[Contribution from the Pioneering Research Division, Textile Fibers Department, E. I. du Pont de Nemours & Co.]

SILICON-CONTAINING CONDENSATION POLYMERS

STANLEY B. SPECK

Received June 9, 1953

DISCUSSION

Introduction. Polysiloxanes such as polydimethylsiloxane possess unique properties of high water repellency, good electrical insulating properties and low degree of variation of viscosity with temperature (1). In order to determine whether some of these properties might be imparted to linear polyamides and polyesters, some dibasic acids and esters containing silicon both as silane and siloxane linkages and a diamine containing a silane linkage were prepared and converted into polyamides and polyesters. The silicon-containing intermediates with some of their properties and analytical data are listed on Table I.

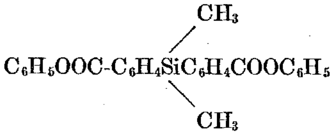
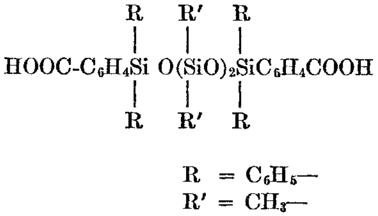
Polyamides containing silicon. The silicon-containing polyamides prepared are listed on Table II with polymerization and polymer data. The polymers which were melt spun into monofils are listed on Table III with some of their fiber properties. The polyamides were prepared by heating the respective salts under reduced pressure. In general the polyamides had properties which appeared to be little different from those of their carbon analogs. (Data have not been published for these carbon analogs that have been prepared in our laboratories.) None of the fibers obtained could be highly oriented by drawing and all of the polymers were amorphous as indicated by x-ray diffraction patterns. The polymers did appear to be unusual in the rather slight effect of temperature on some of their properties. For example they underwent a relatively small change in vibrational modulus (a measure of the stiffness of a fiber when flexurally vibrated) over a rather large temperature range. The polymers were all rather weak, having tenacities of about 1 gram per denier and low elongations of about 5%. In all cases the work recovery values were quite high. (Work recovery may be defined as the ratio of work returned by the fiber on relaxing to the work required to stretch it. Wool-like fibers generally have high work recovery.) None of the polymers was water sensitive. The amount of water absorbed when immersed in water ranged from 1 to 5%. The introduction of larger proportions of silicon in condensation polymers would in all probability result in a greater variation of properties from those of the carbon analogs. However, the problem of synthesizing intermediates containing larger proportions of silicon becomes increasingly difficult.

Molecular weights obtained for the polyamides containing siloxane linkages were disappointingly low. One probable reason for the inability to obtain higher molecular weights was the fact that the melt viscosities of these polymers were extremely high even at 285° despite the fact that their melting points were low. This high melt viscosity tended to make more difficult the removal of water during the later stages of polymerization. Another reason for low molecular weights was that the action of water on siloxanes at high temperature appar-

TABLE I

Organo-silicon Intermediates Prepared

COMPOUND	FORMULA	B.P.		M.P., °C.	ANALYSES AND MISC. DATA
		°C.	Mm.		
Dibenzyldichlorosilane (5)	$(C_6H_5CH_2)_2SiCl_2$	150–165	0.5		N. E., 134.8 (Calc'd, 140.5)
Di-*n*-hexyldichlorosilane	$(C_6H_{13})_2SiCl_2$	97–101	0.5		N. E., 136 (Calc'd, 134.5)
Dibenzyldiethoxysilane	$(C_6H_5CH_2)_2Si(OC_2H_5)_2$	139	0.5		n_D^{25} 1.5250
Di-*n*-hexyldiethoxysilane	$(C_6H_{13})_2Si(OC_2H_5)_2$	95–98	0.5		*Anal.* Calc'd: Si, 9.72; Found: Si, 9.73 n_D^{25}, 1.4265
Di-*p*-tolyldiphenylsilane (7)	$(p\text{-}CH_3C_6H_4)_2Si(C_6H_5)_2$	190–240	0.6	117[a]	*Anal.* Calc'd for $C_{26}H_{24}Si$: C, 85.70; H, 6.65 Found: C, 85.28; H, 6.66. Recryst. from ethanol plus a little benzene
Di-*p*-tolyldimethylsilane	$(p\text{-}CH_3C_6H_4)_2Si(CH_3)_2$	97–105	0.1		*Anal.* Calc'd: Si, 11.7; Found: Si, 12.3
Bis(*p*-bromophenyl)dimethylsilane	$(p\text{-}BrC_6H_4)_2Si(CH_3)_2$	155–170	0.2	72–73	*Anal.* Calc'd: Br, 43.2; Found: Br, 41.3. Recryst. from ethanol
Bis(*p*-cyanophenyl)dimethylsilane	$(p\text{-}NCC_6H_4)_2Si(CH_3)_2$			100–101	*Anal.* Calc'd: N, 10.70; Si, 10.71. Found: N, 10.84; Si, 10.87
Bis(*p*-carboxylphenyl)dimethylsilane	$(p\text{-}HOOC\text{-}C_6H_4)_2Si(CH_3)_2$			283–287	N. E., 153.2 (Calc'd, 150.0)
Bis(*p*-carbomethoxylphenyl)dimethylsilane	$(CH_3)_2Si(C_6H_4COOCH_3)_2$			83–84	*Anal.* Calc'd for $C_{18}H_{20}O_4Si$: C, 66.20; H, 6.09 Found: C, 66.13; H, 5.94 Sap. Eq., 161.2 (Calc'd, 165.7)
Bis(*p*-aminomethylphenyl)dimethylsilane	$(CH_3)_2Si(C_6H_4CH_2NH_2)_2$	180–190	0.5	45–47	*Anal.* Calc'd: N, 10.68; Found: N, 10.36
Bis(*p*-carboxyphenyl)diphenylsilane	$(C_6H_5)_2Si(C_6H_4COOH)_2$			250–257	N. E., 232 (Calc'd, 212)
Bis(*p*-carbomethoxyphenyl)diphenylsilane	$(C_6H_5)_2Si(C_6H_4COOCH_3)_2$			169–170	*Anal.* Calc'd for $C_{28}H_{24}O_4Si$: C, 74.40; H, 5.35 Found: C, 74.32; H, 5.37 Recryst. from 2:1 methanol–benzene
Tetramethyl-1,3-bis(*p*-carboxyphenyl)-disiloxane	$[HOOC\text{-}C_6H_4Si(CH_3)_2\text{—}]_2O$			225–234	N. E., 183 (Calc'd, 187)
Tetramethyl-1,3-bis(*p*-carbomethoxyphenyl)disiloxane	$[CH_3OOC\text{-}C_6H_4\text{-}Si(CH_3)_2\text{—}]_2O$			57–61	Mol. Wt., 407 (Calc'd, 402) Recryst. from hexane

p-Tolyldimethylchlorosilane	$CH_3C_6H_4Si(CH_3)_2Cl$	215–217	atm.		N. E., 179.6 (Calc'd, 184.5)
p-Tolyldiphenylchlorosilane	$CH_3C_6H_4\text{-}Si(C_6H_5)_2Cl$	175–185	0.2		N. E., 298 (Calc'd, 308.5)
p-Tolyldiphenylsilanol	$CH_3C_6H_4Si(C_6H_5)_2OH$			94–95	Recryst. from hexane. *Anal.* Calc'd for $C_{19}H_{18}OSi$: C, 78.62; H, 6.21. Found: C, 78.19; H, 6.25
1,3-Di-*p*-tolyltetramethyldisiloxane	$[C_7H_7Si(CH_3)_2]_2O$	139–141	0.3		
1,3-Di-*p*-tolyltetraphenyldisiloxane	$[C_7H_7Si(C_6H_5)_2]_2O$			156–158	Recryst. from heptane. *Anal.* Calc'd for $C_{38}H_{34}OSi_2$: C, 81.13; H, 6.05. Found: C, 81.67; H, 6.26
Bis(*p*-carboxyphenyl)dimethylsilane, phenyl ester	 $C_6H_5OOC\text{-}C_6H_4Si(CH_3)_2C_6H_4COOC_6H_5$			107–108	Recryst. from ethanol. *Anal.* Calc'd for $C_{28}H_{24}O_4Si$: C, 74.60; H, 5.34. Found: C, 75.04; H, 5.36
	 $HOOC\text{-}C_6H_4SiR_2O(SiR'_2O)_2SiR_2C_6H_4COOH$ $R = C_6H_5\text{—}$ $R' = CH_3\text{—}$			150–152	Recryst. from benzene-hexane N. E., 389 (Calc'd, 385)
Methyl ester of above				134–136	Recryst. from benzene-hexane *Anal.* Calc'd for $C_{44}H_{46}O_7Si_4$: C, 66.3; H, 5.77. Found: C, 69.02; H, 5.64

[a] Melting point previously reported as 176° (8).

TABLE II
Silicon-containing Polymers

NO.	REACTANTS	POLYMERIZATION CONDITIONS			$[\eta]^b$	STICK. TEMP.^{c} (°C.)	REMARKS
		Time (hr.)	Temp. (°C.)	Press. (mm. Hg.)			
1	Hexamethylenediamine salt of bis(*p*-carboxyphenyl)dimethylsilane	1½ ½ ¾	225 283 283	S.T.^{a} atm. 1–2	0.81	190	High melt viscosity. Melt pressed into tough, clear, colorless film. M.p. of salt, 215–220°
2	Decamethylenediamine salt of above acid	2 ⅓ ⅙ 2	220 259 273 273	S.T. atm. atm. 1–2	.80	145	Film was tough, clear and colorless. M.p. of salt, 216–220°
3	Salt of bis(*p*-aminomethylphenyl)dimethylsilane and above acid	⅓ 1 ½	260 273 283	atm. atm. 1–2	.45	215	Clear, colorless. M.p. of salt, 240–245°
4	Hexamethylenediamine salt of 1,3-bis(*p*-carboxyphenyl)tetramethyldisiloxane	1 1 4	225 260 260	S.T. atm. 1–2	.48	140–145	Manually spinnable and drawable. M.p. of salt, 225–230°
5	Salt of bis(*p*-aminomethylphenyl)dimethylsilane and above acid	½ ½ 3	218 273 273	atm. atm. 1–2	.57	165–170	Clear, colorless. M.p. of salt, 140–145°
6	Hexamethylenediamine salt of 1,7-bis(*p*-carboxyphenyl)-1,1,7,7-tetraphenyl-3,3,5,5-tetramethyltetrasiloxane	¼ 1 1	218 260 260	atm. atm. 1–2	.32	135–140	High melt viscosity. Clear, colorless, brittle. M.p. of salt, 205–210°
7	Salt of bis(*p*-aminomethylphenyl)dimethylsilane and above acid	¼ 1 ½	260 260 273	atm. 1–2 1–2	.30	150–155	Very high melt viscosity. Spinnable and drawable. Clear, colorless, brittle. M.p. of salt, 210–215°

8	Ethylene glycol and methyl ester of bis(*p*-carboxyphenyl)dimethylsilane	6 2½ 7	200 260 260	atm. atm. 1-2	.64	134	Catalyst 0.1% $Zn(BO_3)_2$. Melt pressed film was clear, colorless and tough. d^{25}_4 1.27
9	Ethylene glycol and methyl ester of bis(*p*-carboxyphenyl)diphenylsilane	6 2 35	218 260 265	atm. atm. 1-2	.81	185-190	Catalyst: 0.1% $Zn(BO_3)_2$. Clear, hard, brittle. Spinnable and drawable
10	Ethylene glycol and methyl ester of 1,3-bis(*p*-carboxyphenyl)tetramethyldisiloxane	4½ 2½ ½	218 260 260	atm. atm. 1-2	—	—	Catalyst: 0.1% $Zn(BO_3)_2$. Insoluble, infusible gell

[a] S.T. = Sealed in an evacuated tube.

[b] $[\eta]$ = Intrinsic viscosity in *m*-cresol.

[c] Stick. Temp. = Sticking temperature.

TABLE III

Fiber Properties of Some Silicon-containing Condensation Polymers

NO.	POLYMER OBTAINED FROM	Si, %	$[\eta]^c$	STICK. TEMP. (°C.)	SPIN TEMP. (°C.)	DRAW RATIO	TEN.-ELONG. (g./d.)-(%)	WORK RECOVERY, % ELONGATION %			M_i^d	SHRINKAGE IN BOILING H_2O, %	
								1	2	3		Before Heat Setting	After Heat Setting
1	Decamethylenediamine and bis(*p*-carboxyphenyl)dimethylsilane	6.0	0.80	145	—	—	—	—	—	—	—	—	[a]
2	Hexamethylenediamine and above acid	6.8	.90	190	220	2.2×	—	—	—	—	—	62	31[b]
3	Bis(*p*-aminomethylphenyl)dimethylsilane and above acid	10.5	.48	215	230	2×	1.0–5.1	91	97	91	33	2	0
4	Hexamethylenediamine and 1,3-bis(*p*-carboxyphenyl)tetramethyldisiloxane	11.6	.32	140	135	3×	—	—	—	—	—	—	—
5	Bis(*p*-aminomethylphenyl)dimethylsilane and above acid	13.8	.57	165	205	2×	1.1–7.6	99	97	92	30	10	6
6	Above diamine and 1,7-bis(*p*-carboxyphenyl)-1,1,7,7-tetraphenyl-3,3,5,5-tetramethyltetrasiloxane	14.0	.30	150	240	3×	—	—	—	—	—	67	[b]
7	Ethylene glycol and bis(*p*-carboxyphenyl)dimethylsilane	8.6	.64	134	200	3.4×	1.6–2.0	99	95	—	34	80	[b]
8	Ethylene glycol and bis(*p*-carboxyphenyl)diphenylsilane	6.25	.81	185	230	2×	0.9–4.4	96	93	94	30	4.3	0

[a] Fiber disintegrated in boiling water.

[b] Could not be adequately heat-set.

[c] Intrinsic viscosity in *m*-cresol.

[d] M_i: Initial modulus—Young's modulus measured on the straight line portion of the stress-strain curve. This occurs close to the beginning of the curve (13).

ently caused some cleavage of the silicon-carbon bonds and perhaps of the siloxane groups themselves. Very good evidence that cleavage of this type took place was obtained from the fact that the titration of end groups of the polyamide from bis(*p*-aminomethylphenyl)dimethylsilane and bis(*p*-carboxyphenyl)-1,1,7,7-tetraphenyl-3,3,5,5-tetramethyltetrasiloxane ($[\eta]$ 0, 3) gave values for amine and carboxyl ends which gave a calculated molecular weight of about 21,000. This should correspond to an intrinsic viscosity in the neighborhood of 1.0 as estimated from Staudinger's equation (Ref. 4). A possible explanation for this discrepancy would be the hydrolytic cleavage of silicon-carbon or silicon-oxygen bonds. That cleavage of this type does take place has been demonstrated in the case of the action of ethylene glycol on disubstituted diethoxysilanes as described later in this paper.

Some of the fiber properties obtained from melt spun monofils of these polymers are listed on Table III.

Polyesters. The ethylene glycol polyesters of bis(*p*-carboxyphenyl)dimethylsilane and bis(*p*-carboxyphenyl)diphenylsilane were prepared without difficulty in high molecular weight. The polymerization data and some of the polymer properties are shown in Table II. These polymers were rather low melting, the fibers could not be oriented, and they exhibited excessive shrinkage in boiling water. It has been found that the properties of these polymers were very similar to those of the polyester analogs in which the silicon is replaced by carbon or oxygen. All these polymers had rather low softening temperatures, were amorphous, and were not amenable to heat setting treatments which usually reduce the degree of shrinkage of fibers in hot water.

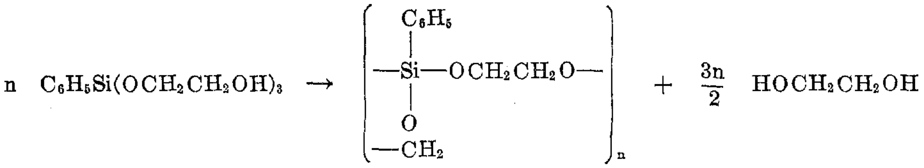
In general it can be said that polyesters and polyamides containing silicon as a silane have properties very similar to those of the carbon analogs. The incorporation of siloxane groups results in a greater variation of the properties of polyamides. However, the replacement of a carbon atom with a siloxane group markedly lowers the melting point of the resulting polymer. The siloxane group cannot be incorporated into ethylene glycol polyesters conveniently due to the ease of cleavage of the silicon-carbon bond by ethylene glycol under polymerization temperatures. (See next topic.)

Subsequent to the completion of this work there was issued to Dow Corning Corp., a patent (5) which describes the preparation of polymeric material by the condensation of carboxyphenylpolysiloxane and polyhydric alcohols. As an example tetramethyl-1,3-dicarboxyphenyldisiloxane and ethylene glycol were heated together to give a "clear, brown resinous thermoplastic material." The conditions used—namely 150° for 90 minutes, were too mild, in the author's opinion, to cause appreciable cleavage of the silicon-carbon bond as described in this paper.

Attempted polymerization of diethoxy-disubstituted silanes. In order to study the condensation of diethoxysilanes with glycols by ester interchange the reaction of diphenyldiethoxysilane with ethylene glycol was investigated. When diphenyldiethoxysilane was heated in an excess of ethylene glycol at 170°, a vigorous reaction set in and ethanol was evolved rapidly. The glycol and silicon ester were not miscible and in order to mix the two together, oxygen-free, dry nitrogen was bubbled from a capillary through the mixture. In the course of 10 to 15 minutes, the mixture became homogeneous. Most of the calculated amount of ethanol came off within the first hour. However, upon raising the temperature and lowering the pressure to effect polymerization of the diglycol ester, it was found that a highly cross-linked, infusible, insoluble material was invariably formed. Further investigation revealed that during the original ester exchange reaction at 200°, a quantity of benzene which corresponded to the removal of about 74% of the phenyl groups of the diphenyldiethoxysilane was collected along with the theoretical amount of ethanol. It was thus shown that aryl groups are cleaved from diaryldialkoxysilanes by the action of ethylene glycol, thus producing a highly cross-linked polymer:

$$(C_6H_5)_2Si(OC_2H_5)_2 + 2HOCH_2CH_2OH \rightarrow (C_6H_5)_2Si(OCH_2\,CH_2OH)_2 + C_2H_5OH$$

$$(C_6H_5)_2Si(OCH_2CH_2OH)_2 + HOCH_2CH_2OH \rightarrow C_6H_5Si(OCH_2CH_2OH)_3 + C_6H_6$$



$$n\ C_6H_5Si(OCH_2CH_2OH)_3 \rightarrow \left[\begin{array}{l} \quad C_6H_5 \\ \quad | \\ -Si-OCH_2CH_2O- \\ \quad | \\ \quad O \\ -CH_2 \end{array}\right]_n + \frac{3n}{2}\ HOCH_2CH_2OH$$

To test the relative stability of dialkyldiethoxysilanes in this reaction, dibenzyldiethoxysilane and di-*n*-hexyldiethoxysilane were treated with an excess of ethylene glycol. In each case the reaction proceeded smoothly with the elimination of ethanol. However, on removal of the excess glycol by heating under reduced pressure, an insoluble infusible material was formed indicating that the same type of silicon-carbon cleavage had taken place. Although the products of the exchange reaction were not identified, it seems likely that alkyl groups also were cleaved by glycol at elevated temperatures.

Silicon esters of the general structure $R_2Si(OR')_2$ were prepared by the reaction of the proper Grignard reagent with ethyl ortho-silicate (2) or by the condensation of the dialkyl- or diaryl-dichlorosilane with the desired dry alcohol (3).

EXPERIMENTAL

Most of the intermediates prepared are listed on Table I with some properties and analytical data.

Preparation of bis(p-carboxyphenyl)dimethylsilane. This dibasic acid was made by two different routes, (a) condensation of dimethyldichlorosilane with *p*-tolylmagnesium bromide and oxidation of the resulting compound to the desired acid, and (b) condensation of dimethyldichlorosilane with the mono-Grignard of *p*-dibromobenzene, conversion to the dinitrile with cuprous cyanide, and hydrolysis of the resulting dinitrile to the diacid.

Route (a): di-p-tolyldimethylsilane. In accordance with the general procedure described by Kipping (8), a solution of 564 g. of *p*-bromotoluene in 300 cc. of absolute ether was added dropwise to mixture of 195 g. of dimethyldichlorosilane, 90 g. of magnesium, and 700 cc. of absolute ether. After the reaction was started the bromotoluene was added at such a rate as to maintain gentle refluxing. After complete addition the mixture was heated under reflux for 2 hours then the ether was removed. The residue was heated at 160° for about 18 hours. The remaining solid was decomposed in cold water and the mixture was extracted twice with ether. The organic layer was washed once with water, dried, and distilled. The fraction distilling at 125–135° (0.1 mm.) was collected as di-*p*-tolyldimethylsilane. The yield was 263 g. (73%).

Anal. Calc'd for $C_{16}H_{20}Si$: Si, 11.7. Found: Si, 12.3.

Oxidation of di-p-tolyldimethylsilane. The oxidation was carried out by adding 380 g. of $KMnO_4$ portionwise to a solution of 100 g. of di-*p*-tolyldimethylsilane and 250 cc. of water in 525 cc. of pyridine while heating on a steam-bath. The permanganate was added at such a rate as to maintain mild refluxing. After complete addition, the mixture was heated for an additional hour and the excess permanganate was destroyed by addition of methanol. The MnO_2 was removed by filtration, and the filtrate was treated with Norit and acidified with HCl. The precipitated acid was collected on a filter, washed with water, then dissolved in sodium carbonate solution, again treated with Norit, and acidified with HCl. A yield of 100 g. (63%) of acid, m.p. 190–240° was obtained.

In order to purify this acid, it was necessary to convert it to the methyl ester which could be conveniently purified by crystallization and subsequently hydrolyzed as described under route (b).

Route (b). Preparation of the dinitrile by the Rosenmund-Von Braun method (9). A mixture of 85 g. (0.325 mole) of bis(*p*-bromophenyl)dimethylsilane (prepared from dimethyldichlorosilane and *p*-dibromobenzene by the Grignard reaction), 50 g. of cuprous cyanide, and 58 cc. of dry pyridine was sealed at atmospheric pressure in a glass tube and the tube was heated at 250° for 1½ hours. During this period the contents were shaken several times. The dark-colored liquid reaction mixture was cooled and then poured into ether. After stirring for a few minutes the mixture was filtered and the dark-colored solid residue was washed thoroughly with ether.

The ether solution was washed several times with concentrated ammonium hydroxide, then with dilute HCl, and finally dried over Na_2SO_4 and then evaporated to dryness. The residual oil was dissolved in 150 cc. of ethanol, treated with Darco, and allowed to crystallize. After one recrystallization from ethanol there was obtained 49 g. (82%) of dinitrile of sufficient purity for conversion to the dibasic acid. Purification for analysis was effected by several recrystallizations from 3:1 hexane-benzene mixture.

Anal. Calc'd for $C_{16}H_{14}N_2Si$: N, 10.70; Si, 10.71.
Found: N, 10.84; Si, 10.87.

Hydrolysis of bis(p-cyanophenyl)dimethylsilane. A solution of 146 g. of the dinitrile and 292 g. of KOH in 880 cc. of ethanol and 480 cc. of water was heated at reflux for about 6 hours. The solution was partially neutralized with HCl, treated with Norit, and acidified. A white precipitate was collected, washed, and dried. The yield of crude acid, m.p. 185–230°, was 148 g. (89%).

In order to purify the acid it was converted to the methyl ester by refluxing with 900 cc. of absolute methanol and 15 cc. of conc'd H_2SO_4 for about 4 hours. Complete solution of the acid resulted after about 15 minutes refluxing. About one-half the methanol was removed and the residue was allowed to cool after treating with Norit. The product which crystallized weighed 83 g. after washing and drying, and melted at 81.5–83°.

The mother liquor from the above filtration was concentrated and distilled. About 13 g. of methyl benzoate was obtained from the distillation. Assuming that the benzoic acid was formed by cleavage of the silicon-benzene linkage during hydrolysis of the dinitrile, this would represent about 17.4% of the dinitrile. From the residue of the above distillation was isolated 17 g. of an ester, m.p. 54–59°. This ester was purified by recrystallization from 4 parts of hexane at −40°. It had a saponification equivalent of about 200 and molecular weight of about 407. The compound was shown to be the methyl ester of tetramethyl-1,3-bis(*p*-carboxyphenyl)disiloxane by its independent synthesis from *p*-tolyldimethylchlorosilane as described below. This ester was hydrolyzed by refluxing in ethanol with the theoretical amount of KOH. The acid was precipitated by acidifying the solution and was purified by redissolving in sodium carbonate, treating with Norit, and reprecipitating. The acid melted at 223–232° and had a neutral equivalent of 183. (Theoretical, 187)

The methyl ester of bis(*p*-carboxyphenyl)dimethylsilane was hydrolyzed in the following manner: A mixture of 83 g. of the ester, 30 g. of KOH, 42 cc. of water, and 380 cc. of ethanol was refluxed for 2 hours. The mixture was poured into an equal volume of water, washed with ether, treated with Norit, and acidified with HCl. A yield of 68.5 g. (91%) of acid, Neut. Equiv., 161 (Calc'd, 150.0) was obtained. After one recrystallization from 340 cc. of dichlorobenzene containing sufficient glacial acetic acid to bring about solution, the acid melted at 280–287° and had a neutral equivalent of 153.2.

Since the completion of this work the preparation of bis(carboxyphenyl)dimethylsilane has been described in a patent (7) issued to the Dow Corning Corporation. Two methods were described: (a) oxidation of ditolyldimethylsilane with alkaline permanganate, and (b) carbonation of the Grignard reagent of dibromophenyldimethylsilane. A melting point of 288° (with decomposition) was reported for the diacid.

bis(p-Carboxyphenyl)diphenylsilane was prepared in the same manner by oxidation of the corresponding ditolyldiphenylsilane (10).

Preparation of bis(p-aminomethylphenyl)dimethylsilane. A charge of 85 g. of bis(*p*-cyanophenyl)dimethylsilane, 100 cc. of liquid ammonia, and 10–15 g. of Raney nickel were shaken in a bomb at 125–130° and 5000 p.s.i. hydrogen pressure for 3 hours. After cooling, the catalyst was removed by filtration and the mixture was distilled. A viscous oil, b.p. 180–190° (0.5 mm.), N. E. 140.36, was obtained. Upon cooling this material crystallized. It was recrystallized from a mixture of one-half its weight of absolute alcohol and twice its weight of absolute ether by cooling to −40°. A yield 26 g. of white crystals, m.p. 45–47° was obtained.

Anal. Calc'd for $C_{16}H_{22}N_2Si$: N, 10.68. Found N, 10.36.

Preparation of 1,3-bis(p-carboxyphenyl)tetramethyldisiloxane. 1,3-Bis(p-tolyl)tetramethyldisiloxane. This material was prepared by the hydrolysis and concurrent dehydration of *p*-tolyldimethylchorosilane (obtained by the Grignard reaction from dimethyldichlorosilane and *p*-tolymagnesium bromide). Since completion of this work the preparation of dimethyltolylchlorosilane has been described in a patent (11) issued to the Dow Corning Corporation. Trimethylchlorosilane and toluene were heated in a bomb at 400° in the presence of a boron or aluminum halide to give dimethyltolylchlorosilane. A boiling point of 110–114° at 30 mm. was reported. The tolyldimethylchlorosilane, 250 g., was placed in a separatory-funnel with 1,000 cc. of ether and was shaken with successive proportions of cold water until the water was no longer acidic. The ether layer was then dried over Drierite and the ether was removed. The liquid residue was distilled and a yield of 157 g. (74%) of a clear colorless liquid, b.p. 139–141° (0.2 mm.), was obtained. A benzene solution of this material did not react with sodium metal indicating the substance to be the disiloxane and not the silanol.

Oxidation of 1,3-bis(p-tolyl)tetramethyldisiloxane. This was carried out in the manner described above for oxidation of di-*p*-tolydimethylsilane. The acid was purified by conversion to the methyl ester and subsequent hydrolysis. Some properties and analytical data are listed on Table I.

Preparation of 1,7-bis(p-carboxyphenyl)-1,1,7,7-tetraphenyl-3,3,5,5-tetramethyltetrasiloxane. This compound was prepared by condensing *p*-tolyldiphenylsilanol with 1,3-dichlorotetramethyldisiloxane in the presence of pyridine. The disiloxane was prepared by partial hydrolysis of dimethyldichlorosilane (12). The *p*-tolydiphenylsilanol was prepared by the hydrolysis of the corresponding chlorosilane.

p-Tolyldiphenylsilanol. The tolyldiphenylchlorosilane (prepared from *p*-bromotoluene and diphenyldichlorosilane by the Grignard method) was hydrolyzed by shaking an ether solution with water as described above for *p*-tolyldimethylchlorosilane. In this case the free silanol, rather than the disiloxane was isolated. It was identified as the silanol by the fact that the benzene solution reacted with sodium and also because the material could be dehydrated to a new compound. Dehydration was carried out by heating a mixture of 72 g. of the silanol and 4 cc. of 0.1 *N* NaOH at 218° for 1.5 hours, during which time water was eliminated. The temperature was then raised to 260° for 1 hour and the melt was allowed to cool. The product was purified by recrystalllization from heptane and a yield of 66 g. of the disiloxane, m.p. 156–158° was obtained. The analytical data shown on Table I confirmed the identity of this material as 1,3-di-*p*-tolyltetraphenyldisiloxane.

Condensation of p-tolyldiphenylsilanol with 1,3-dichlorotetramethyldisiloxane. A solution of 51 g. of the dichlorodisiloxane was added slowly and with constant stirring to a solution of 145 g. of the silanol and 60 g. of pyridine in 400 cc. of dry benzene, while maintaining at room temperature was heated at reflux for about 2 hours. It was then poured into water, ether was added, and the organic layer was washed several times with water, after which it was dried over $CaCl_2$. The ether and benzene were then removed by warming on a steam-bath at reduced pressure. The residue was a viscous colorless liquid weighing 169 g. It was finally induced to crystallize to a rather waxy solid, m.p. 47–52°. All attempts to recrystallize this material from such solvents as petroleum, ether, alcohol, benzene, acetone, etc. were unsuccessful even at very low temperatures. For this reason the material was oxidized directly to the acid without further purification.

Oxidation of the 1,7-di-p-tolyltetrasiloxane. The oxidation was carried out in the manner already described using $KMnO_4$ in aqueous pyridine. Repeated recrystallization of the isolated reaction product from a benzene-hexane (1:2.5) mixture gave a white crystalline material, m.p. 117–122°. However, after heating in a vacuum oven at 100° overnight the material had a neutral equivalent of 389 (Calc'd, 383) and a melting point of 150–152°. It was assumed that the acid had originally crystallized as a partial hydrate.

Attempted preparation of 1,5-bis(p-tolyl)hexamethyltrisiloxane. An attempt was made to prepare this compound first by condensation of *p*-tolyldimethylsilanol with dimethyldichlorosilane. However, attempts to prepare *p*-tolyldimethylsilanol always resulted in the disiloxane instead. Apparently this material dehydrates very readily to form the disiloxane.

Since this silanol could not be isolated readily an attempt was made to prepare it in solution and condense it directly with the dimethyldichlorosilane. The tolyldimethylchlorosilane was hydrolyzed at 0°. Nearly the theoretical amount of 1,3-di-*p*-tolyltetramethyldisiloxane, b.p. 130–147° (2 mm.) was obtained. Apparently the *p*-tolyldimethylsilanol undergoes self-condensation preferentially.

Diphenyldiethoxysilane. The preparation of this material will serve to illustrate the method of preparation of disubstituted diethoxysilanes. This substance may be prepared in two ways: (a) by the action of phenylmagnesium bromide on ethyl silicate or (b) by the alcoholysis of diphenyldichlorosilane with absolute ethanol (6). The latter approach appeared to give a product of greater purity. The diphenyldichlorosilane was a sample supplied by the Dow Corning Corporation. This material was distilled before using, b.p. 119–120° at 0.8 mm. pressure. A total of 253 g. of diphenyldichlorosilane (1 mole) was added slowly to 500 cc. of absolute alcohol while stirring and heating at the reflux. When the addition was complete 180 g. of pyridine was slowly added, after which the solution was refluxed for 2 hours. The solution was then poured into ice-water and the aqueous layer was washed with ether. The combined organic layer and ether washings were washed with water, dried, and then distilled. A yield of 192.5 g. (75%), b.p. 109–110° (0.07 mm.) n_D^{25} 1.5250 was obtained.

Polymer preparation. Polyamides. In general the polyamides were prepared by a salt fusion technique consisting of heating the salt in a sealed evacuated tube for 0–2 hours at 220° followed by an atmospheric heating stage at 260–285° in an atmosphere of nitrogen and finally a finishing stage under high vacuum using a nitrogen bubbling capillary for agitation. The sealed tube stage was found to be somewhat detrimental to polyamides containing siloxane groups apparently due to the fact that the water at high temperature and under pressure caused some cleavage of silicon-carbon bonds.

Salt preparation. The salts prepared along with some of their properties are listed on Table II. The preparation of the hexamethylenediamine salt of bis(*p*-carboxyphenyl)-dimethylsilane will illustrate the general method of preparation: A solution of 12.8 g. of 61.2% hexamethylenediamine solution in methanol (4% excess) was added to a warm solution of 20 g. of bis(*p*-carboxyphenyl)dimethylsilane in 500 cc. of ethanol. The flocculent salt precipitated immediately and after cooling was collected, washed with cold alcohol, then with ether, and dried. The yield was 26 g. (94%) and the salt melted at 215–220°. Due to the insolubility of this salt in alcohol, water, or mixtures thereof, its pH or point of inflection was not obtained.

Polyesters. The preparation of the polyester from bis(p-carboxyphenyl)dimethylsilane and ethylene glycol will be described in order to illustrate the method used. A charge of 5.5 g. (0.017 mole) of bis-p-(carbomethoxyphenyl)dimethylsilane, 3.2 g. (0.052 mole) of ethylene glycol, and 0.006 g. of zinc borate was placed in a glass tube of about 14 mm. diameter and a small boiling stone was added to facilitate ebullition. The tube was heated in an atmosphere of nitrogen at 200° for 6 hours during which time the theoretical amount of methanol was collected as the distillate. The charge was then heated for 2.5 hours at 259° to remove most of the excess glycol. The polymerization was completed by heating for 7 hours at 259° and 1-2 mm. pressure, while bubbling nitrogen into the melt through a capillary tube to provide agitation.

Polymer evaluation. Sticking temperature. The sticking temperature of a polymer was taken as that temperature of a polished copper block at which a chip of polymer, when rubbed against the block, would stick and begin to melt. This temperature is of more practical than theoretical value and should not be taken as the true melting point of the polymer.

Fiber preparation and processing. The polymers were converted into monofil fibers by mechanically extruding the melted polymer from a spinneret. Monofils of 50–100 denier were obtained. None of the fibers could be drawn to a very great extent and all were drawn at elevated temperature. After drawing, the fibers were subjected to heat-setting treatments by holding the fibers at fixed elongation in boiling water 30–60 minutes. The physical properties obtained for the fibers were measured on conventional equipment designed for that purpose.

Acknowledgement. The author wishes to express his appreciation to Dr. R. C. Houtz for his assistance and guidance during the course of this work.

SUMMARY

Silicon has been incorporated into several organic dibasic acids and a diamine from which high molecular weight polyamides and polyesters have been prepared. In general the polymer properties differed only slightly from those of analogous carbon compounds.

WILMINGTON 98, DELAWARE

REFERENCES

(1) BAKER, BARRY, AND HUNTER, *Ind. Eng. Chem.*, **38**, 1117 (1946); COLLINGS, *Chem. Eng. News*, **23**, 1616 (1945).

(2) MCGREGOR AND WARRICK, U. S. Patent 2,380,057 (To Corning Glass Works, Oct. 23, 1941).

(3) ROCHOW, *An Introduction to the Chemistry of the Silicones*, John Wiley and Sons, New York, 1946, p. 37.

(4) STAUDINGER AND HEUER, *Ber.*, **63**, 231 (1930).

(5) BARRY AND GILKEY, U. S. Patent 2,570,090 (To Dow-Corning Corporation, Oct. 2, 1951).

(6) KIPPING AND MURRAY, *J. Chem. Soc.*, 2734 (1927).

(7) TYLER, U. S. Patent 2,517,146 (To Dow-Corning Corporation, Aug. 1, 1950).

(8) KIPPING, *J. Chem. Soc.*, 95, 302 (1909).

(9) KOELSCH AND WHITNEY, *J. Org. Chem.*, **6**, 795 (1941).

(10) GILMAN AND CLARK, *J. Am. Chem. Soc.*, **68**, 358 (1946).

(11) BARRY AND GILKEY, U. S. Patent 2,500,652 (To Dow-Corning Corporation March 14, 1950).

(12) PATNODE AND WILCOCK, *J. Am. Chem. Soc.*, **68**, 358 (1946).

(13) BESTE AND HOFFMAN, *Textile Research J.*, **20**, 443 (1950).