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The Polymerization of Silacyclopentene and -pentane Derivatives

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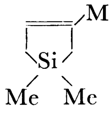
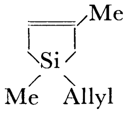
The polymerization of 1,1,3-trimethyl-1-silacyclopentene-3 (I), 1-methyl-, 1-allyl-1,1-diallyl-1-silacyclopentenes and -pentanes with aluminum chloride was carried out. By means of an IR spectroscopic analysis of the resulting polymers, it was established that not only ring opening but also vinyl polymerization due to the C–C double bond occur in this polymerization. Attempts to polymerize I with other catalysts, such as $BF_3 \cdot OEt_2$, AIBN, KOH, and a Ziegler catalyst, were unsuccessful.

Nametkin, Vdovin *et al.*[1] reported the aluminum chloride-catalyzed ring-opening polymerization of silaheterocylic compounds. We have been interested in studying the behavior of silacyclopentene derivatives toward aluminum chloride. Since 1,1,3-trimethyl-1-silacyclopentene-3 (I) contains an unsaturated bond in the ring, it is expected that I can be polymerized either at the C–C double bond or with the opening of the ring. The polymerization of I and its derivatives has been studied in order to obtain some information about the polymerizability of the silacyclo compounds.

Results and Discussion

The silacyclo compounds synthesized in the present work are 1,1,3-trimethyl-1-silacyclopentene-3 (I),[2] 1,3-dimethyl-1-allyl-1-silacyclopentene-3 (II),[3] 1,1-diallyl-3-methyl-1-silacyclopentene-3 (III),[3] 1-methyl-1-allyl-1-silacyclopentane (IV),[3] 1-methyl-1-allyl-2,5-diphenyl-1-silacyclopentane (V),[3] 1,1-diallyl-2,5-diphenyl-1-silacyclopentane (VI), and 1,1,3-trimethyl-1-silacyclopentane (VII).[3]


(I)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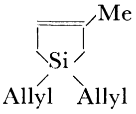
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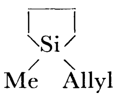
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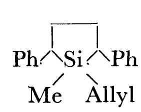
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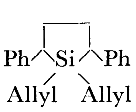
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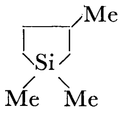
(VII)

These silacyclopentenes and -pentanes were polymerized in the presence of aluminum chloride under various conditions, and studies of the solubilities and IR absorption spectra were carried out with all the polymers obtained. The IR spectrum of VII (Fig. 1) shows three absorption bands, at 1020, 1030, and 1070 cm^{-1}, attributable to a silicon-containing five-membered ring,[4] whereas polymers obtained from VII exhibit an absorption band only at 1070 cm^{-1} in the above region. The disappearance of the absorption bands at 1020 and 1030 cm^{-1} may be taken as an indication of the occurrence of ring-opening polymerization. Consequently, we used these bands for detecting the presence of the five-membered ring in the polymerization products.

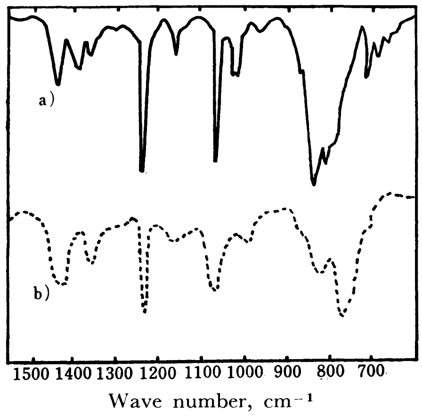

Fig. 1. IR spectra of 1,1,3-trimethyl-1-silacyclopentane (VII) and its polymer.
a) 1,1,3-Trimethyl-1-silacyclopentane (VII)
b) Polymer obtained from VII

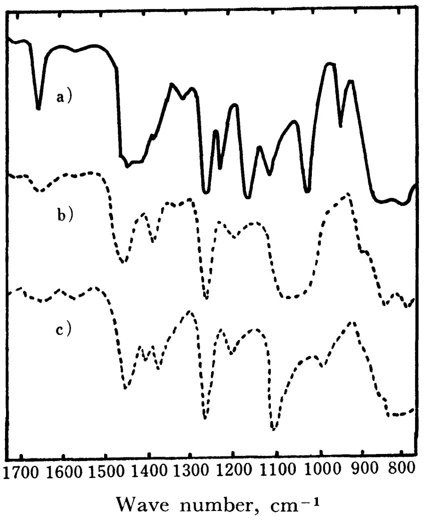

Fig. 2. IR spectra of 1,1,3-trimethyl-1-silacyclopententene-3 and its polymer.
a) 1,1,3-trimethyl-1-silacyclopentene-3 (I)
b) Polymer obtained from I by treating it with $AlCl_3$ at 21°C
c) Polymer obtained from I by treating it with $AlCl_3$ at 120°C

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[1] N. S. Nametkin, V. M. Vdovin, K. S. Pushchevaya, and V. I. Zav'yalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1453, (8) (1965).

[2] D. R. Weyenberg, L. H. Toporcer, and L. E. Nelson, *J. Org. Chem.*, **33**, 1975 (1968).

[3] These are new compounds.

[4] V. M. Vdovin, K. S. Pushchevaya, N. A. Belikova, and R. Syltanov, *Dokl. Akad. Nauk SSSR.*, **136**, 96 (1961).

The IR spectrum of the polymer prepared from I at 21°C showed somewhat weakened absorption bands at 1020 and 1030 cm^{-1}, while the polymer prepared at 120°C showed no absorption band in this region. (Fig. 2) A similar correlation was found between the temperature of polymerization and the intensity of the IR absorption band of the C–C double bond which appears in the 1600 cm^{-1} region in the spectrum. These observations indicate that I, upon treatment with aluminum chloride at a high temperature, polymerized at the C–C double bond as well as by ring opening. On the other hand, as is shown in Table 1, the yield of the polymer obtained from I increased with an increase in the concentration of aluminum chloride in I up to 20%, beyond which the yield decreased instead. Moreover, the addition of a small amount of water to aluminum chloride was found to have no influence on the yield of polymers (Table 2). Attempts to polymerize I with radical, cationic, and anionic catalyst, such as AIBN, $BF_3 \cdot OEt_2$, and KOH, were unsuccessful (Table 4). Therefore, it is conceivable that the aluminum chloride-catalyzed polymerization of I must be explained in terms of a mechanism which is not involved in ordinary vinyl polymerization.

A mechanism of the ring-opening polymerization of five-membered saturated silaheterocyclic compounds was proposed by Nametkin *et al.*[1] on the base of a metal halide-catalyzed disproportionation.[5] This concept of coordinative attack on the α-C of silacyclopentane may also be applied to the polymerization of the unsaturated silaheterocyclic compound. Further, no noticiable polymerization occurred when I and II were treated with a Ziegler cata-

TABLE 1. POLYMERIZATION OF 1,1,3-TRIMETHYL-1-SILACYOLOPENTENE-3 (I) WITH $AlCl_3$
EFFECT OF CATALYST CONCENTRATION

Exp. no.	Cat. concent. (mol%)	Solvent	Reaction Temp. (°C)	Reaction Time (hr)	Yield (%)	Appearance of polymer
1	2.7	CCl_4	15—20	24	0.2	slightly yellow solid
2	4.8	CCl_4	15—20	24	8.6	brown solid
3	13.4	CCl_4	15—20	24	39.0	brown solid
4	21.0	CCl_4	15—20	24	65.6	brown solid
5	31.0	CCl_4	15—20	24	57.1	brown solid
6	42.0	CCl_4	15—20	24	54.7	brown solid

TABLE 2. POLYMERIZATION OF I WITH $AlCl_3$
EFFECT OF A LITTLE AMOUNT OF WATER CONTAINED IN $AlCl_3$

Exp. no.	Mol% of water contained in $AlCl_3$	Concent. (mol%)	Solvent	Reaction Temp. (°C)	Reaction Time (hr)	Yield (%)	Appearance
7	18.4	15.7	CCl_4	27	24	33.5	brown solid
8	28.0	16.0	CCl_4	27	24	35.6	brown solid

TABLE 3. POLYMERIZATION OF I WITH $AlCl_3$
EFFECT OF REACTION TEMPERATURE

Exp. no.	Cat. concent. (mol %)	Solvent	Reaction Temp. (°C)	Reaction Time (hr)	Yield (%)	Appearance of polymer
9	22.0	—	−70	48	not detectable	
10	20.9	CCl_4	25—30	24	66.7	brown solid
11	22.3	—	122	21	54.2	dark brown solid

TABLE 4. POLYMERIZATION OF I WITH INITIATORS OTHER THAN $AlCl_3$

Exp. no.	Catalyst	Cat. concent. (mol %)	Reaction Temp. (°C)	Reaction Time (hr)	Yield
12	AIBN	10	100	5	not detectable
13	$BF_3 \cdot OEt_2$	2.3	21—28	48	not detectable
14	$BF_3 \cdot OEt_2$	10	100	5	not detectable
15	KOH	37	20	27	not detectable
16	KOH	30.8	122	37	not detectable

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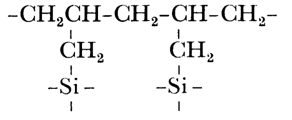
[5] G. A. Russel, *J. Amer. Chem. Soc.*, **81**, 4815 (1959).

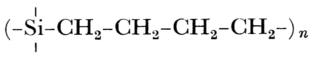
lyst at 60—85°C, although Murahashi *et al.* reported[6]) the successful polymerization of allyl derivatives of methylsilanes with a Ziegler catalyst (Table 5). This difficulty in the polymerization of silacyclopentene derivatives may be attributed to the inactivity of the double bond in the ring toward Ziegler polymerization and to that of the allylic double bond resulting from the steric hindrance of the bulky silacyclopentene ring.

In addition, in order to examine the polymerizability of the allylic double bond in silacyclopentane and -pentene derivatives, the polymerizations of II, III, IV, V, and VI were undertaken and the IR spectra of the polymers were obtained. The results of the experiment (Table 6) show that allyl derivatives of silacyclopentane (IV, V, VI) undergo polymerization faster than their methyl derivatives to give insoluble polymers; this shows that they are crosslinked. In Fig. 3 it can be seen that an absorption band of the allylic double bond which would appear at 1640 cm^{-1} is scarcely observable in the IR spectra of the resulting polymers. These facts lead to the conclusions that polymerization occurs by the allylic double bond as well as by ring opening, and that the polymers are crosslinked through allylic linkages (A) and also by linkages produced by ring opening (B):



$$-\mathrm{CH_2}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ -\mathrm{Si}-\\ |}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ -\mathrm{Si}-\\ |}}{\mathrm{CH}}-\mathrm{CH_2}-$$

(A)



$$(-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-)_n$$

(B)

Furthermore, II and III also undergo polymerization upon treatment with aluminum chloride, giving solid polymers even under such mild conditions where the analogous methyl derivative of silacyclopentene does not polymerize easily (Table 6). Moreover, a remarkable decrease in intensity of the absorption band at 1640 cm^{-1} was observed in the IR spectra of the resulting polymers. Since II and III contain two kinds of double bonds, allylic and endocyclic, the IR absorption bands of which appear in the same region, no decided conclusion about the predominance of allylic polymerization can be drawn from only these experimental data; yet, it may be considered from the foregoing discussion of the facility of the polymerization of allylic derivatives of silacyclopentane, that the allylic polymerization may also play an important role in the case of the polymerization of allyl derivatives of unsaturated silacyclic compounds.

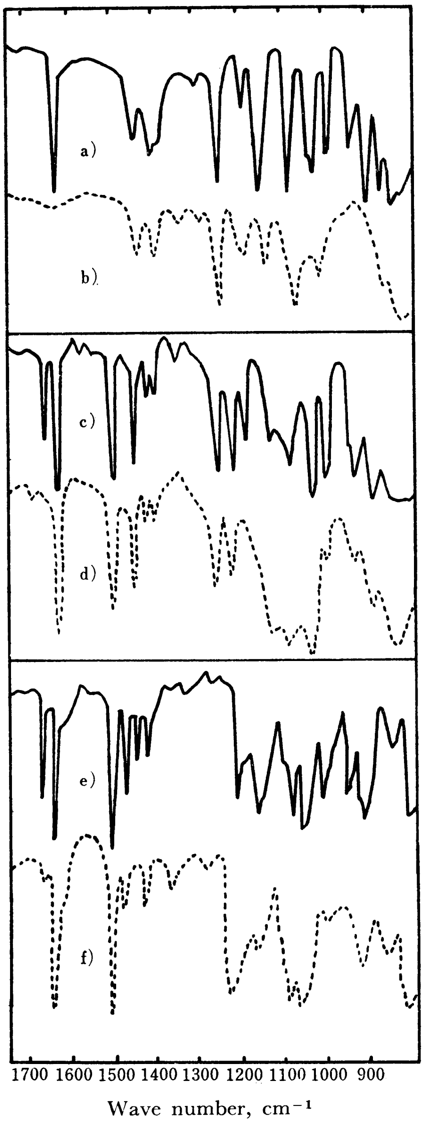


Fig. 3. IR spectra of allyl derivatives of silacyclopentane IV, V, VI, and their polymers.
a) 1-Methyl-1-allyl-1-silacyclopentane (IV)
b) Polymer obtained from IV by treating it with $AlCl_3$
c) 1-Methyl-1-allyl-2,5-diphenyl-1-silacyclopentane (V)
d) Polymer obtained from V by treating it with $AlCl_3$
e) 1,1-Diallyl-2,5-diphenyl-1-silacyclopentane (VI)
f) Polymer obtained from VI by treating it with $AlCl_3$

TABLE 5. POLYMERIZATION OF 1,1,3-TRIMETHYL- (I) AND 1,3-DIMETHYL-1-ALLYL (II)-SILACYCLOPENTENE WITH ZIEGLER CATALYST

Exp. no.	Monomer	Monomer used (mmol)	$AlEt_3$ (mmol)	$TiCl_4$ (mmol)	Solvent	Reaction		Yield
						Temp. (°C)	Time (hr)	
17	I	15.9	1.98	0.80	*n*-hexane	60	25	not detectable
18	II	20.0	1.40	0.40	*n*-heptane	85	48	not detectable

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[6]) S. Murahashi, S. Nozakura, and M. Sumi, This Bulletin, **32**, 670 (1959); *ibid.*, **33** 1760 (1960).

TABLE 6. POLYMERIZATION OF ALLYL DERIVATIVES OF SILACYCLOPENTENE II, III AND -PENTANE IV, V, VI WITH $AlCl_4$[a)]

Exp. no.	Monomer	Cat. concent. (mol%)	Reaction Temp. (°C)	Reaction Time (hr)	Appearance of polymer
19	II	5	70	7	brown solid
20	III	5	70	5	brown solid
21	IV	6	60	4	brown solid
22	V	18	170	20	slightly yellow solid
23	VI	16	room temp.	5	brown solid

a) Yields were not estimated.

TABLE 7. POLYMERIZATION OF 1,1,3-TRIMETHYL-1-SILACYCLOPENANE (VII) WITH $AlCl_3$

Exp. no.	Cat. concent. (mol%)	Solvent	Reaction Temp. (°C)	Reaction Time (hr)	Yield (%)	Appearance of polymer
24	17.2	CCl_4	21	24	61.3	dark brown solid
25	21.0	CCl_4	21	24	67.5	dark brown solid

TABLE 8. YIELD AND PHYSICAL PROPERTIES OF I—VII

Monomer	Yield (%)	Bp (°C/mmHg)	n (°C)	d (°C)	Si analysis Found (%)	Si analysis Calcd (%)
I	28.5	123	1.4462 (25)	0.8144 (25)	22.1	22.2
II	18.4	174	1.4684 (25)	0.8443 (25)	18.3	18.4
III	15.1	209	1.4880 (25)	0.8670 (25)	15.7	15.7
IV	54.0	155	1.4631 (18)	0.8260 (18)	20.4	20.1
V	25.2	152—3/0.1	1.5748 (30)	1.0160 (30)	9.5	9.6
VI	—	170—2/0.4	1.5762 (30)	—	8.6	8.8
VII	88.6	120—123	1.4345 (20)	—	21.9	22.0

Experimental

The infrared spectra were obtained on a Shimadzu IR 27 spectrophotometer.

Preparation of Monomers. Compounds I, II, III, V, and VI were synthesized by the method of Weyenberg *et al.*[2)] Olefins, such as isoprene and styrene, were treated with diorganodichlorosilane $R_1R_2SiCl_2$ (R_1=Me, Allyl; R_2= Me, Allyl) in tetrahydrofuran in the presence of sodium dispersion under a nitrogen atmosphere. After stirring for 20—25 hr at room temperature, filtration and distillation gave I in a 28.5% yield from isoprene and dimethyldichlorosilane, II in a 18.4% yield from isoprene and methylallyldichlorosilane, III in a 15.1% yield from isoprene and diallyldichlorosilane, V in a 25.2% yield from styrene and methylallyldichlorosilane, and VI from styrene and diallyldichlorosilane. IV was synthesized from 1-chloro-1-methyl-1-silacyclopentane, which had itself been synthesized from methyltrichlorosilane and the di-Grignard reagent of 1,4-dibromobutane, by treating it with allylmagnesium bromide in Et_2O. VII was prepared from I by hydrogenating it with hydrogen gas using a Pt–C catalyst in dry *n*-hexane. The yields and physical properties of the above monomers are summarized in Table 8.

Purification of Aluminum Chloride. The $AlCl_3$ catalyst used in this polymerization was obtained from commercial $AlCl_3$ by subliming it and sealing into a glass ampoule.

Polymerization of I and VII with $AlCl_3$. Polymerization was carried out in a three-necked flask equipped with a mechanical stirrer under a nitrogen atmosphere. A monomer and an ampoule containing a given amount of $AlCl_3$ were placed in the flask. Polymerization was started by breaking the ampoule and mixing the ampoule content-$AlCl_3$ with the monomer. After stirring for 4—48 hr at various temperature, polymerization was stopped by the addition of methanol. Dissolving the product in cyclohexane, followed by reprecipitation from a cyclohexane solution, gave a soluble polymer, while an insoluble polymer was obtained from the cyclohexane-insoluble part by washing it with methanol, chloroform, and with dilute alkali.

Polymerization of I and II with a Ziegler catalyst. The triethylaluminum used in this experiment was a product of the Mitsui Toatsu Kagaku Co. *n*-Hexane and *n*-heptane were purified by shaking them with concentrated sulfuric acid, washing them with water and aqueous sodium hydroxide and, after drying over sodium wire, redistilling them under a nitrogen atmosphere just before use. A solution of $AlEt_3$ in *n*-hexane or in *n*-heptane was slowly added, using an injector, to a solution of $TiCl_4$ contained in a flask. A monomer was then added, and polymerization was allowed to proceed for a given period of time. Polymerization was stopped by adding acidic methanol (10 vol. Methanol+1 vol. conc. HCl) to the reaction mixture in the flask. The isolation of the polymer was attempted by pouring the reaction product into a large amount of methanol.

Polymerization of II, III, IV, V, and VI with $AlCl_3$. In a three-necked flask equipped with a mechanical stirrer, aluminum chloride which had been sublimed just before use was placed, a monomer was then stirred into the aluminum chloride under a nitrogen atmosphere. After the reaction flask had been kept at the polymerization temperature for a given period of time, the resulting product was purified by reprecipitation from a cyclohexane solution into methanol, in just the same manner as has been described before.

Polymerization of I with other than $AlCl_3$. Polymerization was carried out in the same manner as in the case of the polymerization of I and VII with $AlCl_3$ except for the use of catalysts other than $AlCl_3$.

The authors are indebted to Dr. H. Nohira for his valuable discussions, to the Shinetsu Kagaku Co. for providing the dimethyldichlorosilan, and to the Mitsui Toatsu Kagaku Co. for supplying the triethylaluminum.