[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Formation of a Cyclic Recurring Unit in the Polymerization of Diallyldimethylsilane[1]

C. S. MARVEL AND R. G. WOOLFORD

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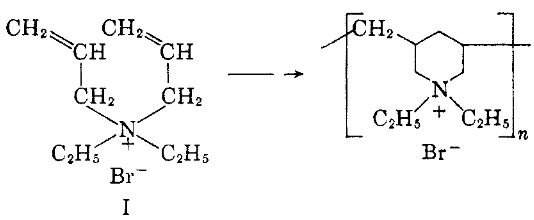
Diallyldimethylsilane has been polymerized with Ziegler-type catalysts to give soluble polymers containing cyclic recurring units.

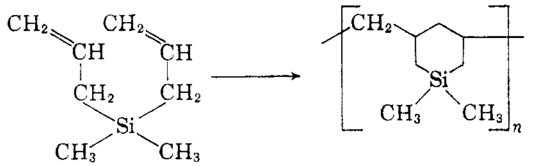
The formation of polymers containing cyclic recurring units by intermolecular-intramolecular polymerization of nonconjugated olefins is now well established. For example,[2] diallyl diethyl ammonium bromide (I) gives a soluble polymer containing recurring piperidine units (II). Similarly,



I

1,5-hexadiene,[3] 1,6-heptadiene,[3] and a series of 2,6-disubstituted 1,6-heptadienes[4] have been polymerized to give polymers containing cyclic recurring units.

It was thought that diallyldimethylsilane (III) might also polymerize to give such a polymer (IV) and such has been found to be the case. Using a



III IV

Ziegler-type catalyst of aluminumtriisobutyl and titanium tetrachloride in heptane solvent at 30°, soluble polymers ranging from moderately viscous oils to high-melting white solids have been obtained. From the preliminary experiments, it seems apparent that the polymerization conditions (amount of solvent, catalyst ratios, etc.) have a marked effect on both the yield and molecular weight of polymer produced. In each case, small amounts (0.9–10% yields) of insoluble, presumably cross-linked polymers, were obtained. Yields of the soluble polymers ranged from 13–91% and in most cases they were very sticky, glassy semisolids. These polymers dissolved completely in benzene, heptane, and chloroform. The results are tabulated in Table I.

The polymer sample from reaction 266A was purified thoroughly by four reprecipitations from benzene solutions into methanol. The soluble portion was able to be divided into two fractions: a white solid, completely insoluble in methanol-benzene solution but freely soluble in benzene (viscosity 0.22), and a viscous oil, moderately soluble in methanol-benzene (viscosity 0.04) which was recovered by boiling off the solvent. These fractions possessed identical infrared spectra (taken in 2.5% solution in chloroform), which contained the following bands (cm.$^{-1}$): 2905 (—C—H stretch); 1441 (—CH$_2$— deformation, normal): 1409 (—CH$_2$— deformation, lowered for CH$_2$ groups next to Si atom); 1339 (—CH< deformation): 1248, 838 (—Si(CH$_3$)$_2$—). In both cases, a very weak band was obtained at 1631 cm.$^{-1}$ (residual double bond). A quantitative comparison of these polymer samples with diallyldimethylsilane (2.5% solution in chloroform) showed that there were 6.0% of the monomer units incorporated in the polymer chain which still retained one double bond. The identical amounts of residual unsaturation in both fractions appear to indicate that, except for molecular weight, the same type of polymer linkage is present in each. The infrared studies are thoroughly consistent with polymer structure IV containing cyclic recurring units. The fraction with the higher viscosity was obtained analytically pure and, on heating, softened and shrank slightly between 100° and 300°. Above 300° it began to turn yellow and at 376° it formed a clear amber melt. When this sample was heated above 300° for more than a few minutes, it began to decompose noticeably.

At this point we learned that Dr. G. B. Butler of the University of Florida was working on this same general problem and we discontinued our work (9-20-58).[5]

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(1) This work was sponsored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, Contract No. AF 33(616)-5486. Reproduction of this paper 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) C. S. Marvel and J. K. Stille, *J. Am. Chem. Soc.*, **80**, 1740 (1958).

(4) C. S. Marvel and R. D. Vest, *J. Am. Chem. Soc.*, **79**, 5771 (1957); also in press.

TABLE I

POLYMERIZATION OF DIALLYLDIMETHYLSILANE AT 30°

No. Sample	Heptane, G.	Aluminum Triisobutyl, G.	Titanium Tetrachloride, G.	Moles Aluminum Triisobutyl / Titanium Tetrachloride, Moles	Monomer, G.	Time, Hr.	Total Yield, %	Insol. Polymer, %	Sol. Polymer, %	η^a (25°)	Polymer Appearance
266A	7.5	0.15	0.144	1.0	4.0	48	32	2.1	30	0.22 (266A-1) 0.04 (266A-2)	White solid Viscous oil
266B	7.5	0.15	0.048	3.0	4.0	48	20	1.3	19	0.08	White solid
266C	15.0	0.15	0.048	3.0	4.0	48	13	0.9	12	0.09	White solid
266D	7.5	0.15	0.144	1.0	4.0	72	37	2.8	35	0.08	Glassy semisolid
266E	7.5	0.30	0.288	1.0	4.0	72	87	10	77	0.06	Glassy semisolid
266F	3.8	0.15	0.144	1.0	2.0	72	91	7.0	84	0.08	Glassy semisolid
266G	15.0	0.30	0.288	1.0	2.0	72	56	3.2	53	0.06	Glassy semisolid

[a] All viscosities were run on 0.25 g. polymer dissolved in 100 ml. of benzene solution.

EXPERIMENTAL[6]

Diallyldimethylsilane (III). A solution of allylmagnesium bromide was made in the usual manner[7] using the following quantities of reagents: allyl bromide (200 g., 1.66 moles), magnesium (97 g., 4.0 g.-atoms), and anhydrous ether (1.5 l.). This solution was decanted into another flask and a solution of allyldimethylchlorosilane (135 g., 1.0 mole) in 300 ml. of anhydrous ether was dropped in at reflux temperature. The reaction mixture was stirred for 12 hr. and hydrolyzed with a saturated solution of ammonium chloride. The ether layer was distilled three times through a 55-cm. packed glass column to yield diallyldimethylsilane (112 g., 80% yield) of b.p. 134–135° (at about 750 mm), n_D^{25} 1.4380. [Petrov *et al.*[8] give: b.p. 135.5° (760 mm.), n_D^{20} 1.4420.]

An infrared spectrum of this compound exhibited the following bands (cm.$^{-1}$): 3070, 2960, 2900 (C—H); 1632 ($CH_2{=}CH$—); 1423, 1395, 1300, 990, 925 (CH and CH_2 deformations); 1253, 830 (—$Si(CH_3)_2$—).

Gas chromatography indicated this silane was free from impurities.

Polymerization studies. Table I lists a series of polymerizations of diallyldimethylsilane. The reaction mixtures were made up in the usual manner.[3] The polymer obtained from reaction 266A was fractionated into two components by repeated reprecipitation from benzene solution into methanol. Fraction 266A-1 was a white, powdery solid, completely insoluble in methanol-benzene solutions, but soluble in benzene, chloroform, and heptane. Fraction 266A-2 was a moderately viscous oil, soluble in methanol-benzene and isolated by boiling off the solvent. This oily fraction represented approximately two thirds of the soluble polymer obtained. No effort was made to fractionate samples 266B–266G. The small amounts of insoluble polymer produced in each reaction were removed by filtering benzene solutions of the original crude polymers from the first reprecipitations. Fine mesh wire screening or ordinary filter paper were used. All samples were purified by reprecipitation and freeze-dried from benzene.

The following physical and chemical data on soluble polymers 266A-1 and 266A-2 were obtained:

266A-1 was a white solid which softened and shrank slightly from 100–300°, formed a clear amber melt at 376°, and was completely soluble in benzene, heptane, chloroform. X-ray diffraction studies indicated this polymer was amorphous.

Anal. Calcd. for $(C_8H_{16}Si)_n$: C, 68.48; H, 11 50; Si, 20.02. Found: C, 68.65; H, 11.48; Si, 19.26.

Infrared spectrum (2.5% in chloroform) (cm.$^{-1}$): 2905 (C—H); 1631 (weak) (residual C=C); 1441 (—CH_2— deformation, normal); 1409 (—CH_2— deformation for CH_2 groups next to Si atom); 1339 (—CH< deformation); 1248,

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(5) Since this manuscript was written, the work of 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); *Chem. Abstr.*, **53**, 8686 (1959) has become available. They have obtained distillable liquids, presumably cyclic trimers and tetramers, by the action of aluminum triethyl/titanium tetrachloride catalysts on diallyldiethylsilane.

(6) We are indebted to Mr. J. Nemeth, University of Illinois and to Clark Microanalytical Laboratories, Urbana, Ill., for the microanalyses, to Mr. P. McMahon for the infrared determinations and to Mr. R. Greenley for the x-ray studies.

(7) O. Grummitt, E. Budewitz, and C. C. Chudd, *Org. Syntheses*, **36**, 60 (1956).

(8) A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1123 (1954); *Chem. Abstr.*, **49**, 7510 (1955).

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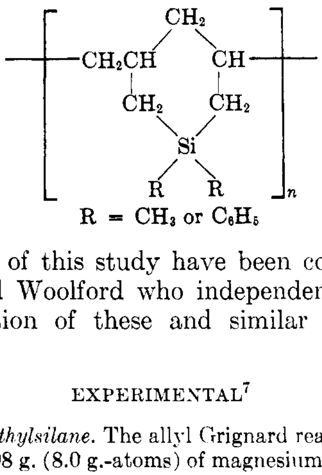
Diallyldimethylsilane and diallyldiphenylsilane have been polymerized with triethylaluminum–titanium tetrachloride complex catalyst to yield soluble polymers.

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:



R = CH_3 or C_6H_5

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.