Stereoregular Polymers. II. Polymerization of Alkenyltrimethylsilanes with Ziegler Catalyst[*]

By Shunsuke MURAHASHI, Shun'ichi NOZAKURA and Masao SUMI

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Isotactic polymers of normal α-olefins have been known to have a maximum melting point at polypropylene (165°C), a minimum value at polyhexene-1 (−55°C), and after that show a gradual increase of melting points with the higher members[1,2]. On the other hand, isotactic polymers of branched α-olefins, which are shown in Table I by the general formulae II and III, have considerably higher melting points than those of the corresponding polymers of normal olefins.

The present study was undertaken to see if (i) the polymerization of alkenyltrimethylsilanes with Ziegler catalyst could lead to crystalline polymers and (ii) the similar melting behaviors could be expected in the case of polyalkenyltrimethylsilane having the same structure of monomer as type III of branched olefins.

A survey of the literature of the subject reveals that the polymers of alkenyltrimethylsilanes hitherto obtained are all liquid polymers of low molecular weight. Kanazashi[3] studied the polymerization of vinyltrimethylsilane with peroxide catalysts at 120°C and with Friedel-Crafts catalysts at 150°C, and obtained oily polymer in the former case and no polymer in the latter case. Polymerization of allyltrimethylsilane was attempted by Sommer[4] with Friedel-Crafts catalysts and also by Petrov[5] and Polyakova[6] at 130°C under a high pressure in the presence of peroxide catalysts. However, in both the cases the product was viscous liquid polymers. Polymerization of 3-butenyltrimethylsilane was also carried out by the latter author[6] to yield only a viscous liquid.

The present authors have prepared three alkenyltrimethylsilanes of the general formula $CH_2=CH(CH_2)_nSi(CH_3)_3 (n=0, 1$ and $2)$, i. e., vinyl-, allyl-, and 3-butenyltrimethylsilane, and subjected them to polymerization by means of Ziegler catalyst. It was found from the experiments that the alkenyltrimethylsilanes could polymerize to high polymeric products having high melting points and, furthermore, the polymers were proved to be highly crystalline by X-ray investigation[**].

Polymerization. — Polymerization was carried out in n-heptane in the presence of Ziegler catalyst, that is, triethylaluminum and titanium tetrachloride. Considering the question from the results of the preceding paper[7], a method which had given a good yield of isotactic polystyrene was adopted in the present study;

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[*] Presented at the 11th Meeting of Chem. Soc. of Japan in Tokyo, April 4, 1958. A brief description of this work was published in *Annual Report of the Institute of Fiber Research (Japan)* (*Sen'ikagaku Kenkyusho Nenpo*), **11**, 23 (1958).

1) F. P. Reding, *J. Polymer Sci.*, **21**, 547 (1956).

2) G. Natta, *Angew. Chem.*, **68**, 393 (1956).

3) M. Kanazashi, This Bulletin, **28**, 44 (1955).

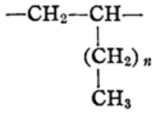
4) L. H. Sommer, L. J. Tyler, F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948).

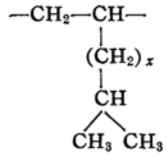
5) A. D. Petrov et al., *Doklady Akad. Nauk S. S. S. R.*, **99**, 785 (1954).

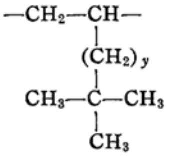
6) A. M. Polyakova, et al., *Izvest. Akad. Nauk S. S. S. R., Otdel Khim. Nauk*, **1956**, 978.

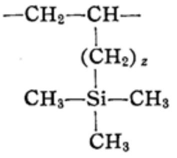
[**] Quite recently Natta and his collaborators have presented a letter and we have learned that they succeeded to prepare the crystalline polymers of allylsilane and of allyltrimethylsilane. G. Natta et al., *J. Polymer Sci.*, **31**, 181 (1958).

TABLE I. MELTING POINTS OF ISOTACTIC POLY-α-OLEFINS


(I)


(II)


(III)


(IV)

n	m. p., °C	x	m. p., °C	y	m. p., °C	z	m. p., °C
0	165, 165*	0	245, 300*			0	340
1	128, 120*	1	205, 235*	1	320	1	258
2	80, 70*	2	130			2	206
3	−55*						
4	−40*						
5	−38*						
9	45*						
15	70*						

The values with asterisks are reported by Reding1) and the others except the type IV are reported by Natta2). The values of type IV are presented by the present authors.

TABLE II. POLYMERIZATION OF ALKENYLTRIMETHYLSILANES WITH ZIEGLER CATALYSTS AT 70°C$^{a)}$

$AlEt_3$, g.	$TiCl_4$, g.	Monomer	Wt., g.	Polymn. time, hr.	Conversion, %
0.66	0.47	Vinyltrimethylsilane	2.77	5.5	2.4
0.44	0.27	Allyltrimethylsilane	5.54	9.0	30.2
0.34	0.23	3-Butenyltrimethylsilane	2.76	6.0	44.6

a) Twenty ml. of n-heptane were used as a solvent in each run.

TABLE III. SEPARATION OF CRYSTALLINE POLYMERS FROM CRUDE POLYMERS

Polymer	Extracting solvent	Fraction, %	Analysis of fractions					
			C, %		H, %		Si, %	
			Found	Calcd.	Found	Calcd.	Found	Calcd.
Polyvinyl-trimethylsilane	Hot toluene	Extract, 44	80.26	$85.6^{a)}$	12.49	$14.4^{a)}$		
		Residue, 55	58.94	59.91	11.83	12.07	29	28.02
Polyallyl-trimethylsilane	Toluene	Extract, 23	64.89	63.14	12.70	12.69	23.03	24.59
		Residue, 72	63.70		12.43		24.19	
Poly-3-butenyltri-methylsilane	Hot ether	Extract, 26	65.93	65.57	12.48	12.49	21.20	21.90
		Residue, 70	65.90		12.66		21.47	

a) Calcd. for $(C_2H_4)_n$, polyethylene.

that is, the catalysts were prepared without stirring and polymerizations were carried out also without stirring.

The conversions of both allyl- and 3-butenyltrimethylsilane were moderately high, but the conversion of vinyltrimethylsilane was very low (Table II).

Separation of Crystalline Polymers.— In the polymerizate of vinylmethylsilane, the existence of polyethylene was recognized from the analytical data and X-ray diffraction pattern. The separation of the polyethylene was effected by extraction with hot toluene. The occurrence of the polyethylene is considered to be due to the polymerization of ethylene which evolved during the preparition of the heterogeneous catalyst7). Polyvinyltrimethylsilane is insoluble in most organic solvents.

The amorphous polymer in the polymerizate of allyltrimethylsilane could be separated from the crystalline part by extraction with toluene. It was found that the crystalline part is soluble only in hot high-boiling solvents such as α-methylnaphthalene and dioctylphthalate.

In the case of 3-butenyltrimethylsilane, the separation of amorphous polymer was effected by hot extraction with ether, and also the extraction with cold n-heptane was found to be effective, wherein the

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7) S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, This Bulletin, in press.

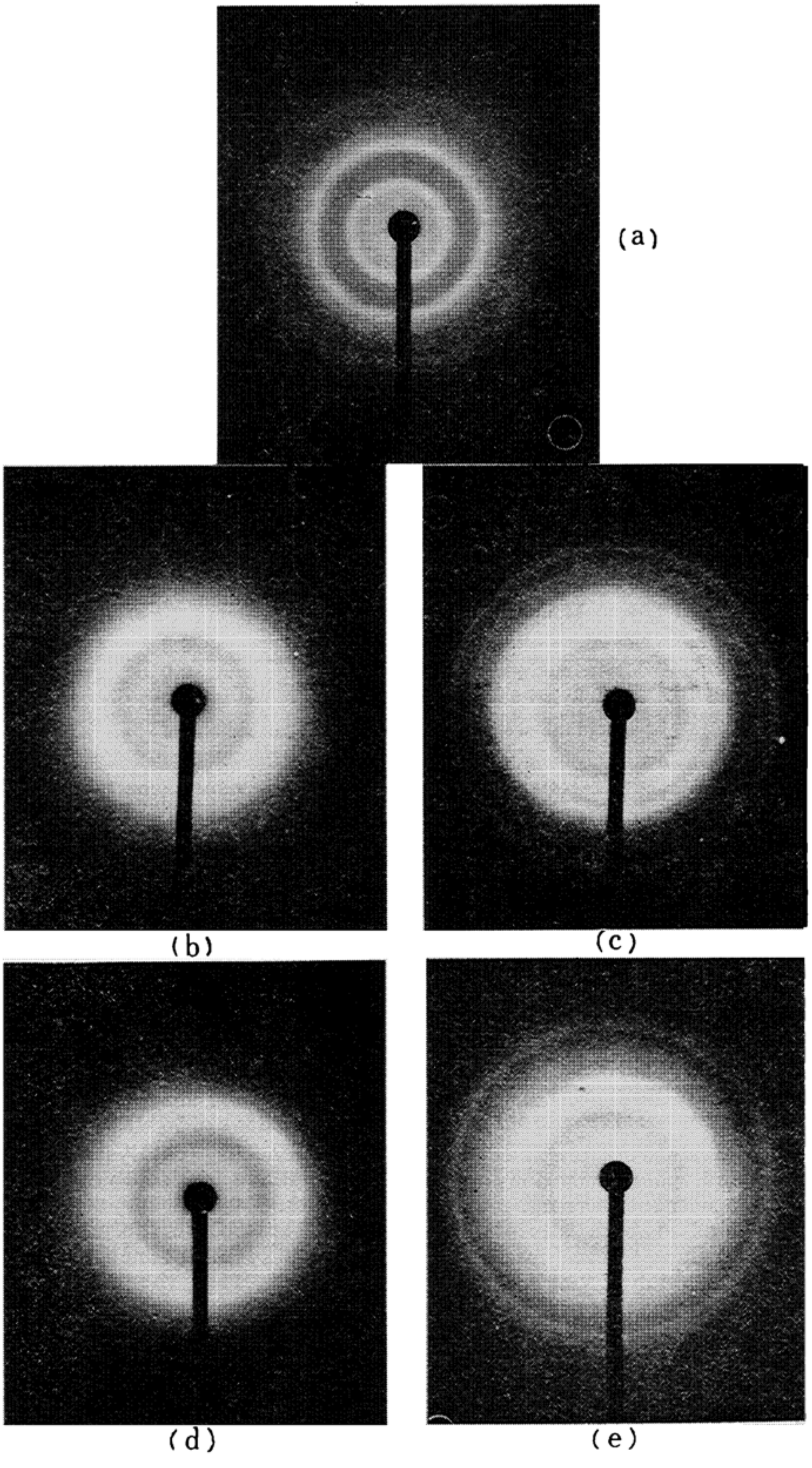

Fig. 1. X-ray diffraction patterns of polyalkenylsilanes.

(a) Polyvinyltrimethylsilane, the insoluble part in hot toluene.
(b) Polyallyltrimethylsilane, the soluble part in toluene.
(c) Polyallyltrimethylsilane, the insoluble part in toluene.
(d) Poly-3-butenyltrimethylsilane, the soluble part in hot ether.
(e) Poly-3-butenyltrimethylsilane, the insoluble part in hot ether.

TABLE IV. SOME PROPERTIES OF POLYALKENYLTRIMETHYLSILANES

Polymer		m. p., °C	*Tg*, °C	Density[a]	Appearance
Polyvinyltrimethylsilane		340[b]	—	0.95	White powder
Polyallyltrimethylsilane	amorph.	—	114	—	Soft solid
	cryst.	258	—	0.895	Hard and brittle
Poly-3-butenyltrimethylsilane	amorph.	—	132	—	Soft solid
	cryst.	206	—	0.889	Hard and brittle

a) Measured at room temperature by flotation method.

b) Upon being heated on a free flame in a nitrogen atmosphere the polymer decomposed to a volatile liquid.

crystalline part was insoluble. It was found to be soluble in decalin and hot tetralin. The experimental results of extraction and the analytical data of both the amorphous and crystalline fractions were summarized in Table III.

Physical Properties.—The X-ray photograph of the extraction residue of polyvinyltrimethylsilane showed a sharp Debye reflection, indicating the highly crystalline nature of the polymer. The photographs of the fractions of polyvinyl-, polyallyl-, and poly-3-butenyltrimethylsilane were presented in Fig. 1. In all the cases the residual part of solvent extraction showed marked crystalline patterns, while the extracts showed only minor extents of crystallinity. From the crystalline part of poly-3-butenyltrimethylsilane an extruded filament was obtained, which could be drawn at 100°C to several times of its original length, and gave a fine X-ray fiber diagram. From the analysis of the fiber diagram, a helical structure containing three monomeric units per identity period was established as follows***.

$$\text{Rhombic} \left[\begin{array}{l} a=10.97\ \text{Å} \\ b=20.02\ \text{Å} \\ c=6.46\ \text{Å (fiber axis)} \end{array} \right.$$

No. of monomeric unit in unit cell = 6

ρ (X-ray) = 0.902 g./cm^3

ρ (obsd.) = 0.889 g./cm^3

The crystalline polymers of other monomers than 3-butenyltrimethylsilane considered to be isotactic by analogy to the case of poly-3-butenyltrimethylsilane, but their fiber diagrams could not be obtained because of the difficulty of drawing.

Melting points and glass transition temperatures were determined dilatometrically on the amorphous as well as the crystalline parts of the polymers. The results and other properties are shown together in Table IV. As was expected, the melting points of the crystalline parts are very high in all cases and the polymer with the larger branch has the lower melting points. Particularly, the first member of this series, polyvinyltrimethylsilane has an extremely high melting point and was completely insoluble in all organic solvents examined.

Experimental

Monomers. — Vinyltrimethylsilane was synthesized through two different ways. One is the methylation of vinyltrichlorosilane by methylmagnesium bromide[8]. Refluxing the ethereal reaction mixture for 6 hr. gave 58% of the product, b. p. 55.0∼55.2°C. The other way is the Wurtz-Wittig's reaction between trimethylchlorosilane and vinylchloride[9]. The yield was 55.6% based on trimethylchlorosilane used, b. p. 55.0∼55.2°C.

Allyltrimethylsilane was also synthesized through two alternating methods. One is the methylation of allyltrichlorosilane**** by methylmagnesium bromide[10] and the other is the reaction of allylmagnesium bromide on trimethylchlorosilane[5]. The former yielded 53% of allyltrimethylsilane calculated from allyltrichlorosilane used and the latter yielded only 19.3% of the product after refluxing the ethereal solution for 8.5 hr.

3-Butenyltrimethylsilane was synthesized according to Petrov's method: that is the reaction between allylbromide and trimethylsilylmethylmagnesium chloride[5]. After refluxing the ether solution for 5 hr., 35.2% of the product was obtained, b. p. 118.5∼111.7°C.

Materials.—Triethylaluminum was the product of Mitsui Chem. Ind. Co. Thirty percent solution in *n*-heptane was prepared in a modified Schlenk's apparatus and separated in small portions into sealed ampoules.

*** Details of the structural annalysis of the polymer will be published elsewhere by Mr. Y. Chatani of Nitta's laboratory. We are very grateful to him for the X-ray data.

8) R. Nagel and H. W. Post, *J. Org. Chem.*, **17**, 1379 (1952).

9) M. Kanazashi, This Bulletin, **26**, 493 (1953).

**** Allyltrichlorosilane was kindly offered by Dr. R. Okawara at Faculty of Engineering, Osaka University.

10) C. A. Burkhard, *J. Am. Chem. Soc.*, **72**, 1078 (1950).

Titanium tetrachloride was the product of Osaka Titanium Co. and 21% solution in *n*-heptane was used.

n-Heptane was purified by shaking with fuming sulfuric acid, washing with water and aqueous sodium hydroxide, and was dried over calcium chloride, distilled and stored over sodium chips.

Polymerization. — Polymerization was carried out in the same apparatus as in the preceding paper[7]. The solution of $AlEt_3$ was added first to *n*-heptane and mixed thoroughly, and the solution of $TiCl_4$ was dropped slowy along the wall of the vessel without stirring. The solid brown mass was observed to form at the bottom of the flask. Finally the monomer was added and the polymerization was carried out without stirring.

Polymerization was stopped by adding 2 ml. of methanol and 0.3 ml. of concentrated hydrochroric acid, and the reaction mixture was poured onto about 100 ml. of methanol. After being kept overnight, the polymer was collected and washed thoroughly with methanol. The results of polymerization were given in Table II.

Separation of Crystalline Polymers from Crude Products. — When the crude polyvinyltrimethylsilane was extracted with hot toluene, a precipitate was obtained from the cooled extract. The precipitate was ascertained to be polyethylene from the analytical data and X-ray powder pattern. The insoluble part was nearly pure polyvinyltrimethylsilane.

Crude polyallyltrimethylsilane was refluxed gently with a large volume of toluene for several hours. After being cooled, the insoluble part was separated from the solution by a centrifuge. The intrinsic viscosity of the amorphous part in toluene was 0.087 at 30°C.

In the case of poly-3-butenyltrimethylsilane, the separation was effected by hot extraction with ether using a modified Soxhlet apparatus. The separation could also be done by cooling the hot solution of the crude polymer in *n*-heptane; only the crystalline polymer was precipitated when being cooled, while the amorphous polymer still remained in solution. Intrinsic viscosities of the amorphous and the crystalline part in decalin were 0.169 and 1.21 at 30°C, respectively.

Analysis of Silicon. — Analysis of silicon in the polymers was carried out by wet digestion using fuming sulfuric acid in a platinum crucible. The ignited silica was ascertained by treating with 60% hydrofluoric acid.

Properties. — Melting points and glass transition temperatures were determined dilatometrically. The polymer was melted in vacuum to form a small rod prior to measurement.

Density was measured by the flotation method at room temperature using the mixtures of carbon tetrachloride and alcohol.

Summary

Vinyl-(I), allyl-(II), and 3-butenyl-trimethylsilane(III) were polymerized at 70°C in *n*-heptane with the heterogeneous catalyst of Ziegler's type. The monomer I gave only a small yield of polymer, while the monomers II and III gave moderate amounts of polymers.

The amorphous and crystalline polymers of these monomers were separated by extraction with appropriate solvents. As regards the crystalline polymers, solubility property, density, dilatometrical melting point, and X-ray spectra were described. Glass transition temperatures of the amorphous polymers are also determined.

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Department of Chemistry
Faculty of Science
Osaka University
Kita-ku, Osaka