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Alkoxysilanes. V. The Preparation of Polyalkyl(aryl) Silicates

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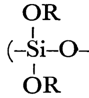
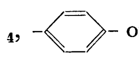
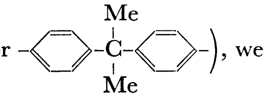
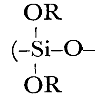
Silicon-containing novel polymers, polyalkyl(aryl) silicates  $(-\overset{OR}{\underset{OR}{Si}}-O-R'-O-)_n$ ($R=Bu^t$ and $(Bu^tO)_3Si$, $R'=-(CH_2)_{2\text{ or }4}$,  or ), were prepared by the reaction of diaminosilanes with aliphatic or aromatic diols. The products were a white powder (fused at about 300°C), a highly viscous liquid, or a glassy solid; these products were soluble in common organic solvents, but insoluble in methanol. The results of the molecular-weight determination by the vapour-pressure method indicated that some of polymers had a molecular weight of 5000 or 6000. A study of the thermal stability of the polymers by means of TGA and DTA analysis made clear that the polymers with the aryloxy group in the molecular main chain were remarkably more stable than those with the alkoxy group. The former indicated a weight loss of about 50% at 350—400°C. An investigation of the TGA curve and thermal decomposition products allowed us to discuss the probable process for the degradation of the polymers. The reaction of the diaminosilanes with 1,4-butanediol afforded distillable products rather than the expected polymers; these products were identified as being cyclic alkoxysilanes.

In order to obtain thermally-stable polymers, many experiments[1] have been carried out concerning the preparation of polymers containing metal atoms. Although it is well-known that polyalkylsiloxanes have a superior thermal stability, they are also pyrolyzed at temperatures higher than 300°C to form ring compounds of a low molecular weight. Therefore, an attempt has been made to prevent the degradation and to increase the thermal stability by replacing the side[2] and main[3] chain of the polysiloxane by other groups or metals. Recently, Dunnavant[4] has synsesized polyaryloxysilanes with aryloxy groups in the main chain and the phenyl group in the side chain; his polyaryloxysilanes have excellent thermal and mechanical properties.

Polyalkyl(aryl) silicate  $(-\overset{OR}{\underset{OR}{Si}}-O-R'-O-)_n$, however, has not been prepared; in it both the main and side chain are replaced by an alkoxy or aryloxy group. Probably, the reason is that the alkoxysilanes $(RO)_nSiX_{4-n}$ ($n=2$ and 1) have various functional groups and their reactivities have not yet been investigated. Since we have already reported on our study of the preparation and reaction of alkoxysilanes containing functional groups,[5,6] in this experiment we tried to prepare polyalkyl(aryl) silicates and to investigate their thermal stability.

Experimental

Material. The di-*t*-butoxydiaminosilane[7] and bis(tri-*t*-butoxysiloxy)diaminosilane[6] were prepared by the reaction of the corresponding dichlorosilanes with dry ammonia gas. The ethylene glycol and 1,4-butanediol were purified by distillation after having been dehydrated over anhydrous sodium sulfate. The hydroquinone and bisphenol A were recrystallized from methanol and benzene respectively.

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[1] D. N. Hunter, "Inorganic Polymers," John Wiley & Sons, New York (1963); V. V. Korshak, "Progress of Polymer Chemistry," Izdatelystovo Nauka, Moskva (1965), p. 323.

[2] S. M. Atlas and H. F. Mark, *Angew. Chem.*, **72**, 249 (1960).

[3] C. M. Murphy, C. E. Saunder and D. C. Smith, *Ind. Eng. Chem.*, **42**, 246 (1950).

[4] W. R. Dunnavant, R. A. Markle and P. B. Stickney, *J. Polym. Sci., Part A-1*, **5**, 707 (1967).

[5] Y. Abe and I. Kijima, This Bulletin, **42**, 1118 (1969).

[6] Y. Abe and I. Kijima, *ibid.*, **42**, 2570 (1969).

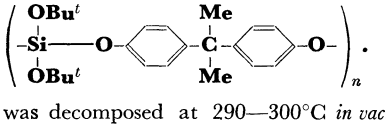
[7] C. S. Miner, L. A. Bryan, R. P. Holysz and G. W. Pedlow, *Ind. Eng. Chem.*, **39**, 1368(1947).

Polymerization and Measurement of the Reaction Rate. To a solution of diols dissolved into dry ethyl ether or benzene, diaminosilanes were added. After the solvent (ether) had been removed off along with stirring and the introduction of dry nitrogen gas, the residue was polymerized under the conditions shown in Tables 1 and 2. When the benzene was used as a solvent, the mixture was refluxed under the boiling point of the solvent. When the reaction was carried out without a solvent, the mixture was heated at the temperatures shown in Tables 1 and 2. The raw product (a highly viscous liquid or a glassy solid) thus formed was dissolved into benzene, and filtered off; the filtrate was then added, drop by drop, into vigorously stirred methanol. The precipitate was separated by decantation and dried *in vacuo*. When a white precipitate was produced from the reaction mixture, it was filtered off, extracted with benzene, and dried *in vacuo*.

The polymerization rate in the reaction of the diaminosilanes with hydroquinone or bisphenol A was determined by introducing ammonia evolved under the following conditions into a sulfuric acid solution: a mixed solution was heated up to 70°C for 30 min, and then the ether was removed. When the temperature rose to 70°C during the next 30 min, the residue was further heated for 170—180°C. The results are shown in Fig. 1.

The Reaction of Di-*t*-butoxydiaminosilane with 1,4-Butanediol. A mixture of 21.8 g (0.1055 mol) of the diaminosilane, 9.5 g (0.1055 mol) of 1,4-butanediol, and 50 m*l* of benzene was refluxed with stirring. After 3.5 hrs' heating (45%, ammonia evolved), the solvent was evaporated off; the residue was then further heated for 7.5 hr at 150—160°C (80.4%, ammonia evolved). The distillation of the residue *in vacuo* gave 11.0 g of a distillate (bp 115°C/21 mmHg) and 17.3 g of a brown, highly viscous liquid. The redistillation of the distillate yielded 7.5 g of a colorless, transparent liquid. The results of elemental analysis, the measurement of the NMR spectra, and the yield are shown in Table 3.

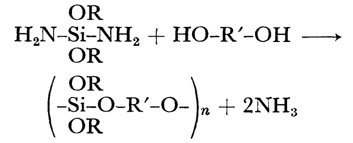
The Reaction of Bis(tri-*t*-butoxysiloxy)diaminosilane with 1,4-Butanediol. A mixture of 11.0 g (0.0188 mol) of the diaminosilane, 1.7 g (0.0188 mol) of 1,4-butanediol, and 30 m*l* of toluene was heated while being stirred. The mixture was refluxed for 6.5 hr (93%, ammonia evolved), and the solvent was removed off. Then the residue was distilled *in vacuo* to give 8.3 g of a solid; 160—161°C/1 mmHg. The solid was recrystallized with petroleum ether with a boilling point below 45°C, giving a needle crystal. The results are shown in Table 3.

Thermal Decomposition of the Polymer . A sample (9.1 g) was decomposed at 290—300°C *in vacuo* to form a gas, which was trapped into a vessel cooled by dry ice-acetone. The weight loss of the polymer was 2.1 g (23%). The residue (T-1), insoluble in solvents, was finely powdered, extracted with benzene, and subjected to elemental analysis (Found: C, 54.39; H, 5.08; Si, 9.48%) and IR-spectra measurements (Fig. 6). The gas, becaming a liquid under the cooling, was absorbed into a carbon tetrachloride-bromine solution. The solution was washed, dehydrated over anhydrous calcium chloride, and subjected to gas chromatography.

The T-1 (7.0 g) was further pyrolyzed at 480°C *in vacuo* to form a volatile liquid and a solid. To the mixture, carbon tetrachloride was added. Then the solid was filtered off and recrystallized with the solvent to give a crystal; mp 151—152°C (bisphenol A). The filtrate, having a phenolic odor and showing a positive color test for ferric chloride, was brominated to give a precipitate, which was then recrystallized with an aqueous alcohol, mp 91—93°C (tribromophenol). The weight loss of T-1 was 2.9 g (55%, total weight loss in relation to the initial polymer). The residue which remained was subjected to elemental analysis (Found: C, 41.60; H, 3.92; Si, 15.87%) and IR-spectra measurements (Fig. 6) after it had been treated as has been described above.

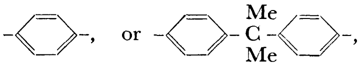
Results and Discussion

Preparation of Polyalkyl(aryl) Silicates. Polyalkyl(aryl) silicates were obtained by the following reactions:



$$H_2N\text{-}\overset{\text{OR}}{\underset{\text{OR}}{\text{Si}}}\text{-}NH_2 + HO\text{-}R'\text{-}OH \longrightarrow \left(\text{-}\overset{\text{OR}}{\underset{\text{OR}}{\text{Si}}}\text{-}O\text{-}R'\text{-}O\text{-}\right)_n + 2NH_3$$

where R=Bu^t and (Bu^t O)$_3$Si, R'=-(CH$_2$)$_2$-, -(CH$_2$)$_4$-,



At first, the reactivity of the diols to the diaminosilanes was investigated by measuring the ammonia evolved by the reaction of the diaminosilanes with hydroquinone or bisphenol A under definite conditions. The results are shown in Fig. 1. Figure 1 indicates that the reactions are completed within about 3 hr (90%, ammonia evolved); thus, it is clear that the polymerization proceeds easily. This figure also suggests that di-*t*-butoxydiaminosilane reacts more easily with hydroquinone or bisphenol

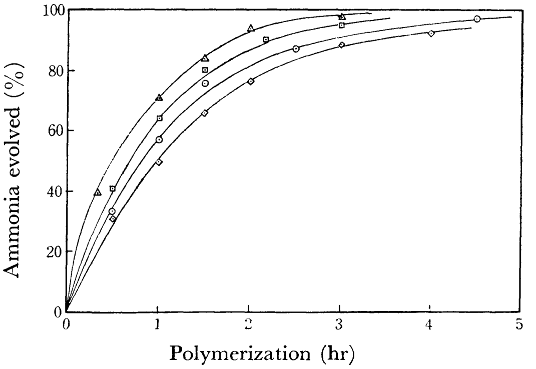
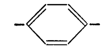
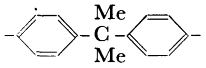


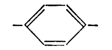
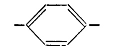
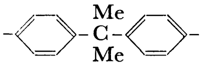
Fig. 1. The rate in the reaction of diaminosilanes with hydroquinone or bisphenol A.
△: c, ⊡: d, ⊙: C, ◇: D

TABLE 1. REACTION CONDITIONS AND PRODUCTS IN THE REACTION OF $(\mathrm{Bu}^t\mathrm{O})_2\mathrm{Si}(\mathrm{NH}_2)_2$ WITH HO-R′-OH

		Reaction Condition				Product		
Exp. No.	R′	Reaction Temp., °C	Reaction Time, hr	Solvent	Mp, °C	Anal., Found (Calcd) %		
						C	H	Si
a-1	$-(\mathrm{CH}_2)_2-$	70—80	2.5	Benzene	300	21.24 (51.25)	6.34 (9.46)	23.44 (11.19)
b-1	$-(\mathrm{CH}_2)_4-$	7C—80	3.5	Benzene	Liq	53.32 (54.92)	10.75 (9.99)	10.52 (10.70)
b-2	$-(\mathrm{CH}_2)_4-$	184—208	4.5	—	Liq	54.09 (54.92)	10.80 (9.99)	— (10.70)
c-1		136—204	3.5	Ether	79-84	58.29 (59.54)	8.48 (7.85)	9.71 (9.96)
d-1		120—160	2.5	Ether	68-75	67.81 (68.96)	8.51 (8.06)	6.98 (7.01)

Molar ratio=1:1, Liq=liquid

TABLE 2. REACTION CONDITIONS AND PRODUCTS IN THE REACTION OF $[(\mathrm{Bu}^t\mathrm{O})_3\mathrm{SiO})]_2\mathrm{Si}(\mathrm{NH}_2)_2$ WITH HO-R′-OH

		Reaction Condition				Product		
Exp. No.	R′	Reaction Temp., °C	Reaction Time, hr	Solvent	Mp, °C	Anal., Found (Calcd) %		
						C	H	Si
A-1	$-(\mathrm{CH}_2)_2-$	81-83	6.0	Benzene	300	50.60 (50.80)	10.29 (9.50)	13.72 (13.70)
A-2	$-(\mathrm{CH}_2)_2-$	100-199	1.5	—	300	— (50.80)	— (9.50)	13.75 (13.70)
A-3	$-(\mathrm{CH}_2)_2-$	80-84	2.0	Benzene	160-170	50.92 (50.80)	10.59 (9.50)	13.26 (13.70)
B-1	$-(\mathrm{CH}_2)_4-$	150-231	4.5	—	125-135	52.02 (52.30)	10.39 (9.71)	12.80 (13.10)
C-1		200-260	4.0	Ether	Liq	53.36 (54.35)	9.50 (8.82)	12.57 (12.71)
C-2		250-285	1.5	Ether	56-63	49.54 (54.35)	7.75 (8.82)	12.58 (12.71)
D-1		165-194	4.0	Ether	53-56	60.42 (59.96)	9.01 (8.77)	10.05 (10.78)

Molar ratio 1:1 or 1 : 2 diol (A-3)

A than with bis(tri-*t*-butoxysiloxy)diaminosilane. This results from the smaller steric hindrance of the *t*-butoxy group than that of the tri-*t*-butoxysiloxy group. Further, in comparison with bisphenol A, hydroquinone is more reactive to di-*t*-butoxydiaminosilane (or bis(tri-*t*-butoxysiloxy)diaminosilane). This may be explained by the stronger acidity of hydroquinone than that of bisphenol A.

On the basis of the above results, polymerization was attempted; it gave the polymers shown in Tables 1 and 2. The products were a white powder (A-1, 2, 3; B-1; a-1; c-1), a highly viscous liquid (b-1,2; C-1), and a glassy solid (C-2; d-1; D-1); some of them (c, C, d, and D) form fiber when fused at elevated temperatures. The a-1, A-3, and B-2 polymers are soluble in hot benzene, but A-1 and 2 are insoluble in solvents. The others are soluble in all common organic solvents, such as benzene, *n*-hexane, ether, acetone, and carbon tetrachloride, but not methanol; hence, the polymers can be purified by adding them, dissolved in benzene, into vigorously-stirred methanol. The results of elemental analysis after the purification are shown in Tables 1 and 2. The tables indicate that the values, except for in the cases of a-1 and C-2, agree with those calculated for the linear structure $(-\mathrm{Si(OR)}_2-\mathrm{O}-\mathrm{R}'-\mathrm{O}-)_n$. It seems to support the above structure that the products are soluble in organic solvents and form fiber. The IR spectra are essentially identical and show absorption peaks at 2900 (Me), 1605 and 1505 (Ph), 1390 and 1365 (Bu^t), and 1100—1000 (Si–O–Si, Si–O–C) cm^{-1}. As Fig. 2 shows, the NMR spectra of the polymer (d) exhibit the proton signals at 2.87—3.27 (Ph), 8.38 (Me), and 8.66 (Bu^t) τ. These spectroscopic data also imply that the above

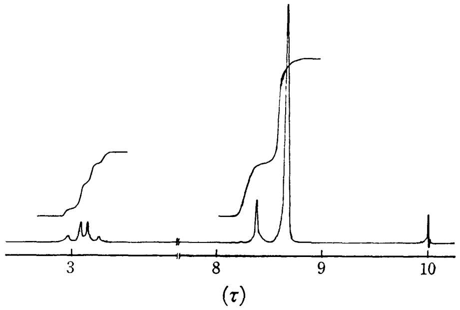


Fig. 2. NMR spectrum of polyaryloxy silicate d.

structure is reasonable. The polymer C and especially the polymer c are apt to discolor, probably due to the susceptibility of hydroquinone to oxidation. The results of the molecular-weight determination for D and d in benzene by the vapor-pressure method indicated the values of 6100 and 4800, which corresponded to the degrees of polymerization of 8 and 16 respectively. The X-ray powdery diffraction of D also showed no crystallinity. In general, it has been established that alkyl silicate are susceptible to hydrolysis and alcoholysis, but these polyalkyl(aryl) silicates have a remarkable stability.

The results of the elemental analysis for a-1 and C-2 are different from the values calculated for the structure. It is found that the deviation in the case of a-1 is due to a cross-linking of the polymer by ethylene glycol, which results from the alcohol-exchanging reaction between the *t*-butoxy and the hydroxy group of ethylene glycol, for *t*-butyl alcohol was detected in the gas chromatography of the solvent removed from the reaction mixture. Additional evidence of the cross-linking lies in the IR spectra of the product; a strong absorption peak appears at 3425 (OH) cm^{-1}, while the peaks at 1390 and 1360 cm^{-1} due to the *t*-butyl group almost disappear. Therefore, the product is a polymer partially crosslinked by ethylene glycol; however, the degree of the cross-linking seems to be low, for it is soluble in hot benzene. The deviation in c-2 may be ascribed to a partial decomposition during the course of polymerization at a high temperature (280°C).

On the other hand, distillable products rather than polymeric substances were obtained when the reaction of the diaminosilanes with 1,4-butanediol was carried out using toluene as the solvent. These products were found to be cyclic alkoxysilanes by elemental analysis, by molecular-weight determination (Table 3), and by means of examining the NMR spectra (Fig. 3). In the reaction of di-*t*-butoxydiaminosilane with the diol, a polymeric substance was formed in addition to the cyclic alkoxy silane; the ratio of the products was about 5 : 3 (by weight). On the other hand, in the reaction of bis(tri-*t*-butoxysiloxy)diaminosilane, only a distillable product was obtained.

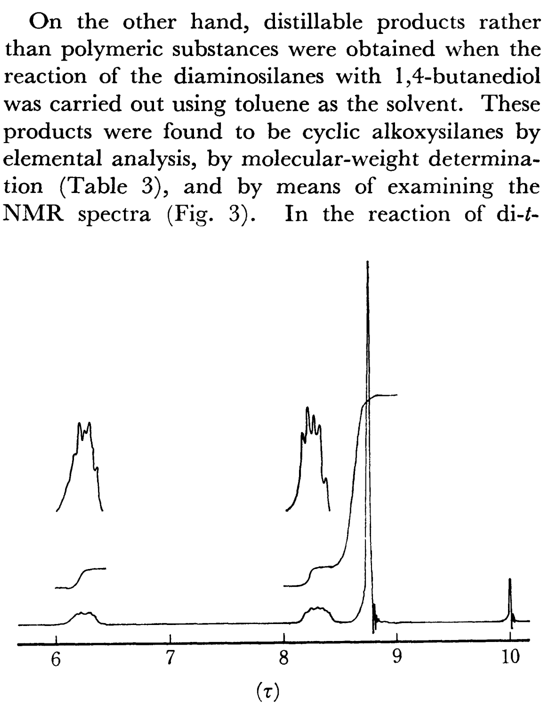
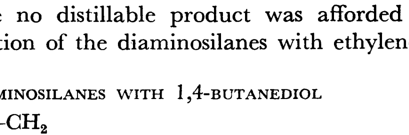


Fig. 3. NMR spectrum of cyclic alkoxysilane (R=Bu^t).

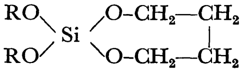


$$\begin{matrix}RO\\RO\end{matrix}\!\!>\!Si\!<\!\!\begin{matrix}NH_2\\NH_2\end{matrix} + HO\text{-}(CH_2)_4\text{-}OH \longrightarrow \begin{matrix}RO\\RO\end{matrix}\!\!>\!Si\!<\!\!\begin{matrix}OCH_2CH_2\\ |\\ OCH_2CH_2\end{matrix} + 2NH_3$$

where R=Bu^t and (Bu^{t}O)$_3$Si.

The tendency toward cyclization rather than the expected polymerization seems due to the length of the methylene linkage and the steric hindrance, since no distillable product was afforded by the reaction of the diaminosilanes with ethylene glycol

TABLE 3. PRODUCTS IN THE REACTION OF DIAMINOSILANES WITH 1,4-BUTANEDIOL



$$\begin{matrix}RO\\RO\end{matrix}\!\!>\!Si\!<\!\!\begin{matrix}O\text{-}CH_2\text{—}CH_2\\ |\\ O\text{-}CH_2\text{—}CH_2\end{matrix}$$

R	Yield %	Bp, °C/mmHg (Mp, °C)	Mol. wt. Found (Calcd)	Analysis Found (Calcd) %			NMR (τ) (Proton Ratio)		
				C	H	Si	Me	CH$_2$	CH$_2$
Bu^t	40	106.5/1 n_0^{20} 1.4217	261 (261)	54.94 (54.93)	10.75 (9.98)	10.70 (10.52)	8.92 (4.5)	8.16–8.37 (1)	6.1 –6.35 (1)
(Bu^{t}O)$_3$ Si	70	160–161/1 (62–63)		52.57 (52.30)	10.30 (9.71)	12.95 (13.10)	8.71 (14.7)	8.15–8.36 (1)	6.02–6.22 (1)

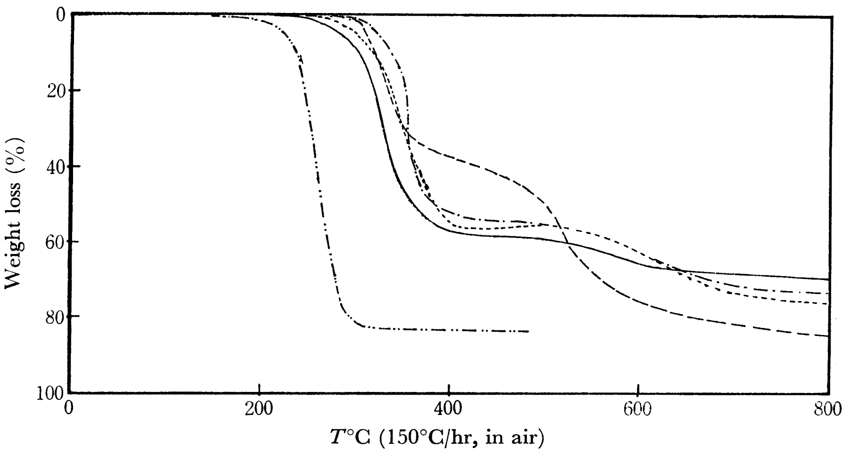


Fig. 4. TGA curve of A (—··—), C (———), D (—·—), c (·········), and d (----).

and only the cyclic alkoxysilane was formed in the case of bis(tri-*t*-butoxysiloxy)diaminosilane. These facts suggest that the seven-membered ring is more favorable to ring formation than the five-membered ring and that the steric hindrance of tri-*t*-butoxysiloxy group greatly contributes to the cyclization. Probably, the reactions proceed *via* the initial formation of the intermediate $(RO)_2Si(NH_2)(OCH_2CH_2CH_2CH_2OH)$, and at this stage it may undergo an intramolecular condensation, for the intermolecular condensation appears to be more difficult due to the steric hindrance of the RO groups. Indeed, the assumption that the intermediate is formed seems to be supported by the reports by Miner[7] and by our previous investigation.[6]

Thermal Properties of Polyalkyl(aryl) Silicates. The TGA curves of polyalkyl(aryl) silicates (Fig. 4) indicate that the weight loss of A-1 amounts to about 80% at 200—300°C, whereas those of c, C, d, and D amount to about 50—60% at 350—400°C and 70—80% at 900°C. Obviously the polymers with aromatic rings in the molecular main chain have a superior thermal stability to the A-1 with the methylene linkage. When c, C, or D is compared with d, no remarkable difference in thermal stability is observed, except that the weight loss of d is less than that of the others at 400—500°C. However, as Tables 1 and 2 show, there is a tendency for the fusing points of polymers with a butoxy group in the side chain are to be higher than those with a tri-*t*-butoxysiloxy group. This seems to be explained by considering that the flexibility of the molecule increased by the Si–O–Si linkage in the side chain of C and D results in a lowering their fusing points compared with those of c and d without the linkage.

The results of the differential thermal analysis of D and d are shown in Fig. 5. Figure 5 indicates that D and d have endo- or exothermic peaks at about 60 and 360°C. The endothermic peaks at about 60°C correspond to the fusing points, which are in good accordance with the results shown in Tables 1 and 2. The peaks at 360°C are due to decomposition, but the thermal behavior is

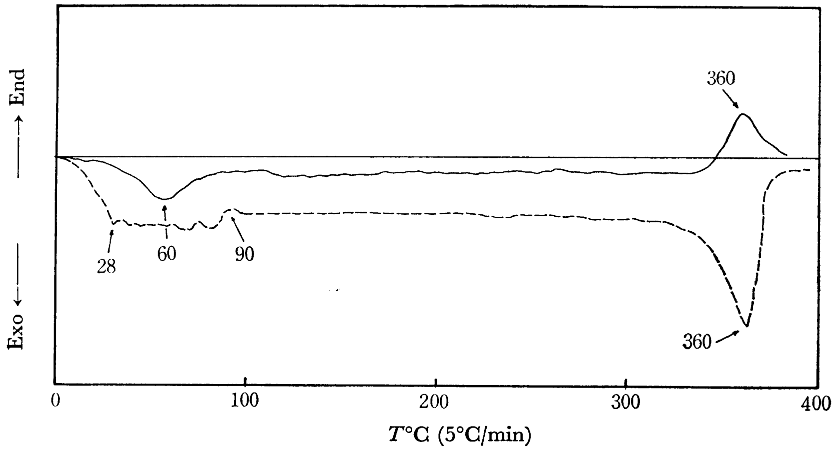


Fig. 5. DTA curve of D (----) and d (——).

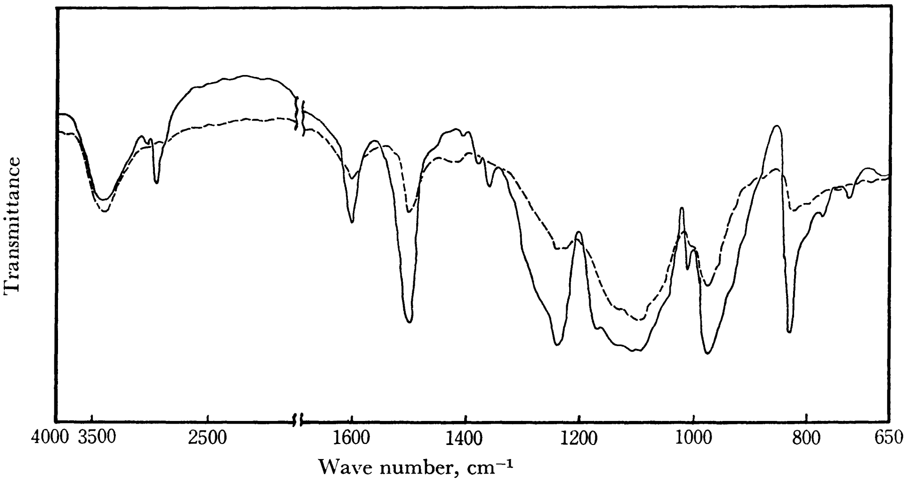
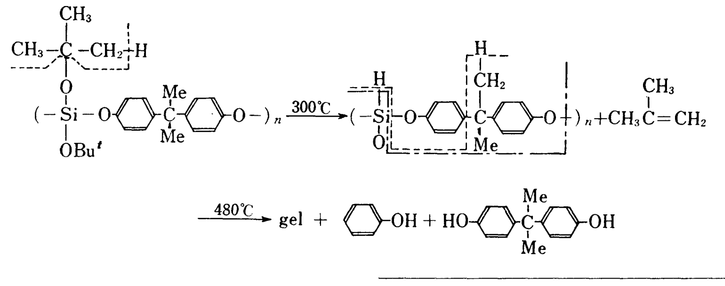


Fig. 6. IR spectra of T—1 (——) and T—2 (----).

different, as may be seen when d is compared with D. This may be thought to be caused by the different side chains, the butoxy and butoxysiloxy groups.

During the investigation of the thermal stability by means of the TGA curves, it has been observed that the decomposition of all the polymers except A proceeds through two steps, as is shown by Fig. 4. This suggests that either step is caused by the degradation of the side or main chain; hence, the identification of thermal decomposition products would allow us to discuss the process of the degradation. With this in view, the d polymer was pyrolyzed at 300 and 480°C *in vacuo*; a gas evolved, and the residue was subjected to analysis. Consequently, the following facts were made clear: 1. The gas evolved at 300°C was confirmed to be 2-methyl propene by means of gas chromatography after it had been brominated. Moreover, as is shown in Fig. 6, the IR spectra of the residue (T-1) at this temperature exhibited absorption peaks at 1500 and 820 cm^{-1} due to the phenyl group, but lack the peaks at 1380 and 1360 cm^{-1} attributed to the branching of the alkyl group; therefore, the above facts seem to support the idea that the first step is the degradation of the side chain. 2. The volatile substances obtained at 480°C were identified as phenol and bisphenol A; besides, the IR spectra of the residue (T-1) at 480°C lack the peaks ascribed to not only the branching of the alkyl group, but to the phenyl group. These facts imply that the second step is the decomposition of the main chain. On the basis of the above results, it is thought that the probable decomposition process of the polymers proceeds step by step, as is shown by the following scheme:



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