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The Formation of Linear Polymers from Diene Monomers by the Cyclopolymerization Mechanism. X. Polymers Containing Cyclohexamethylenesilyl and Cycloheptamethylenesilyl Ring Structures†

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SUMMARY

In an effort to determine the feasibility of formation of larger rings from dialkenyl silanes by the cyclopolymerization mechanism through use of Ziegler-type initiators, four new silane monomers were synthesized and their polymerization studied. Allyldimethyl-(3-butene-1)-silane (I) and allyl-diphenyl-(3-butene-1)-silane (III) are functionally capable of producing polymers containing a seven-membered ring. Dimethyl-bis-(3-butene-1)-silane (II) and diphenyl-bis-(3-butene-1)-silane (IV) are functionally capable of producing polymers containing an eight-membered ring. The diphenyl monomers gave benzene-soluble, solid polymers containing a low degree of residual unsaturation, interpreted as evidence that the predicted cyclization had occurred. The dimethyl derivatives, on the contrary, gave only viscous oils or semisolid products which could not be well characterized.

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†For previous paper in this series, see *J. Macromol. Sci.,* A3, 821 (1969).

INTRODUCTION

The high probability of formation of five- and six-membered rings in organic compounds is well known. An earlier study [1] of the tendency for formation of rings of various sizes by cyclopolymerization of 1,X-dienes has shown that this tendency essentially parallels that in monomeric structures. In view of the larger size of the silicon atom in comparison to carbon, and the known tendency of silicon to form eight-membered siloxane rings [2] rather than the preferred six-membered ring in the carbon compounds, we undertook a program to compare the relative tendencies of dialkenylsilanes toward formation of seven- and eight-membered rings. In a previous study [3], we have shown that diallylsilanes undergo cyclopolymerization to form polymers which possess no detectable unsaturation in the infrared spectrum, indicating that cyclization is essentially complete when the favorable six-membered ring is formed.

RESULTS AND DISCUSSION

The monomers for use in this study were prepared by Grignard reagent substitution reactions on the appropriate halosilanes. During the course of the snythetic work a new halosilane, allyldiphenylchlorosilane **(V)** was also synthesized. The monomers synthesized were allyldimethyl-(3-butene-1)-silane **(I)**, allyldiphenyl-(3-butene-1)-silane **(III)**, dimethyl-bis-(3-butene-1)-silane **(II)**, and diphenyl-bis-(3-butene-1)-silane **(IV)**. The physical properties and analyses for these compounds are reported in Table 1.

Polymerization experiments were conducted using heptane as solvent, and an initiator system consisting of aluminum triethyl and titanium tetrachloride. The results of the polymerization studies and analytical results on the polymers are reported in Table 2. As indicated previously, the dimethyl monomers gave only viscous oils or semisolid products which could not be fully characterized.

The diphenyl polymers were obtained only in low conversion, and some insoluble polymer was obtained, indicating that as the required ring size becomes less favorable cross-linking occurs. No cross-linking was observed in the diallyl monomers [3], which lead to six-membered rings. In addition, the polymers obtained in the present study also contained considerable unsaturation as determined from the NMR spectrum.

The more satisfactory results obtained on the diphenyl monomers in comparison to the dimethyl monomers can be accounted for, at least in

Table 1. New Silane Monomers Synthesized

		Boiling point				Analytical[a]						
						Calculated			Found			
Compound	Halosilane used	°C	Pressure, mm	n_D^{20}	d_4^{20}	%C	%H	%Si	%C	%H	%Si	% Yield
(I)	Allyldimethylchlorosilane	71-72	40	1.4436	0.7746	70.04	11.75	18.22	69.86	11.51	18.36	60.0
(II)	Dimethyldichlorosilane	90-90.5	40	1.4457	0.7843	71.34	11.97	16.69	71.47	12.24	16.79	44.0
(III)[b]	Allyldiphenylchlorosilane	141	0.8	1.5678	0.9897	81.95	7.96	10.09	81.47	8.18	10.13	61.6
(IV)[c]	Diphenyldichlorosilane	128	0.3	1.5618	0.9740	82.13	8.27	9.60	82.01	8.15	9.62	73.0
(V)[d]	Allyltrichlorosilane	113	0.45	1.5790	1.0976	69.63	5.80	10.86	69.30	5.95	11.04	43.3

[a] The structural assignments were also confirmed by the infrared spectra of the compounds.

[b] The NMR spectrum showed CH_2-Si/CH_2-vinyl/$CH_2=/CH=$ area ratios 1.00/1.78/2.18/1.09 (theory 1/2/2/1).

[c] The NMR spectrum showed CH_2-Si/CH_2-vinyl/$CH_2=/CH=$ area ratios 1.82/1.64/2.27/1.00 (theory 2/2/2/1).

[d] Cl: calculated: 13.70; found: 13.60.

Table 2. Properties of Soluble Polymers[a]

Polymer	% Conversion		Melting range, °C	Inherent viscosity[b]	Residual unsaturation[c], %	sp^2/sp^3 Hydrogens ratio[d]		Calculated			Found		
	Insoluble	Soluble				Monomer	Polymer	%C	%H	%Si	%C	%H	%Si
Poly **(III)**	0.17	0.36	80-93	0.04	7	1/1	1/14.2	81.95	7.96	10.08	81.37	8.32	9.86
Poly **(IV)**	4.3	5.3	90-102	0.09	13	1/1.3	1/6.6	82.12	8.27	9.60	81.17	8.60	9.84

[a] The infrared spectra of the polymers were similar to the spectra of the monomers, but showed greatly reduced unsaturation bands.

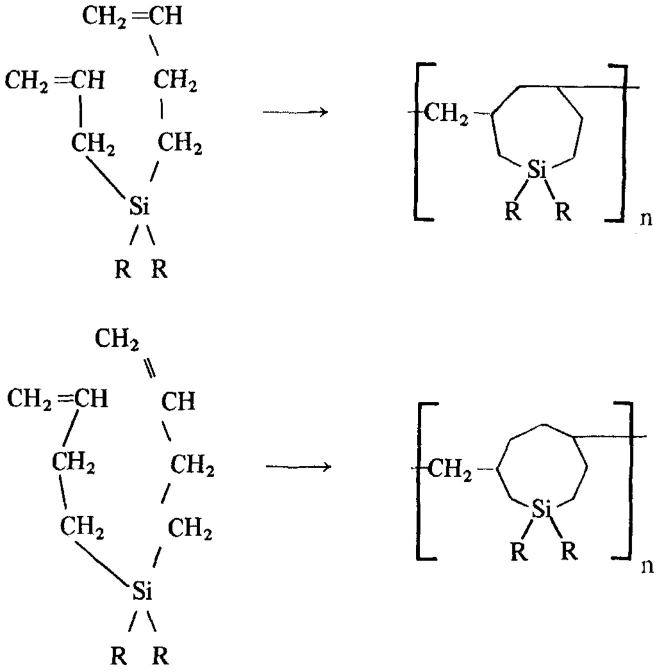
[b] At 25°C, 0.25% concentration in benzene. The intrinsic viscosity could not be determined because inverted plots were obtained.

[c,d] From the NMR spectral areas. The residual unsaturation was given by $sp^2/(sp^2 + sp^3)$; the phenyl hydrogens were neglected.

part, by the following: (1) the higher molecular weight per mer unit; (2) the increased steric acceleration due to the phenyl groups, which reduces the freedom of rotation of the alkenyl groups and forces them closer together; and (3) increased stabilization of the transition state in the anionic polymerization by the electron-withdrawing effect of the phenyl groups.

Table 2 shows that the seven-membered ring formed to a greater extent than the eight-membered ring, as indicated by the decrease in the sp^2/sp^3 hydrogen ratio from 1:1 in the monomer to 1:14.2 in the polymer. This ratio decreased only from the value of 1:1.3 in the monomer required to form the eight-membered ring to 1:6.6 in the corresponding polymer. Also, the ratio of cross-linked to soluble polymer was greater in the latter case, a result which is consistent with a lower tendency to cyclize during the propagation step. A much lower conversion in the case of the allyl-3-butene-1)-monomer can possibly be accounted for on the basis of the increased entropy factor in formation of the cyclic structure.

On the basis of the results obtained in this study, the conclusion may be drawn that the cyclic structures indicated below can be used to represent the major portion of the soluble polymers obtained, and that the major course of the propagation is by way of the cyclopolymerization mechanism:



R = methyl or phenyl

However, it may also be concluded that the tendency toward formation of seven- and eight-membered rings is less than that toward formation of six-membered rings, an observation which is consistent with previous findings.

EXPERIMENTAL

The silanes were synthesized using the same procedure outlined for triallylmethylsilane [4]. The halosilanes used in the Grignard substitution reactions are listed in Table 1. Allylmagnesium bromide or 3-butene-1-magnesium bromide were used as Grignard reagents. One halosilane (allyldiphenylchlorosilane) had not been previously reported. It was synthesized as follows:

Allyldiphenylchlorosilane

Into a 1-liter, three-necked flask, previously flamed out and flushed with nitrogen (a nitrogen static pressure was maintained throughout the preparation), and fitted with stirrer, reflux condenser, and addition funnel, were placed 44.0 g (0.25 mole) of allyltrichlorosilane and 70 ml of dry ether. The flask was cooled with an ice bath, and then 350 ml of 1.43 M ether solution (0.5 mole) of phenyl lithium [5] were added dropwise, with stirring, over a 2-hr period. Stirring at room temperature was continued for 30 min after the addition was completed; then the lithium bromide precipitated was filtered out and washed with ether. After removal of the solvent, one fractionation gave 28.0 g (43.3%) of allyldiphenylchlorosilane. Refractionation gave 19.5 g of pure product, with the physical constants listed in Table 1.

Polymerization

The same procedure was followed for all monomers. The optimum conditions had been previously determined through an extensive study of the polymerization of diallyldiphenylsilane. The following is a typical procedure:

Poly(diphenyl-bis-(3-butene-1)-silane). A 125-ml Erlenmeyer flask was flamed out and flushed with nitrogen, then sealed with a rubber injection gasket. The flask was introduced into a dry box (where the complete polymerization was carried out); then the following reagents were injected in the order given: dry heptane, 10 ml; aluminum triethyl, 2.7 ml of

1 M heptane solution; titanium tetrachloride, 1.4 ml of 0.5 M heptane solution; after shaking for 1 min, 10 g (0.034 mole) of diphenyl-bis-(3-butene-1)-silane. (Catalyst ratios: 10% molar on monomer, 4/1 $AlEt_3/TiCl_4$.) After occasional shaking for 2 days, the reaction mixture was poured, with stirring, into 100 ml of methanol, then left to stand in the cold. Filtration gave 0.96 g (9.6% conversion) of polymer. Addition of benzene dissolved 0.53 g; after three reprecipitations from methanol, 0.29 g of a white solid was obtained, whose physical properties are reported in Table 2.

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