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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The use of $MeSiHCl_2$ as a comonomer in the preparation of polycarbosilanes has provided materials with improved pyrolytic yields of silicon carbide ceramic compositions. These polymers, prepared by potassium metal dechlorination of mixtures of chlorosilane monomers in tetrahydrofuran, incorporate $MeSiHCl_2$ both as trifunctional $MeSi\equiv$ units and as difunctional $-MeSiH-$ units.

$Me Si(3-)$

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<u>ORGANOSILANE POLYMERS, V</u>:

<u>HYDROSILYL-MODIFIED POLYCARBOSILANE</u>

<u>PRECURSORS FOR SILICON CARBIDE</u>

by

C. L. Schilling Jr. and T. C. Williams

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Tarrytown, New York   10591

September 1983

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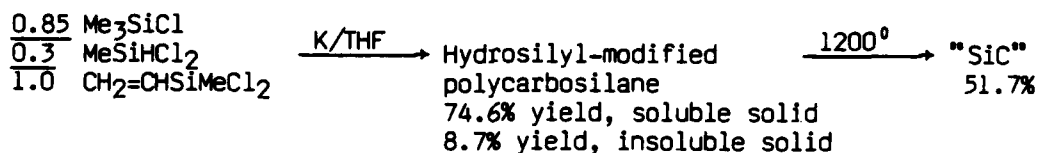
PRECURSORS FOR SILICON CARBIDE

INTRODUCTION

Several organosilicon polymer approaches to ceramic compositions have recently been developed, including branched polycarbosilane precursors for silicon carbide.[1] These thermoplastic polymers were prepared in high yield through potassium metal dechlorinations of mixtures of vinylic or chloromethyl ($ClCH_2-$) chlorosilanes with other methylchlorosilanes in tetrahydrofuran solvent. Monomer mixtures were selected to maximize formation of backbone "SiC" bonds, while maintaining high synthetic yield, tractability, and high yields of silicon carbide ceramic compositions on unconfined pyrolysis. A typical preparation as

$$\frac{\begin{array}{l}0.85 \;\; Me_3SiCl\\ 0.3 \;\;\;\; Me_2SiCl_2\end{array}}{1.0 \;\;\;\; CH_2CHSiMeCl_2} \xrightarrow{K/THF} \begin{array}{l}\text{Polycarbosilane}\\ \text{97.3\% yield as}\\ \text{soluble solid}\end{array} \xrightarrow{1200^0} \begin{array}{l}\text{"SiC"}\\ \text{31.4\%}\end{array}$$
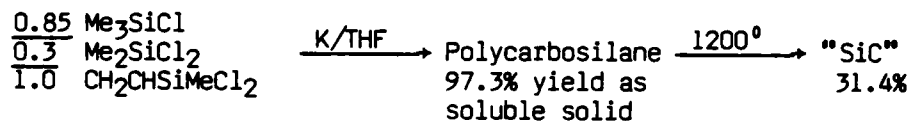
shown yields a polymer which, in unfractionated form, provides a 31.4% yield of SiC ceramic composition on pyrolysis.

RESULTS AND DISCUSSION

The substitution of $MeSiHCl_2$ for Me_2SiCl_2 in the above preparation provides a somewhat lower yield of tractable polymer, which in turn yields significantly more SiC composition on pyrolysis.
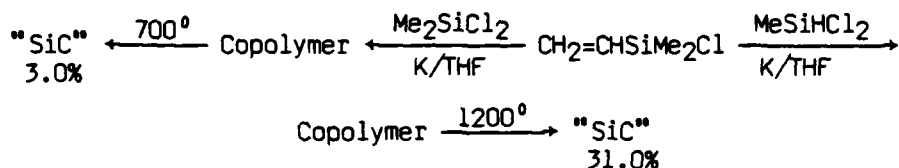
$$\frac{\begin{array}{l}0.85 \;\; Me_3SiCl\\ 0.3 \;\;\;\; MeSiHCl_2\end{array}}{1.0 \;\;\;\; CH_2=CHSiMeCl_2} \xrightarrow{K/THF} \begin{array}{l}\text{Hydrosilyl-modified}\\ \text{polycarbosilane}\\ \text{74.6\% yield, soluble solid}\\ \text{8.7\% yield, insoluble solid}\end{array} \xrightarrow{1200^0} \begin{array}{l}\text{"SiC"}\\ \text{51.7\%}\end{array}$$

Improved ceramic yields were also obtained when $MeSiHCl_2$ was substituted for Me_2SiCl_2 in other copolymerizations.

For example, a linear copolymer prepared from $Me_2SiCl_2/CH_2=CHSiMe_3$[2] provides a very low ceramic

$$\begin{array}{c}\text{"SiC"}\\ 0.3\%\end{array} \xleftarrow{590^0} \underset{\underset{SiMe_3}{|}}{[SiMe_2CH_2CH]} \xleftarrow[K/THF]{Me_2SiCl_2} CH_2=CHSiMe_3 \xrightarrow[K/THF]{MeSiHCl_2}$$

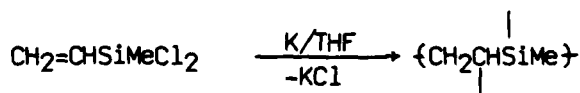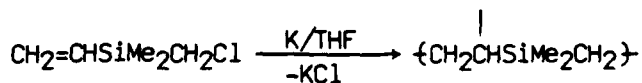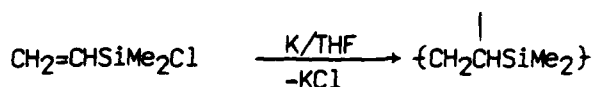$$\text{Copolymer} \xrightarrow{1200^0} \begin{array}{c}\text{"SiC"}\\ 28.5\%\end{array}$$
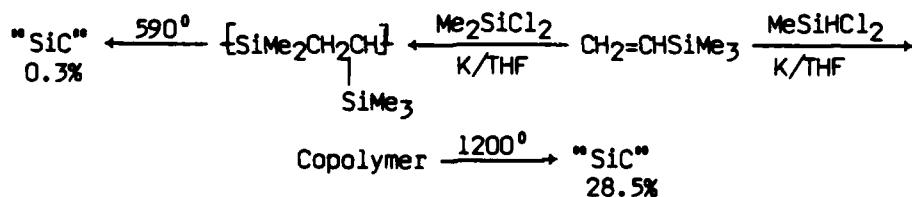
yield after pyrolysis, while a similar polymer prepared with $MeSiHCl_2/CH=CHSiMe_3$ provides a significantly higher ceramic yield. Equivalent results are obtained from coplymers prepared from Me_2SiCl_2 or $MeSiHCl_2$ and $CH_2=CHSiMe_2Cl$, or from Me_2SiCl_2 or $MeSiHCl_2$ and $CH_2=CHSiMe_2CH_2Cl$. In the latter comparison, a 2/1

$$\text{"SiC"} \xleftarrow{\;700°\;} \text{Copolymer} \xleftarrow[K/THF]{Me_2SiCl_2} CH_2=CHSiMe_2Cl \xrightarrow[K/THF]{MeSiHCl_2}$$
$$3.0\%$$

$$\text{Copolymer} \xrightarrow{\;1200°\;} \text{"SiC"}$$
$$31.0\%$$

$$\text{"SiC"} \xleftarrow{\;680°\;} \text{Copolymer} \xleftarrow[K/THF]{2Me_2SiCl_2} CH_2=CHSiMe_2CH_2Cl \xrightarrow[K/THF]{1.5MeSiHCl_2}$$
$$0.3\%$$

$$\text{Copolymer} \xrightarrow{\;1200°\;} \text{"SiC"}$$
$$27.8\%$$
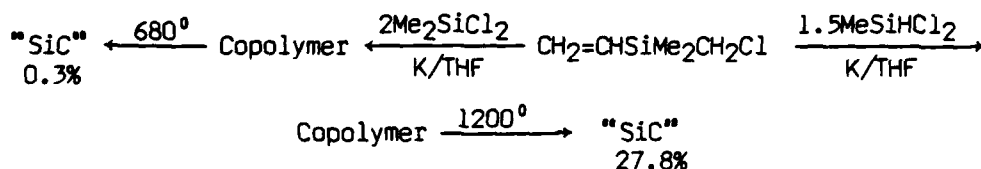
molar ratio of $Me_2SiCl_2/CH_2=CHSiMe_2CH_2Cl$ was used, with a 1.5/1 molar ratio of $MeSiHCl_2/CH_2=CHSiMe_2CH_2Cl$.

Since the backbone branching in these polycarbosilane types is responsible for their effective pyrolytic conversion to SiC,[1] it appears that $MeSiHCl_2$ provides such branching, either by forming trifunctional MeSi≡ units during synthesis (with loss of H-groups) or during pyrolysis, by reactions of difunctional -MeSiH- groups.

It should be noted that the polymeric units derived from $CH_2=CHSiMe_2Cl$ or $CH_2=CHSiMe_2CH_2Cl$ provide backbone branching at carbon, rather than at silicon, and do not contribute to ceramic yield, while $CH_2=CHSiMeCl_2$ provides units with backbone branching at silicon which do contribute to ceramic yield.

$$CH_2=CHSiMe_2Cl \xrightarrow[-KCl]{K/THF} \{CH_2\overset{|}{CH}SiMe_2\}$$

$$CH_2=CHSiMe_2CH_2Cl \xrightarrow[-KCl]{K/THF} \{CH_2\overset{|}{CH}SiMe_2CH_2\}$$

$$CH_2=CHSiMeCl_2 \xrightarrow[-KCl]{K/THF} \{CH_2\overset{|}{\underset{|}{CH}}SiMe\}$$

Model reactions suggest that the majority of the hydrosilyl groups are lost in the preparative step. Reaction of 2/1 $Me_3SiCl/MeSiHCl_2$ with K/THF provides a low yield of the tetrasilane, $MeSi(SiMe_3)_3$,[3] as the major volatile product, rather than $MeSiH(SiMe_3)_2$. Proton NMR analyses of the $MeSiHCl_2$-derived copolymers show that about 20% of the hydrosilyl groups remain, while 80% are

$$MeSiHCl_2 \xrightarrow[-KCl]{K/THF} \underset{H}{\overset{Me}{-Si-}} + \underset{}{\overset{Me}{-Si-}}$$
$$\phantom{MeSiHCl_2 \xrightarrow[-KCl]{K/THF}} \quad 20\% \quad 80\%$$
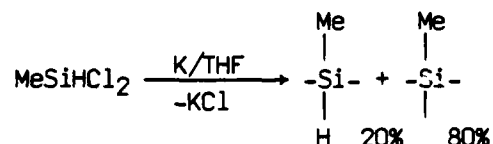
converted to trifunctional branching units. The degree of loss of hydrosilyl functionality may be dependent on the active metal, since lithium causes complete loss,[4] while sodium retains most of the hydrosilyl groups,[5] in respective reactions with Me_2SiHCl.

$$HSiMe_2SiMe_2H \xleftarrow{\quad Na \quad} Me_2SiHCl \xrightarrow[THF]{Li} (SiMe_2)_6$$

POLYMER PROPERTIES

The soluble solid from dechlorination of 0.85/0.3/1.0 $Me_3SiCl/$ $MeSiHCl_2/CH_2=CHSiMeCl_2$ is a colorless resin which thermosets before melting, remaining solid to 300°, at which point pyrolytic degradation commences. TGA Scans of that polymer (Figure I) and the corresponding 0.85/0.3/1.0 $Me_3SiCl/$ $Me_2SiCl_2/CH_2=CHSiMeCl_2$ polymer (Figure II) also demonstrate the higher ceramic yield from the $MeSiHCl_2$-derived polymer. The TGA yield figures are somewhat lower than those obtained from bulk pyrolyses, probably due to the higher TGA heating rate and the small TGA sample size.
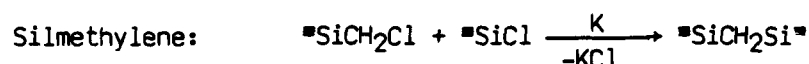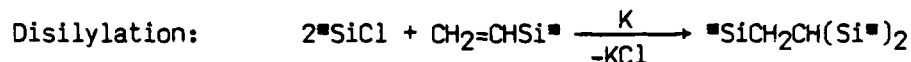
A series of polymers were prepared with relatively lower contents of units derived from $MeSiHCl_2$, as in 0.85/0.3/0.3/1.0, 0.85/0.2/0.2/1.0, and 0.85/0.3/0.1/1.0 polymers from $Me_3SiCl/Me_2SiCl_2/MeSiHCl_2/CH_2=CHSiMeCl_2$ monomer mixtures, to provide materials with better melt properties. The latter two polymers were solids at room temperature, remained fluid after melting to 300°, and were melt-spun to preceramic polycarbosilane fibers.[6]

Fractionation of the 0.85/0.3/1.0 terpolymer from $Me_3SiCl/MeSiHCl_2/$ $CH_2=CHSiMeCl_2$ from THF into nonsolvent acetone provided high and low molecular weight fractions in approximately equal amounts.

The high molecular weight fraction provided 53.5% of SiC ceramic composition on pyrolysis, while the low molecular weight fraction yielded 43.2%. Actual molecular weights were not determined, although the polymers are amenable to analysis by gel permeation chromatography.

These polymers do not provide exact elemental analyses[7] due to oxygen incorporation during hydrolytic termination, loss of hydrogen from ■SiH groups, and problems in total combustion of preceramic materials.

The major-polymer forming reactions are disilylation of vinyl groups, creation of silmethylene groups, or formation of silicon-silicon bonds. Model

Disilylation: $2■SiCl + CH_2=CHSi■ \xrightarrow[-KCl]{K} ■SiCH_2CH(Si■)_2$

Silmethylene: $■SiCH_2Cl + ■SiCl \xrightarrow[-KCl]{K} ■SiCH_2Si■$

Si-Si Bonds: $2■SiCl \xrightarrow[-KCl]{K} ■SiSi■$
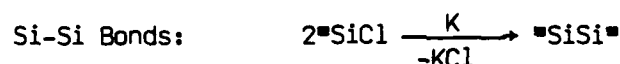
reactions[1] have shown that formation of ■Si-C■ bonds by the first two reactions is genererally favored, and instrumental analyses (IR, NMR, IV) are consistent with that fact.

CONCLUSIONS

The use of low levels of $MeSiHCl_2$ in modifying potassium-derived poly-carbosilanes provides significant improvements in yields and qualities of SiC ceramic compositions obtained therefrom. Most of the $MeSiHCl_2$ reacts to form trifunctional MeSi■ groups, with about 20% being incorporated as difunctional -MeSiH- units. Residual hydrosilyl groups provide proportionate in situ cross-linking during pyrolysis.

EXPERIMENTAL

All chlorosilanes were freshly distilled before use. THF was reagent grade, dried over Linde 4A molecular sieves. K Metal was purchased as practical grade ingots; all K metal transfers were made under nitrogen in a dry box. All reactions (preparations and pyrolyses) were run under argon or nitrogen. Routine NMR spectra were recorded on a Perkin-Elmer R24A spectrometer - VPC Analyses were run on a Hewlett-Packard 5840A gas chromatograph. Pyrolyses up to 700° were run in quartz reactors in a Lindberg 54242 tube furnace and those up to 1200° were run in an alumina reactor in a Lindberg 54233 tube furnace. Both furnaces have programmable controllers, which allow attendent-free operation from charging to removal of products. Conversions to SiC compositions were confirmed by x-ray diffraction.

Reaction of 1/1 $MeSiHCl_2/CH_2=CHSiMe_3$ with K/THF

In a 1l 3N RB flask were combined 31.6g (0.81 mol) of K metal and 422.9g anhydrous THF. Flask was fitted with mechanical stirrer (stainless steel blade), thermometer, heating mantle, addition funnel, and nitrogen flow valves. Mixture was heated to reflux (66°), melting the K, and addition of a mixture of 38.5g (0.39 mol) of $CH_2=CHSiMe_3$ and 44.3g (0.39 mol) of $MeSiHCl_2$ begun and

completed in 40 min., lowering the reflux temperature to 64°. Heating was resumed at reflux for 5-1/2 hr, followed by cooling on wet ice bath, termination with 6.5g H_2O/48.6g THF solution (dropwise addition), and neutralization with 6.4g conc. HCl. Filtration, trituration, and dissolution of the salts (H_2O) left a trace amount of insoluble solid product. The THF reaction solution and trituration solvent were dried over $MgSO_4$, filtered, and vacuum distilled, yielding 0.38g up to 35°/1.0 mm plus 24.36g (44%) of heavies. VPC Analysis suggested 20.8g (54%) of $CH_2=CHSiMe_3$ was unreacted and was removed by stripping. Pyrolysis of the heavies to 1200° in two steps provided 28.5% of SiC composition, showing a weak X-ray diffraction pattern for microcrystalline β-SiC.[8]

A similar copolymer prepared from Me_2SiCl_2/$CH_2=CHSiMe_3$,[1,2] provided only 0.3% ceramic on pyrolysis to only 590°.

Reaction of 0.85/0.3/1.0 Me_3SiCl/$MeSiHCl_2$/$CH_2=CHSiMeCl_2$ with K/THF

The procedure above was repeated using a 2l flask, 106.4g (2.72 mols) of K metal, 807.1g of tetrahydrofuran, and a mixture of 69.7g (0.64 mol) of Me_3SiCl, 25.9g (0.225 mol) of $MeSiHCl_2$, and 105.9g (0.75 mol) of $CH_2=CHSiMeCl_2$. Workup as above yielded 8.7% of insoluble solid product, 9.5% of volatile products, b.p. up to 65°/0.5 mm, and 74.6% of soluble solid product. Pyrolysis of the latter to 1200° in two steps yielded 51.7% of SiC composition having the correct x-ray diffraction pattern for microcrystalline β-SiC.

Analytical:	% C	% H	% Si	% Cl	% O
Calc'd:	48.33	10.22	41.45	0	0
Found:	45.48	9.10	39.63	0.044	5.65
(% O by difference)					

The soluble solid (analysis above) was submitted to Albany International Research Company for spin screening. Under melt spinning conditions, it crosslinked to an insoluble solid.

The procedure was repeated to prepare polymers from 0.85/0.3/0.3/1.0, 0.85/0.2/0.2/1.0, and 0.85/0.3/0.1/1.0 ratios of Me_3SiCl/Me_2SiCl_2/$MeSiHCl_2$/ $CH_2=CHSiMeCl_2$. The latter two polymers were successfully melt-spun to preceramic fibers. The respective bulk pyrolysis yields of SiC ceramic compositions were 41.6%, 40.8%, and 35.5%.

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7. Elemental analyses by Galbraith Laboratories, Knoxville, Tenn.

8. S. Yajima, et. al., Nature, $\underline{279}$, 706 (1979).

FIGURES

ORGANOSILANE POLYMERS, V

Figure I

TGA Scan of Terpolymer from 0.85/0.3 /1.0
Me3SiCl/MeSiHCl2/CH2=CHSiMeCl2

ORGANOSILANE POLYMERS, V
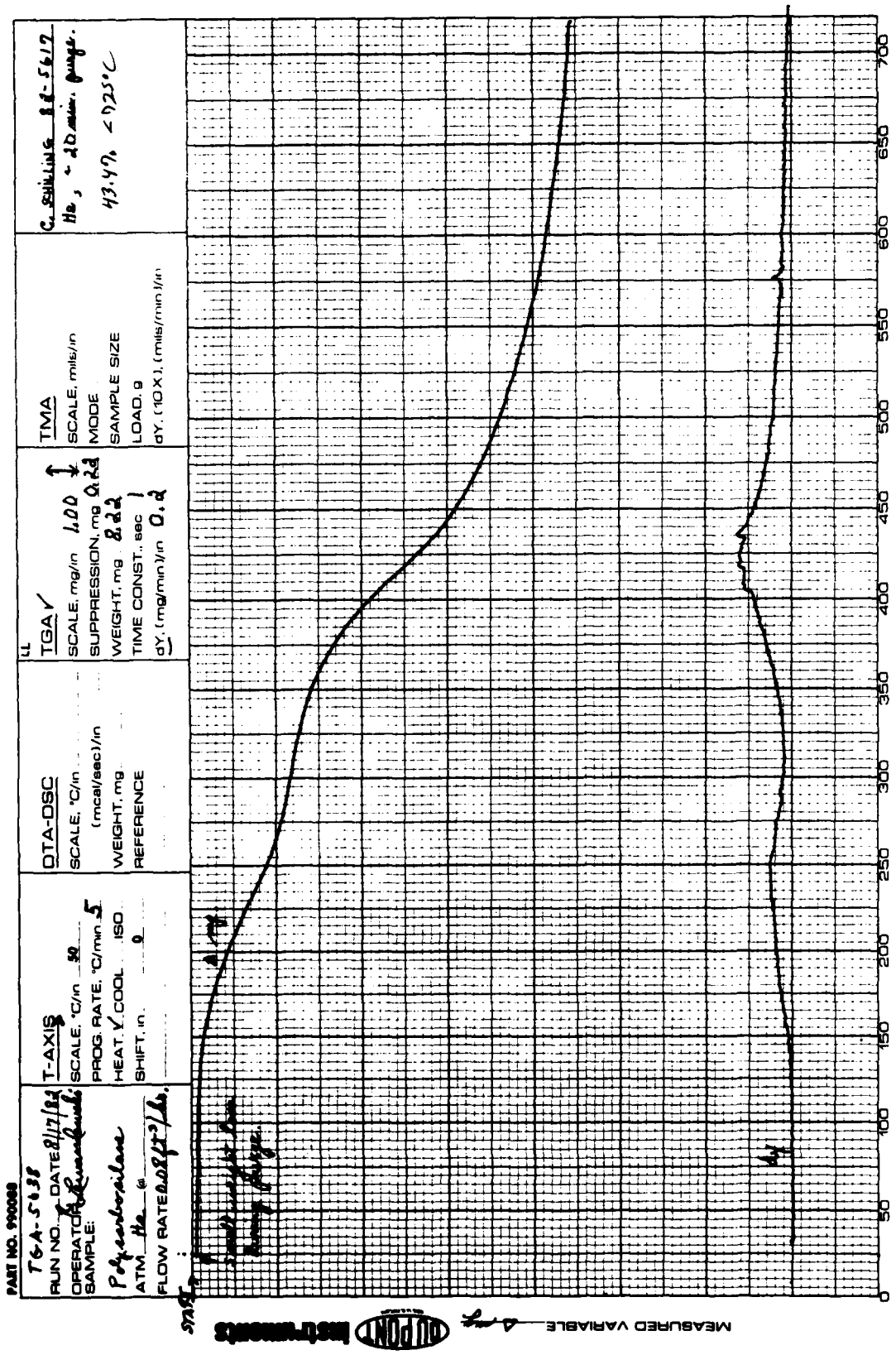
Figure II
TGA Scan of Terpolymer from 0.85/0.3/1.0
Me$_3$SiCl/Me$_2$SiCl$_2$/CH$_2$=CHSiMeCl$_2$

C. Schilling 82-5616
He, ~ 20 min purge
24.3 % < 725°C

TEMPERATURE, °C (CHROMEL/ALUMEL)

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