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Yearly Report on Polymer Precursors for Ceramic Matrix Composites

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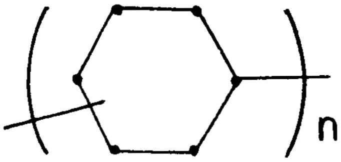
Summary

The general objective of this research was to synthesize a polymer which has a high theoretical SiC char yield. To achieve this objective, a six-membered silicon ring structure of the type shown below was proposed.



(Each dot represents a silicon atom with sufficient methyl groups attached to bring the total valency of silicon to four.)

The theoretical char yield for this polymer is 75%.

To synthesize a polymer of the type shown above, one needs a bifunctional monomer. Various methods were tried to synthesize such a monomer, and the one finally opted for was metal coupling of $PhMeSiCl_2$ and Me_2SiCl_2. The procedure gives six-membered ring compounds with all degrees of phenyl substitution, from none to hexaphenyl. The compounds with groups from 0-2 were isolated and characterized. The fraction with degree of phenyl substitution equal to 2, a mixture of <u>cis</u> and <u>trans</u> 1,2-; 1,3-; and 1,4- isomers, was isolated in 32% yield.

Pure 1,4-diphenyldecamethylcyclohexasilane was isolated from the

mixed diphenyl compounds and characterized.

Diphenyldecamethylcyclohexasilanes were dephenylated to dichlorodecamethylcyclohexasilanes by treating with H_2SO_4/ NH_4Cl in benzene. The latter were purified and polymerized by reacting with sodium in toluene.

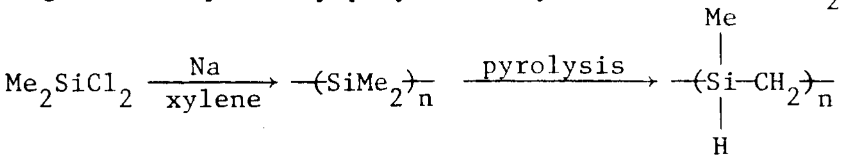
The polymers were characterized by HPGPC, elemental analysis, proton NMR, and IR.

Thermogravimetric analyses were carried out on the polymers. As the yield of residual SiC was low, polymers were heat-treated to increase the residual char yield. As high as 51.52% residual char yield was obtained in one case.

Introduction

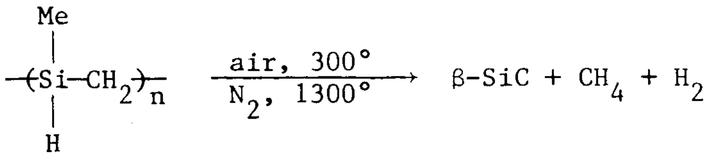
Silicon carbide has been recently attracting keen interest of various scientists as a high temperature structural material because of its resistance to oxidation, corrosion, and thermal shock. Exploratory research has shown that new silicon-based preceramic polymers have the potential to be formed into desired shapes using conventional low temperature plastic processes, then fired to form high temperature fibers and structures [1,2]. The polymer processing route to ceramics has the potential to advance structural materials.

In 1975, Yajima and his coworkers [3] discovered that polysilane polymers could be used as precursors to β-SiC. The process for making β-SiC begins with permethylpolysilane synthesized from Me_2SiCl_2 and Na.



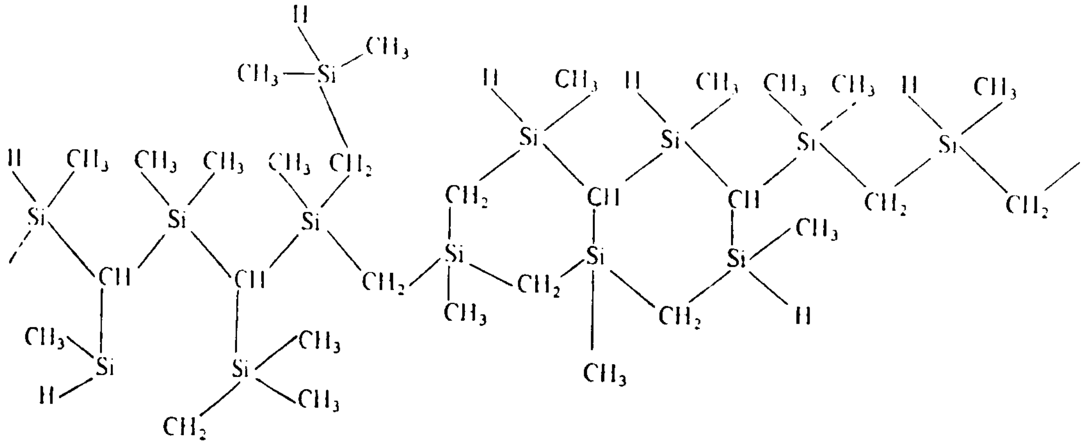
$$Me_2SiCl_2 \xrightarrow[xylene]{Na} -(SiMe_2)_n- \xrightarrow{pyrolysis} -(\overset{Me}{\underset{H}{Si}}-CH_2)_n-$$

Fibers can be melt spun from the hexane soluble, non-volatile portion of the rearranged polymer. These are cross-linked by surface oxidation in air and then further pyrolized up to 1300°C in a N_2 atmosphere to make β-SiC fibers.

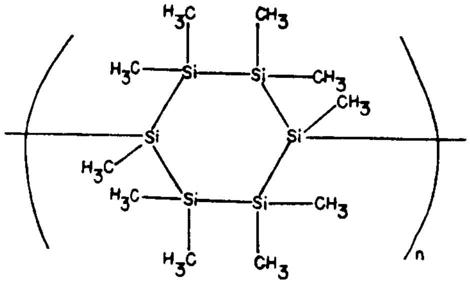


$$-(\overset{Me}{\underset{H}{Si}}-CH_2)_n- \xrightarrow[N_2,\ 1300^\circ]{air,\ 300^\circ} \beta\text{-SiC} + CH_4 + H_2$$

The proposed structure of polycarbosilane (by Yajima) is shown below.



The structure has many cyclized units in it and it is well known that linear poly(dimethylsilanes) tends to cyclize and volatilize when heated. The volatilization can be prevented by replacing some methyl groups by phenyl groups (West's polysilastyrene) [4,5]. However, the yield of SiC drops since the percent volatiles increases. In addition, graphite tends to form. We felt that a way around both the problems of volatilization and low char yield was to make polymers of already cyclized molecules. The hypothesized structure is shown below.



The structure shown above would probably be crystalline. This would be useful to make fibers. A mixture of 1,2-; 1,3-; and 1,4-substituted rings would generate an amorphous polymer which could act as a binder. The theoretical char yield for such a polymer is 75% if only hydrogen and methane would be lost.

The project was undertaken in two phases:

Phase I: Working out synthetic route for monomer.

Phase II: Preparation of polymer and its characterization.

This report summarizes results in these two phases. Section I deals with synthesis of diphenyldecamethylcyclohexasilanes while Section II deals with the preparation, characterization and thermogravimetric analysis of polymers.

References

1. S. Yajima, J. Hayashi, M. Omori and K. Okamura, Nature, 261 (1976) 683.

2. R.H. Baney, J.H. Gaul, Jr., and T.K. Hilty, Organometallics, 2 (1983) 859.

3. S. Yajima, J. Hayashi and M. Omori, Chem. Lett., (1975) 931.

4. R. West, L.D. David, P.I. Djurovich, H. Yu, and R. Sinclair, Ceramic Bull., 62 (1983) 899.

5. R. West, L.D. David, P.I. Djurovich, K.L. Stearley, K.S.V. Srinivasan, and H. Yu, J. Am. Chem. Soc., 103 (1981) 7352.

Synthesis and Characterization of 1,4-Diphenyldecamethylcyclohexasilane

Section I

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Introduction

Phenylated permethylcyclohexasilane derivatives are generally prepared by the reaction of phenyl magnesium chloride (PhMgCl) with chloropermethylcyclohexasilanes [1]. The method is basically used to purify the chloro compounds, as the phenyl derivatives are much easier to handle in air and can be quantitatively converted back to the chloro compounds. Monochloroundecamethylcyclohexasilane has been prepared by the reaction of dodecamethylcyclohexasilane with HCl in the presence of $AlCl_3$ as catalyst [1]. Reaction of dodecamethylcyclohexasilane in the presence of $AlCl_3$ with trimethylchlorosilane [2-4], or CH_3COCl [5] gives a mixture of 5-membered mono- and dichloro- products. Recently West and his coworkers [6] reported a method of synthesizing mono- and dichloropermethylcyclohexasilanes by reacting dodecamethylcyclohexasilane with trichlorosilane and $PtCl_4$. As the chloro derivatives tend to hydrolyse in air, they are not easily purified. For ease of handling and getting pure chloro compounds, we decided to prepare phenylated permethylcyclohexasilanes directly; these can then be converted to the corresponding pure chloro derivatives. West [7] has also reported the syntheses of some of the phenylated permethylcyclohexasilanes. In this paper we report the detailed procedure of the preparation, purification, and characterization of 1,4-diphenyldecamethylcyclohexasilane.

Results and Discussion

Synthesis

The method used to synthesize the phenyl substituted permethylcyclohexasilanes was alkali metal coupling of $PhMeSiCl_2$ and Me_2SiCl_2 (eq. 1).

$$PhMeSiCl_2 + 2Me_2SiCl_2 \xrightarrow[THF]{Na-K} Me_{12-x}Ph_xSi_6 + MCl \qquad (1)$$

$$(x = 0\text{-}6) \qquad (M = Na, K)$$

Though the method gave compounds with all degrees of phenyl substitution, from none to hexaphenyl, only those compounds with 0-2 phenyl groups were isolated and characterized. The best yield of diphenyl derivatives was obtained with a slow addition of the mixed dihalosilanes to Na-K alloy in refluxing THF, and was optimized for 32% isolable yield of the isomeric diphenyldecamethylcyclohexasilanes. Table 1 shows the percent yield of various isolated derivatives.

TABLE 1. PERCENT YIELD OF VARIOUS ISOLATED DERIVATIVES

$Me_{12-x}Ph_xSi_6$		Yield	
x	wt(%)	mol(%)	mol(%)(theoretical)
0	8	11	8.8
1	24	27	26.3
2	32	32	32.9
3	36	30	21.9
4			8.2
5			1.6
6			0.1

The theoretical yields were obtained by assuming that the coupling of dimethylsilyl and methylphenylsilyl groups was random, and using a binomial expansion to calculate the values. Theory agreed with experiment, showing that the coupling of dihalosilanes was random. In experiments where all the silanes were added to the reaction rapidly instead of being added slowly, a large amount of dodecamethylcyclohexasilane and the higher polyphenylated compounds were obtained, with only a small yield of diphenyl compound.

The isomeric mixture of diphenyl derivatives was further separated into solid and liquid fractions. High pressure liquid chromatography using a μ Bondapak C18(reverse-phase) column with an 80% methanol/ 20% THF mobile phase showed that the solid fraction was a mixture of at least 5 isomers.

Pure 1,4-diphenyldecamethylcyclohexasilanes [1], mp = 167-70°C, was obtained by repeated recrystallization of the solid fraction. Its chromatogram shows only a single peak under the above mentioned conditions. The structure of 1,4-diphenyl derivative was confirmed by its ^{1}H (Fig. 1), ^{13}C, and ^{29}Si NMR. The chemical shift data are given in Table 2. The 1,4-diphenyl derivative is probably the trans form. Though there is no certain evidence, the trans derivative would be expected to have the highest melting point of all the diphenyl isomers, and thus would be most easily isolated.

TABLE 2. ^{1}H-, ^{13}C-, AND ^{29}Si- NMR CHEMICAL SHIFTS FOR PURE 1,4-DIPHENYLDECAMETHYLCYCLOHEXASILANE

^{1}H(No. of Methyl Groups) (δ ppm)[a]	^{13}C(No. of Carbon) (δ ppm)[b]	^{29}Si(No. of Silicon) (δ ppm)[c]
0.530 (2)	-4.32 (4)	-41.08 (4)
0.330 (4)	-6.49 (2)	-41.40 (2)
0.198 (4)	-6.71 (4)	
	134.68 (o,4)	
	127.86 (p,2)	
	127.71 (m,4)	
	146.98 (i,2)	

a - CH_2Cl_2(δ 5.35) was used as an internal reference.

b - $CDCl_3$(δ 77.0) was used as an internal reference.

c - TMS(δ 0.0) was used as an internal reference.

^{1}H NMR

The spectrum of pure 1,4-diphenyldecamethylcyclohexasilane shows only three peaks (Fig. 1) due to methyl protons. Peak positions of the 1,4-derivative were assigned on the basis of chemical shifts in the cyclohexane system. The bulkier phenyl groups are expected to go to the equatorial position (preferred conformation); methyl groups attached to the 1,4 Si atoms appear at δ 0.530. As the equatorial methyl groups at positions 2, 3, 5, and 6 lie in the deshielding region of the benzene rings, they are expected to be downfield and assigned to the peak at δ0.330, while the axial methyl groups are shielded and appear upfield at δ0.198. Also, if the 1,4-diphenyl derivative is cis, that is, if one of the phenyl groups were axial (at the 4 position, for example), the axial methyl groups at positions 3 and 5 should be strongly shielded. Such peaks appear in the spectra of the mixed compounds, at δ 0.134. Proton NMR of the solid and liquid factions show a complicated pattern (Fig. 1) and both fractions seem to contain all of the possible isomers, though the peaks which are strong in one spectrum are weak in the other spectrum.

^{13}C NMR

^{13}C NMR chemical shifts for pure 1,4-diphenyldecamethylcyclohexasilane are shown in Table 2. In contrast with proton spectra an upfield shift was observed for the 1,4 methyls. The methyls which are cis to the phenyl groups appear downfield and methyls which are trans to the phenyl groups appear upfield. [No comparison was made with dodecamethylcyclohexasilane]. These assignments are consistent with the results of Helmer and West [7]. In the case of the solid and liquid fractions which are mixtures of isomers, the spectra are quite complicated and it is difficult to assign peaks to particular positions.

^{29}Si NMR

^{29}Si NMR chemical shifts for pure 1,4-diphenyldecamethylcyclohexasilane are shown in Table 2. The 1,4-silicon resonances appear at $-\delta 41.40$ while the other silicon resonances appear at $-\delta 41.08$. This assignment of peaks is based on the results of Sharp et al. [8]. Again, for the solid and liquid fractions, ^{29}Si NMR spectra are complicated and it is difficult to assign various peaks to particular positions.

Experimental

Dimethyldichlorosilane and methylphenyldichlorosilane were obtained from Aldrich Chemical Co., and were distilled before use. Tetrahydrofuran (THF) was predried over $LiAlH_4$ and distilled from Na/benzophenone. The liquid chromatograph used was Varian 8500 with Waters μ Bondapak C18 (reverse phase) column. The solvent used was 80% methanol/20% THF at a flow rate of 1 ml/min. Ultraviolet (UV) absorbance detector was set at 254 nm. All NMR spectra were run using $CDCl_3$ as solvent on a Varian XL-200 spectrometer. Methylene chloride

(δ5.35) was used as an internal standard in the case of ^{1}H NMR. Chloroform (δ77.0) was used for referencing the ^{13}C NMR peaks.

TMS (δ0.0) was used as an internal standard for the ^{29}Si NMR measurements. They were run in 10 mm tubes with a small amount of $Cr(acac)_3$ added to shorten the silicon spin-lattice relaxation times and eliminate the negative NOE due to proton decoupling. Infrared spectra were recorded on a Digilab Model FT-IRS-14. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Mass spectra were obtained on FINNIGAN mass spectrometer. Elemental analyses were done by Galbraith Laboratories.

Preparation of 1,4-Diphenyldecamethylcyclohexasilane

A one liter, three-necked, round-bottomed flask was equipped with a tru-bore mechanical stirrer, a condenser, a nitrogen inlet, and a rubber septum. The system was dried thoroughly and flushed with nitrogen. The flask was charged with 300 ml of dry freshly distilled THF by means of a syringe. The rubber septum was replaced quickly with a stopper. Na-K alloy was prepared in the reaction flask from 22.9 g (0.587 mol) of K, and 3.82 g (0.166 mol) of Na (78% K by weight), as reported by West et al. [9]. The stopper was removed and quickly replaced by a pressure-equalized addition funnel fitted with a rubber septum. Freshly distilled $PhMeSiCl_2$ (20 g, 0.105 mol), and Me_2SiCl_2 (27 g, 0.210 mol) in 50 ml of dry THF were placed in the dropping funnel by syringe. The stirrer was started and Na-K/THF mixture was brought to a mild reflux. At this point, the solution of dihalosilanes in THF was added dropwise to the reaction flask. After the addition of 1-2 ml of solution, the color of the reaction mixture turned golden yellow. Slow addition of dihalosilanes was maintained until the addition was complete in 2 hrs. The heating was continued overnight while stirring. At this point, the color of the reaction mixture was light blue, or white. The mixture was then cooled, at which time 250 ml of hexane was added and the excess of Na-K alloy was destroyed by the gradual and very slow addition of water. Once the evolution of hydrogen gas ceased, more water was added till the salt dissolved. The hexane-THF layer was separated, washed with saturated aqueous NaCl and dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator and a viscous liquid weighing 24.5 g (99.2% yield) was obtained.

Thin layer chromatography (silica) using hexane as a solvent showed this liquid as a mixture of at least 5 products. Three products, dodecamethylcyclohexasilane, monophenylundecamethylcyclohexasilane, and diphenyldecamethylcyclohexasilane were isolated using flash column chromatography [10]. A detailed procedure for isolating these products is as follows: a glass column of 5.7 cm diameter was filled up to 17.8 cm with 40-63 μ silica gel 60 and packed with hexane using air pressure as described by Still et al. [10]. 13 g of crude product was loaded on this column and it was eluted with hexane at a rate where the liquid level in the column dropped by 5 cm/min. 125 ml fraction were collected. The products isolated from various fractions were characterized as follows:

Fractions 4-6: dodecamethylcyclohexasilane (1.64 g, 8%); NMR ($CDCl_3$, δ ppm) 0.182(s, 36H); mp 251-3°C (lit(9)254-7°C).

Fractions 14-16: monophenylundecamethylcyclohexasilane, recrystallized from ethanol, (3.12 g, 24%); mp 109-10°C (lit(7) 110-11°C).

Fractions 17-28: diphenyldecamethylcyclohexasilanes (4.16 g, 32%), the isomeric mixture of 1,2-; 1,3-; and 1,4- cis and trans derivatives. It becomes semisolid after standing overnight at room temperature. A small amount of ethanol was added to it and the solid fraction was isolated by filtration. (Found: C, 55.70; H, 8.53; Si, 35.83. $Si_6H_{40}C_{22}$ calcd.: C, 55.85; H, 8.52; Si, 35.62%). Mass spectrum(m/z): 472 (M^+).

The evaporation of the ethanol solution gave a viscous liquid. (Found: C, 56.09; H, 8.47; Si, 35.18. $Si_6H_{40}C_{22}$ calcd.: C,55.85; H, 8.52; Si, 35.62%).

The solid fraction was recrystallized thrice with ethanol and 60 mg of pure trans 1,4-diphenyldecamethylcyclohexasilane was obtained, mp 167.5-170° C, identified from its NMR spectra. Also, HPLC using a μ Bondapak C18(reverse-phase) column with 80% methanol/20% THF shows a single peak. NMR($CDCl_3$, δ ppm): 0.198(s, 12H); 0.330(s, 12H) 0.530(s, 6H); 7.42(m, 10H). IR spectrum (ν, cm^{-1}): 3060m, 3040m, 2950s, 2890s, 1420m, 1400m, 1245br,m, 1090m, 835s, 800s, 770s, 727s, 695s, 650m, 630m. Mass spectrum(m/z): 472 (M^+).

Acknowledgement

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References

1. M. Ishikawa and M. Kumada, Synth. Inorg. Metal-Org. Chem., 1 (1971) 191.
2. M. Ishikawa and M. Kumada, ibid., 1 (1971) 229.
3. T.J. Drahnak, R. West and J.C. Calabrese, J. Orgmet. Chem., 198 (1980) 55.
4. M. Ishikawa and M. Kumada, Chem. Comm., (1969) 567.
5. H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, Tetrahedron Letters, (1966) 5493.
6. R. West, Pure and Applied Chem., 54 (1982) 1041.
7. B.J. Helmer and R. West, J. Orgmet. Chem., 236 (1982) 21.
8. K.G. Sharp, P.A. Sutor, E.A. Williams, J.D. Cargioli, T.C. Farrar and K. Ishibitsu, J. Am. Chem. Soc., 98 (1976) 1977.
9. R. West, L. Brough and W. Wojnowski, Inorg. Synth., XIX (1975) 265.
10. W.C. Still, M. Kahn and A. Mitra, J. Org. Chem., 43 (1978) 2923.

Preparation and Thermogravimetric Analysis of Poly(decamethylcyclohexasilanes)

Section II

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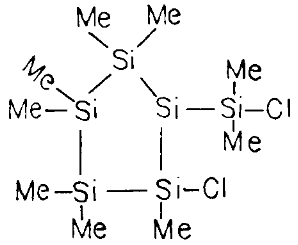
Introduction

Various approaches were taken to synthesize the disubstituted ring monomers. Reaction of dodecamethylcyclohexasilane in the presence of $AlCl_3$ with HCl or CH_3COCl [1] gives a five-membered ring with a pendant chlorodimethylsilane group. The major dichlorinated isomer was shown to be the following structure [2].



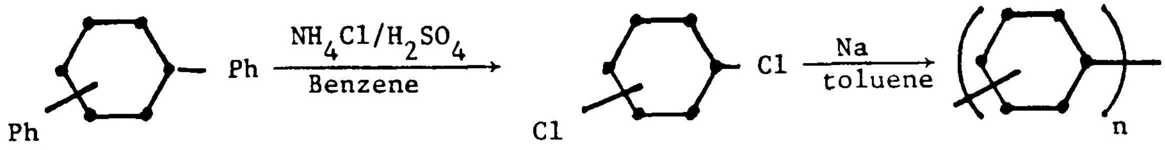
Generally such substitution results in a weak polymer.

As the chloro derivatives tend to hydrolyse in air, they are not easily purified. A general method to purify chlorosilanes is to make their phenyl derivatives, which can be handled in air. Once pure phenyl derivative is obtained, it can be converted back to the chloro derivative quantitatively.

Results & Discussion

Details of the synthesis of the diphenyldecamethylcyclohexasilanes are discussed in Section I.

The isomeric mixture of diphenyldecamethylcyclohexasilanes was separated into solid and liquid fractions. Both of these fractions were used to synthesize polymers. Diphenyldecamethylcyclohexasilanes were converted to dichlorodecamethylcyclohexasilanes by reacting with H_2SO_4/NH_4Cl in benzene. The latter were purified by sublimation and polymerized by reacting with sodium in toluene as shown in equation 1.



(1)

Fig. 2 and Fig. 3 show the GPC elution profiles of the two polymers. Both the polymers exhibited a bimodal molecular weight distribution. The polymer synthesized from the solid fraction (polymer 25) has somewhat higher molecular weight than the polymer synthesized from the liquid fraction (Polymer27).

Elemental analysis which showed the presence of oxygen by difference was repeated for oxygen analysis. The results obtained are given in Table 1. Elemental analysis for this type of polymer is not reproducible due to the formation of residual SiC.

Proton nuclear magnetic resonance spectra of the two polymers show broad peaks which cannot be assigned to particular positions of methyl groups (Fig. 4 and Fig. 5). The absence of peaks in the downfield region show that there were no remaining phenyl substituents.

TABLE 1 ELEMENTAL ANALYSIS OF POLYMER25 AND POLYMER27

Polymer	Analytical	% C	% H	% Si	% O
Polymer25	Calcd.:	37.74	9.43	52.83	0
	Found:	33.52	8.69	48.22	9.57 (by difference)
Repeat	Found:	34.40	8.51	-----	None or Trace
Polymer27	Calcd.:	37.74	9.43	52.83	0
	Found:	38.10	9.65	48.70	3.55 (by difference)
Repeat	Found:	40.14	9.23	-----	0.16

Infrared spectra of the polymers were scanned from 4000 cm^{-1} to 400 cm^{-1} (Fig. 6 and Fig. 7). The broad peak at 1025 cm^{-1} indicates the presence of Si-O bonds which arise from the termination of chains and impurities on the Na metal used for coupling (Na_2O, NaOH, etc.).

Differential scanning calorimetry of these polymers did not give much information as they start decomposing at the softening temperature.

Thermogravimetric analysis under N_2 of polymers 25 and 27 at a heating rate of 10°C/min gave about 5% yield of residual SiC. As the theoretical char yield for these polymers is 75%, an effort to raise the yield was made. The polymer was crosslinked by heat treating it under vacuum before TGA analysis. Polymer25, sealed under vacuum in a glass tube, was heat-treated at various temperatures and thermogravimetric analyses were carried out. The results under various conditions are listed in Table 2.

TABLE 2 THERMOGRAVIMETRIC ANALYSIS OF POLYMER25 CURED AT VARIOUS TEMPERATURES

Temperature/Time	Char Yield %	Heating Rate
Polymer25	27.39	1.5°C/min
124° ± 4°C/4 hrs (a)	18.75	10° C/min
200° ± 1°C/5 min	20.85	10° C/min
250° ± 5°C/15 min	(a) 20.80	10° C/min
	(b) 48.27	10° C/min
200° ± 1°C/5 hrs	(c) 51.52	10° C/min
	17.74	10° C/min
	36.47	10° C/min
	25.71	15° C/min
	19.64	1.5°C/min

(a) Hexane soluble fraction (59.8% of total polymer).

(b) Gel (12.67% of the total polymer.

(c) A piece of polymer was used, rather than ground powder.

As evidenced from Table 2, reproducibility of the results is poor; the maximum residual yield of 51.52% was obtained in one case only (Fig. 8).

Infrared spectra of residual SiC was very similar to the one reported in literature [3].

Another set of thermogravimetric analyses was carried out on a mixture of Polymer25 and Polymer27 which had been sealed in a glass tube under vacuum and heated at 200°C for 10.45 hours. The results are listed in Table 3.

TABLE 3 THERMOGRAVIMETRIC ANALYSIS OF POLYMER MIXTURE CURED AT 200°/10.45 HR.

Sample Condition	Weight Used mg.	Residual Yield %	Heating Rate
Powdered	9.0258	31.42	10°C/min
Powdered	8.9867	27.55	10°C/min
Powdered	8.5065	27.27	10°C/min
Powdered	9.6796	34.77	10°C/min
Pressed(a)	8.4453	32.19	20°C/min
Pressed	8.5599	13.11	15°C/min
Pressed	8.6156	25.50	15°C/min
Pressed	8.3768	25.04	10°C/min
Pressed	7.9245	29.63	10°C/min
Pressed	8.7687	22.20	5°C/min
Pressed	9.0147	20.81	5°C/min
Pressed	8.9067	5.58	2.5°C/min
Pressed	8.8139	10.96	2.5°C/min

(a) Powdered sample was pressed into a pellet in a KBr press and pieces of the pellet were used.

As one can observe, there is a trend to higher yields at higher heating rates, but the reproducibility of the results is poor and more work needs to be done.

A few isothermal runs were carried out with the heat-treated mixed polymers; the results are tabulated in Table 4.

TABLE 4 ISOTHERMAL RUNS OF POLYMER MIXTURE CURED AT 200°/10.45 HR.

Starting Temp. (°C)	Heating Rate (°C/min)	Isothermal Temp. (°C)	Isothermal Time (min)	Yield (%)	Heating Rate (°C/min)	Final Temp. (°C)	Residual Yield (%)
50	160	500	60	22.68	------	--	-
50	160	280	60	90.00	10	900	32.37
50	160	280	60	67.60	------	--	-
50	160	280	600	40.40	10	900	2.49
50	160	280	600	43.26	10	900	5.84
50	160	240	60	87.55	------	--	-

Experimental

Toluene was distilled from Na benzophenone before use. The gel permeation chromatograph used was Beckman 1104 with three microstyragel columns (porosity ranges 10^5, 10^4, 10^3). The solvent used was HPLC grade THF at a flow rate of 1 ml/min. UV absorbance detector was set at 254 nm. All NMR spectra were run using $CDCl_3$ as a solvent on a Varian XL-200 spectrometer. Methylene chloride was used as an internal standard. Elemental analyses were done by Galbraith Laboratories. Thermogravimetric analyses (TGA) of polymers were carried out in a nitrogen flow of 35 cm^3 min^{-1}. Measurements were made on a Perkin-Elmer TGS-2 system equipped with a System 4 microprocessor controller.

Preparation of Isomeric Mixture of Dichlorodecamethylcyclohexasilanes

A 250 ml, two-necked, round bottomed flask was fitted with a magnetic stirrer, a stopper, a pressure-equalized addition funnel, and a nitrogen inlet. The system was dried thoroughly and flushed with dry nitrogen. The flask was charged with 63 ml of conc. H_2SO_4 and cooled in an ice-bath. A mixture of isomeric diphenyldecamethylcyclohexasilanes (3 g, 0.63 mmol) in 50 ml of benzene was placed in the dropping funnel. It was added dropwise in the H_2SO_4 over the period of 30 min. The mixture was stirred in the cold for an additional 30 min. To it was then added 4.5 g of NH_4Cl in several portions. The organic layer was separated and solvent was stripped off by distillation. The distillation of residue using Kugelrohr gave 1.85 g (74.9%) of product subliming in the range of 115-130 °C/0.05 - 0.1 mm of Hg.

Preparation of Poly(decamethylcyclohexasilanes) (Polymer25)

A 100 ml, three-necked, round bottomed flask was equipped with a condenser, a magnetic stirrer, a pressure-equalized addition funnel, a nitrogen inlet, and a rubber septum. The system was dried thoroughly and flushed with dry nitrogen. The flask was charged with 15 ml of dry freshly distilled toluene by means of a syringe. Sodium (0.276 g, 1.2 mmol) was added to the flask and mixture was brought to a reflux. Sodium dispersion was formed by stirring the mixture. A solution of 1.85 g (0.48 mmol) of isomeric mixture of dichlorodecamethylcyclohexasilanes(a) in 10 ml of dried toluene was added dropwise. Addition required 10-15 min, during which time the reaction mixture turned from gray to dark purple. After the addition was completed, the mixture was refluxed for 2.45 h. At this point, heating was turned off and the reaction mixture was stirred overnight. The reaction was quenched by the dropwise addition of EtOH/H_2O. Additional water was added to dissolve the salt. The organic layer was separated and washed with water. A very small amount of insoluble polymer was separated by centrifugation. The solvent was dried over anhydrous $MgSO_4$ and stripped off on a rotary evaporator. A small amount of petroleum ether was added to the white solid, to remove the last

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(a) Dichlorodecamethylcyclohexasilanes were obtained from the isomeric mixture of the solid diphenyldecamethylcyclohexasilanes.

traces of toluene. Removal of solvent gave white brittle product weighing 1.1 g (73.3%).

Preparation of Poly(decamethylcyclohexasilanes) (Polymer27)

Most of the reaction conditions were the same as described for Polymer25. The few differences are listed below.

1. Dichlorodecamethylcyclohexasilanes obtained from the isomeric mixture of the liquid diphenyldecamethylcyclohexasilanes were used.
2. Mechanical stirrer rather than magnetic stirrer was used.
3. Addition was completed in 1-2 min instead of 10-15 min.
4. The mixture was refluxed with stirring for 10 hours.
5. The yield of polymer was 72.6%.

Heat-Treatment of Polymer25 or Polymer Mixture

A known amount of the Polymer25 or polymer mixture was taken in a polymerization tube. The tube was evacuated for at least 3 hours at about 10^{-3} torr and then sealed. Heat-treatments were carried out by dipping the whole tube in a temperature controlled oil bath, at a certain temperature for a certain period of time. See Tables 2 and 3 for the details.

References

1. H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, Tetrahedron Letters, (1966) 5493.
2. T.J. Dralinik, R. West and J.C. Calabrese, J. Organomet. Chem. 198, (1980) 55.
3. S. Yajima, K. Okamura, S. Hayashi, Chem. Lett., (1975) 1209.

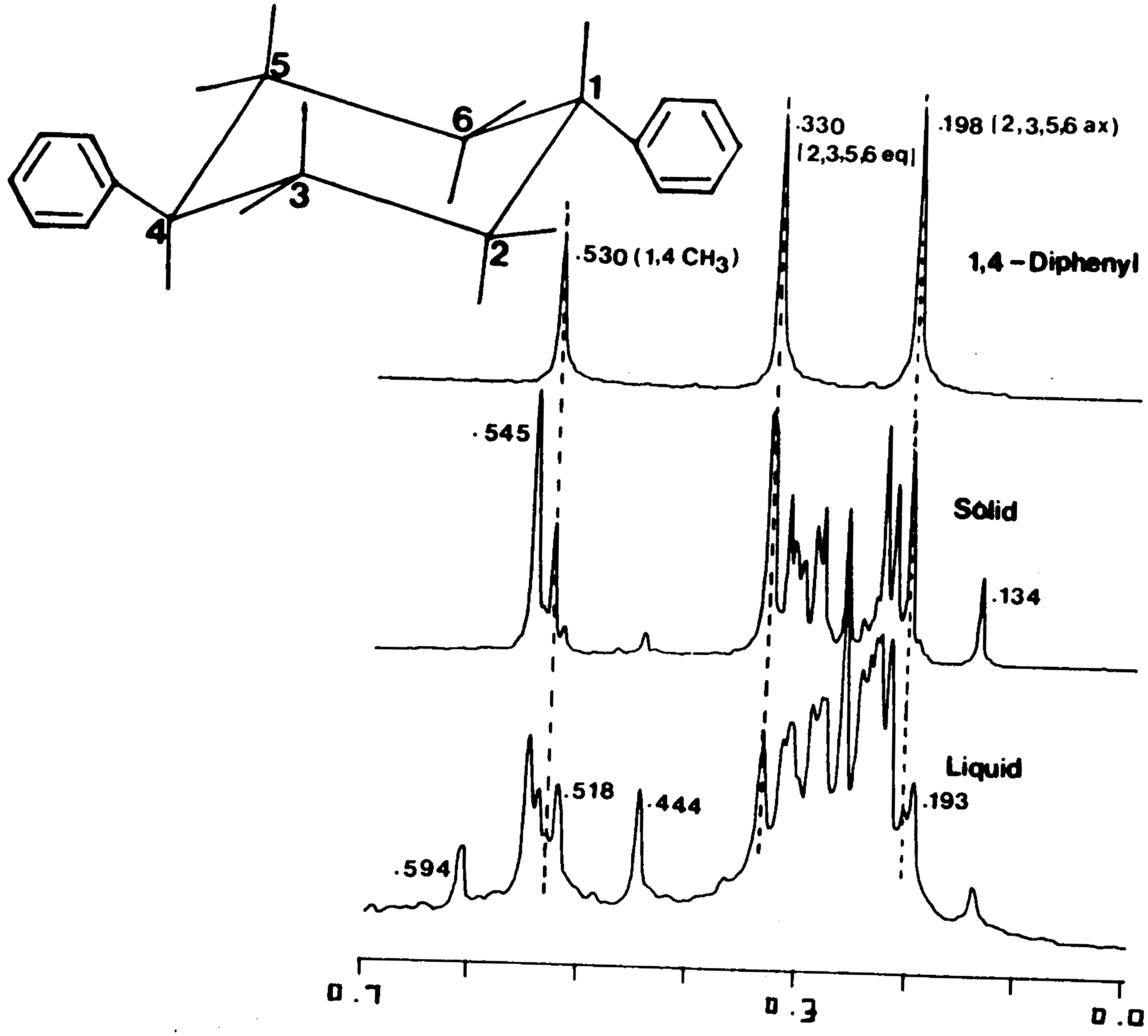
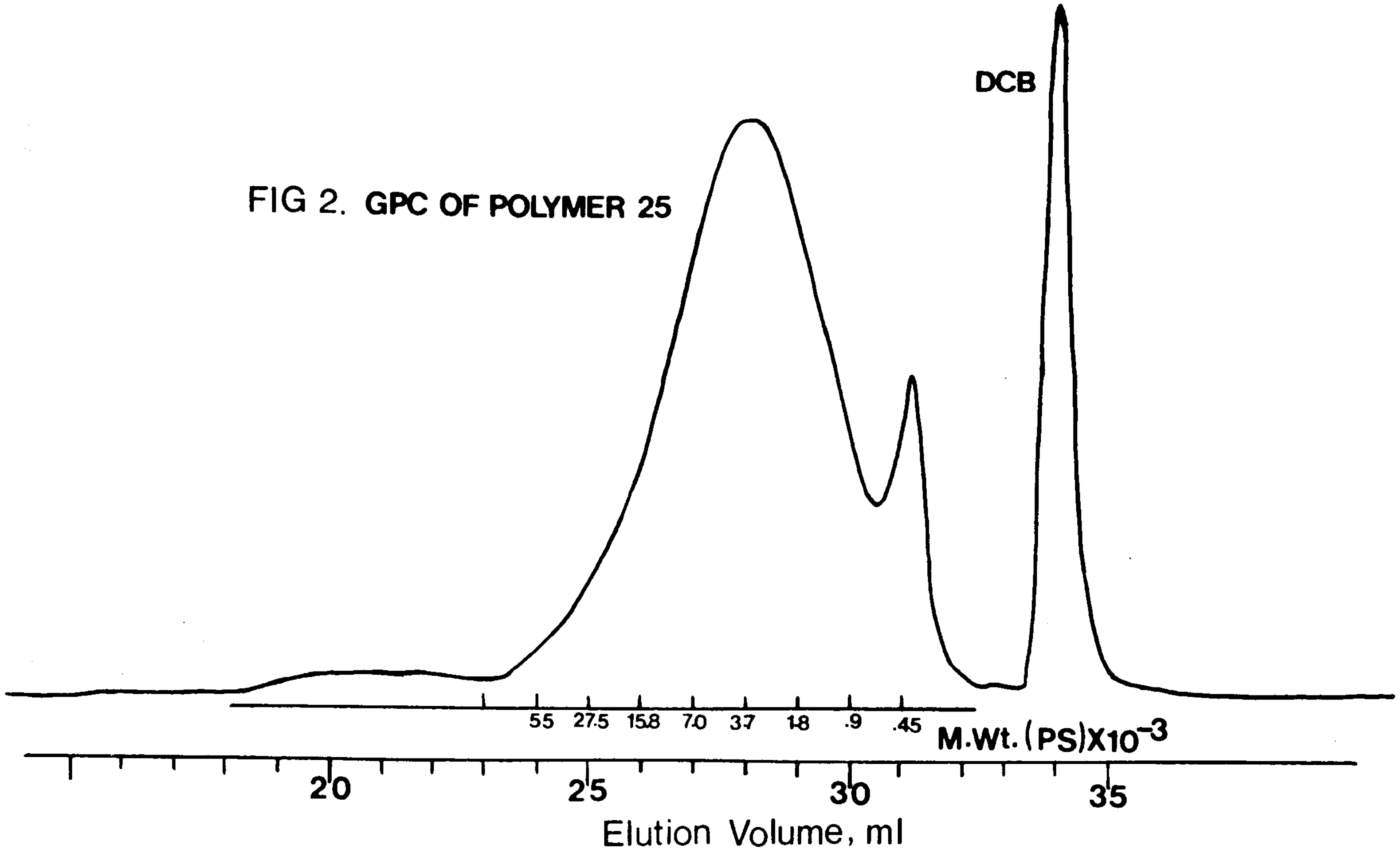


FIG 1. NMR OF DIPHENYLDECAMETHYLCYCLOHEXASILANE

FIG 2. **GPC OF POLYMER 25**



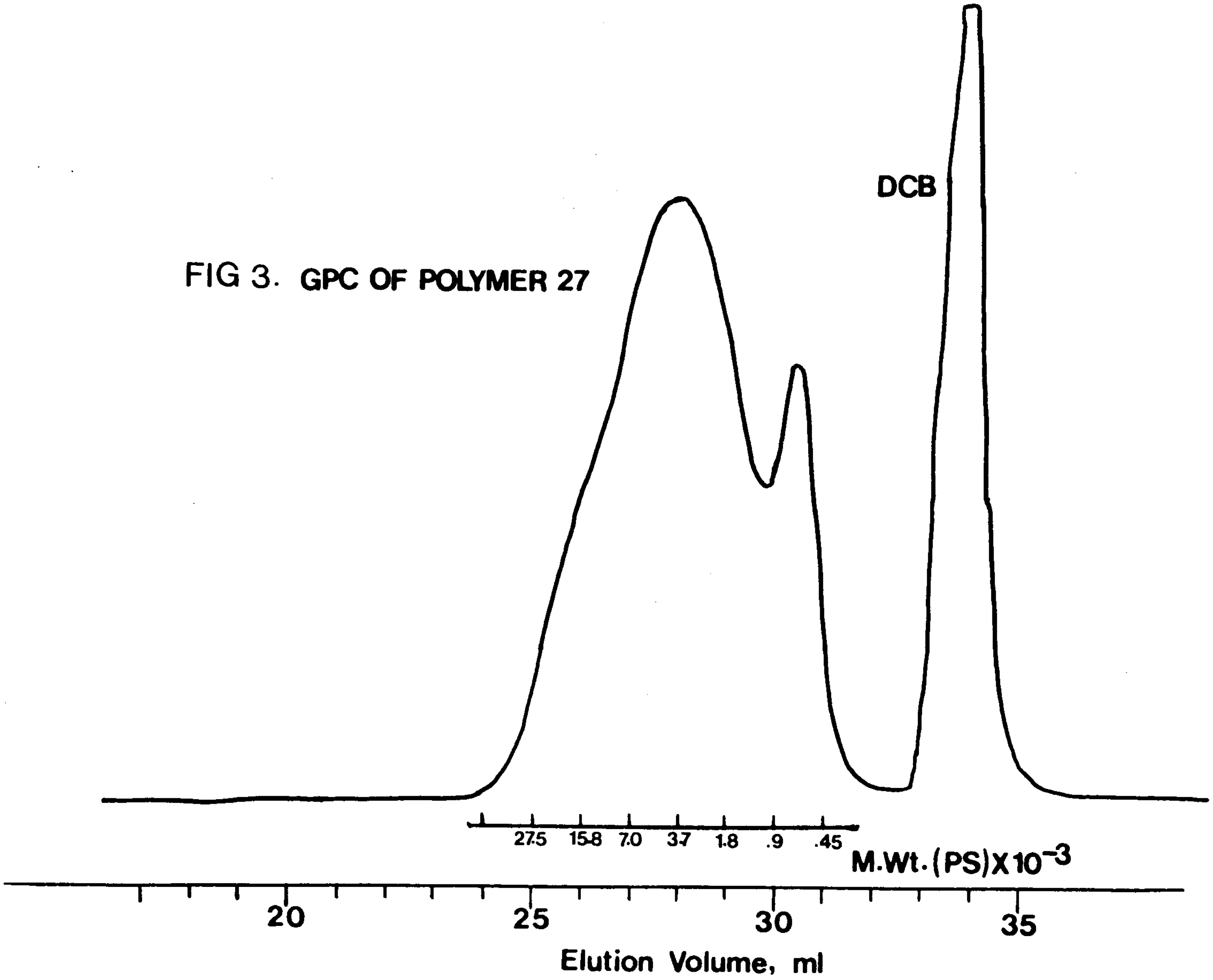
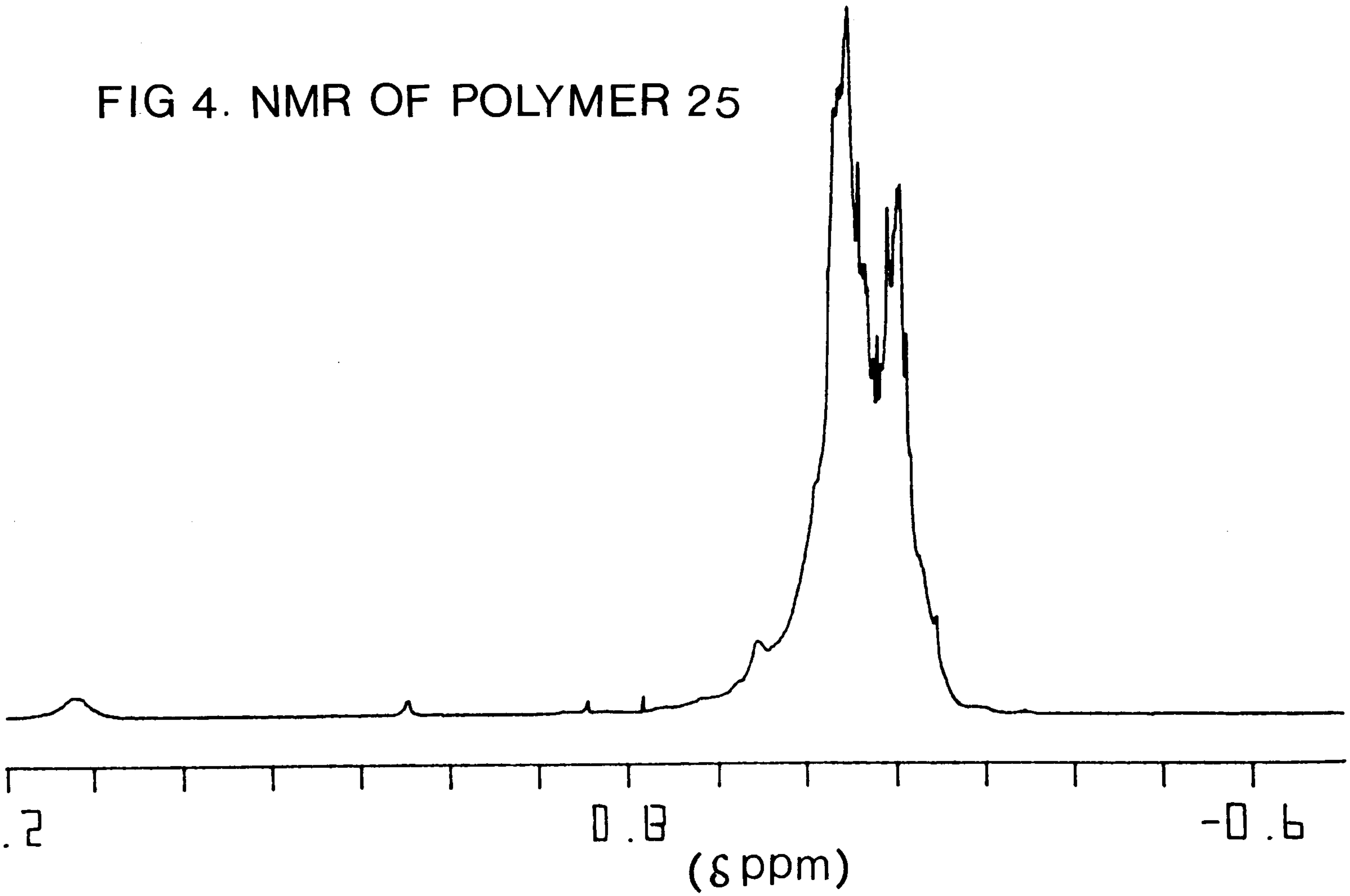


FIG 3. **GPC OF POLYMER 27**

FIG 4. NMR OF POLYMER 25



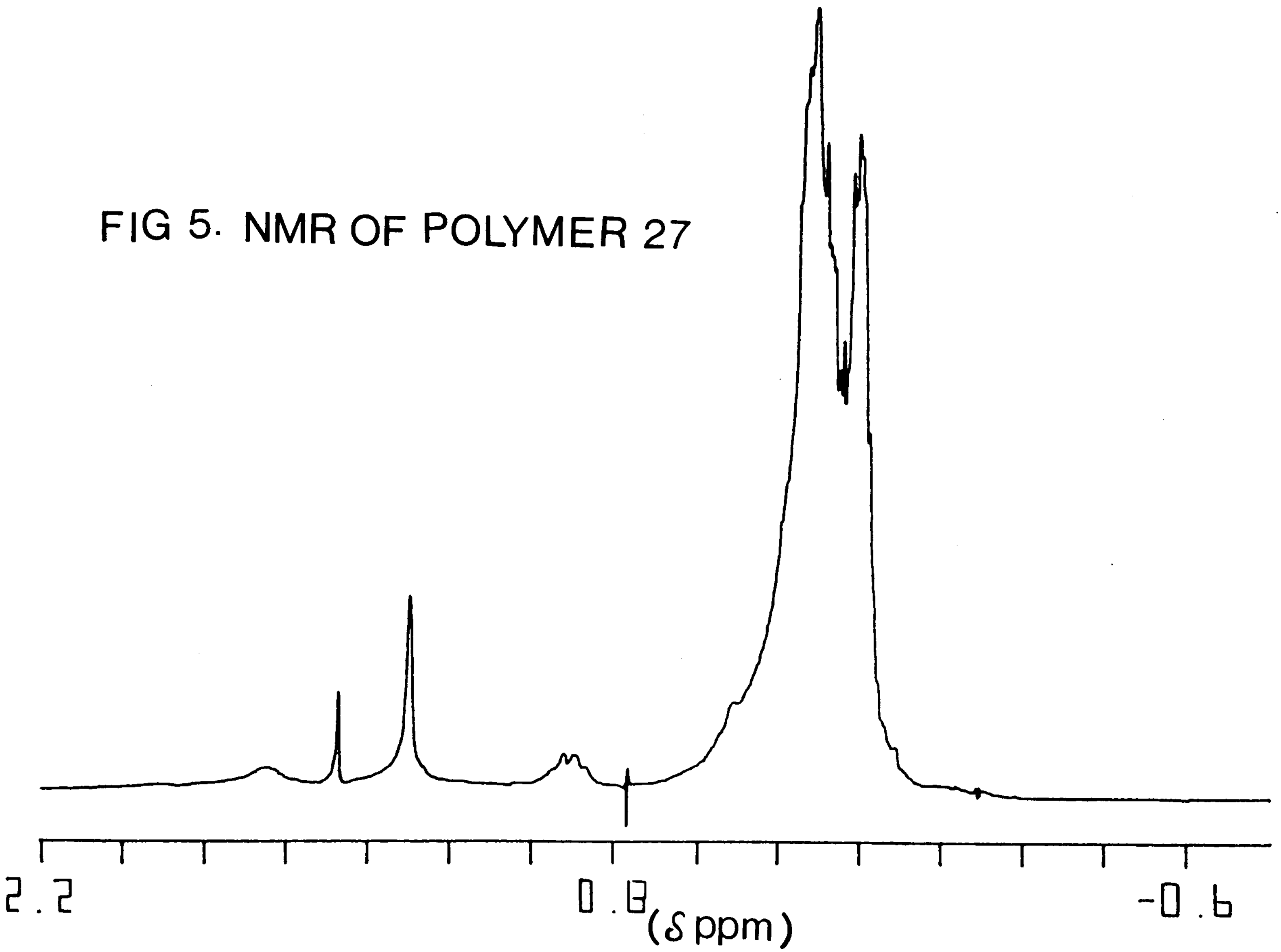


FIG 5. NMR OF POLYMER 27

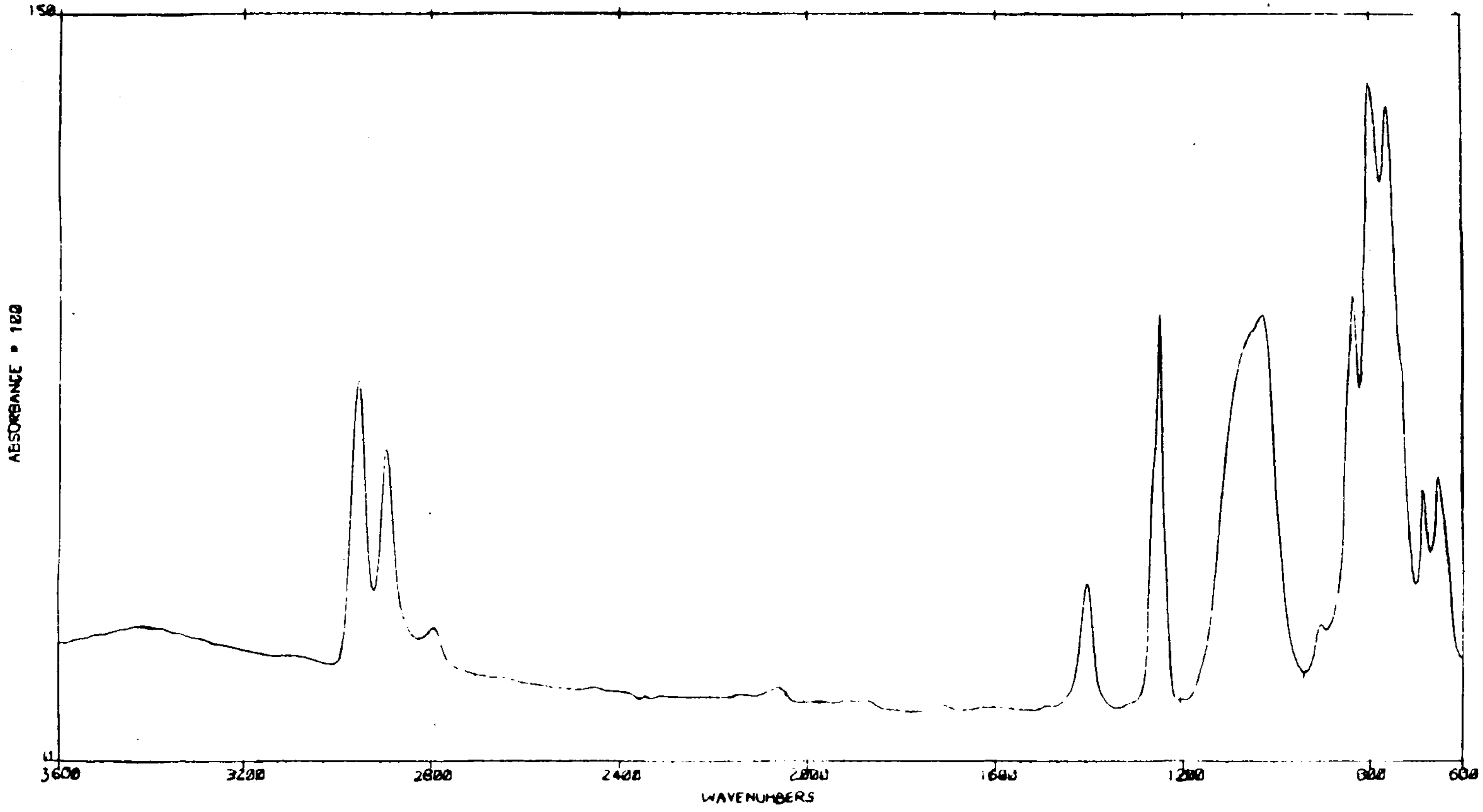


FIG 6. IR OF POLYMER25

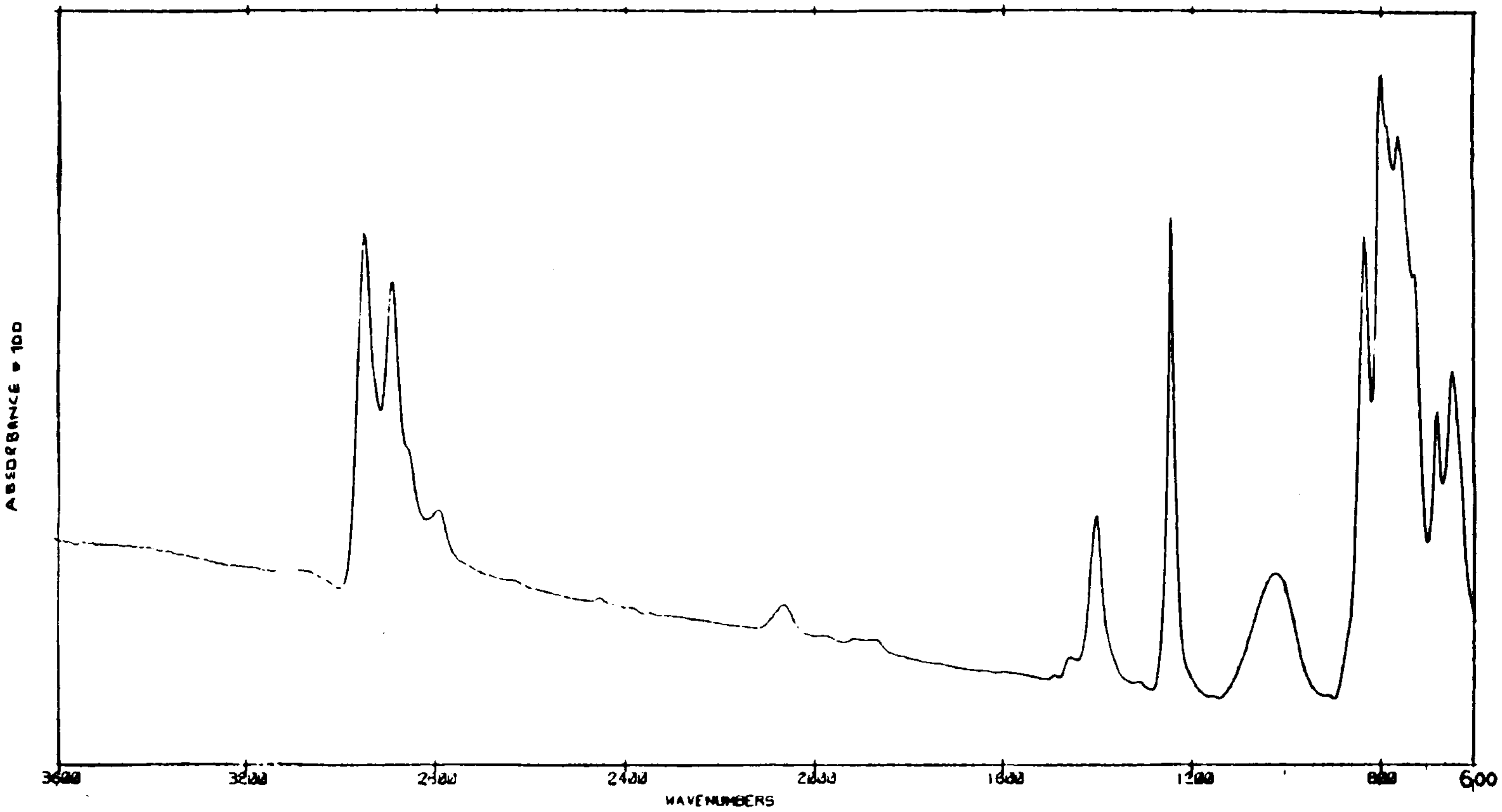


FIG 7. IR OF POLYMER27

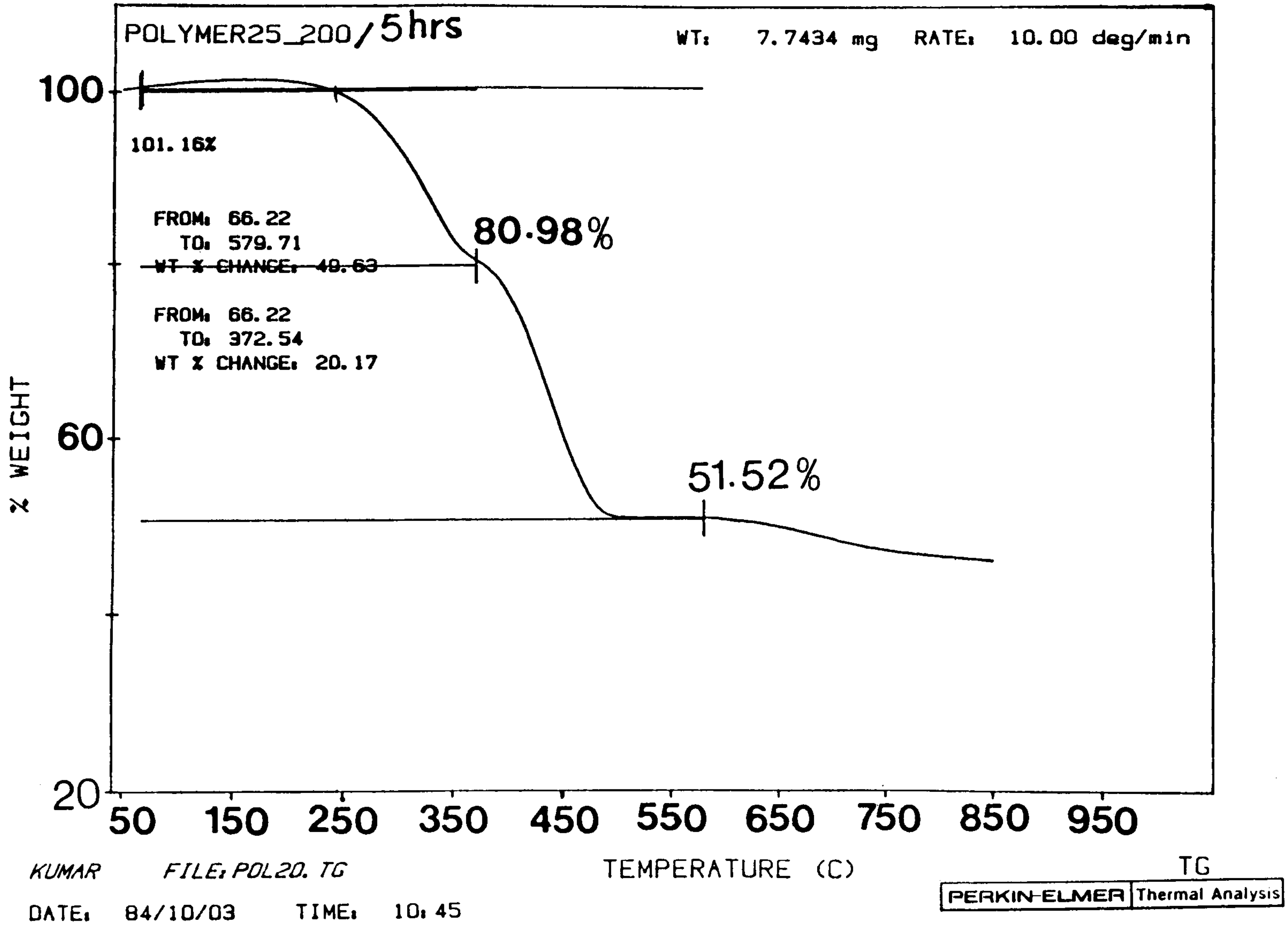

POLYMER25_200/5hrs
WT: 7.7434 mg
RATE: 10.00 deg/min
101.16%
FROM: 66.22
TO: 579.71
~~WT % CHANGE: 49.63~~
FROM: 66.22
TO: 372.54
WT % CHANGE: 20.17
80.98%
51.52%
100
60
20
% WEIGHT
50
150
250
350
450
550
650
750
850
950
TEMPERATURE (C)
KUMAR
FILE: POL20. TG
DATE: 84/10/03
TIME: 10:45
TG
PERKIN-ELMER
Thermal Analysis

FIG 8. TGA

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4. Title and Subtitle Yearly Report on Polymer Precursors for Ceramic Matrix Composites	5. Report Date December 1986
	6. Performing Organization Code
7. Author(s) Morton H. Litt and Kanta Kumar	8. Performing Organization Report No. None
	10. Work Unit No. 506-43-11
9. Performing Organization Name and Address Case Western Reserve University Department of Macromolecular Science Cleveland, Ohio 44106	11. Contract or Grant No. NAG3 446
	13. Type of Report and Period Covered Contractor Report Annual
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135	14. Sponsoring Agency Code

15. Supplementary Notes

Project Manager, Frances I. Hurwitz, Materials Division, NASA Lewis Research Center.

16. Abstract

The synthesis and characterization of a polycyclohexasilane is reported. Because of its cyclic structure, it is anticipated that this polymer might serve as a precursor to SiC having a high char yield with little rearrangement to form small, volatile cyclic silanes, and, as such, would be of interest as a precursor to SiC composite matrices and fibers, or as a binder in ceramic processing. Several approaches to the synthesis of a bifunctional cyclic monomer were attempted; the most successful of these was metal coupling of $PhMeSiCl_2$ and Me_2SiCl_2. The procedure gives six-membered ring compounds with all degrees of phenyl substitution, from none to hexaphenyl. The compounds with from 0-2 groups were isolated and characterized. The fraction with degree of phenyl substitution equal to 2, a mixture of <u>cis</u> and <u>trans</u> 1,2-; 1,3-; and 1,4-isomers, was isolated in 32 percent yield. Pure 1,4-diphenyldecamethylcyclohexasilane was isolated from the mixed diphenyl compounds and characterized. Diphenyldecamethylcyclohexasilanes were dephenylated to dichlorodecamethylcyclohexasilanes by treating with H_2SO_4/NH_4Cl in benzene. The latter were purified and polymerized by reacting with sodium in toluene. The polymers were characterized by HPGPC, elemental analysis, proton NMR, and IR. Thermogravimetric analyses were carried out on the polymers. As the yield of residual SiC was low, polymers were heat treated to increase the residual char yield. As high as 51.52 percent residual char yield was obtained in one case.

17. Key Words (Suggested by Author(s)) Organometallic polymers Ceramic precursors Polysilanes	18. Distribution Statement Unclassified - unlimited STAR Category 23

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