TABLE II

POLYMERIZATION STUDIES

Monomer	Polymer (Approximate Values) % Residual Alcohol Bond	% Residual Acid Bond	% Cyclization	Approximate % Conversion	Gel Time (hr.)	Inherent Viscosity (g. polymer/100 ml. solution)	Observations
Ia[a]	15	60	25	10	110	0.046 (0.198)	—
Ib	—	—	—	—	—	—	No polymer with 2% Bz_2O_2[d] at 100° for 45 days or 2% AIBN[e] at 75° for 14 days
Ic[b]	11	58	31	10	[c]	0.039 (0.207)	—
Id	—	—	—	—	—	—	No solid polymer with 2% Bz_2O_2 at 100° for 29 days
Ie	—	—	—	—	—	—	No polymer with 2% Bz_2O_2 at 100° for 14 days or 2% AIBN at 75° for 14 days
IIa	—	—	—	—	—	—	No solid polymer with 2% Bz_2O_2 at 100° for 22 days or 2% AIBN at 25° for 11 days
IIb	—	—	—	—	—	—	No polymer with 2% Bz_2O_2 at 100° for 25 days or 2% AIBN at 75° for 12 days
IIc	—	—	—	—	—	—	No solid polymer with 2% Bz_2O_2 at 100° for 25 days or 2% AIBN at 75° for 12 days

[a] Calcd. for $(C_7H_{10}O_2)_n$: C, 66.64; H, 7.99. Found: C, 66.37; H, 7.90. [b] Calcd. for $(C_8H_{12}O_2)_n$: C, 68.54; H, 8.63. Found: C, 68.37; H, 8.29. [c] No gelation after 32 days at 100° using 2% Bz_2O_2. [d] Benzoyl peroxide. [e] Azobisisobutyronitrile.

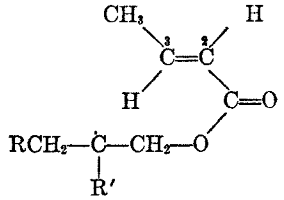
Residual unsaturation was determined as previously described[3] (Table II).

Inherent viscosity measurements were carried out in glacial acetic acid at 30.0° using a modified Ubbelohde viscometer (Table II).

Results and discussion. As indicated in Table II only allyl crotonate (Ia) and β-methallyl crotonate (Ic) gave solid, titratable polymers. Crotyl crotonate (Ib), crotyl vinylacetate (IIb) and *N*-allylcrotonamide (Ie) gave no polymeric material; allyl vinylacetate (IIa), β-methallyl vinylacetate (IIc) and propargyl crotonate (Id) afforded only viscous oils which resisted crystallization.

The relatively low degree of cyclization in poly(allyl crotonate) and poly(β-methallyl crotonate) is not surprising in view of the great difference in reactivities between the alcohol and acid bonds. This effect of differences in bond reactivities as reflected in linear *vs.* cyclopolymerization has been noted earlier.[3]

In addition to the anticipated absorption in the C=C stretching (1640–1655 cm.$^{-1}$) and carbonyl (1725–1740 cm.$^{-1}$) regions the infrared spectra (solid film from carbon tetrachloride) of the solid polymers showed a strong band at 1770–1772 cm.$^{-1}$ characteristic of a 5-membered lactone ring.[7] These findings were surprising, for although molecular models indicated somewhat less steric hindrance to attack of the initially-formed free radical at C_2 of



R' = —H, —CH_3

the acid (5-membered lactone ring) rather than at C_3 (6-membered lactone ring), attack at C_3 should be favored by virtue of the resonance-stabilized radical formed at C_2.

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Preparation of Hexaphenylcyclotrisiloxane by the Reaction of Diphenyldichlorosilane with Zinc Oxide

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In recent papers,[1] the senior author has described some methods which involve direct synthesis of

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hexaphenylcyclotrisiloxane (hereafter called trimer) from diphenyldichlorosilane (DPDS).

It has now been found that the trimer can be obtained readily by the reaction of DPDS with zinc oxide: When one mol. of DPDS was added to one and one half to two mol. of zinc oxide in inert solvents, reaction occurred exothermally. Trimer was obtained from the reaction product in a yield of 96 % (mean). Zinc chloride was determined as zinc hydroxide by neutralization with aqueous base.

Stoichiometry supports the following equation:

$$ZnO + (C_6H_5)_2SiCl_2 \longrightarrow ZnCl_2 + 1/3[(C_6H_5)_2SiO]_3$$

Other anhydrous reagents[2] (cupric oxide, lead oxide, silver oxide, manganese dioxide, cupric sulfate, ferric sulfate, zinc sulfate, nickel sulfate, ferric oxalate, cupric carbonate basic, etc.) were found to react with DPDS in substantially similar manner.

EXPERIMENTAL

Reagents. Purified-grade diphenyldichlorosilane was received from the Shin-etsu Chemical Industrial Co. Reagent-grade zinc oxide was finely powdered after prolonged drying. Methyl acetate was purified according to the ordinary method.

Procedure. A typical procedure is as follows: When a solution of diphenyldichlorosilane in methyl acetate (50 g., 0.2 mol., of DPDS, dissolved in 100 ml. of methyl acetate) was added portion-wise to a shaking flask which contained 24 g., 0.3 mole, of zinc oxide and 200 ml. of methyl acetate, an exothermic reaction occurred gradually. After the addition of DPDS was complete, the reaction mixture was gently refluxed for about 10 min., the color change of crystal violet[3] was used to determine completion of the reaction.

Benzene (200 ml.) was added to the reaction mixture to dissolve the silicon-containing product, and the resulting mixture, cooled to room temperature, was filtered by suction. The filtrate was shaken with about 400 ml. of distilled water to remove zinc chloride.

The top layer was separated, ethanol (200 ml.) was added to it, and the solution was evaporated to dryness on a water bath. A white crystalline mass melting at 177–180° and mixed with a small amount of oily liquid, was obtained. Further purification was effected by recrystallization from ethyl acetate, whereby 38 g. (97%) of pure trimer melting at 188–189° was obtained as elongated hexagonal plates.

Anal. Calcd. for $C_{36}H_{30}Si_3O_3$: Si, 14.16; OH/mol., 0.00; mol. wt., 594. Found: Si, 14.8; OH/mol., 0.0 (Karl Fischer titration[4]); mol. wt., 580–600 (Rast).

The x-ray powder pattern of the trimer obtained showed the major part to be orthorhombic trimer[5] and a minor amount to be triclinic trimer.[5]

From the bottom layer, 19 g. (96%) of zinc hydroxide was obtained by aqueous treatment with ammonium hydroxide using phenolphthalein as an indicator.

Although some other oxides and sulfates were also found to produce trimer and chlorides, respectively, most effective results (highest yield of trimer, greatest simplicity in procedure) were achieved by using zinc oxide as a reactant, whereby the marked dehydrating effect of the chloride resulted in almost a quantitative formation of the trimer.

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(2) Thorough investigations will soon appear in *J. Chem. Soc. Japan (Ind. Chem. Sect.)*.

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Synthesis of Tetra(perfluoroalkoxy)silanes

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The first reported synthesis of a tetraalkoxysilane was made by von Ebelman.[1] Since that time many tetraalkoxysilanes have been reported in literature.[2,3,4,5] Reaction 1 is most generally used for the preparation of these compounds:[6,7]

$$4SiCl_4 + 10\ ROH \longrightarrow ROSiCl_3 + (RO)_2SiCl_2 + (RO)_3SiCl + (RO)_4Si + 10HCl \quad (1)$$

A modification of the method of Helferich and Hausen[8] was employed to make a number of previously unreported tetra(perfluoroalkoxy)silanes. The method consisted of reacting tetrachlorosilane and a 10% molar excess of perfluorinated alcohols in an anhydrous medium at −10°. Hydrogen chloride produced during the reaction was removed by refluxing and by purging the reaction mixture with dry inert gas. The desired silanes were recovered by vacuum distillation.

Molar excesses of alcohol were used, not only to promote the formation of the tetra-substituted silanes, but also to prevent any reaction between silicon tetrachloride and the tetra-substituted silanes during refluxing or distillation.[9]

$$SiCl_4 + Si(OR)_4 \longrightarrow 2Cl_2Si(OR)_2 \quad (2)$$

Before distillation, the crude mixture of silanes was percolated through a column of activated, dry silica gel to remove the acidic materials which

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