^4 to 1.75 x 10^6 peak M's) provided the calibration curve. These standards were mixed as a single solution and injected each day before analyzing an experimental material. This procedure, developed previously [4], guarded against day-to-day fluctuations in the chromatographic system.

E. Formulation/Cure Technology

Two formulations (Table 1) were investigated. All of the formulated rubbers were milled for 15 minutes on a micro rubber mill, left overnight, vulcanized under pressure for 20 min in a 4.25 x 4.75 x 0.054 in. preheated (338°F) mold, then removed from the mold and cured for 16 hr in a 450°F oven.

TABLE 1. FORMULATIONS

Formulation	Polymer	Santocel[a]	Super Floss[a]	Peroxide
1	25.0g	1.25g	2.50g	0.20g VAROX[b]
2	25.0g	1.25g	2.50g	0.44g DI-CUP40C[c]

a. Fumed silica fillers
b. 2,5-Dimethyl-2,5-di(t-butyl-peroxy)hexane
c. Dicumyl peroxide

F. Thermal Analysis

A DuPont 1090 Thermal Analyzer with 951 Thermogravimetric Analyzer Module was used to acquire thermogravimetric analyses (TGA) of the formulated methylvinylsilphenylene-siloxane polymer and a formulated commercial methylvinylsilicone gum. Gradient (20 deg/min, 25 to 800°C) and isothermal (400°C for 24 hr) analyses were conducted in both air and nitrogen. The analyses for the experimental elastomer (weight average molecular weight of 1.81 x 10^6) are shown in Figures 1 and 2. The glass transition temperatures for the formulated experimental elastomer (weight average molecular weight of 1.81 x 10^6) and the commercial silicone were determined with a DuPont 910 Differential Scanning Calorimeter System (Fig. 3).

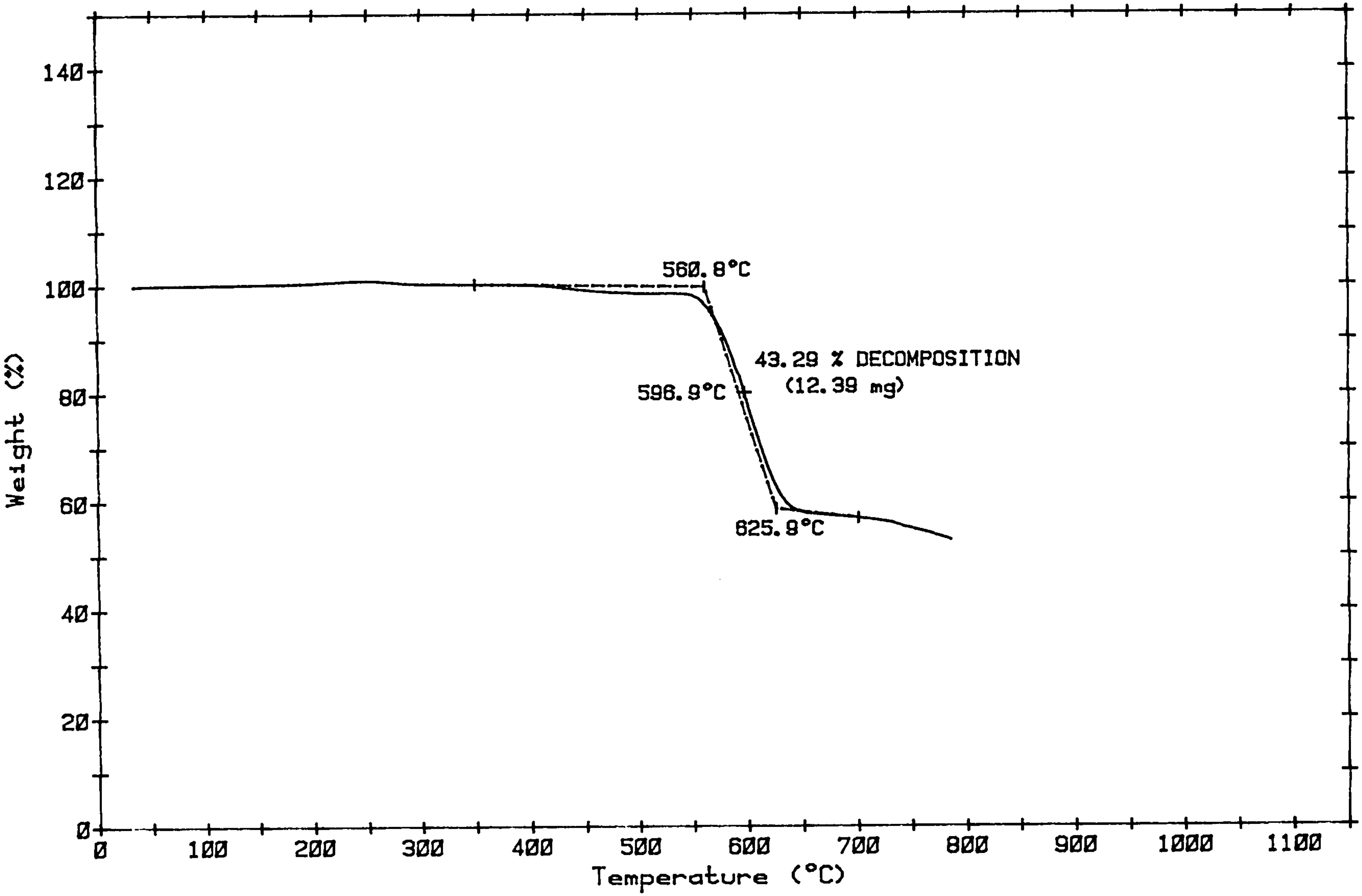


Figure 1. TGA for experimental elastomer in air.

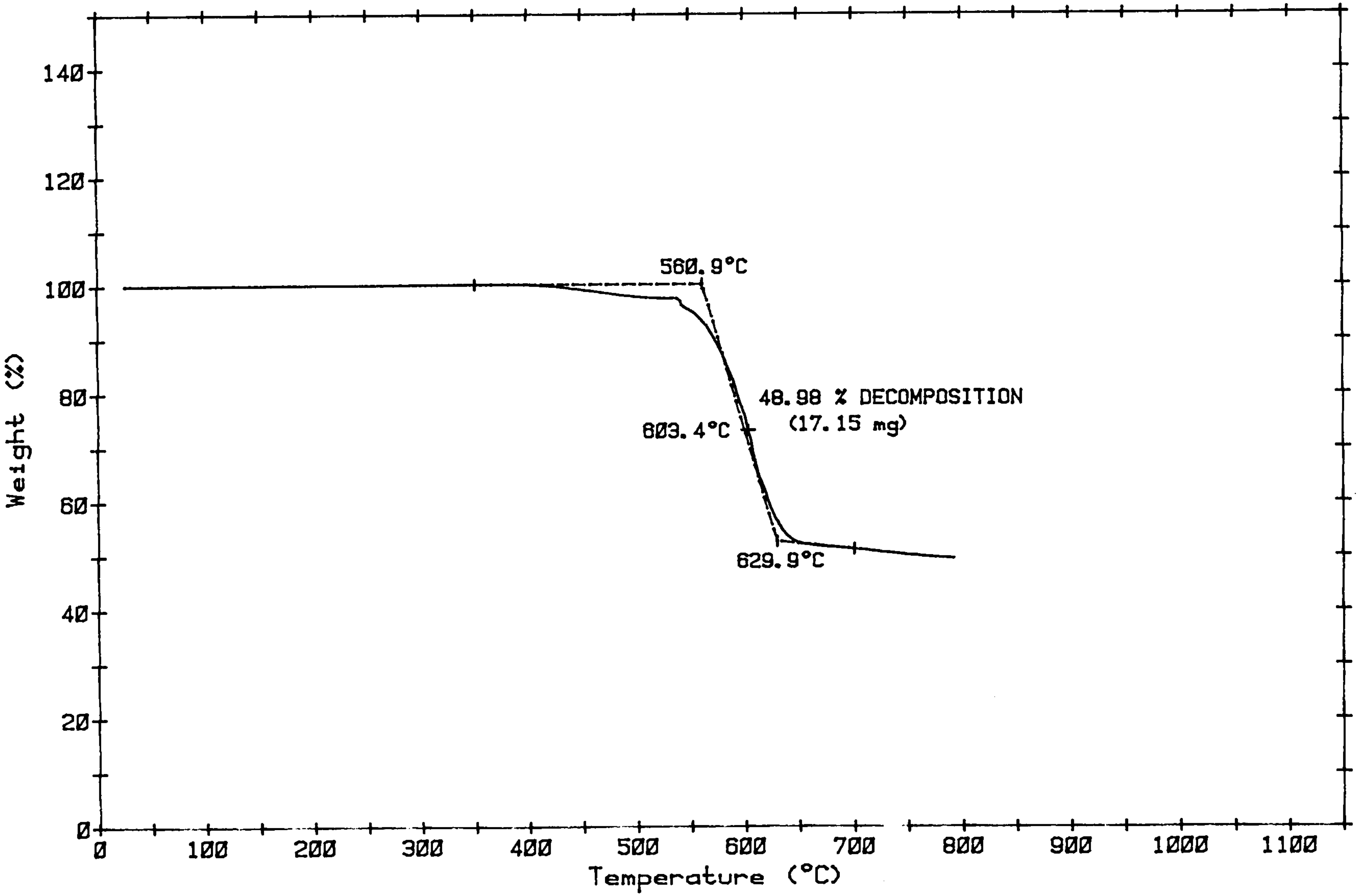


Figure 2. TGA for experimental elastomer in nitrogen.

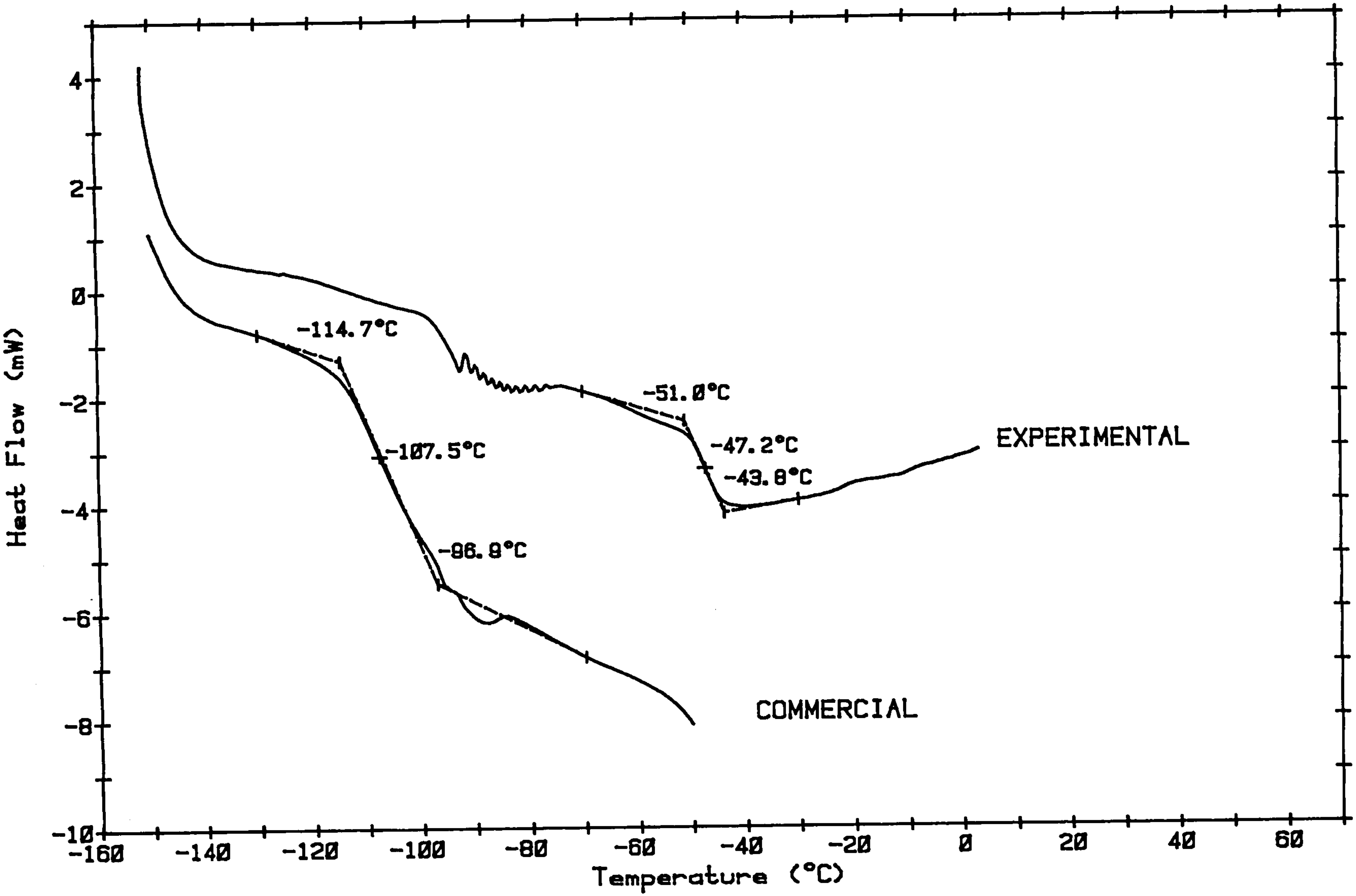


Figure 3. Comparative DSC for experimental elastomer versus commercial silicone.

G. Mechanical Analysis

All mechanical analyses were performed on an Instron 1125 Mechanical Tester. The ultimate strength, Young's modulus, and percent elongation at failure were determined for two formulations of both the experimental and the commercial materials. These properties were also assessed after 16 hr at 550°F. The tear strength of the experimental rubber and the formulated commercial gum were determined by ASTM D 624 using Die C.

IV. RESULTS AND DISCUSSION

Four different lots of the experimental methylvinylsilphenylene-siloxane with molecular weights above 9×10^5 were synthesized (Table 2) from prepolymers whose molecular weights ranged from 5.2×10^4 to 3.48×10^5. Both prepolymer and polymer were successfully synthesized in 200 gram quantities. The large-scale prepolymer synthesis resulted in higher molecular weights at lower aminosilane concentrations (92.5 mol percent) than were previously reported [4]. This was attributed to more efficient mixing provided by the mechanical stirrer, as opposed to the stirring bar which had been used for the smaller scale syntheses.

TABLE 2. PREPOLYMER/POLYMER MOLECULAR WEIGHT DATA

Prepolymers			Polymers		
Silane Mol (%)	Viscosity [η] (dL/g)	M_w[a]	Viscosity [η] (dL/g)	M_w[a]	Lot
95.1[b]	1.103	3.48×10^5	2.305	9.02×10^5	A
94.6[b]	0.244	5.20×10^4	3.244	1.23×10^6	B1
94.6[b]	0.244	5.20×10^4	2.441	9.94×10^5	B2
92.5[c]	0.572	1.64×10^5	1.559[c]	1.81×10^6	C

a. Determined by gel permeation chromatography.
b. 100 gram scale-up.
c. 200 gram scale-up.

The incorporation of the vinyl moiety along the polymer chain provided the expected crosslink sites for vulcanization, as indicated by formation of low-tack, thermoset elastomers following peroxide vulcanization. Two gum formulations were investigated. These formulations were compared on the basis of ultimate strength, Young's modulus, and percent elongation at failure (Table 3).

TABLE 3. VARIATION IN MECHANICAL PROPERTIES WITH FORMULATION

Gum	Formulation	Ultimate Strength (psi)	Young's Modulus (psi)	Elongation at Failure (%)
COMMERCIAL	1	157±3	204±4	233±29
B1	1	166±0	230±53	139±10
COMMERCIAL	2	135±13	189±42	212±31
B2	2	201±15	250±40	188±33

Formulation 3 was chosen for more extensive analysis. Utilizing this formulation, vulcanized samples of the commercial material as well as three experimental polymer lots, representing a range of prepolymer molecular weights, were compared on the basis of mechanical properties (Table 4). Prepolymer molecular weight appeared to influence the mechanical properties of the cured material; polymer A, whose prepolymer had the highest molecular weight, exhibited the lowest values for ultimate strength and Young's modulus. This effect was expected on the basis that higher molecular weight prepolymers have relatively lower reactive end-group concentrations, and incorporate fewer vinyl crosslink sites in the subsequent conversion to high polymer. Polymer A's molecular weight only increased by a factor of 2.6 during the second stage, in contrast to 11 for polymer C and 19 for polymer B2.

TABLE 4. VARIATION IN MECHANICAL PROPERTIES WITH POLYMER GUM STOCK

Gum-Formulation	Ultimate Strength (psi)	Young's Modulus (psi)	Elongation at Failure (%)	Tear Strength (lb/in.)
COMMERCIAL-2	135±13	189±42	212±31	23.1
C-2	242±21	127±23	319±17	34.6
B2-2	201±15	250±40	188±33	–
A-2	168±43	81±9	359±66	–

The data from Tables 3 and 4 demonstrate that equivalent or superior mechanical properties were achieved for the experimental elastomer as compared to the commercial material. Formulation 3 appeared to result in a higher crosslink density, as evidenced by the higher strength and modulus data. This may be an indication of a more efficient vulcanization mechanism for the dicumyl peroxide.

Further evidence of the effect of crosslink site concentration is presented in Table 5. A comparison of prepolymer molecular weights from Table 2 with resulting mechanical properties (Table 4) indicates a positive correlation with both Young's modulus and elongation. Decreasing prepolymer molecular weight (M_W) (which increases cure site and crosslink density) drives the cured elastomer to higher modulus and lower elongation. This is the expected mechanical response of a more highly crosslinked rubber. The mechanical properties did not appear to correlate with final molecular weight of the polymer gum stocks.

TABLE 5. CORRELATION OF PREPLOYMER MOLECULAR WEIGHT WITH ELASTOMER PROPERTIES

Formulation	Prepolymer M_W	Young's Modulus (psi)	Elongation (%)
A-2	3.48×10^5	81	359
C-2	1.64×10^5	127	319
B2-2	5.20×10^4	250	188

The relative thermal/oxidative stability of the vulcanized experimental and commercial materials were assessed by thermogravimetric analysis. The superior thermal/oxidative stability of the experimental material is clearly demonstrated in Figures 4 and 5. This enhanced stability was further illustrated by isothermal exposure at 400°C (Figs. 6 and 7), which resulted in rapid degradation of the commercial silicone but demonstrated the stability of the experimental formulation.

The inherent thermal stability reflected by the TGA measurements was not observed to the same extent in the mechanical properties. After being exposed to 550°F for 16 hr, both elastomers exhibited extensive degradation of mechanical properties (Table 6). Although there was insufficient material for tear strength measurements, it was obvious from handling the samples that the commercial material was more brittle and easily torn.

TABLE 6. EFFECT OF ELEVATED TEMPERATURE ON MECHANICAL PROPERTIES

Gum-Formulation	Ultimate Strength (psi)		Young's Modulus (psi)		Elongation At Failure (%)	
	Before	After	Before	After	Before	After
Commercial-2	135±13	160±13	189±42	140±14	212±31	55±33
C-2	242±21	173±7	127±23	110±18	319±17	97±56

V. CONCLUSIONS AND RECOMMENDATIONS

A vinyl moiety was successfully incorporated into the silphenylene-siloxane polymers while maintaining molecular weights above one million. Additionally, the feasibility of synthesizing this material on a 200 gram scale was demonstrated.

The vinyl-modified silphenylene-siloxane polymer was shown to be amenable to conventional silicone processing technology. The vulcanized experimental elastomer exhibited enhanced thermal/oxidative instability when compared to an identically formulated commercial methylvinyl silicone, and possessed equivalent or superior mechanical properties.

The experimental data indicated a correlation of lower molecular weights with increasing modulus and decreasing elongation. This demonstrated the sensitivity of the experimental elastomer properties to vinyl cure site concentration.

A possible extension of this study would involve an expansion of the formulation matrix. Changes in filler type and/or concentration might further enhance the properties of this material. Additional improvement in thermal/oxidative stability might result from incorporation of an antioxidant [6].

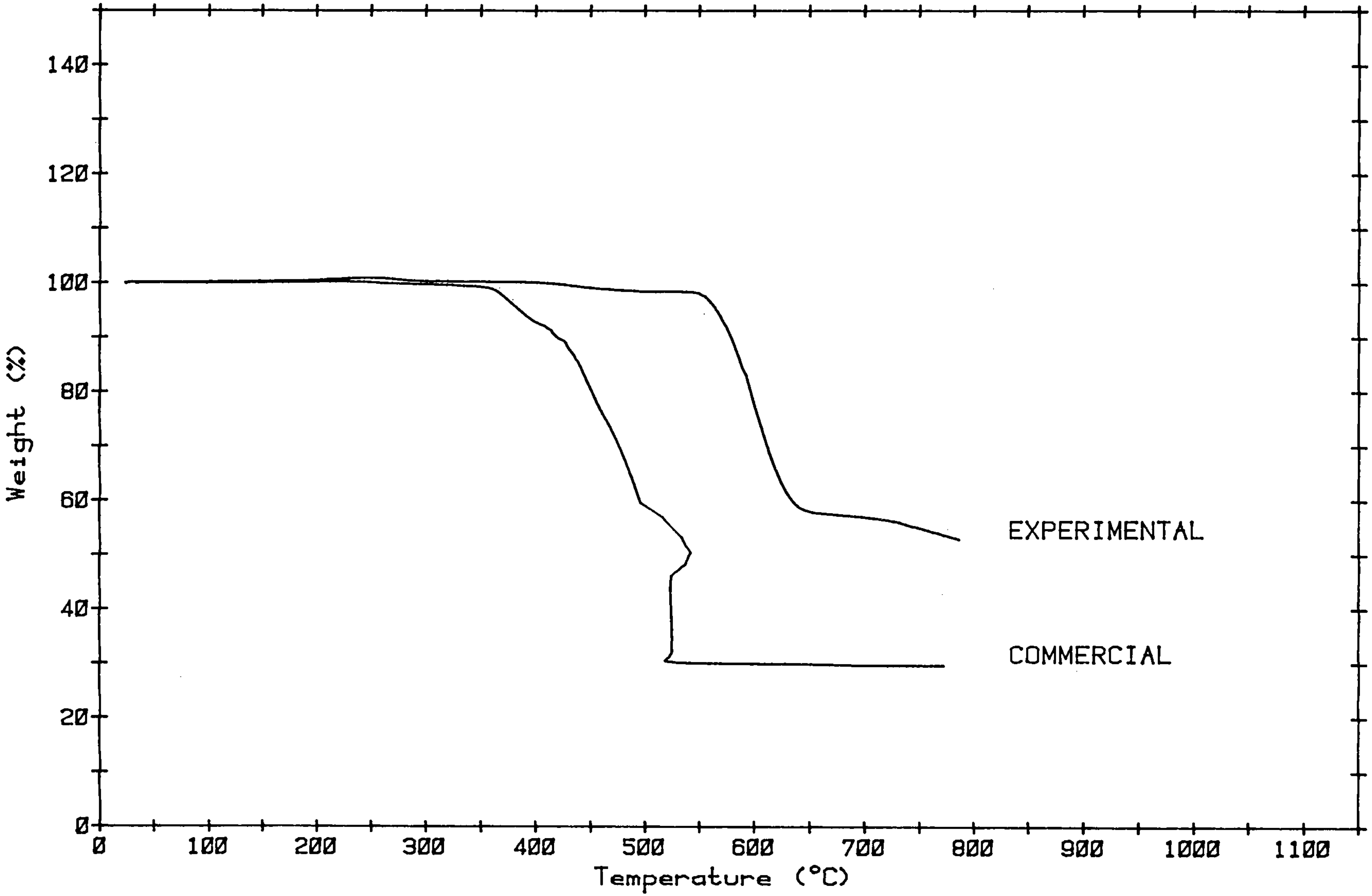


Figure 4. Comparative TGA for experimental elastomer versus commercial silicone in air.

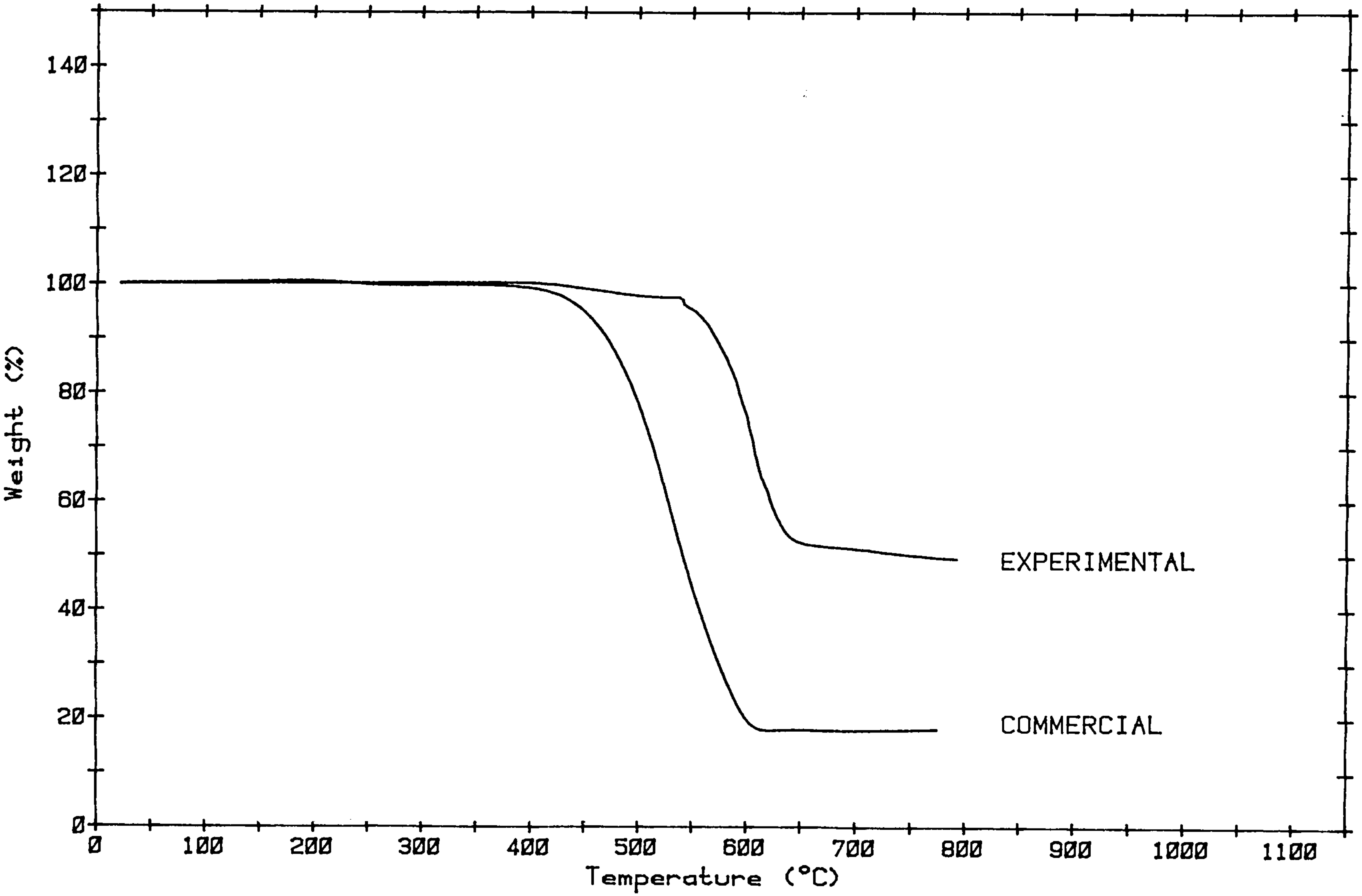


Figure 5. Comparative TGA for experimental elastomer versus commercial silicone in nitrogen.

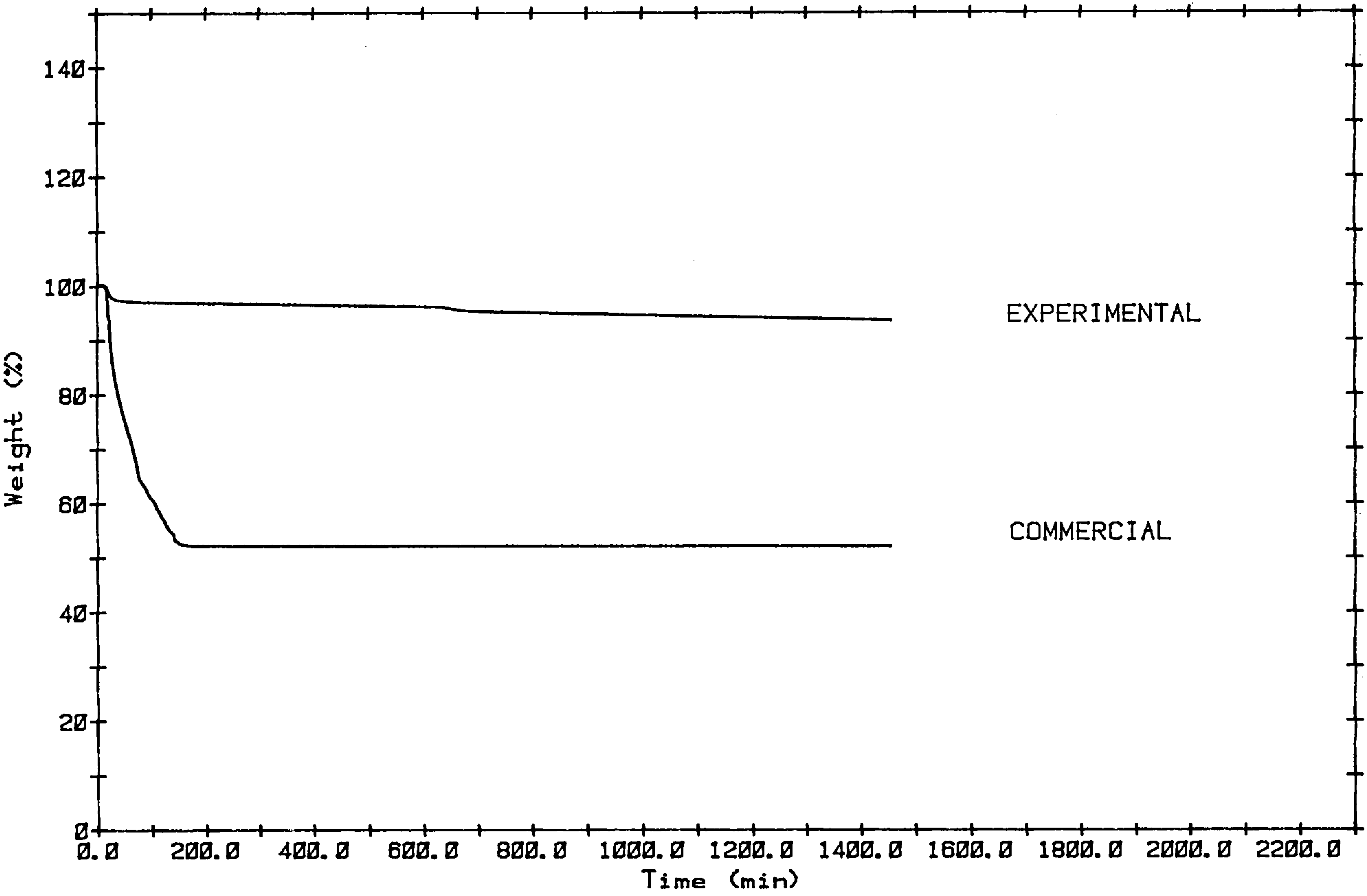


Figure 6. Isothermal TGA for experimental and commercial elastomers in air.

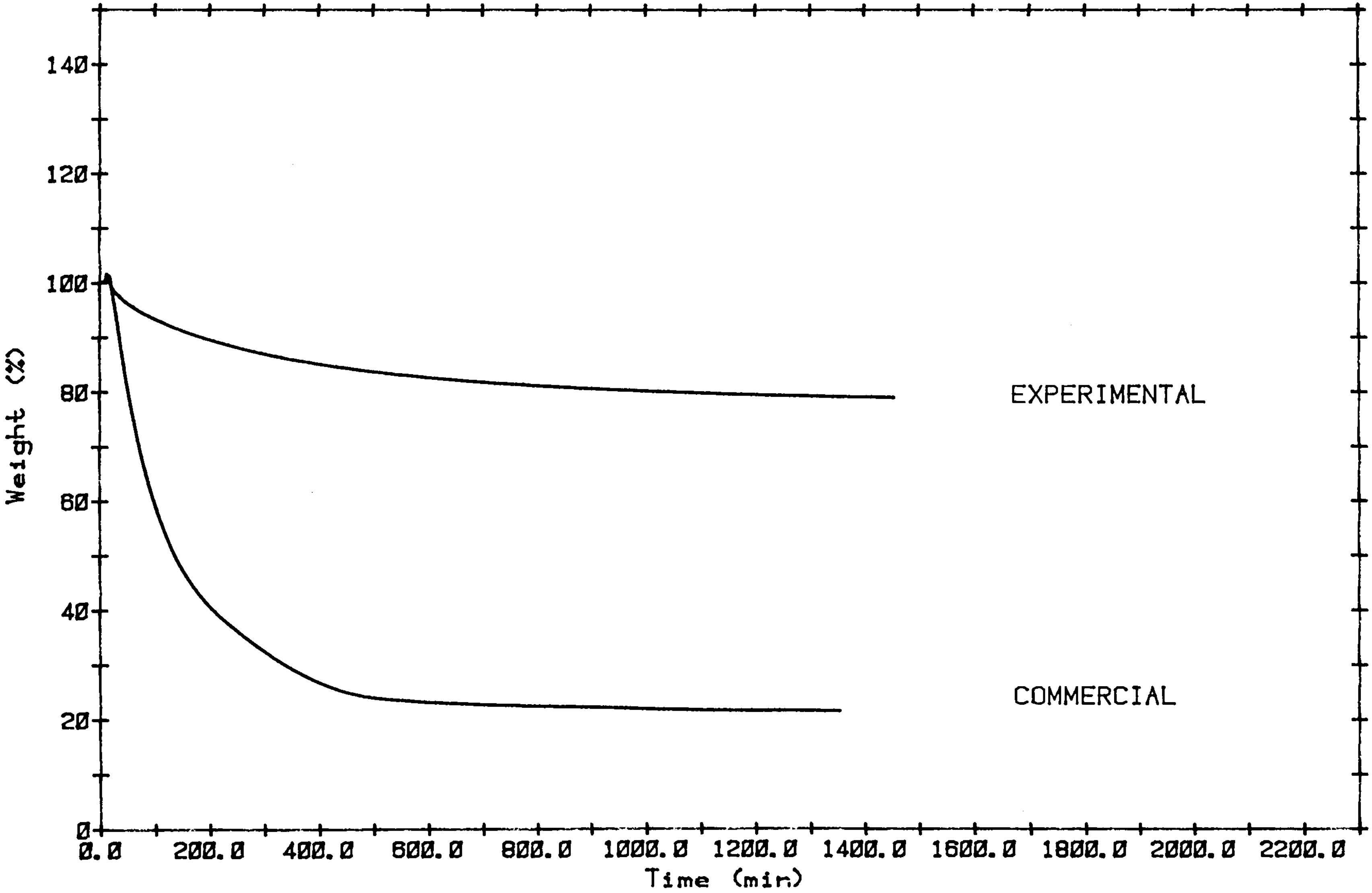


Figure 7. Isothermal TGA for experimental and commercial elastomers in nitrogen.

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16. ABSTRACT

Molecular weights above one million were achieved for methylvinylsilphenylene-siloxane terpolymers using a two-stage polymerization technique which was successfully scaled up to 200 grams. The resulting polymer was vulcanized by two different formulations and compared to an identically formulated commercial methylvinyl silicone on the basis of ultimate strength, Young's modulus, percent elongation at failure, and tear strength.

Relative thermal/oxidative stabilities of the elastomers were assessed by gradient and isothermal thermogravimetric analyses performed in both air and nitrogen. The experimental elastomer exhibited enhanced thermal/oxidative stability and possessed equivalent or superior mechanical properties.

The effect of variations in prepolymer molecular weight on mechanical properties was also investigated.

17. KEY WORDS Elastomer, High Molecular Weight Oxidative Stability, Polymer, Silicone, Siloxane Silphenylene-Siloxane, Thermal Degradation	18. DISTRIBUTION STATEMENT Unclassified - Unlimited Subject Category 27

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