838 (—$Si(CH_3)_2$—). A quantitative comparison of this polymer with diallyldimethylsilane showed that there were 6.0% of the monomer units incorporated in the polymer chain which still retained one double bond.

266A-2 was a moderately viscous oil which was completely soluble in benzene, heptane, and chloroform. It had an infrared spectrum identical with that of 266A-1, including the amount of residual unsaturation in polymer.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. VI. Polymerization Studies of Some Diallylsilanes[1]

GEORGE B. BUTLER AND ROBERT W. STACKMAN

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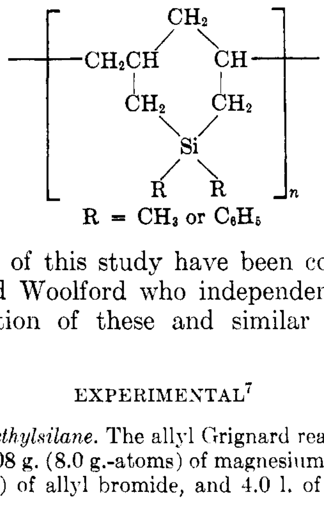
Diallyldimethylsilane and diallyldiphenylsilane have been polymerized with triethylaluminum–titanium tetrachloride complex catalyst to yield soluble polymers.

During the period following the original proposal[2] that 1,6-heptadienes can polymerize by an alternating intra-intermolecular mechanism to produce soluble, linear polymers, a wide variety of such monomers and the resulting polymers have been prepared and studied.[3] We now wish to report the synthesis and results of the polymerization studies of diallyldimethylsilane and diallyldiphenylsilane.

While both monomers studied in this work have previously been reported,[9,11] their significance was not realized until the advent of the intra-intermolecular mechanism for polymerization of 1,6-dienes and the Ziegler-type catalysts for polymerization of hydrocarbons. A kinetic study of radical catalyzed polymerization of allyltrimethylsilane and diallyldimethylsilane has been made,[4] and low molecular weight polymers were reported. More recently, polymerization of diallyldimethylsilane and diallyldiethylsilane by use of a triethylaluminum–titanium tetrachloride complex catalyst has been reported.[5] These authors reported that both liquid and solid polymers were obtained. From the liquids could be isolated trimers, tetramers, and pentamers; however, the solid polymers were insoluble in ether, benzene, and carbon tetrachloride, but swelled in heptane.

The polymers reported in this study are soluble in benzene. The absence of unsaturation in the polymers in conjunction with their solubility properties suggests the following structure for the polymers:



The results of this study have been confirmed by Marvel and Woolford who independently studied polymerization of these and similar monomers.[6]

EXPERIMENTAL[7]

Diallyldimethylsilane. The allyl Grignard reagent was prepared from 208 g. (8.0 g.-atoms) of magnesium turnings, 448 g. (4.0 moles) of allyl bromide, and 4.0 l. of sodium-dried ether.[8]

Titration of the solution showed that it contained 3.7 equivalents (94% yield) of Grignard reagent. To 2.3 l. (2.3 equivalents) of the Grignard reagent was added 129 g. (1.0 mole) of dimethyldichlorosilane over a period of 4 hr.; the mixture was stirred for 20 hr. at room temperature. Hydrolysis was accomplished by pouring the contents of the reaction flask into a chilled hydrochloric acid solution. The ether layer and one 100-ml. ether extract of the aqueous phase were dried over calcium chloride; removal of the solvents by distillation left an oil which, when fractionated, gave 106 g. (76.3%) of diallyldimethylsilane, b.p. 135° (760 mm.), n_D^{20} 1.4405 [reported[9] b.p. 135.0–136.0° (760 mm.), n_D^{20} 1.4402]. The infrared spectrum of this compound[10] was identical with the spectrum of diallyldimethylsilane reported previously.[9]

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(1) This research was supported by the United States Air Force through the Materials Laboratory, Wright Air Development Center of the Air Research and Development Command, under Contract Number AF 33(616)-5808. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957).

(3) A previous paper in this series [M. D. Barnett, A. Crawshaw, and G. B. Butler, *J. Am. Chem. Soc.*, **81**, 5946 (1959)] contains many pertinent references.

(4) O. Mikulasova and A. Hvirik, *Chem. zvesti*, **11**, 645 (1957).

(5) A. V. Topchiev, N. S. Nametkin, S. G. Durgar'yan, and S. S. Dyankov, *Khim i Prakt. Primenenie Kremneorg. Soedinenii, Trudy Konf. Leningrad*, No. **2**, 118 (1958).

(6) C. S. Marvel and R. G. Woolford, *J. Org. Chem.*, **25**, 1641 (1960).

(7) All melting and boiling points are uncorrected.

(8) The procedure for the preparation of allyl Grignard reagent was obtained from Peninsular ChemResearch, Inc.

(9) L. D. Nasiak and H. W. Post, *J. Org. Chem.*, **24**, 489 1959).

(10) The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer by Mr. George Price and Mr. Leo Pijanowski.

TABLE I

POLYMERIZATION OF DIALLYLDIMETHYLSILANE

Heptane, ml.	$Al(C_2H_5)_3$, g.	$TiCl_4$, g.	$\frac{\text{Moles } Al(C_2H_5)_3}{\text{Moles } TiCl_4}$	Monomer, g.	Temperature	Time, hr.	Polymer, g.	Conversion %
10	0.15	0.10	2.5	3	60	30	0.3	10
50	0.60	0.40	2.5	10	65	48	0.7	7
50	0.40	0.20	3.3	10	85	48	0.9	9
50	0.70	0.50	2.4	10	85	24	1.0	10

TABLE II

POLYMERIZATION OF DIALLYLDIPHENYLSILANE

Heptane, ml.	$Al(C_2H_5)_3$, g.	$TiCl_4$, g.	$\frac{\text{Moles } Al(C_2H_5)_3}{\text{Moles } TiCl_4}$	Monomer, g.	Temperature	Time, hr.	Polymer, g.	Conversion, %
5	0.10	0.08	2.2	3	60	24	1.5	50
10	0.15	0.10	2.5	5	65	24	1.5	30
40	0.60	0.40	2.5	8	70	16	2.0	25
50	0.80	0.30	4.4	10	85	24	5.6	56

Diallyldiphenylsilane. The above procedure was repeated using 1.5 l. (1.5 equivalents) of allyl Grignard reagent and 126 g. (0.5 mole) of diphenyldichlorosilane. Fractionation of the product yielded 91 g. (71%) of diallyldiphenylsilane, b.p. 137–138° (1.5 mm.), n^{20}_{D} 1.5742 [reported[11] b.p. 140.5° (2 mm.), n^{20}_{D} 1.5750]. The previously reported spectrum of diallyldiphenylsilane[9] was identical with that obtained for this compound.

Polymerization studies. The catalyst for the polymerizations was prepared in a dry box. Triethylaluminum was dissolved in heptane; this was followed by the addition of a measured quantity of titanium tetrachloride which appeared to react immediately to give a brown suspension. After the flask was capped and removed from the dry box, the monomer was added, with stirring, to the suspension. The contents of the flask were then heated to the specified temperature. After varying intervals of time the polymerization mixtures were poured into methanol to decompose the catalyst.

Polydiallyldimethylsilane. Table I shows the results of the polymerization of diallyldimethylsilane. Purification of the polymers was accomplished by dissolving them in benzene; the resulting solution was poured into methanol from which the compounds precipitated. The analytical samples were obtained by repeating this process at least four times. The purified polymers melted between 80° and 110° and began to darken between 300° and 330° (open capillary). The infrared spectrum exhibits peaks for aliphatic hydrogen (2900–2800 cm.$^{-1}$) and for silicon dimethyl (1260–1240 cm.$^{-1}$, 815–800 cm.$^{-1}$). The bands for the double bond (1640 cm.$^{-1}$) and for the terminal methylene group (895 cm.$^{-1}$) are absent from the spectrum. An intrinsic viscosity determination in benzene gave a value of 0.13.

Anal.[12] Calcd. for $(C_8H_{16}Si)_n$: C, 68.52; H, 11.50; Si, 19.98. Found: C, 65.84; H, 10.95; Si, 19.73.

Polymerizations were also carried out using di-*t*-butyl peroxide as an initiator. The polymers were purified in a similar manner. The polymer obtained with 1.2% peroxide melted at 80–100° and began to darken at 280°. The infrared spectrum was similar to that of the Ziegler catalyst–initiated polymer but there were small peaks for the double bond (1640 cm.$^{-1}$) and for the terminal methylene group (895 cm.$^{-1}$) indicating some residual unsaturation.

Polydiallyldiphenylsilane. Table II shows the results of the polymerization of diallyldiphenylsilane. The method used for purifying the polymers was the same as that with polydiallyldimethylsilane. The polymers obtained melted from 125–155° and began to darken above 330° (open capillary). The weight-average molecular weight, as obtained by light scattering measurements,[13] was 6.0 × 10^{4}. A value of 0.065 was found for the intrinsic viscosity on a benzene solution of the polymer. The infrared spectrum possesses peaks for phenylsilicon (1430 cm.$^{-1}$, 1110 cm.$^{-1}$), aliphatic hydrogen (2900 cm.$^{-1}$), and aromatic hydrogen (3030 cm.$^{-1}$). The spectrum exhibits no absorption for the double bond (1641 cm.$^{-1}$) or for the terminal methylene group (895 cm.$^{-1}$).

Anal. Calcd. for $(C_{18}H_{20}Si)_n$: C, 81.78; H, 7.63; Si, 10.60. Found: C, 80.74; H, 7.60; Si, 10.40.

Polymerizations carried out on diallyldiphenylsilane with di-*t*-butyl peroxide gave similar polymers. A polymer prepared with 6% peroxide had a melting range of 115–140° and began to darken at 315°. An intrinsic viscosity of 0.04 was obtained for a sample of this polymer dissolved in benzene. The infrared spectrum of this polymer and the infrared spectrum of the Ziegler catalyst–initiated polymer are identical.

GAINESVILLE, FLA.

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[11] A. D. Petrov, V. F. Mironov, and V. G. Glukhotsev, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk,* 1123 (1954).

[12] Microanalyses were performed by Spang Microanalytical Laboratory and Clark Microanalytical Laboratory.

[13] The light scattering measurements were performed with a Brice-Phoenix Universal Light Scattering Photometer by Mr. Carey Rushing.