in vacuo yielded a constant refractive index plateau product which had a purity of 99 mole %. No improvement in purity was shown when the material was hydrogenated once more and was purified by distillation and percolation through silica gel.

1,1-Dicyclohexylhexane.—Another portion of the olefin was hydrogenated to the saturated compound directly by using an equal volume of methylcyclohexane and 15% by wt. of U.O.P. nickel catalyst. Reduction of the double bond and of the aromatic nuclei occurred at 130° and at 170–180° at 1500 p.s.i., respectively. Purification consisted of a single fractionation in a Podbielniak column followed by percolation through silica gel.

1,6-Diphenyl-3-hexanol.—A solution of 6,580 g. (33 moles) of γ-phenylpropyl bromide (b.p. 122° at 10 mm.) in 6 l. of dry ether reacted with 710 g. (29.4 g. atoms) of magnesium covered with 8 l. of dry ether in a 30-gal. reactor. A solution of 3676 g. (27.4 moles) of freshly-distilled hydrocinnamaldehyde in 4 l. of dry ether condensed with the Grignard reagent and the reaction mixture was stirred for 12 hours. An emulsion formed during hydrolysis with 10% hydrochloric acid was broken by adding acid of increased concentration (15%). The product layer was worked up in the usual manner and the yield of 1,6-diphenyl-3-hexanol obtained after distillation was 5720 g. (82%); b.p. 196–199° at 3 mm. and n^{20}_{D} 1.5547. When the oil was dissolved in petroleum ether and chilled, a solid was obtained which melted at 35–35.5°.

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.96; H, 8.70.

1,6-Diphenyl-3-hexene.—A solution of 5610 g. (22.1 moles) of the carbinol dissolved in 3 l. of benzene was passed through a tube packed with alumina and maintained at 350–375°. The theoretical amount of water was obtained and the olefinic product recovered from the distillation was 4980 g. (95% yield). A subsequent fractional distillation gave an olefin with the following properties: m.p. −8.41°, b.p. 340° (dec.) at 760 mm. and 167° at 3.5 mm., n^{20}_{D} 1.5551 and d^{20} 0.96766 g./ml.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.36; H, 8.59.

The reduction of the ozonide prepared from a sample of the 1,6-diphenyl-3-hexene gave hydrocinnamaldehyde which was characterized as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 152.5–156°. This identified the olefin as 1,6-diphenyl-3-hexene. No evidence was found to indicate the presence of the isomeric 1,6-diphenyl-2-hexene which would also be expected as a product of this dehydration reaction.

1,6-Diphenylhexane.—An ethanol solution of 1,6-diphenyl-3-hexene was hydrogenated in a Parr apparatus at room temperature by the use of Adams catalyst. The yield was quantitative and the product was obtained in satisfactory purity by a single fractionation.

The Wurtz reaction involving the coupling of γ-phenylpropyl bromide in the presence of sodium was used as an independent synthesis. Finely divided sodium was obtained by heating 200 g. (8.7 g. atoms) in 1 l. of toluene while maintaining vigorous stirring. After cooling to room temperature, 1701 g. (8.5 moles) of γ-phenylpropyl bromide was added over a period of 6 hours, the reaction flask being intermittently cooled to keep the temperature below 25°. After the addition was completed, the temperature was kept at 50–70° while stirring was maintained for 48 hours. Water was added gradually to the cooled reaction mixture to consume the unreacted sodium. The hydrocarbon layer, after removal, was washed, dried and distilled. Since it gave a positive test for unsaturation, the material was reduced following the same procedure used for 1,6-diphenyl-3-hexene. Subsequent fractionation gave 429 g. (42% over-all yield) of 1,6-diphenylhexane in a state of purity comparable to that of the product obtained from the Grignard synthesis.

1,6-Dicyclohexylhexane.—A charge consisting of 908 g. (3.8 moles) of 1,6-diphenylhexane in an equal volume of methylcyclohexane with 100 g. of U. O. P. nickel catalyst was reduced at 180–190° at a pressure of 1700 p.s.i. in a 3-l. bomb. The catalyst was filtered out and the solvent was distilled from the product. The fractional distillation of the remaining material gave 892 g. (94%) of 1,6-dicyclohexylhexane which was percolated through silica gel prior to the determination of the physical properties.

CLEVELAND, OHIO

RECEIVED APRIL 2, 1951

[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

Synthesis of Alkoxy Silanols and Siloxanes[1]

BY C. R. MORGAN, W. F. OLDS AND ANNE LYONS RAFFERTY

The alkoxysilanol, -disiloxanol and -trisiloxanol derivatives of methylisobutylcarbinol have been prepared and isolated in good yields. The silanol and disiloxanol have been employed in the stepwise synthesis of linear alkoxyltrisiloxanes, and linear and branched alkoxytetrasiloxanes. Attempted preparations of a linear and branched pentasiloxane were unsuccessful, as was the isolation of the alkoxysilanol derivative of 2-ethylhexanol.

In an examination of the effects of siloxane chain structure upon the liquid properties of alkoxysiloxanes it was desired to synthesize certain tri-, tetra- and pentasiloxanes by routes which avoid the inherent difficulties of chlorosiloxanes[2] or orthosilicate esters[3] as starting materials. A stepwise synthesis has been examined, based upon single condensation reactions of alkoxysilanol and alkoxychlorosilane derivatives of methylisobutylcarbinol and 2-ethylhexanol. Because of the somewhat general instability of alkoxysilanols but two references have been made to their isolation and these are limited to derivatives of *t*-butyl alcohol,[4,5] where steric factors appear to favor stability. No stepwise condensations of the materials were reported, but Backer[4] has described the hexaalkoxydisiloxane as a very high melting solid. Our desire to study liquid alkoxysiloxanes ruled out further investigation of systems derived from *t*-butyl alcohol.

Of the two alcohols selected only methylisobutylcarbinol gave a trialkoxysilanol (IV) of sufficient stability for isolation. This product as well as the corresponding di-(IX) and trisiloxanol (XI) derivatives were prepared in good yields. Figure 1 illustrates the preparation of these materials and the utilization of IV and IX in the syntheses of the disiloxane (V), linear trisiloxane (VI) and the branched and linear tetrasiloxanes (VII and X). Repeated attempts to prepare the linear pentasiloxane by reaction between the trisiloxanol (XI) and the chlorodisiloxane (VIII) were not successful. Also, the branched

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(1) This paper is taken from a portion of the research sponsored by the Hodges Research and Development Company, Redwood City, California. Further work on this subject is being conducted by the Oronite Chemical Company, San Francisco, California.

(2) W. C. Schumb and D. Holloway, THIS JOURNAL, **63**, 2753 (1941).

(3) E. Konrad, O. Bächle and R. Signer, *Ann.*, **474**, 276 (1929).

(4) H. J. Backer and H. A. Klasens, *Rec. trav. chim.*, **61**, 500 (1942).

(5) C. S. Miner, *et al.*, *Ind. Eng. Chem.*, **39**, 1368 (1947).

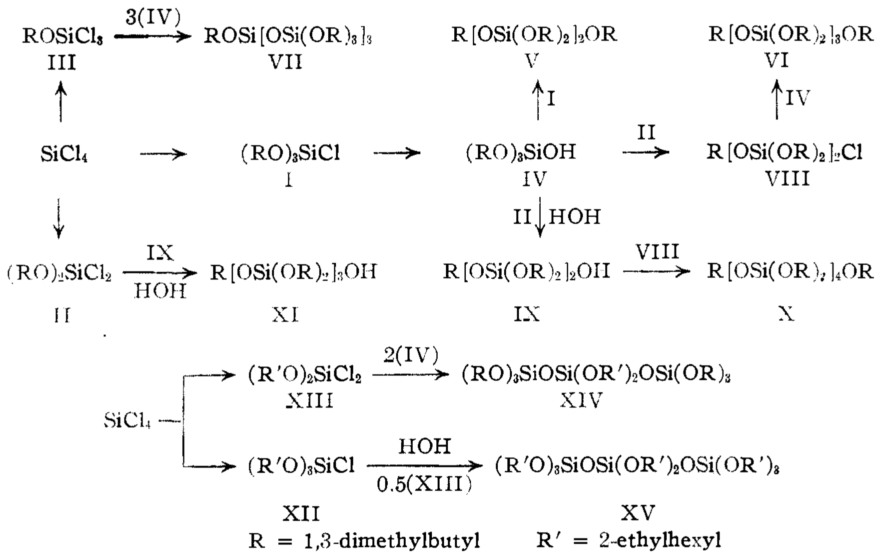

Fig. 1.

pentasiloxane could not be prepared by reaction of the silanol (IV) with silicon tetrachloride.

Although the trialkoxysilanol derived from 2-ethylhexanol could not be isolated, reaction of this compound *in situ* was effected yielding the trisiloxane (XV). Another linear trisiloxane (XIV), containing both the 2-ethylhexyl and 1,3-dimethylbutyl radicals, was prepared as indicated in Fig. 1.

Acknowledgment.—The services of Miss Verne M. Bass and Mr. Carleton B. Scott in the analytical and synthetic work are gratefully acknowledged.

Experimental[6]

Alkoxychlorosilanes.—All alkoxychlorosilanes were prepared by addition of the appropriate amount of methylisobutylcarbinol or 2-ethylhexanol to an anhydrous benzene solution of silicon tetrachloride. The properties of these intermediates are described in Table I.

TABLE I

PROPERTIES OF ALKOXYCHLOROSILANES

Compound[a]	Boiling point °C.	Boiling point Mm.	$n^{20}\mathrm{D}$
(RO)$_3$SiCl (I)	80	0.3	1.4219
(RO)$_2$SiCl$_2$ (II)	62	0.2	1.4235
ROSiCl$_3$ (III)	165	760	....
(R'O)$_3$SiCl (XII)	150	0.2	1.4391
(R'O)$_2$SiCl$_2$ (XIII)	116	0.2	1.4380

[a] R = 1,3-dimethylbutyl; R' = 2-ethylhexyl.

Tris-(1,3-dimethylbutoxy)-silanol (IV).—To a solution of 100 ml. of pyridine in 400 ml. of water at 10° there was added dropwise with stirring 399 g. (1.09 moles) of I. After complete addition the layers were separated and the organic layer was washed three times with an equal volume of water, dried over magnesium sulfate, and distilled. An 82% yield (310 g.) of IV was obtained at 105–106° at 0.3 mm., $n^{20}\mathrm{D}$ 1.4241.

Anal. Calcd. for $C_{18}H_{40}O_4Si$: Si, 8.04; *MR*D, 97.9. Found: Si, 8.03, 8.17; *MR*D, 97.8.

Hexakis-(1,3-dimethylbutoxy)-disiloxane (V).—Under anhydrous conditions 54 g. (0.155 mole) of IV was added dropwise to a cold, stirred mixture of 57 g. (0.155 mole) of I and 16 g. (0.20 mole) of dry pyridine. After washing with water and drying over magnesium sulfate, 70 g. (66% yield) of V was distilled at 179° and 0.5 mm., $n^{20}\mathrm{D}$ 1.4260.

Anal. Calcd. for $C_{36}H_{78}O_7Si_2$: Si, 8.26; *MR*D, 192.4; mol. wt., 679. Found: Si, 8.25, 8.15; *MR*D, 192.2; mol. wt., 674, 692.

Octakis-(1,3-dimethylbutoxy)-trisiloxane (VI). Mixed Alkoxytrisiloxane (XIV).—To a cold solution of 100.4 g. (0.289 mole) of IV in 24 g. (0.30 mole) of dry pyridine there was added dropwise with stirring 43.6 g. (0.145 mole) of II. Stirring was continued for 1 hour following complete addition and the mixture was allowed to stand overnight. After water washing and drying over magnesium sulfate there was obtained 55.4 g. (41%) of VI by distillation at 210° and 0.1 mm., $n^{20}\mathrm{D}$ 1.4297.

Anal. Calcd. for $C_{48}H_{104}O_{10}Si_3$: Si, 9.09; *MR*D, 259.0; mol. wt., 925. Found: Si, 9.15, 9.38; *MR*D, 259.1; mol. wt., 899, 907.

In a similar fashion the mixed octa-alkoxytrisiloxane (XIV) was prepared in 73% yield from reaction of the dichloro derivative (XIII) with two equivalents of the silanol (IV).

Anal. Calcd. for $C_{52}H_{112}O_{10}Si_3$: Si, 8.58; *MR*D, 277.4; mol. wt., 982. Found: Si, 8.67, 8.70; *MR*D, 277.0; mol. wt., 986, 988.

Decakis-(1,3-dimethylbutoxy)-tetrasiloxane, Branched (VII).—To a cooled mixture of 33.3 g. (0.141 mole) of 1,3-dimethylbutoxytrichlorosilane (III) in 84 g. (1.06 moles) of dry pyridine and 100 ml. of dry benzene there was added dropwise with stirring 174 g. (0.50 mole) of the silanol (IV). After standing at room temperature over the week-end the reaction mixture was washed with water and dried. By distillation 15 g. of VII was collected at 250° and 0.2 mm., $n^{20}\mathrm{D}$ 1.4320.

Anal. Calcd. for $C_{60}H_{130}O_{15}Si_4$: Si, 9.58; *MR*D, 325.3; mol. wt., 1172. Found: Si, 9.60, 10.5; *MR*D, 322.0; mol. wt., 1107, 1112.

Pentakis-(1,3-dimethylbutoxy)-chlorodisiloxane (VIII).—The alkoxysilanol (IV), 60.7 g. (0.175 mole), was added with stirring to a cooled mixture of 52.5 g. (0.175 mole) of II and 17.3 g. (0.22 mole) of dry pyridine in 70 ml. of dry benzene. After complete addition the pyridine hydrochloride precipitate was filtered from the reaction mixture, and benzene was removed by means of a water aspirator. Dissolved pyridine hydrochloride was removed by heating the crude product under high vacuum, and subsequent distillation through a 25-cm. Vigreux column gave 73.6 g. (70%) of VIII at 150° and 0.3 mm., $n^{20}\mathrm{D}$ 1.4250.

Anal. Calcd. for $C_{30}H_{65}ClO_6Si_2$: Si, 9.15; *MR*D, 168.1; mol. wt., 613. Found: Si, 9.28, 9.35; *MR*D, 168.1; mol. wt., 606, 611.

Pentakis-(1,3-dimethylbutoxy)-disiloxanol (IX).—Fifty-eight grams (0.167 mole) of IV was added dropwise to a cold, stirred mixture of 51 g. (0.170 mole) of II and 52 g. (0.66 mole) of dry pyridine. After complete addition of IV, 70 ml. of water was added rapidly and stirring was maintained for 1 hour. The reaction mixture was extracted with ether, the ether extract washed with water and then dried over magnesium sulfate. After ether removal 85 g. of IX was collected by distillation at 165° and 0.3 mm., $n^{20}\mathrm{D}$ 1.4270. Based upon the silanol (IV) a yield of 86% was obtained.

Anal. Calcd. for $C_{30}H_{66}O_7Si_2$: Si, 9.43; *MR*D, 162.6; mol wt., 595. Found: Si, 9.54, 9.60; *MR*D, 164.7; mol. wt., 593, 595.

Decakis-(1,3-dimethylbutoxy)-tetrasiloxane, Linear (X).—Under anhydrous conditions 29.7 g. (0.05 mole) of IX was dissolved in 16 g. (0.20 mole) of pyridine, and 30.6 g. (0.05 mole) of VIII was added dropwise, with cooling and stirring, over a 20-minute period. Stirring was continued for 1 hour and the reaction mixture was allowed to stand

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(6) Molecular weights were determined by the cryoscopic method in benzene. Molecular refractivities were calculated according to E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

overnight. After washing with water and drying, the crude product was distilled, yielding 19.4 g. (33%) of X at 240–242° and 0.05 mm., $n^{20}D$ 1.4318.

Anal. Calcd. for $C_{60}H_{130}O_{13}Si_4$: Si, 9.58; *MR*D, 325.3; mol. wt., 1172. Found: Si, 9.84, 10.01; *MR*D, 321.7; mol. wt., 1143.

Heptakis-(1,3-dimethylbutoxy)-trisiloxanol (XI).—Eighty-five grams (0.143 mole) of the disiloxanol (IX) was added dropwise with stirring to a cold mixture of 42 g. (0.140 mole) of II and 30 g. of dry pyridine. After an hour 70 ml. of water was added rapidly and stirring was continued for an additional hour. The organic layer was extracted with ether, washed with water, and dried over magnesium sulfate. After removal of ether the crude product was distilled, yielding 75 g. (65%) of XI at 185° and 0.1 mm., $n^{20}D$ 1.4255.

Anal. Calcd. for $C_{42}H_{92}O_{10}Si_3$: Si, 10.0; *MR*D, 230.8; mol. wt., 841. Found: Si, 10.5, 10.9; *MR*D, 228.2; mol. wt., 840, 843.

Octakis-(2-ethylhexoxy)-trisiloxane (XV).—Efforts to isolate the trialkoxysilanol derived from 2-ethylhexanol were unsuccessful and this silanol was prepared *in situ* by addition with stirring of 66.7 g. (0.148 mole) of the chlorosilane (XII), over a period of 2 hours, to 2.66 g. (0.148 mole) of water in 100 ml. of dry pyridine. During the next half-hour 24.6 g. (0.074 mole) of bis-(2-ethylhexoxy)-dichlorosilane (XIII) was added, and stirring was continued for an additional half-hour. The reaction mixture was washed with water, dried and distilled. Thirty-five grams (41%) of XV was collected at 260–269° and 0.05 mm., $n^{20}D$ 1.4428.

Anal. Calcd. for $C_{64}H_{136}O_{10}Si_3$: Si, 7.32; *MR*D, 332.9; mol. wt., 1150. Found: Si, 7.90, 7.92; *MR*D, 329.8; mol. wt., 1111, 1134.

CAMBRIDGE 42, MASS. RECEIVED MAY 16, 1951

[CONTRIBUTION NO. 294 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

Tracer Studies of Oxidation–Reduction Polymerization and Molecular Weight of "Teflon" Tetrafluoroethylene Resin

BY K. L. BERRY AND J. H. PETERSON

The objective of this work was to determine the molecular weight of polytetrafluoroethylene. Since the polymer is insoluble and infusible, attempts were made to introduce and determine radiosulfur-containing end groups derived from persulfate initiator. Polymers initiated by persulfate activated thermally or by reaction with Fe^{++} or bisulfite did not contain sulfur from the persulfate. When bisulfite containing radiosulfur was employed in oxidation–reduction initiation reactions with persulfate or Fe^{+++}, polymers with non-hydrolyzable sulfur-containing end groups from the bisulfite were obtained. These results are explained on the basis that the following are the most probable radical-producing reactions in decreasing order of effectiveness for initiating tetrafluoroethylene polymerization.

$$S_2O_8^{=} + Fe^{++} \longrightarrow Fe^{+++} + SO_4^{=} + SO_4^{\dot{-}} \quad (1)$$

$$HSO_3^{-} + Fe^{+++} \longrightarrow Fe^{++} + HSO_3\cdot \quad (2)$$

$$S_2O_8^{=} + HSO_3^{-} \longrightarrow SO_4^{=} + SO_4^{\dot{-}} + HSO_3\cdot \quad (3)$$

The translation of radioactive end group determinations to molecular weights is based upon the foregoing view of the initiator reactions and the assumptions (1) that there is no chain transfer or disproportionation in the polymerization, and (2) that termination is by combination of radicals. The number average molecular weights of some relatively low molecular weight polytetrafluoroethylenes are in the range 142,000–534,000.

Introduction

No data on the molecular weight of polytetrafluoroethylene have yet been reported because the insolubility and extremely high melt viscosity of this polymer[1] have precluded determinations by conventional methods. In this paper we report the use of radioactive sulfur in bisulfite and persulfate initiator components for determining end groups and molecular weights of some polytetrafluoroethylenes prepared under various conditions.

Examination of this polymer by end group analysis is singularly informative in view of evidence[1] that there is no branching in the polymer. The results have given additional information on the chemical nature of end groups derived from several initiator systems and on the oxidation–reduction reactions involved in persulfate–bisulfite systems.

Experimental Details

Preparation of S^{35}*-Containing Persulfate and Bisulfite.—The radiosulfur used in this investigation was obtained as irradiated potassium chloride from Oak Ridge National Laboratory and was allocated by the U. S. Atomic Energy Commission. Preparation of potassium persulfate containing radioactive sulfur has been described.[2]

Sodium bisulfite containing radiosulfur was prepared by burning the sulfur (0.1–0.8 g.) in a large excess of oxygen streaming through a heated glass tube, and absorbing the sulfur dioxide in sodium hydroxide solution at 0°. The weighed sulfur sample was placed in a small test-tube which was inserted in the hot tube at a point where the temperature was 250–275°. The sulfur slowly volatilized and burned evenly at the mouth of the test-tube. The gases then traveled through a zone where the maximum temperature was about 550°. The exit gases were bubbled through approximately 0.1 *M* NaOH solution in the amount calculated on the weight of sulfur to produce $NaHSO_3$. Some oxidation of SO_2 to SO_3 occurred during combustion, and there was also some oxidation of bisulfite in the solution by oxygen. Recoveries of sulfur as bisulfite, however, were 91 to 96%. The bisulfite was used in the solution as prepared. The solutions were stored at 2–4° under a nitrogen atmosphere, and the bisulfite content determined before each use.

Purity and Handling of Monomer.—Tetrafluoroethylene was purified by distillation under pressure at 4.5 atm. at which pressure the boiling point is −43°. Each batch was analyzed for oxygen, and only material containing less than 10 p.p.m. of oxygen was used. The monomer in the gas phase was stored at approximately 100 lb./sq. in. in a steel cylinder at ambient temperature behind a barricade in an isolated location and piped through a pressure reducing valve to the reactor.

Polymerization.—The apparatus in which polymerizations were conducted comprised a Model A Parr hydrogenation unit[3] modified by providing a pressure gage connected to the 325-ml. Pyrex brand glass reaction vessel. The latter was equipped with a glass thermocouple well containing an iron–constantan thermocouple for indicating the tempera-

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(1) W. E. Hanford and R. M. Joyce, THIS JOURNAL, **68**, 2082 (1946).

(2) W. E. Mochel and J. H. Peterson, *ibid.*, **71**, 1426 (1949).

(3) Manufactured by the Parr Instrument Company, Moline, Ill.