The Formation of Linear Polymers from Diene Monomers by the Cyclic Polymerization Mechanism. IX. Further Polymerization Studies on Silane Monomers

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SUMMARY

A number of unsaturated silanes which are functionally capable of polymerizing by the cyclopolymerization mechanism have been synthesized and their polymerization studied. Allyl-substituted silanes studied include diallylmethylphenylsilane, diallylcyclotetramethylenesilane, and diallylcyclopentamethylenesilane. The latter two compounds have been characterized, and their physical properties are reported since they are new structures. Methallyl-substituted silanes studied include dimethallyldimethylsilane, dimethallyldiphenylsilane, dimethallylmethylphenylsilane, and dimethallylcyclopentamethylenesilane. The latter compound has been characterized, and its physical properties are reported since it is a new structure. Also, allylvinyldimethylsilane was prepared, characterized, and studied, since this compound is functionally capable of producing a five-membered ring in the repeating unit of the polymer. All of the diallylsilanes yielded polymers of low molecular weight by use of coordination catalysts of the Ziegler type. The dimethallylsilanes failed to yield polymer via coordination initiators but yielded low polymers by a free radical machanism. Allylvinyldimethylsilane yielded a low, noncyclic polymer via coordination initiation in which only the allyl double bond participated. By the free radical mechanism, polymers of similar structure were obtained.

INTRODUCTION

In a previous paper from this laboratory [1] the formation of cyclic polymers from diallyldimethylsilane and the corresponding diphenyl compound via coordination complex and free radical initiation was reported. Some further studies along these lines are reported herein, including several additional diallylsilanes, several dimethallylsilanes, and one allylvinyl-silane. The diallyl compounds are examples of substituted 1,6-heptadienes and would be expected to participate in a coordination complex-initiated polymerization as 1,6-heptadiene does [2]. On the other hand, the dimethallyl compounds, being structurally related to alkenes branched at C-2, would not be expected to participate readily in this type of initiation [3]. However, even though 2-methyl-1-pentene yielded only a low-molecular-weight oil in low conversion, 2,5-dimethyl-1,5-hexadiene gave quantitative conversion to a cyclic polymer having an intrinsic viscosity of 0.11 dl/g [2]. These results were interpreted to be indicative of an unusual driving force in the polymerization process during cyclic polymerization of such monomers.

Allylvinyldimethylsilane is an example of a substituted 1,6-hexadiene; unsubstituted 1,6-hexadiene has been shown to undergo metal alkyl coordination-catalyzed polymerization to yield a polymer containing five-membered rings in the repeating unit [2]. However, it has been reported [3] that a-olefins with branching closer than the 3- or 4-position relative to the double bond cannot be polymerized by the coordination complex method of initiation. In view of this and the fact that the larger size of the silicon atom compared with that of carbon would be detrimental to formation of the five-membered ring system required by cyclic polymerization of this monomer, polymerization by this mechanism does not appear probable. Also, it is well known that silicon has a tendency, particularly in the siloxanes, to form an eight-membered ring as the most stable structure [4].

RESULTS AND DISCUSSION

Consistent with the results previously reported [1], the diallylsilanes studied in this work were found to undergo cyclic polymerization by use of metal alkyl coordination complex initiation. All gave polymers which were soluble in benzene, although small fractions of a few polymers were insoluble. The soluble polymers exhibited little or no residual unsaturation

as determined from the infrared spectra. It can be concluded that the polymers were formed by the cyclic polymerization mechanism [1], and the following interesting spiro structures can be assigned to those polymers arising from diallylcyclotetramethylenesilanes (I) and diallylcyclopentamethylene silanes (II), respectively:

(I)   (II)
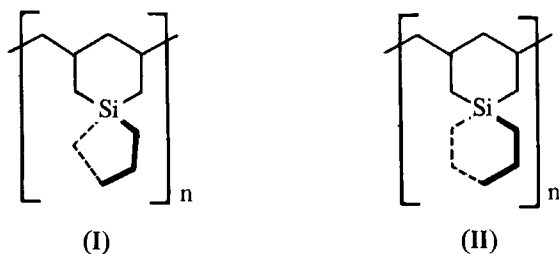
A similar structure has been assigned to the polymer of diallylmethylphenylsilane. These polymers are not of high molecular weight, as confirmed by intrinsic viscosity values of 0.12, 0.11, and 0.04 dl/g, respectively, for the methylphenyl, cyclotetramethylene, and cyclopentamethylene derivatives. The results of these studies are shown in Tables 1–3.

Attempts were made, without success, to convert dimethallyldimethylsilane to polymer by use of coordination complex initiation. These results are consistent with previously published reports on attempts to polymerize olefins with branching close to the double bond [3], but they are inconsistent with the results obtained with 2,5-dimethyl-1,5-hexadiene [2], a compound which has branching similar to that of this silane and which gave 100% conversion to cyclic polymer via coordination complex initiation. Free radical initiation, however, led to soluble, low-molecular-weight polymers from all of the dimethallyl compounds studied. These polymers exhibited little or no residual unsaturation as determined from the infrared spectra, which supports the proposed cyclic structure for the products. The conditions and results of these polymerization studies are shown in Table 4.

Allyldimethylvinylsilane is functionally capable of undergoing cyclic polymerization to yield a polymer containing five-membered rings in the repeating unit. The infrared spectrum of this compound exhibits two distinct peaks for the two carbon-carbon double bonds at 1635 and 1595 cm^{-1}. The peak at 1595 cm^{-1} was assigned to the vinyl group bonded to silicon, and the peak at 1635 cm^{-1} to the allyl double bond. These

assignments are consistent with other similarly substituted silanes. The shift of the vinyl absorption indicates that the carbon-carbon double bond of the group is of lower energy than is that of the allyl group, which suggests a polarization of the double bond due to the bonding to silicon. This polarization, due to the "electron sink" effect of silicon, would be expected to stabilize a free radical formed from initiator attack on the vinyl group. This postulate is supported by the fact that free radical chlorination of tetraethylsilane gives exclusively the a-chloro compound [5]. The stability of this radical would be expected to be detrimental to participation of the vinyl group in a free radical-initiated polymerization. The results of attempts to convert this monomer to polymer by use of di-t-butyl peroxide led to a highly viscous liquid polymer and an insoluble solid. The infrared spectra of these products were similar and showed absorption for both allyl and vinyl groups, with the concentration of the allyl double bond having been reduced relative to the monomer much more than the vinyl double bond. These results are consistent with the above structural considerations and suggest that the less reactive vinyl double bond can participate in a cross-linking reaction, leading to insoluble polymer. The low-molecular-weight, soluble polymer is indicated to have arisen through polymerization of the allyl double bond, leaving the vinyl group pendant.

Attempts to polymerize this monomer by coordination complex initiation gave a polymer which was a highly viscous liquid, obviously of low molecular weight. In the coordination complex case, the vinyl double bond does not take part in the polymerization due to steric factors [3]. The infrared spectrum of the polymer indicated this to be borne out, as the major changes in the spectrum of the polymer, relative to the monomer, were associated with a decrease or disappearance of the allyl double bond content, with the vinyl double bond absorption remaining relatively constant. These results indicate that only the allyl double bond is involved in the coordination complex-initiated polymerization.

The results of the carbon analysis of the polymers are in many cases quite far from the theoretical values. It is reported [4] that in the analysis of silicon-containing polymers, combustion of the sample may lead to the formation of some silicon carbide which is not completely oxidized. Formation of this compound would account for the low value for carbon found in the polymers. The results of the silicon analysis would not be affected by this phenomenon since the silicon analyses are performed on a separate sample using wet oxidation methods.

EXPERIMENTAL

Preparation of Monomers

Diallylmethylphenylsilane. To 1.2 liters (1.2 eq) of allyl Grignard reagent were added 100 g (0.52 mole) of methylphenyldichlorosilane 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, 10% hydrochloric acid solution. The ether layer and one 50-ml ether extract of the aqueous phase were dried over calcium chloride; removal of the solvent by distillation left an oil that, when fractionated, gave 80.3 g (75%) of diallylmethylphenylsilane, bp 124°C (15 mm), n_D^{20} 1.5200 (reported [6] bp 123.5–124.4°C [20.5 mm], n_D^{20} 1.5221). Gas-liquid chromatography indicated that the compound was pure. The infrared spectrum exhibited the following bands (cm^{-1}): 3060, 2970, 2950, 2875 (C–H); 1960, 1880, 1800 (phenyl); 1635 (CH_2=CH–); 1485, 1390, 1300, 987, 893 (CH and CH_2 deformations); 1426, 1112 (Si–phenyl); and 1250, 830 (–Si(CH_3)–).

Diallylcyclotetramethylenesilane. To a solution of 1.05 eq of allyl Grignard reagent were added 67 g (0.43 mole) of dichlorocyclotetramethylenesilane over a period of 2 hr. The mixture was then treated in the same manner as were the previous preparations, to give 56 g (79%) of diallylcyclotetramethylenesilane, bp 98–101°C (35 mm), n_D^{24} 1.4857, d_4^{24} 0.8825, MR_D 54.3 (calculated [7], 54.3). Gas-liquid chromatography indicated that the compound was pure. An infrared spectrum exhibited the following bands (cm^{-1}): 3050, 2930, 2850 (C–H); 1635 (CH_2=CH–); 1450, 1415, 1400, 1380, 1290, 990, 894 (CH and CH_2 deformations); and 1245, 855 (Si–R). Anal: Calculated for $C_{10}H_{18}Si$: C, 72.20; H, 10.90; Si, 16.88. Found: C, 69.80; H, 11.64; Si, 17.33.

Diallylcyclopentamethylenesilane. To a solution of 1.48 eq of allyl Grignard reagent were added 100 g (0.59 mole) of dichlorocyclopentamethylenesilane, over a period of 3 hr. The mixture was stirred for an additional 8 hr and was then treated in the same manner as was the previous preparation to give 72 g (68%) of diallylcyclopentamethylenesilane, bp 104°C (24 mm), n_D^{24} 1.4888, d_4^{24} 0.8779, MR_D 59.9 (calculated [7], 60.6). Gas-liquid chromatography indicated that the compound was pure. The infrared spectrum exhibited the following bands (cm^{-1}): 3080, 3030, 2900, 2850, 2800 (C–H); 1635 (CH_2=CH–); 1450, 1420, 1400, 1300,

990, 900 (CH and CH_2 deformations); and 915 (cyclopentamethylene silicon ring) [8]. Anal: Calculated for $C_{11}H_{20}Si$: C, 73.28; H, 11.18; Si, 15.54. Found: C, 72.07; H, 10.82; Si, 15.06.

Dimethallyldimethylsilane. To a suspension of methallyl Grignard reagent, prepared from 1.0 mole of methallyl chloride, were added 25 g (0.2 mole) of dimethyldichlorosilane over a period of 1 hr. After the mixture was stirred for 12 hr at room temperature, it was treated in the same manner as were the previous preparations to give 24 g (71.5%) of dimethallyldimethylsilane, bp 75–79°C (25 mm), n_D^{20} 1.4525 (reported [6] bp 71–71.6°C [22 mm], n_D^{20} 1.4538). Gas-liquid chromatography indicated that the compound was pure. The infrared spectrum exhibited the following bands (cm^{-1}): 3030, 2850, 2770 (C–H); 1640 (CH_2=CH–); 1450, 1440, 1370, 1276, 997, 870 (CH and CH_2 deformations); and 1247, 830 (–$Si(CH_3)_2$–).

Dimethallyldiphenylsilane. To a suspension of methallyl Grignard reagent, prepared from 1.0 mole of methallyl chloride, were added 63 g (0.25 mole) of dichlorodiphenylsilane over a period of 1 hr. The mixture was then treated in the same manner as were the previous preparations to give 41 g (55%) of dimethallyldiphenylsilane, bp 148°C (0.5 mm), n_D^{22} 1.5650 (reported [6] bp 193.8–194.1°C [14.5 mm], n_D^{20} 1.5693). The infrared spectrum exhibited the following bands (cm^{-1}): 3050, 2980, 2910, 2720 (C–H); 1960, 1880, 1800 (phenyl); 1635 (CH_2=CH–); 1450, 1370, 1300, 1280, 975, 875 (CH and CH_2 deformations); 1430, 1110 (Si–phenyl); and 1190 (Si–R).

Dimethallylmethylphenylsilane. To a suspension of methallyl Grignard reagent, prepared from 1.5 moles of methallyl chloride, were added 70 g (0.37 mole) of dichloromethylphenylsilane over a period of 1 hr. The mixture was then treated in the same manner as were the previous preparations to give 43 g (51%) of dimethallylmethylphenylsilane, bp 138°C (12 mm), n_D^{22} 1.5180 (reported [6] bp 142–143°C [20 mm], n_D^{20} 1.5221). The infrared spectrum exhibited the following bands (cm^{-1}): 3050, 2980, 2910, 2850, 2720, (C–H); 1960, 1880, 1800, (phenyl); 1635 (CH_2=CH–); 1450, 1400, 1370, 1305, 1280, 980, 875, (CH and CH_2 deformations); 1430, 1120 (Si–phenyl); and 1255, 835 (Si–R).

Dimethallylcyclopentamethylenesilane. To a suspension of methallyl Grignard reagent, prepared from 1.8 moles of methallyl chloride, were

added 32 g (0.45 mole) of dichlorocyclopentamethylenesilane over a period
of 1 hr. The mixture was treated in the same manner as were the previous
preparations, to give 58 g (59.5%) of dimethallylcyclopentamethylenesilane,
bp 95°C (2 mm), n_D^{24} 1.4907, d_4^{24} 0.8770, MR_D 68.8 (calculated [7],
68.9). Gas-liquid chromatography indicated that the compound was pure.
The infrared spectrum exhibited the following bands (cm^{-1}): 3100, 2970,
2900, 2800 (C–H); 1640 (CH$_2$=CH–); 1450, 1400, 1380, 1345, 1280,
993, 875 (CH and CH$_2$ deformations); 915 (cyclopentamethylene silicon
ring) [8]. Anal: Calculated for $C_{13}H_{24}Si$: C, 74.94; H, 11.61; Si, 13.45.
Found: C, 74.01; H, 11.36; Si, 13.77.

Allyldimethylvinylsilane. (a) To a solution of 1.8 eq of vinyl Grignard
reagent in tetrahydrofuran were added 134 g (1.0 mole) of allyldimethyl-
chlorosilane, dropwise over a period of 5 hr. The mixture was then treated
in the same manner as were the previous preparations to give 64 g (51%)
of allyldimethylvinylsilane, bp 111°C (760 mm), n_D^{22} 1.4315, d_4^{24} 0.7540,
MR_D 43.39 (calculated [7], 44.23). Gas-liquid chromatography indicated
that the compound was pure.

(b) To a solution of 1.0 eq of allyl Grignard reagent were added 130 g
(1.0 mole) of vinyldimethylethoxysilane over a period of 1 hr. The mix-
ture was then stirred at reflux temperature (40°C) for 48 hr. At the end
of this period no reaction had occurred. To the reaction flask 500 ml of
benzene were then added, and 500 ml of ether were removed by distilla-
tion. The mixture was stirred at 70°C for 24 hr. At the end of this period
a large amount of salt had formed in the flask. The mixture was then
treated in the same manner as were the previous preparations to yield 35 g
(28%) of allyldimethylvinylsilane, bp 111°C (760 mm). The refraction in-
dex and gas-liquid chromatography retention time for this compound were
the same as those for the product obtained in preparation (a). Both pro-
ducts also possessed identical infrared spectra. The spectrum exhibited the
following bands (cm^{-1}): 3080, 3000, 2950, (C–H); 1635, 1600
(CH$_2$=CH–); 1450, 1425, 1390, 1300, 1010, 990, 895 (CH and CH$_2$ de-
formations); and 1255, 850 (–Si(CH$_3$)$_2$–). Anal: Calculated for $C_7H_{14}Si$:
C, 66.57; H, 11.17; Si, 22.24. Found: C, 66.61, H, 10.95; Si, not
determined.

Polymerization of Monomers

General Procedures. *Ziegler catalyst polymerization.* Into a 50- or
100-ml reaction flask, equipped with a reflux condenser, mechanical stirrer,

gas addition tube, and rubber injection gasket, was injected a measured amount of dry heptane. The flask was swept with dry nitrogen. Measured amounts of triethylaluminum and titanium tetrachloride were then injected into the flask. The dark-brown catalyst suspension was heated and stirred for a definite period to age the catalyst. After this period the monomer was added and the mixture was allowed to react for various periods of time. At the end of the polymerization period the mixture was hydrolyzed by pouring it into methanol. The polymer was removed from the mixture by filtration, washed with a 10% hydrochloric acid solution, and dissolved in benzene. The solution was filtered to remove any insoluble polymer, and then the soluble polymer was reprecipitated by adding the solution to rapidly stirred methanol. The polymers were further purified by repeated reprecipitations from benzene solution. The solvent was then removed by storing the polymers in a vacuum desiccator.

Free radical polymerization. Into a 20-mm test tube, equipped with a reflux condenser, was placed a solution of the monomer and the free radical initiator (di-t-butyl peroxide). After thoroughly sweeping with dry nitrogen, the solution was heated by placing the tube in a bath maintained at 135°C by refluxing xylene. At the end of the polymerization period the heat was removed. The polymers were removed from the tube and purified in the same manner as were the polymers obtained with the Ziegler catalyst.

Specific Procedures. *Diallylmethylphenylsilane.* Polymerization of this monomer was accomplished by use of the Ziegler catalyst. The results are shown in Table 1. The infrared spectrum exhibited the following bands (cm^{-1}): 3000, 2950, 2875 (C–H); 1960, 1880, 1800 (phenyl); 1485, 1440, 1395 (CH_2 and CH_3 deformations); 1426, 1112 (Si–phenyl); and 1250, 830 (Si–CH_3). Anal: Calculated for $(C_{13}H_{18}Si)_n$: C, 77.15; H, 8.96; Si, 13.88. Found: C, 71.60; H, 8.72; Si, 13.79.

Diallylcyclotetramethylenesilane. This monomer was polymerized with the Ziegler catalyst. The results of the polymerizations are shown in Table 2. The infrared spectrum exhibited the following bands (cm^{-1}): 2950, 2900, 2830 (C–H); 1635 weak (CH_2=CH–); 1455, 1400 (CH_2 deformation); and 1250, 860 (Si–R). Anal: Calculated for $(C_{10}H_{18}Si)_n$: C, 72.20; H, 10.90; Si, 16.88. Found: C, 69.80; H, 11.64; Si, 17.41.

Diallylcyclopentamethylenesilane. Polymerization of this monomer was accomplished by use of the Ziegler catalyst to give white, solid polymers in addition to other lower-molecular-weight compounds. The results of these polymerizations are shown in Table 3. The infrared spectrum

Table 1. Polymerization of Diallylmethylphenylsilane[a]

Heptane, ml	AlEt₃, g	TiCl₄, g	Moles AlEt₃/moles TiCl₄	Monomer, g	Reaction time, hr	Polymer, g	Yield, %	Melting range, °C	Intrinsic viscosity
50	0.60	0.33	4.5	5.0	24	trace	–	–	–
50	0.68	0.40	3.7	10.0	24	0.4	4	90–110	0.12
50	0.60	0.33	4.5	10.0	48	1.0	10	95–120	–
50	0.60	0.33	4.5	10.0	24	0.4	4	–	–
50	0.60	0.33	4.5	10.0	24	0.6	6	90–115	0.07
50	0.60	0.30	4.9	9.0	48	0.5	56	87–95	–
25	0.60	0.33	4.5	10.0	48	2.6	26	98–112	0.09

[a]Polymerization performed at 85°C.

Table 2. Polymerization of Diallylcyclotetramethylenesilane [a]

Heptane, ml	AlEt$_3$, g	TiCl$_4$, g	Moles AlEt$_3$/moles TiCl$_4$	Monomer, g	Reaction time, hr	Polymer, g	Yield, %	Melting range, °C	Intrinsic viscosity
50	0.45	0.20	5.4	6.0	24	0.3	15	110–130	—
50	0.30	0.15	4.5	3.0	24	0.8	27	120–140	0.11
50	0.60	0.33	4.4	5.0	24	0.5	10	100–115	—
50	0.60	0.33	4.4	10.0	24	0	—	—	—
25	0.30	0.16	4.3	6.0	72	2.9	48	80–100	0.05

[a] Polymerizations performed at 85°C.

Table 3. Polymerization of Diallylcyclopentamethylenesilane [a]

Heptane, ml	AlEt$_3$, g	TiCl$_4$, g	Moles AlEt$_3$/moles TiCl$_4$	Monomer, g	Reaction time, hr	Polymer, g	Yield, %	Melting range, °C	Intrinsic viscosity
50	0.30	0.15	4.5	4.0	48	0.5	13	80–105	—
50	0.07	0.40	0.5	5.0	24	trace	—	—	—
50	0.60	0.30	4.8	6.0	24	0	—	—	—
50	0.60	0.50	4.8	10.0	24	0.7	7	95–108	0.04
25	0.60	0.38	4.4	4.0	48	3.0	75	95–110	0.04

[a] Polymerizations performed at 85°C.

exhibited the following bands (cm^{-1}): 3030, 2880, 2800 (C–H); 1635 weak (CH$_2$=CH–); 1460, 1450, 1400 (CH$_2$ deformations); and 915 (cyclo-pentamethylene silicon ring) [8]. Anal: Calculated for (C$_{11}$H$_{20}$Si)$_n$: C, 72.23; H, 11.18; Si, 15.54. Found: C, 69.07; H, 10.58; Si, 15.95.

Dimethallyldimethylsilane. Attempts to polymerize this monomer with the Ziegler catalyst give no polymer. Polymerization was accomplished with di-t-butyl peroxide as the initiator. The results of the polymerization are shown in Table 4. The infrared spectrum exhibited the following bands (cm^{-1}): 3100, 3030, 2960, 2850 (C–H); 1640 very weak (CH$_2$=CH–); 1460, 1425, 1380, 1280, 980 weak, 880 weak (CH$_2$ and CH$_3$ deforma-tions); 1255, 825 (–Si(CH$_3$)$_2$–). Anal: Calculated for (C$_{10}$H$_{20}$Si)$_n$: C, 71.34; H, 11.97; Si, 16.68. Found: C, 71.04; H, 11.31; Si, 16.75.

Dimethallyldiphenylsilane. Polymerization of this monomer was accom-plished with di-t-butyl peroxide as the initiator. The results are shown in Table 4. The infrared spectra of the polymers exhibited the following ab-sorption bands (cm^{-1}): 3100, 3000, 2920, (C–H); 1960, 1880, 1800 (phenyl); 1460, 1380, 1300 (CH$_2$ and CH$_3$ deformations); 1425, 1120 (Si–phenyl); 1190 (Si–R). Anal: Calculated for (C$_{20}$H$_{24}$Si)$_n$: C, 82.12; H, 8.27; Si, 9.60. Found: C, 80.88; Si, 8.72; Si, 9.43.

Dimethallylmethylphenylsilane. Polymerization of this monomer with di-t-butyl peroxide gave a white, benzene-soluble solid. The polymerization conditions and properties of the polymer obtained are listed in Table 4. The infrared spectrum exhibited the following absorption bands (cm^{-1}): 3100, 3000, 2920 (C–H); 1960, 1880, 1800 (phenyl); 1640 very weak (CH$_2$=CH–); 1450, 1375, 1300 (CH$_2$ and CH$_3$ deformations); 1425, 1120 (Si–phenyl); and 1200 (Si–R). Anal: Calculated for (C$_{15}$H$_{24}$Si)$_n$: C, 78.18; H, 9.62; Si, 12.18. Found: C, 76.31; H, 9.33; Si, 12.76.

Dimethallylcyclopentamethylenesilane. This monomer was polymerized with di-t-butyl peroxide. A white solid was obtained which was soluble in benzene. The results are shown in Table 4. The infrared spectrum ex-hibited the following bands (cm^{-1}): 3010, 2900, 2820 (C–H); 1640 very weak (CH$_2$=CH–); 1450, 1400, 1380, 1350, 1290 (CH$_2$ and CH$_3$ deforma-tions); and 915 (cyclopentamethylene silicon rings) [8]. Anal: Calculated for (C$_{13}$H$_{24}$Si)$_n$: C, 75.46; H, 10.74; Si, 13.60. Found: C, 73.68; H, 10.84; Si, 14.77.

Allyldimethylvinylsilane. Polymerization of this monomer was attempted with both Ziegler catalysts and free radical initiators. The Ziegler catalyst polymerization gave heavy, brown oils which would not solidify at -70°C. The infrared spectrum exhibited the following bands (cm^{-1}): 3080, 2900, 2850 (C–H); 1635 weak, 1595 (CH$_2$=CH–); 1450, 1380, 1350, 1010, 990,

Table 4. Polymerization of Dimethallylsilanes[a]

Monomer	Di-t-butyl peroxide, %	Reaction time, hr	Monomer, g	Polymer, g	Yield, %	Melting range, °C	Intrinsic viscosity
Dimethallyldimethylsilane	5	48	5.5	1.9	35	—	0.04
	2.5	48	4.0	1.5	38	—	—
	5	24	3.0	0.5	17	—	—
Dimethallyldiphenylsilane	5	48	4.0	3.0	75	110–125	0.026
	3.5	66	11.0	7.0	64	115–120	0.03
Dimethallylphenylmethylsilane	3	48	5.0	2.0	40	65–75	0.03
Dimethallylcyclopentamethylenesilane	4	48	5.0	2.3	50	75–90	0.04

[a] Polymerizations performed at 135°C.

950, 890 (CH, CH_2, and CH_3 deformations); and 1255, 850 $(-Si(CH_3)_2-)$.

Polymerization was also accomplished by use of di-t-butyl peroxide. Use of 2% by weight of the initiator yielded an oil similar to that obtained with the Ziegler catalyst, after 2 days. An insoluble solid was obtained after 4 days. The infrared spectra of these products were similar to those of the oils described above.

Benzoyl peroxide (5%) as initiator gave a heavy, brown oil after 1 week at 70°C. The infrared spectrum of this oil was similar to that of the Ziegler catalyst-initiated polymer except that the bands for the allyl double bond were much stronger. Attempted polymerization with 5% a,a'-azobisisobutyronitrile at 70°C for 1 week gave appreciably no polymer.

ACKNOWLEDGMENT

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