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PREPARATION AND EVALUATION OF EXACTLY ALTERNATING SILARYLENE-SI--ETC(U)
AUG 78 R W LENZ, P R DVORNIC N00014-76-C-0700

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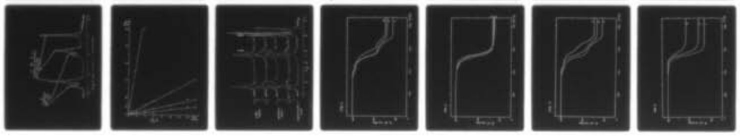

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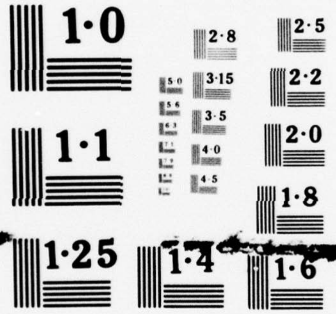

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Silarylene polymers; siloxane polymers; disilanol monomers; ureidosilane monomers; alternating silarylene-siloxane polymers; elastomers; thermally-stable polymers; vinylsiloxane monomers; molecular weight of silicone polymers.
20. ABSTRACT (Continue on reverse side if necessary and identify by block number):

Four monomers needed for the preparation of exactly alternating silarylene-siloxane polymers of high molecular weight were prepared in high purity. The polymerization reaction based on the combination of a disilanol monomer (either the p-phenylene or the p,p′-diphenyl ether) with a diureidosilane monomer (either the dimethyl or the methylvinyl) was applied successfully to the preparation of polymers and copolymers having weight average

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ANNUAL TECHNICAL REPORT

"PREPARATION AND EVALUATION OF EXACTLY ALTERNATING SILARYLENE-SILOXANE ELASTOMERS"

by

Robert W. Lenz
and
Petar R. Dvornic

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Chemical Engineering Department
and
Polymer Science and Engineering Department
University of Massachusetts, Amherst

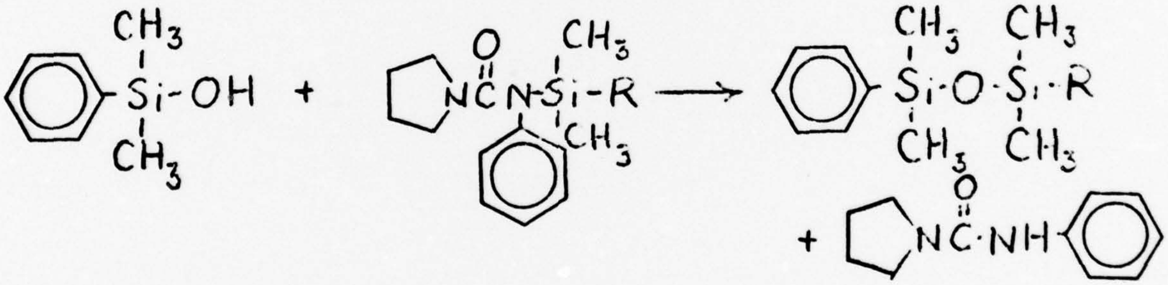
August 1, 1978

SUMMARY

Four monomers needed for the preparation of exactly alternating silarylene-siloxane polymers of high molecular weight were prepared in high purity. The polymerization reaction based on the combination of a disilanol monomer (either the p-phenylene or the p,p'-diphenyl ether) with a diureidosilane monomer (either the dimethyl or the methylvinyl) was applied successfully to the preparation of polymers and copolymers having weight average molecular weights greater than 100,000. A particularly important problem in these preparations was the stability of the ureidosilane monomer. The glass temperatures of the two dimethylsiloxane-diol homopolymers as determined by DSC were -64° and -24°C for the p-phenylene and the p,p'-diphenyl ether polymers, respectively. The thermal stabilities of these homopolymers and copolymers as determined by TGA were fairly simple in behavior in nitrogen but quite complex in air. Incorporation of the methylvinylsiloxane units into the exactly alternating copolymers resulted in considerable increases in thermal stability.

INTRODUCTION

Initial investigations in this grant research program were directed at evaluating the step-growth, condensation polymerization reaction, which has been developed for the preparation of alternating carborane-siloxane polymers,(1) to the preparation of closely analogous arylene-siloxane polymers. The basic reaction involved is the nucleophilic substitution of a ureidosilane with a silanol to form the desired siloxane unit and also an unsymmetrical urea as the by-product, as follows:



The urea moeity was selected as the leaving group because of its low basicity and reactivity to the siloxane unit.

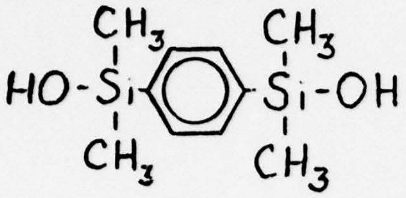
It was determined in these investigations that this reaction was capable of generating high molecular weight, alternating arylene-siloxane polymers, and these products had good thermal stabilities and promising mechanical properties. The reaction system was somewhat complicated, however, by the instability of the ureidosilane monomer, and the present phase of the research program has been concerned with this problem as well as with the selection of the best candidate monomers and optimization of the polymerization reaction conditions.

It was recognized at the start that the two principal problems involved in the synthesis of high molecular weight polymers were: (1) preparation of very pure monomers, particularly the ureido silane monomers which were observed to be unstable on storage, and (2) selection of the best procedures to carry out and monitor the polymerization reactions. Intensive investigations in these areas during the past year have led to the development of procedures for the consistent preparation of high molecular weight polymers in much shorter reaction times than previously required. Most recently polymerization reaction times have been reduced from 5 to 6 down to 1 to 2 days.

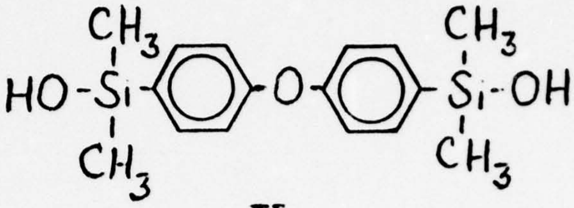
The procedure developed has been applied to the preparation of high molecular weight homopolymers and copolymers of two different disilanol monomers with two different ureidosilane monomers as discussed in the following report. These polymers have been characterized for composition, structure, molecular weight, molecular weight distribution, physical properties, and thermal stability.

MONOMER SYNTHESIS

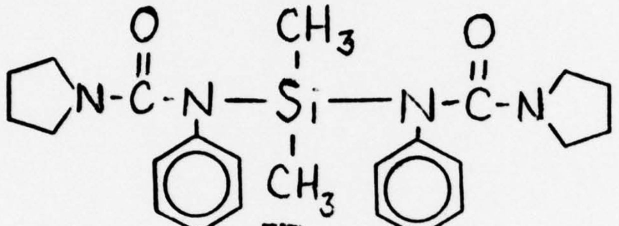
Investigations carried out during the first year of this grant on four different disilanol monomers indicated that the most promising candidates were 1,4-bis(hydroxydimethylsilyl)benzene, I, termed the p-diol, and 4,4'-bis(hydroxydimethylsilyl)phenyl ether, II, termed the ether-diol.(2) This selection was made on the basis of ease of preparation and purification, reactivity in polymerization with bis(1,1-tetramethylene-3-phenylureido)-dimethylsilane, III, ability to prepare high molecular weight polymers, and polymer properties.



I



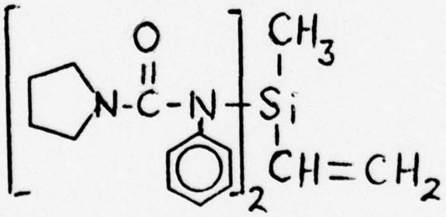
II



III

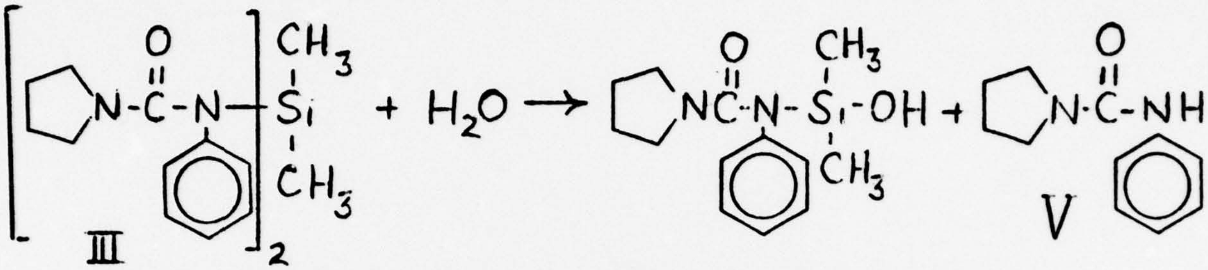
Detailed procedures for preparations of these monomers were given in a previous technical report.(2) These procedures have also been applied to the synthesis of a second ureidosilane monomer to be used for the preparation of crosslinked polymers; namely bis(1,1-tetramethylene-3-phenylureido)-methylvinyl silane, IV:

IV



Polymers and copolymers prepared from different combinations of these four monomers are listed in Table 1 according to their letter designations to be used in subsequent discussions.

The dimethylureidosilane monomer, III, was synthesized by the reaction of phenylisocyanate with bis(N-pyrrolidinyl)dimethylsilane, and this monomer was much more difficult to prepare in high purity than the silanols. The crude product always contained some amount of 1,1-tetramethylene-3-phenylurea, V, which varied in content from 5 to 30% and which is believed to be formed by hydrolysis with adventitious amounts of water:



Numerous attempts to extract the urea, V, from the monomer were never completely successful, for one reason or another, with a wide variety of common solvents. Toluene was effective to some degree for this purpose, but it was difficult to subsequently completely remove that solvent from the monomer. The best procedure, but one still not entirely satisfactory, was to selectively dissolve the urea from the crude product with very carefully dried diethyl ether. Treatment of the solvent with n-butyllithium and direct distillation into the reaction flask was a satisfactory drying procedure.(3)

The purity of the ureidosilane monomer was also a function of the temperature at which phenyl isocyanate was added to bis(pyrrolidinyl)dimethylsilane, with lower reaction temperatures yielding higher purity products. Presumably the lower temperatures reduced the rate and importance of the hydrolysis reaction.

Nevertheless, by using the ether extraction procedure, monomers almost completely free of the unsymmetrical urea could be obtained after approximately 36 hours of continuous extraction. The NMR spectrum of this product in deuterated chloroform contained the following peaks: 0.18 δ (s) $Si\text{-}CH_3$, 2.00 δ (quint.) $-CH_2\text{-}CH_2-$ 3.50 δ (t) $-N\text{-}CH_2-$, and 6.90-7.50 δ (m) phenyl.

In chlorobenzene, the first three peaks appear at 0.98, 1.78 and 3.38 δ, respectively. The spectrum of the urea by-product, V, contained the following peaks: 1.98 δ (quint.) $-CH_2-CH_2-$, 3.63 δ (t) $-N-CH_2-$ and 7.00 δ (broad s) -N-H. Because of the different characteristic peaks for the monomer, III, and the urea, V, NMR could be used as an analytical method for determining the amount of this impurity present. As an example, the NMR spectrum in Figure 1 is for a crude monomer containing 25 mole % of V.

The high sensitivity of the ureidosilane monomer to hydrolysis became a problem in its storage, and the effect of storage conditions on the rate of urea formation was determined with the results collected in Figure 2. The storage conditions used to obtain the data in this figure were the following: A. exposed to air at room temperature; B. stored under vacuum at -5°C; C. stored under a nitrogen atmosphere at room temperature; D. stored under a nitrogen atmosphere at -20°C. It is apparent that storage under vacuum was ineffective in excluding water from contacting the sample.

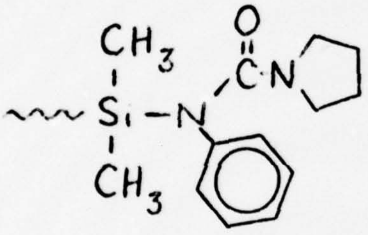
POLYMER PREPARATIONS

Polymerization reactions of the silanol monomers, I or II, with the ureidosilane, III, were carried out in chlorobenzene, which is a good solvent for ureido monomers and polymers but a very poor solvent for the urea by-product, V. Because of the sensitivity of the ureidosilane monomer to water and the uncertainty of its exact purity, the normal procedure of using stoichiometric amounts of the two monomers in a step-growth polymerization reaction could not be used with confidence. Instead the procedure developed by previous workers for the synthesis of the carboranesiloxane polymers was applied in which the course of the polymerization reaction was followed by NMR spectroscopy.(1) The most convenient method for doing this was to monitor unreacted ureidosilane monomer and endgroups in the reaction mixture, and the appropriate chemical shifts for this purpose are collected in Table 2.

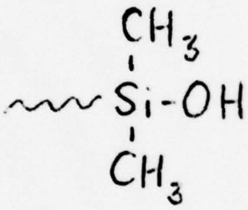
By this approach the typical synthetic route used was to begin the reaction with a slight excess of the diol monomer over the ureidosilane monomer and add, consecutively, small amounts of the latter until the first appearance of unreacted ureidosilane groups was observed. After sufficient time was allowed for these groups to react, additional amounts of the diol monomer were added to achieve the exact functional group equivalence. This procedure was capable of forming high molecular weight polymers, but it is undesirably slow and tedious.

A typical polymerization reaction based on this procedure for the p-diol monomer is described below:

5.0974 g (22.536 m mole) of p-diol was placed in a three-neck round-bottom flask, equipped with a nitrogen inlet and outlet as well as with a magnetic stirrer. Nitrogen gas was purified by passing it through H_2SO_4 and through columns filled with KOH, P_2O_5 and molecular sieves. After the inert atmosphere was achieved by flushing with nitrogen, the falsk was cooled in a acetone-dry ice bath, which was maintained at a temperature between -34° and -26°C. Chlorobenzene, which had been refluxed twice over CaH_2 for 24 hours and distilled was used as the polycondensation solvent. 8.7449 g (20.057 m mole) of ureidosilane was dissolved under nitrogen in 50 ml of chlorobenzene and added to the solid p-diol in the reaction flask over a period of 1.5 hours. The molar ratio of the two monomers at this point (diol to silane was 1.124. The reaction mixture was slowly warmed to room temperature and stirred under nitrogen over night. An NMR spectrum of a sample taken from the reaction mixture was obtained, and as it did not show any unreacted ureidosilane, another 0.3805 g (0.872 m mole) of ureidosilane dissolved in 4 ml of chlorobenzene was slowly added at room temperature. This procedure was repeated several times until the NMR spectrum indicated the presence of a slight excess of ureidosilane as shown in Figure 3. At this point, the endgroups were predominantly, if not entirely, the ureidosilane functional groups, VI, instead of the silanol function groups VII:

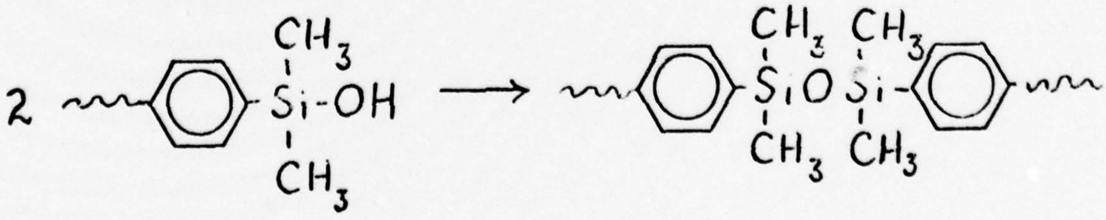


VI



VII

Solid p-diol was then added to the reaction mixture until the NMR peaks due to unreacted ureidosilane slowly disappeared as shown in Figure 3. The molar ratio of two comonomers calculated at that point was 1.03, which indicated that some self-condensation of the silanol groups probably occurred during the reaction, as follows:



The reaction mixture was filtered to separate solid urea by-product from the polymer solution, and the liquid phase was slowly added into a six-fold excess of well-stirred methanol, upon which white, rubberlike polymer precipitated. The polymer was filtered off and dried in a vacuum oven at 25°C over a period of 48 hours. A yield of 6.04 g (95%) of a very viscous, liquid-like polymer was isolated. By using the identical procedures, 6.41 g of the polymer from the ether-diol (90% yield) was obtained. This product was even more viscous but still liquid-like.

POLYMER CHARACTERIZATION

Homopolymers and copolymers prepared by the procedure described above were characterized for structure and composition by elemental analysis - Table 3, NMR spectroscopy - Table 4, and IR spectroscopy - Table 5. Elemental analyses were obtained by the Microanalysis Laboratory of the University of Massachusetts, infrared spectra were obtained on a Perkin-Elmer Spectrometer Model 283, and NMR spectra on a Perkin Elmer R-32 instrument with chemical shifts given in Table 4 relative to methylene chloride as the standard.

Intrinsic viscosities of dilute polymer solutions were determined in tetrahydrofuran at 30 ± 0.5°C using an U-belhode dilution viscometer. In all determinations concentrations ranged from 0.570 g/dl to 0.510 g/dl and five different concentrations were always used. Intrinsic viscosities obtained in such a manner are listed in Table 6.

With the exception of Polymer A (4), values for Mark-Houwink constants for these polymers were not known. Using $K = 7.86\ 10^{-5}$ and $a = 0.757$ for polymer A, the calculated value for $\overline{M}_v$ was 112,700 which agrees fairly well with $\overline{M}_w$ value obtained for the same polymer by GPC (see Table 6). On the basis of the $[\eta]$ values for the other polymers it can be assumed that their molecular weights should be close to or higher than that of Polymer A.

Preliminary GPC analyses were made for Polymers A and C. Molecular weight distributions characteristic for condensation polymers were obtained. For GPC determinations tetrahydrofuran was used as the solvent at room temperature and calculations were based on polystyrene standards.

THERMOGRAVIMETRIC ANALYSIS

A DuPont 950 Thermogravimetric Analyzer in line with a DuPont 900 Thermal Analyzer was used for TGA analysis. Polymers were tested in air and in a nitrogen atmosphere at a heating rate of 15°C/min. The results obtained are presented in Tables 7 and 8, respectively, and selected thermograms are shown in Figures 4-7.

General conclusions which can be drawn from these TGA results are the following:

(1) The mechanisms of degradation in air, Figure 4, and in nitrogen, Figure 5, were entirely different in nature. While decomposition by a single process apparently occurred in nitrogen, in air a three-step process seemed to be involved.

(2) In all cases degradation started at lower temperatures in air than in nitrogen.

(3) With the exception of the 100% vinyl polymers, 50% weight loss was achieved at lower temperatures in a nitrogen atmosphere than in air.

(4) Vinyl substituted polymers were generally more stable than the dimethylsilyl polymers and resistance to thermal degradation apparently increased with increasing vinyl content as seen in Figures 6 and 7 for degradation in air and nitrogen, respectively.

(5) In nitrogen polymers from the diphenylether diol monomer were more stable than those from the p-diol monomer, and while the copolymer of the 50 mole % diol monomer mixture was in between, the situation was reversed in air as seen in Figures 4 and 5.

DIFFERENTIAL SCANNING CALORIMETRY

A Perkin Elmer Differential Scanning Calorimeter, model DSC2 was used to determine glass transition temperatures of most polymers. Heating rates of 20°C/min and 5°C/min in the temperature interval for -100°C to 0°C were employed. The results obtained are presented in Table 7.

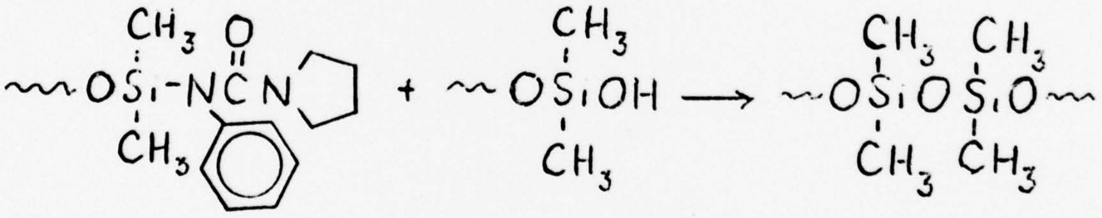
TABLE 7 - Glass Transition Temperatures of Alternating Silarylene-Siloxane Polymers

Polymer	Tg (°C) h.rate = 20°C/min	Tg (°C) h.rate = 5°C/min
A	-64	-62
B	--	--
C	-24	-26
D	-24	-27
E	--	--
F	-35	-34
G	-43	-40

CONCLUSIONS

The most difficult problem encountered in the preparation of high molecular weight polymers was in obtaining and maintaining highly pure ureidosilane monomers. These compounds readily decomposed to unsymmetrical ureas, which were not in themselves detrimental to the polymerization (indeed the ureido monomer was selected for that reason), but the uncertainty of monomer purity and the possibility of further hydrolysis during polymerization made it very difficult to establish the exact equivalence of arylene silanol and ureidosilane functional groups which is required for the achievement of high molecular weight products in this step-growth polymerization reaction. As a result, the reactions had to be continuously monitored by NMR and the monomers added sequentially.

An additional potential problem resulting from the ureidosilane hydrolysis could be the possible formation of disiloxane units in the final polymer from the reaction of the ureidosilanol so formed with another ureidosilane:



These units if present in small amounts would not be observed by the NMR analysis of the final polymer but could possibly be sites of thermal instability.

For monitoring the polymerization reaction by NMR, the most convenient peaks to follow were those at 0.98 δ and 3.40 δ for the ureidosilane functional group. At the early stages of the reactions the spectra were quite complex, but as the molecular weight of the polymers increased to a relatively high value, the spectra simplified into two principal, intense singlets at 0.35 δ and 0.1 δ. These peaks, in the intensity ratio of 2:1, were for the methyl groups on the silarylene and siloxane units, respectively.

The thermal stabilities of the linear, alternating silarylene-siloxane homopolymers and copolymers showed some variabilities, but, in general, the polymers based on the ether-diol monomer were more stable than those based on the p-diol monomer. In both air and nitrogen atmospheres, increasing thermal stabilities were observed with increasing contents of the methylvinylsiloxane in the polymers (replacing the dimethy siloxane). This observation suggests that the presence of the vinylsilane units may have caused crosslinking reactions in the polymers during thermal degradation resulting in the formation of more thermally stable residues. The most stable polymer was Polymer D formed from the ether-diol and the methylvinylureidosilane. In nitrogen this polymer began to degrade at 490°C, showed a leveling-off weight loss of approximately 35% of its initial weight at approximately 740°C and lost no additional weight up to the final temperature of the test up to 980°C. In air this polymer and all of the others showed a much more complex weight-loss behavior.

Literature References

1. E.N. Peters, E. Hedaya, J.H. Kawakami, G.T. Kwiatkowski, R.W. Tulis and D.W. McNeil, Union Carbide Report CRL-T 795, July 17, 1974; J. Polymer Sci. Chem. Ed., 15, 2229 (1977).

2. R.W. Lenz, N. Koide and P.R. Dvornic, Office Naval Research, Contract No. N00014-76-C-0700, Annual Report, June 1, 1977.

3. D.R. Burfield, K. Lee and R.H. Smithers, J. Org. Chem., 42, 3060 (1977).

4. C.U. Pittman, Jr., W.J. Patterson and S.P. McManus, J. Polymer Sci., Polymer Chem. Ed., 14, 1715 (1976).

TABLE 1 - Alternating Silarylene-Siloxane Homopolymers and Copolymers*

Homopolymer	Disilanol	Ureidosilane
A	I	III
B	I	IV
C	II	III
D	II	IV
Copolymer		
E	II	0.925 III + 0.075 IV
F	0.5 I + 0.5 II	III
G	0.5 I + 0.5 II	IV

*I-p-diol; II-ether-diol; III dimethylureido silane; IV methylvinylureidosilane

TABLE 2 - Assignments for the Characteristic NMR Peaks in the Spectra of Samples from the Polymerization Reaction Mixture

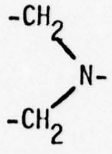
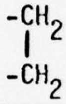
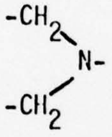
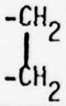
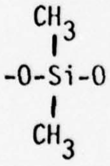
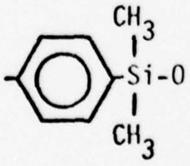
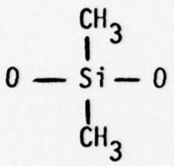
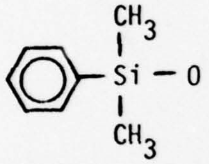
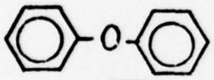
	Group	Chemical Shift(δ)	Type of Signal
Ureidosilane Monomer	$Si-CH_3$	0.98	singlet
		3.90	triplet
	 $\begin{array}{l}-CH_2\\ \mid\\ -CH_2\end{array}$	1.80	quintet
Urea By-Product		3.65	triplet
	 $\begin{array}{l}-CH_2\\ \mid\\ -CH_2\end{array}$	1.98	quintet
Polymer	 $\begin{array}{c}CH_3\\ \mid\\ -O-Si-O\\ \mid\\ CH_3\end{array}$	0.55	singlet
		0.80	singlet

TABLE 3 - Elemental Analysis of Alternating Silarylene-Siloxane Polymers

Polymer	% C		% H		% Si		% O	
	Calc'd	Obs'd	Calc'd	Obs'd	Calc'd	Obs'd	Calc'd	Obs'd
A	51.06	48.08	7.80	8.36	29.79	29.98	11.35	13.58
B	53.06	51.97	7.48	7.26	28.57	28.67	10.88	12.10
C	57.75	55.60	6.95	6.76	22.46	23.14	12.84	14.50
D	59.07	59.43	6.74	6.66	21.76	21.70	12.43	12.21
E	57.84	57.64	6.93	7.01	22.40	22.89	12.80	12.46
F	54.88	54.93	7.32	7.58	25.61	25.30	12.19	12.19
G	56.47	56.01	7.06	7.15	24.71	24.37	11.76	12.47

TABLE 4 - PMR Assignments for Alternating Silarylene-Siloxane Polymers

Assignment	Chemical Shift δ (ppm)*						
	polymer A	B	C	D	E	F	G
 $O-Si(CH_3)_2-O$	0.10 s.	0.15s	0.10s	0.10s	0.10s	0.10s	0.10s
	0.35s	0.35s	0.35s	0.35s	0.35s	0.35s	0.35s
	--	--	7.05d 7.55d	7.05d 7.55d	7.05d 7.55d	7.05d 7.55d	7.05d 7.55d
	7.60s	7.60s	--	--		7.60s	7.60s
$-CH=CH_2$	--	5.95(g)	--	5.95	6.30	--	5.95
				0.05s	0.05s		

*Relative to methylene chloride.

TABLE 5 - IR Assignments for Alternating Silarylene-Siloxane Polymers

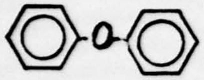
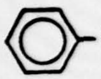
	Polymer Absorbtion Bands						
Assignments	A	B	C	D	E	F	G
C-H stratching (CH$_3$)	2900-3080	2900-3080	2900-3080	2900-3080	2900-3080	2900-3080	2900-3080
	2960	2960	2960	2960	2960	2960	2960
	--	1595	1585	1585	1585	1585	1585
	1395	1380	1395	1395	1390	1380	1410
	1410	1405	1410	1410	1410	1410	
Si-CH$_3$	1310	--	1310	1305	1310	1310	--
	1240-1260	1240-1260	1240-1260	1240-1260	1240-1260	1240-1260	1240-1260
Si	1175	1140	1175	1175	1175	1175	1175
O-Si-O	1115	1040	1115	1115	1115	1115	1115
	1040		1040	1040	1040	1040	1140
Ch$_2$=CH-	--	960	940	--	960	--	960
Si-CH$_3$	870	--	860	870	870	870	870
	825	820	825	825	825	825	825
	790	780	790	780	780	790	775
n.a.	--	1730	--	1730	1730	1730	1730
	--	740	--	--	745	735	745
	690-700	685	690-700	690-700	690-700	690-700	690-700

TABLE 6 - Intrinsic Viscosities and GPC Results for Alternating Silarylene-Siloxane Polymers*

Polymer	[η](dl/g)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
A	0.524	66 646	126 434	1.90
B	0.486			
C	0.667	100 480	214 259	2.13
D	0.464			
E	0.625			
F	0.405			
G	0.387			

*All measurements were made in THF solutions at 30 ± 0.5°C.

TABLE 7 - Thermogravimetric Analysis of Silarylene-Siloxane Polymers in Air

Polymer	Onset of degrad. (°C)	50% loss (°C)	End of degrad. (°C)	Wt. remained (%)
A	345	665	735	39.5
B	420	--	725	58.5
C	335	610	720	26.5
D	425	675	730	41
E	405	630	720	35
F	360	635	730	37
G	420	670	730	46

TABLE 8 - Thermogravimetric Analysis of Silarylene-Siloxane Polymers in N_2

Polymer	Onset of degrad. (°C)	50% loss (°C)	End of degrad. (°C)	Wt. remained (%)
A	400	545	660	30.5
B	450	--	690	75
C	450	518	650	33
D	490	--	740	66.5
E	465	600	720	43
F	390	527	750	31.5
G	415	--	785	53

Figure Captions

1. NMR spectrum of crude dimethylureidosilane monomer in chlorobenzene
2. Rate of formation of the unsymmetrical urea by-product obtained from the degradation of the dimethylureidosilane monomer under various storage conditions.
3. Changes in the NMR spectra of the reactants during polymerization.
4. TGA in air for three dimethylureidosilane polymers: A-p-diol homopolymer; C-ether-diol homopolymer; F-50/50 copolymer.
5. TGA in nitrogen for polymers of Figure 4.
6. Effect of methylvinylsilane units on the TGA in air for three ether-diol polymers: C - 0%, E - 7.5% and D - 100% methylvinylsilane units.
7. TGA in nitrogen for polymers of Figure 6.

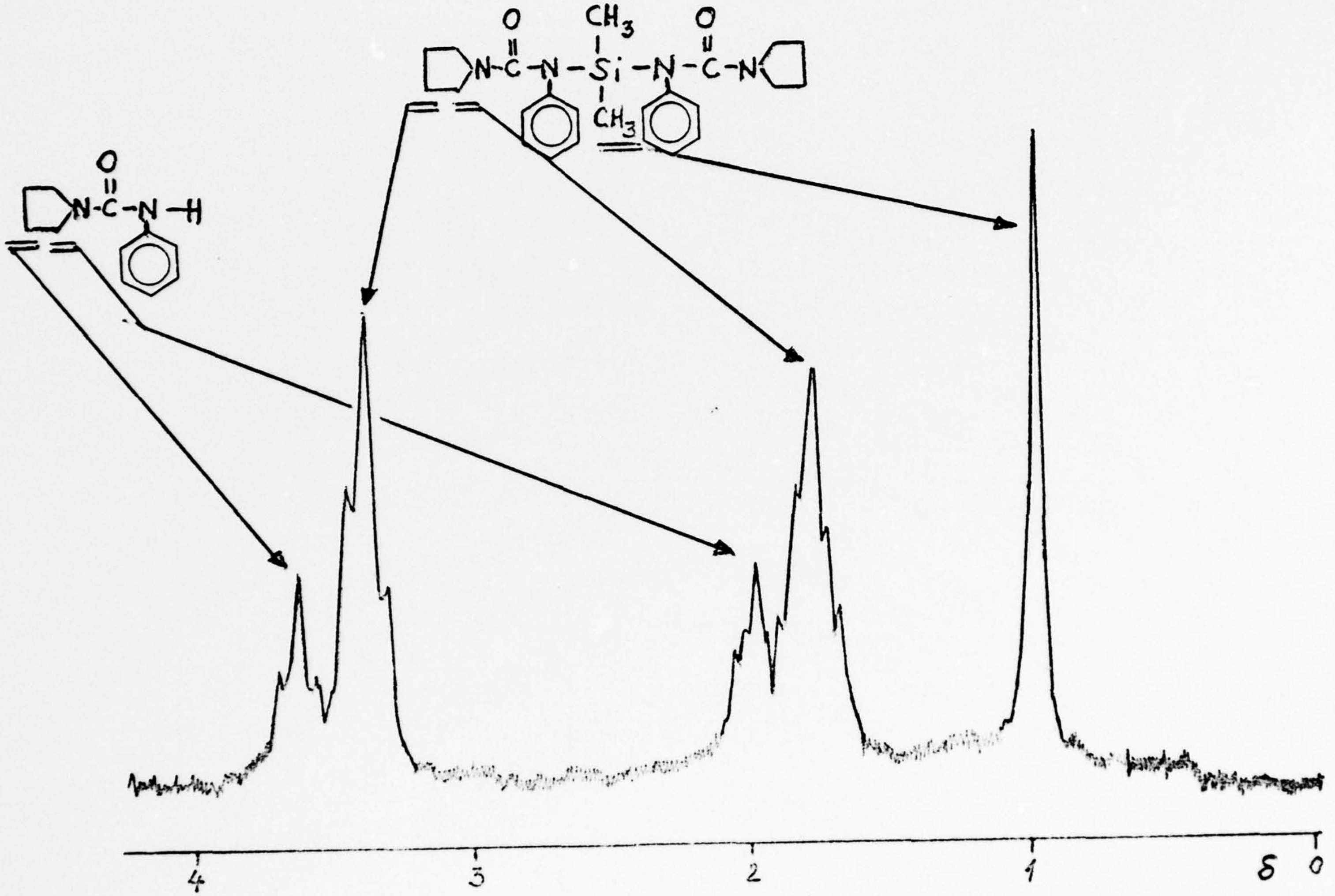


Fig. 1 crude ureidosilane in chlorobenzene

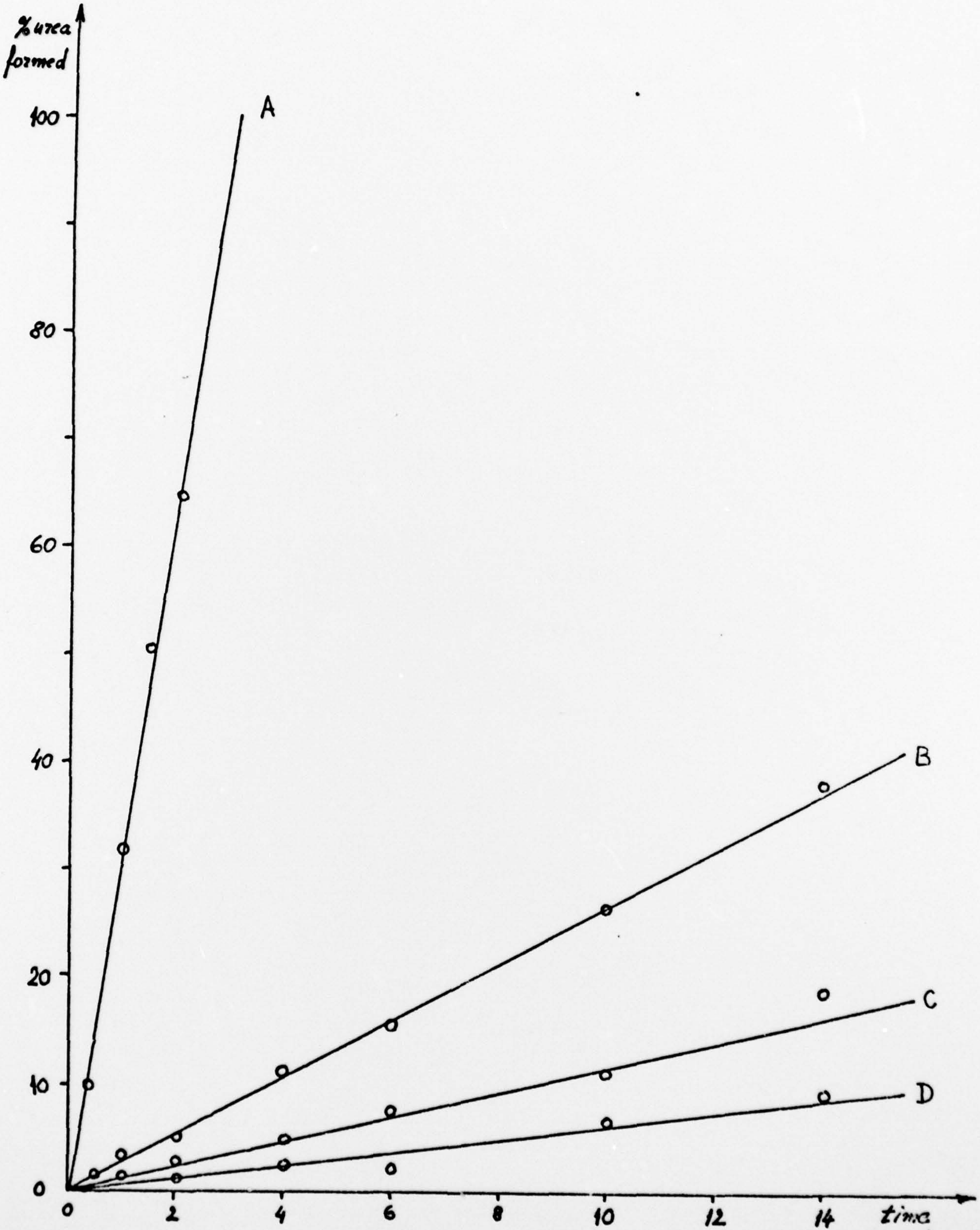


Fig. 2

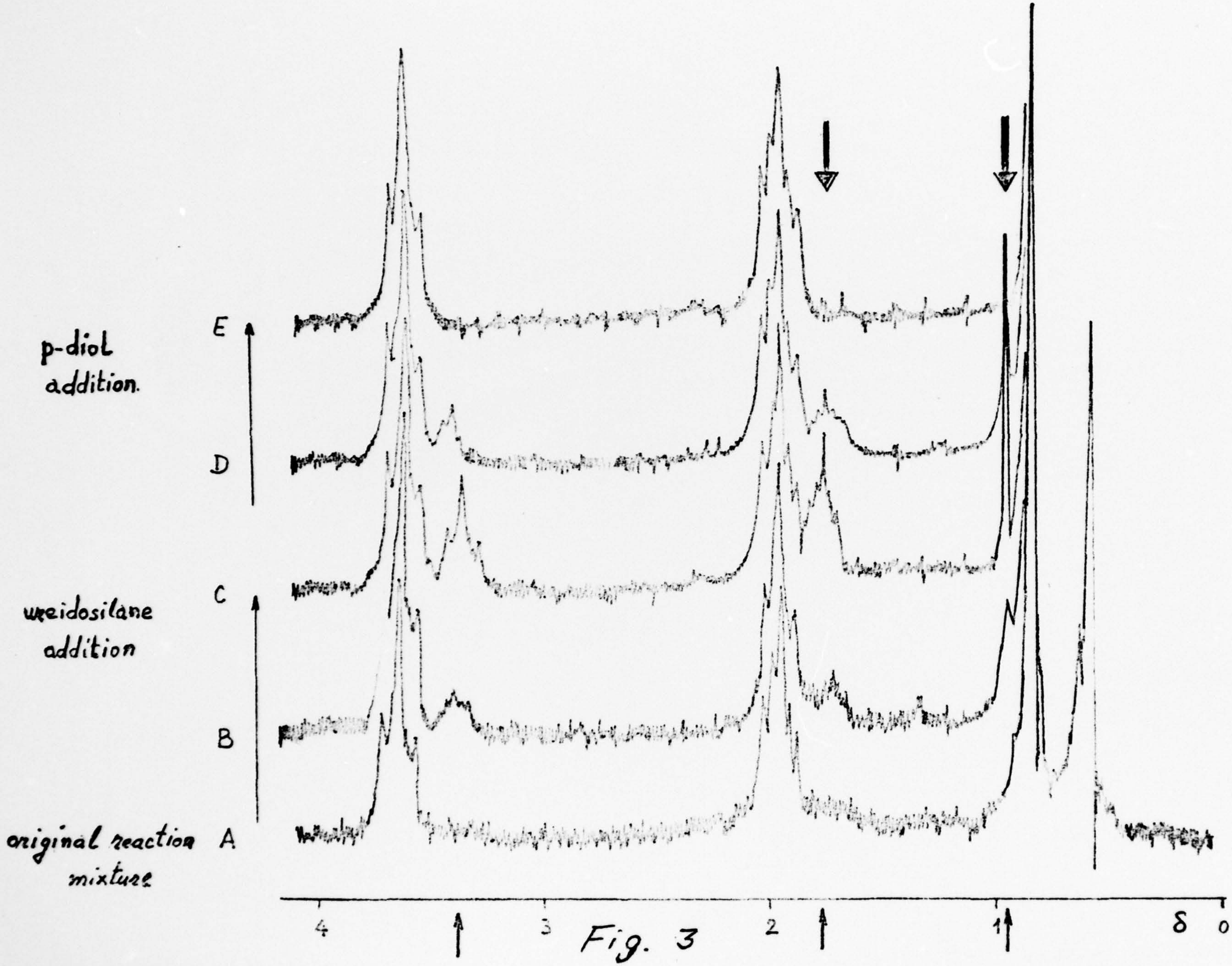

p-diol addition.
E
D
ureidosilane addition
C
B
original reaction mixture
A
4
3
2
1
δ 0

Fig. 3

FIG. 4

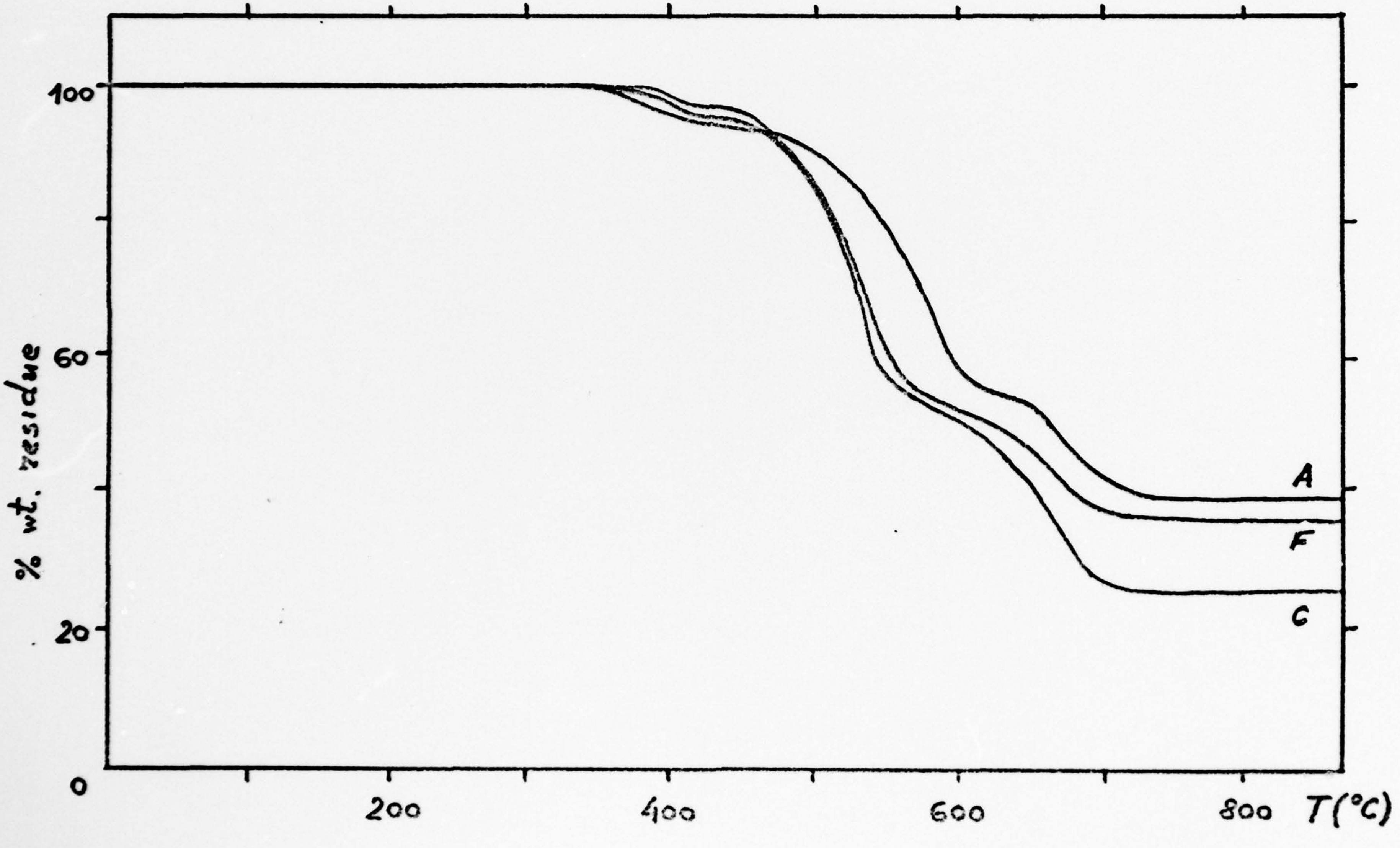


FIG. 5

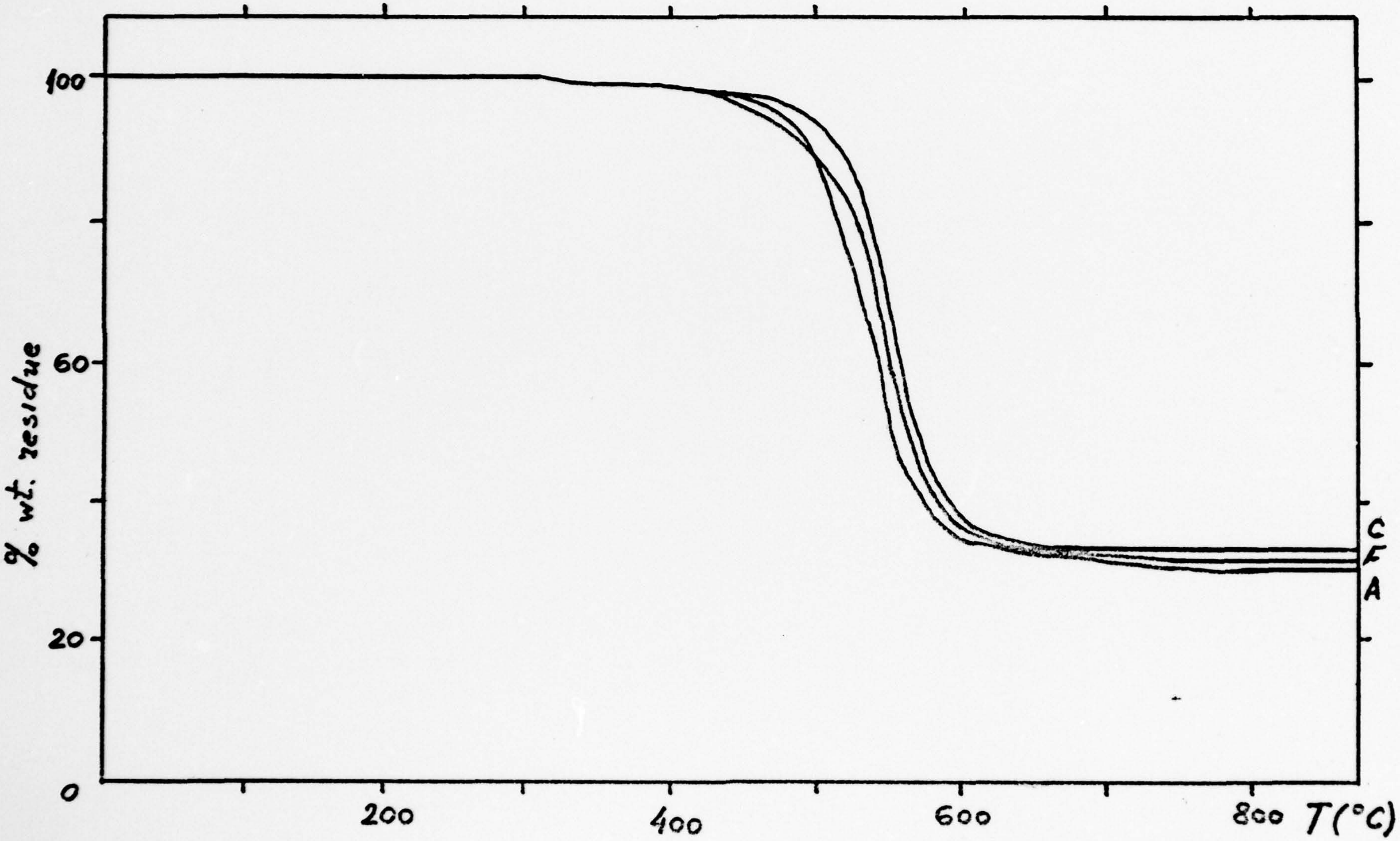


FIG. 6

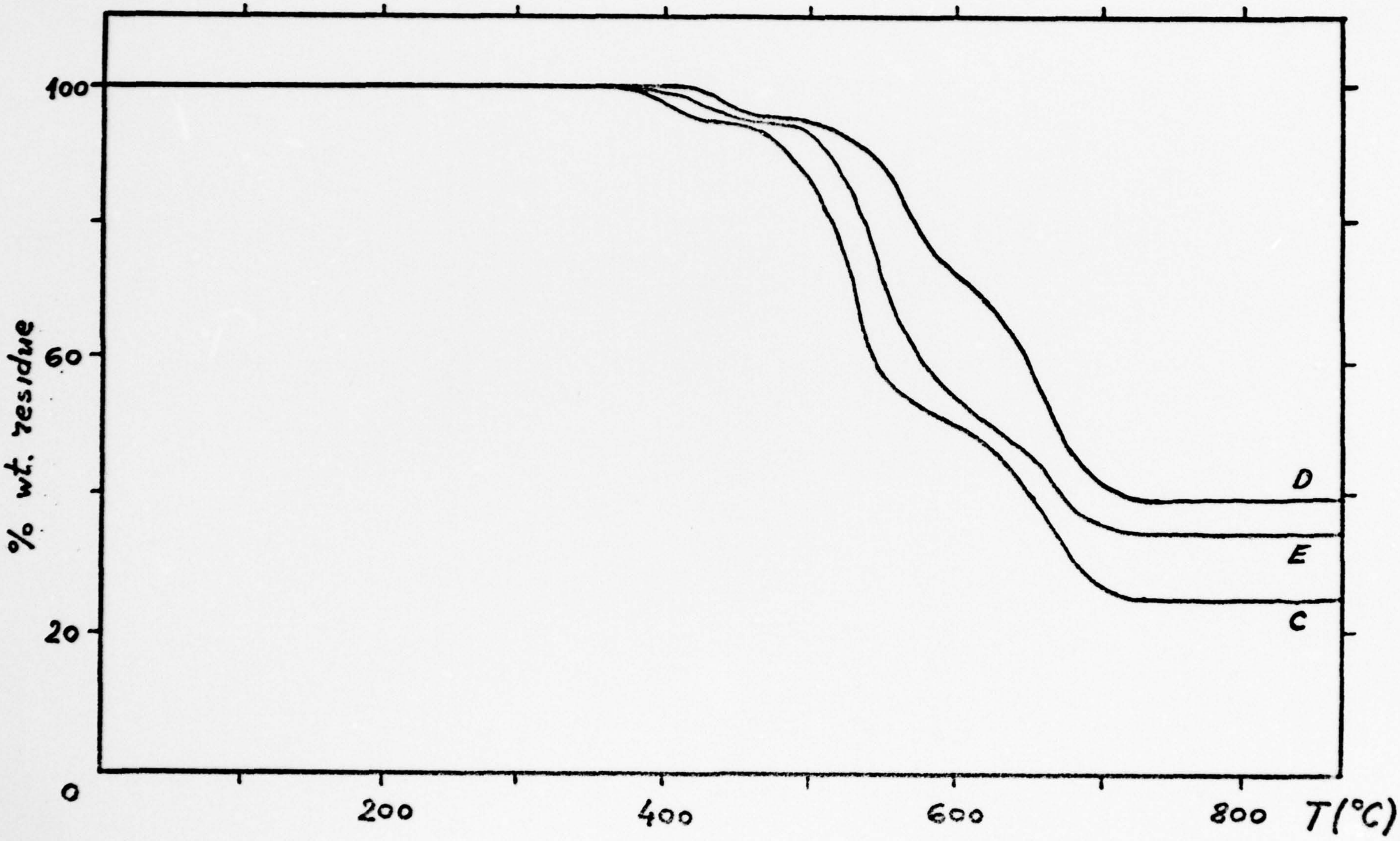


FIG. 7