

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Preparation and Properties of Polyallenes. I. Polymerization of Allene by Ziegler-Type Catalysts

R. Havinga^a; A. Schors^a

^a Centraal Laboratorium TNO Delft, The Netherlands

To cite this Article Havinga, R. and Schors, A.(1968) 'Preparation and Properties of Polyallenes. I. Polymerization of Allene by Ziegler-Type Catalysts', *Journal of Macromolecular Science, Part A*, 2: 1, 1 – 20

To link to this Article: DOI: 10.1080/00222336808053343

URL: <http://dx.doi.org/10.1080/00222336808053343>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Preparation and Properties of Polyallenes. I. Polymerization of Allene by Ziegler-Type Catalysts

R. HAVINGA and A. SCHORS

*Centraal Laboratorium TNO
Delft, The Netherlands*

Summary

The polymerization of allene induced by organoaluminum-vanadium oxytrichloride catalysts has been investigated in aliphatic hydrocarbons and at normal pressure. For the catalysts investigated, the polymerization activity decreases at decreasing order of alkylation of the aluminum alkyl: $\text{AlR}_3 > \text{AlR}_2\text{X} > \text{AlRX}_2$ (R is Et or *i*-Bu; X is halogen). Compared with other aluminum trialkyls, trimethylaluminum shows a low activity. For the Al-*i*-Bu₃-VOCl₃ system, the effects of catalyst ratio, reaction time, and temperature have been studied.

The polyallenes obtained are generally highly crystalline and melt between 115 and 125°C.

The structure of the polymers was investigated by means of an NMR-infrared analysis.

The activity of the initiating systems has been related to reactions taking place between the catalyst components. It is concluded that active catalysts are formed under conditions that favor the formation of vanadium (II or III)-aluminum complexes of a relatively low solubility and stability. A polymerization mechanism is proposed in which the propagation starts with a coordination of the monomer with a vanadium center. In the next step the monomer is inserted into the vanadium-carbon bond of the growing polymer chain. It is assumed that the chain grows at the central carbon atom of the monomer unit. Vinyl and internal double bonds may have been formed as a result of isomerization of the chain end by a proton shift.

In the years between 1961 and 1964 the polymerization of allenes has been studied in this laboratory, using radical, conventional ionic, and complex metal catalysts. Radical-induced polymerization of

allene in solution (initiator dibenzoyl peroxide) and in emulsion (potassium persulfate, 50°C; redox-system cumene hydro-peroxide-ferrous pyrophosphate, 0–10°C) did not yield reaction. Solid linear polymers of allene and of some of its homologues were obtained when Ziegler catalysts were applied [1]. Some cationic catalysts gave rise to more or less cross-linked polymers.

Until then, the only authentic high molecular weight polyallene had been reported by Baker [2, 7]. The polymer was obtained by polymerization of allene using triisobutylaluminum-transition metal salt combinations as catalysts, and could be obtained in an amorphous as well as a crystalline form. Its structure appeared to be composed of blocks of vinylidene-, vinyl-, and cis-olefin structures. Recently, a polyallene of a more regular structure, composed predominantly of vinylidene units, was reported by Otsuka et al. [3] and Griesbaum [4]. This polymer was obtained from allene using π -complexes of nickel as catalysts.

Our results on the polymerization of allene induced by Ziegler-type catalysts are presented in this paper. A second paper describes in some detail the dependence of the physical state of this polyallene on the polymerization conditions and after-treatments [1, 5], while a third paper will deal with the polymerization of some homologues of allene with Ziegler-type catalysts [1, 6].

POLYMERIZATION OF ALLENE BY ZIEGLER-TYPE CATALYSTS

Introductory experiments showed that high polymerization activity was especially obtained with Ziegler catalysts containing vanadium. Therefore, the systematic investigation reported here has been performed with catalysts based on vanadium oxytrichloride and aluminum alkyls. In this investigation were studied the effect of various aluminum alkyls, of catalyst ratio, of temperature, of time of polymerization, and of the presence of small quantities of propyne on the polymerization and the properties and structure of the polymers. All experiments were carried out at normal pressure under nitrogen. Because of a possible influence of small amounts of impurities on the polymerization, by preference only experiments have been compared that were performed with reagents of the same supply.

EFFECT OF SOME PARAMETERS ON THE POLYMERIZATION ACTIVITY

Unless stated otherwise, all polymerization experiments were carried out according to the following scheme. Into the flask containing the solvent, gaseous allene was added with vigorous shaking of the flask until the desired quantity of monomer was dissolved.

Subsequently, vanadium oxytrichloride and aluminum alkyl were added successively, as molar solutions in the solvent used, giving rise in the majority of cases to the development of a violet to dark brown turbidity. For the duration of the experiment, allene was passed over at the rate of approximately 100 ml/min. The polymerization started at once, and generally the polymer separated as a gel. In some experiments, however, the polymer appeared as a fine powder or as fibers. The reaction proceeded under the evolution of heat. Isopropanol was added to the reaction mixture to decompose the catalyst. The white polymer was collected on a filter, pulverized in methanol in a Braun household mixer, again collected on a filter, washed with methanol, and dried in vacuo over phosphorous pentoxide. It was stored under nitrogen in ampoules.

Organoaluminum Compound

The influence of the organoaluminum compound on the yield of polyallene was investigated in a series of experiments. The time of polymerization was 15 min. In Table 1 the varying reaction conditions and the results are given.

TABLE 1. Influence of the Aluminum Compound on the Conversion of Allene (10 g of allene (250 mmoles) dissolved in 300 ml of cyclohexane, 0.4 mmole VOCl_3 , varying quantities of aluminum alkyl, allene introduced for 15 min, room temp.)

Al compound ^a	Al/V, molar	Color developed	Polyallene, g	Monomer converted, moles/mole VOCl_3
Al-i-Bu ₃	9	Violet → brown	4.2	263
AlEt ₃	9	Violet → brown	2.2	138
AlHex ₃	9	Violet → brown	3.6	215
AlMe ₃	9	Red → brown	0.21	13
Al-i-Bu ₂ Cl	9	Violet → brown	0.20	13
Al-i-Bu ₂ Br	13	Violet → brown	1.1	69
AlEt ₂ Br	9	Violet → brown	0.39	24
AlEt ₂ Br	13	Violet → brown	0.37	23
Al-i-BuBr ₂	9	Yellow → brown	0	0
Al-i-BuBr ₂	26	Yellow → brown	0	0
AlEtBr ₂	9	Yellow → brown	0	0
AlEtBr ₂	27	Orange → brown	0	0
AlMeBr ₂	9	Red → brownish	0	0
AlMeBr ₂	26	Red → brownish	0	0

^aEt, ethyl; Hex, hexyl; i-Bu, isobutyl; Me, methyl.

As will be seen from this table, the organoaluminum compound has a distinct influence on the activity of the catalyst. With the exception of trimethylaluminum, the highest alkylated compounds have the highest activity, then follow the dialkylaluminum monohalogenides, whereas monoalkylaluminum dihalogenides are inactive: $\text{AlR}_3 > \text{AlR}_2\text{X} > \text{AlRX}_2$ ($\text{X} = \text{Cl}, \text{Br}$). Of the aluminum-trialkyls, triisobutylaluminum seems to have the highest activity. In the following experiments, triisobutylaluminum–vanadium oxytrichloride was used as a catalyst combination.

$\text{AlR}_3/\text{VOCl}_3$ Ratio

Keeping the concentration of the vanadium compound constant, the ratio of the catalyst components was varied. There is a distinct increase in activity with increasing Al/V ratio up to Al/V = 2–3, but after that the yield of polymer is practically independent of this ratio (Fig. 1).

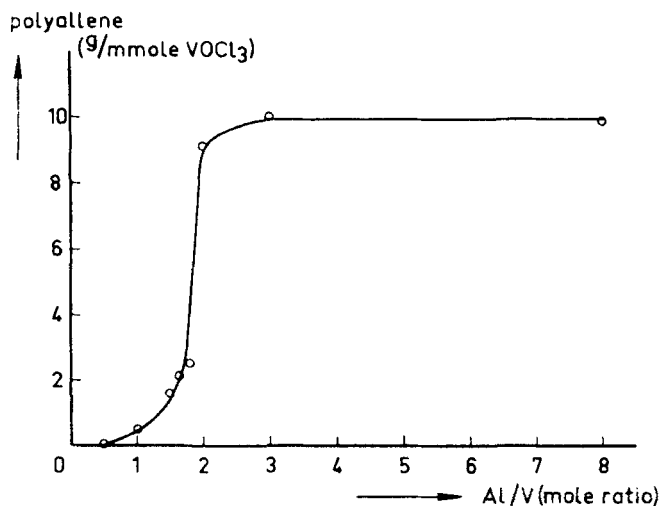


FIG. 1. Yields of polyallene at varying Al-*i*- $\text{Bu}_3/\text{VOCl}_3$ ratios (300 ml of cyclohexane, 10 g of allene, 0.5 mmole of VOCl_3 , polymerization time 15 min, initial temperature: room temperature, allene passed over during the experiment).

Polymerization Time

The rate of polymerization decreases with increasing polymerization time (see Fig. 2). Right from the beginning the activity of the catalyst rapidly decreases, and is very low after about 5 min.

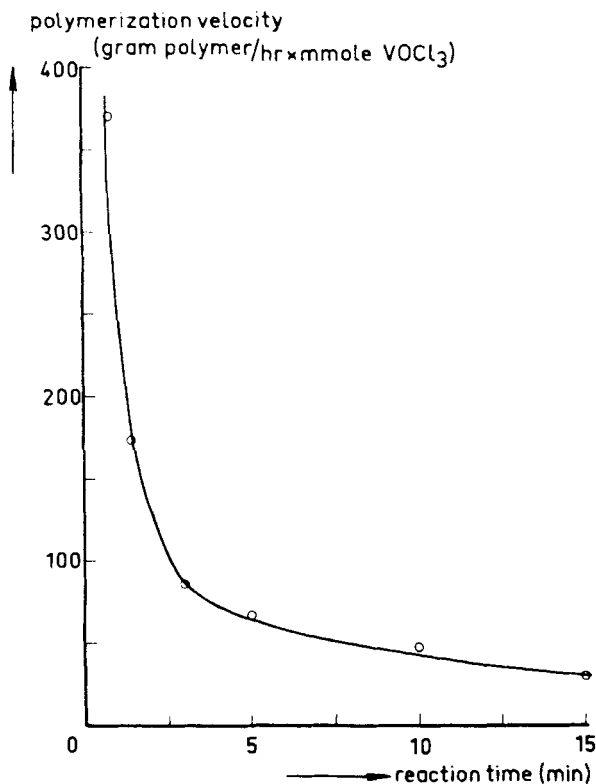


FIG. 2. Rate of polymerization vs. reaction time (300 ml of cyclohexane, 10 g of allene, 0.4 mmole of VOCl_3 , $\text{Al/V} = 9$, allene passed over during the reaction).

Reaction Temperature

The influence of the reaction temperature on the activity of the polymerization was studied in cyclohexane (Table 2) and in heptane (Fig. 3). Both series of experiments display an increase of the polymerization activity with increasing temperature between 0 and 80°C. The activity in heptane at temperatures below 0°C is very low. In both series the temperatures stated are initial temperatures. The true reaction temperatures, however, are rather indefinite, particularly for the experiments at higher temperatures, where much heat was developed, owing to the high conversions. Consequently, much of the dissolved monomer was set free again during these experiments.

TABLE 2. Influence of the Polymerization Temperature on the Yield and the Viscosity of Polyallene (600 ml of cyclohexane, 10 g of allene, 0.5 mmole of VOCl_3 , 4.4 mmoles Al-i-Bu_3 , time 15 min, $[\eta]$ determined in $\text{C}_6\text{H}_5\text{Br}$ at 110°C)

Temp. $^\circ\text{C}$	Polymer, g	$[\eta]$, dl/g
7	1.1	6.3
20	2.7	7.0
50	4.9	10-11

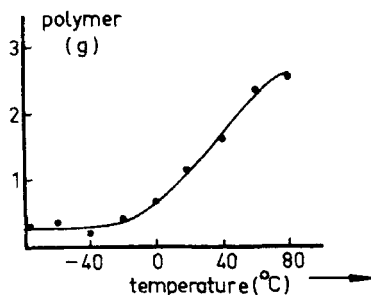


FIG. 3. Yield of polyallene vs. reaction temperature (reaction in 300 ml of *n*-heptane; 10 g of allene, 0.35 mmole of VOCl_3 , 3.2 mmole of Al-i-Bu_3 , polymerization time 2 hr (-80 to -40°C) and 15 min (-40 to 80°C)).

PROPERTIES AND STRUCTURE

General Properties

The polymers of allene generally are white, coarse powders or fibers; some products were obtained as very fine powders. Elementary C-H analyses were in good agreement with the formula $(\text{C}_3\text{H}_4)_n$. Ash contents varied from 0.04 to 0.50 wt.%; in the ashes aluminum and vanadium were detected spectrographically. At elevated temperatures (130 – 160°C), polyallene can be pressed to films that are light brown and brittle. Densities of these films at 22.5°C vary from 1.02 to 1.03. Polyallene shows a marked tendency to crystallize: its crystallinity is generally high, and greatly depends

on the conditions of preparation [5]. The polymers generally melt between 115 and 125°C (double-refraction melting-point microscope).

The change of the shear modulus and damping of a compression-molded specimen with the temperature is shown in Fig. 4 Apart

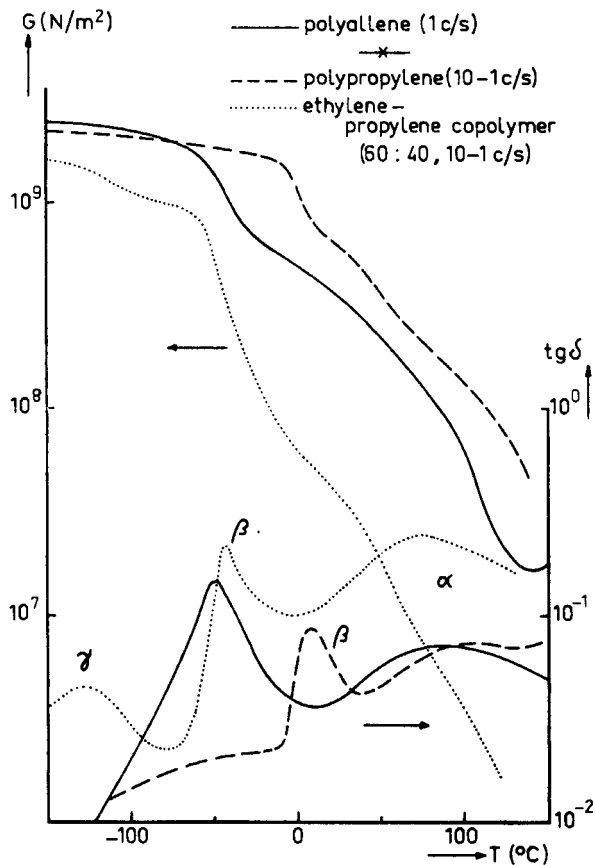


FIG. 4. Shear modulus vs. temperature and damping vs. temperature curves of polyallene at 1 cycle/sec. For comparison, the corresponding curves for isotactic polypropylene and for an ethylene-propylene copolymer [8] are included.

from its very low glass transition temperature (damping peak for 1 cycle/sec at $-50^{\circ}C$), the dynamic mechanical behavior of polyallene appears to be very similar to that of isotactic polypropylene [8] (damping peak for 1 cycle/sec at about $0^{\circ}C$).

All the investigated polymers of allene swell in hot aliphatic and aromatic solvents such as isooctane, benzene, and monochlorobenzene. They are practically entirely soluble in monochlorobenzene at 130°C. The solubility in solvents with a lower boiling point greatly depends on the molecular weight and the crystallinity of the polymer. The following picture is based on a series of extractions of several samples of polymer; it may be regarded as representative for the solubility of the Ziegler-type polyallene: (1) not soluble in *n*-pentane or diethyl ether; (2) for a small part soluble in hot *n*-hexane; (3) for the greater part, or entirely, soluble in boiling benzene, cyclohexane, *n*-heptane, *n*-octane, and trichloroethylene; (4) entirely soluble in toluene, tetralin, and halogenated aromatic hydrocarbons at temperatures higher than 100°C.

When the polymers are stored in air for a long time they become yellowish. This yellowing effect is accompanied by oxidative degradation and cross-linking. This instability of polyallene can be attributed to the high content of activated hydrogen atoms and double bonds, and is promoted by metallic residues [9, 10], particularly vanadium, which occur in the samples in varying quantities. A distinct increase in stability was obtained, however, when the polymers were stored under exclusion of oxygen. Accordingly, the polymers were, as soon as possible after their isolation, kept in sealed tubes under nitrogen. Thus stored they were found to be still completely white after more than 1 year.

Viscosity Measurements

The instability of polyallene is of influence on the determination of the viscosity. Initially it was difficult to perform somewhat reliable viscosity determinations, owing to oxidative and thermal decomposition while dissolving the samples in the hot solvent. Although a distinct improvement was observed when certain stabilizers were added, degradation could not be avoided completely. As a result, the original viscosities presumably are higher than those measured after the samples had been dissolved. In the systematic viscosity measurements this disadvantage was evaded by taking the contact time between polymer and solvent equal for all determinations. The following procedure proved to be successful: the polymer was dissolved under nitrogen in monobromobenzene at 110°C in a concentration of 0.01–0.05 g/100 ml, in the presence of phenyl- β -naphthylamine (0.5 wt. % with respect to the solvent). After a heating time of 3 hr, the viscosity was measured in an Ubbelohde viscometer at 110°C. It is seen that (1) the viscosity as a function of the Al/V ratio follows the same curve as the polymerization activity against this ratio (Fig. 5); (2) the viscosity increases with increasing reaction time and reaches a constant value after some minutes (Fig. 6); and (3) the viscosity increases with increasing polymerization temperature (Fig. 7 and Table 2).

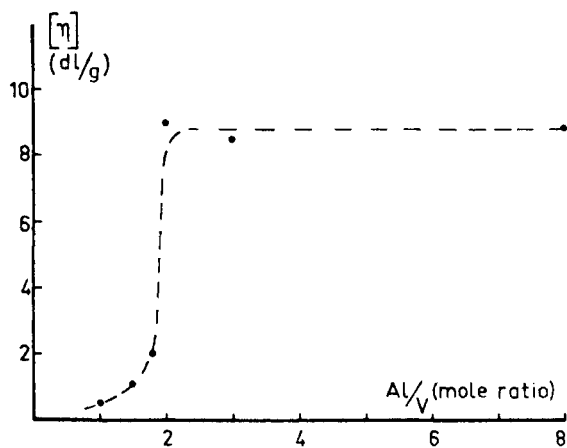


FIG. 5. Intrinsic viscosity vs. Al/V ratio (see Fig. 1) (monobromobenzene, 110°C).

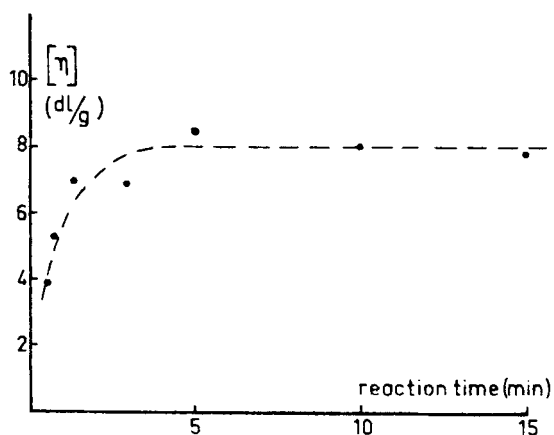


FIG. 6. Viscosity vs. time of polymerization (see Fig. 2).

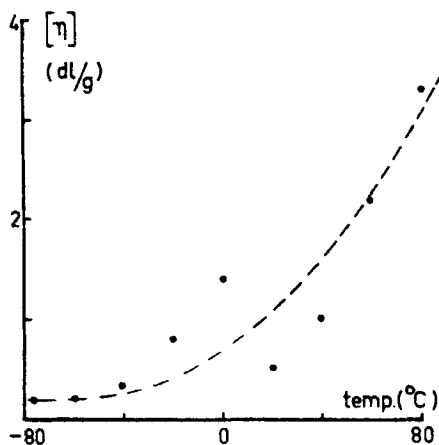


FIG. 7. Viscosity vs. polymerization temperature (see Fig. 3).

Chemical Structure

The structure of the polyallenes has been investigated by infrared and by nuclear magnetic resonance.

Infrared Investigation. A typical spectrum of polyallene (KBr disks) is given in Fig. 8. In agreement with the results of Baker [2],

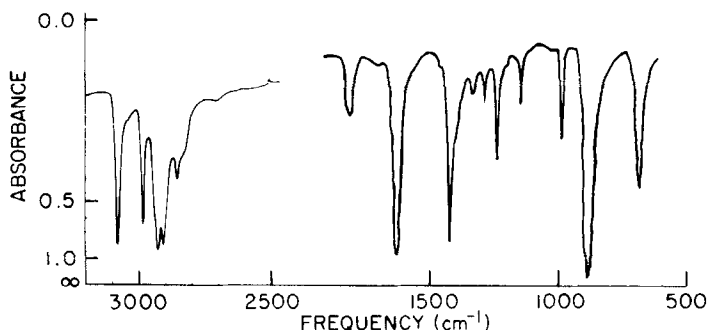
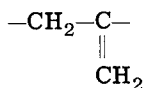


FIG. 8. Infrared spectrum of a Ziegler polyallene.

three types of unsaturation appear to be present: in high concentration the vinylidene group (the intensive absorption band at 880 cm^{-1} corresponding with the C—H out-of-plane deformation vibra-

tion of $>C=CH_2$) corresponding with the structural unit



and in much lower concentrations—vinyl and internal ethene—cis groups (the bands at 990 and 690 cm^{-1} , respectively). The band at 1635 cm^{-1} is attributed to the C=C valency vibration. The band at 1425 cm^{-1} corresponds with the C—H in-plane deformation vibration of $>C=CH_2$ and $-CH=CH_2$. The scissoring of the $-CH_2$ group, which normally is present at 1465 ± 20 cm^{-1} , upon closer investigation appears to occur at approximately 1435 cm^{-1} as a shoulder of the band at 1425 cm^{-1} . Apparently this band has shifted to lower frequencies under the influence of neighboring vinylidene groups. Baker [2] situates the $-CH_2$ scissoring in polyallene at 1425 cm^{-1} . Bellamy [11] states that shift of the frequency of the scissoring of the saturated $-CH_2$ group in $-C=C-CH_2-$ to lower frequencies can occur when the double bond is part of a ring, as in some sterols. Nakanishi [12] mentions that the scissoring of $-CH_2-$ in $-CH_2-C=C-$ lies at 1445–1430 cm^{-1} and shifts to a lower frequency when the $-CH_2$ group lies between two double bonds.

NMR Investigation. The NMR investigation has been performed at 5 wt.% gelatinous solution of polymer in *o*-dichlorobenzene at temperatures of about 100°C. A typical spectrum is shown in Fig. 9. It displays two intensive peaks at $\tau = 5.08$ and 7.27. $\tau = 5.08$ is a good value for terminal $=CH_2$ groups. $\tau = 7.27$ is a reasonable value for the $=C-CH_2-C-$ grouping (Jackman [13] gives 7.1). Moreover, both peaks have the same surface, so it may be concluded that the NMR spectrum is in agreement with the presence of the repeating unit

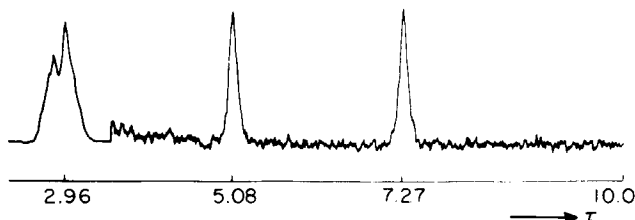
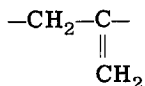
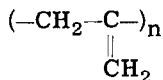


FIG. 9. NMR spectrum of polyallene.

No indications could be found for the presence of the vinyl and internal cis groupings, however. Nonterminal cyclic olefinic protons absorb at $\tau = 4.45-4.95$.

The results from the infrared and NMR investigation are supported by the dynamic mechanical behavior (Fig. 4). This is in agreement with a rather high percentage of crystallinity, i.e. a fairly regular structure. Its low glass transition in comparison with, e.g., isotactic polypropylene (0°C) [8] might be caused by the regular successions of unsaturated groups (compare, e.g., poly-cis-isoprene-1, 4 [14] and poly-cis-butadiene-1, 4 [15], glass transitions at approx. -50 and -95°C, respectively). The width of the glass transition peak, especially at the side of lower temperatures (<-50°C) indicates that the composition of the polymer chain is not completely homogeneous*; next to the presence of blocks of the main structure



links of increased mobility must be present too (vinyl, cis). The spectrum of polyallene does not show the presence of the so-called γ -peak, which occurs in the ethylene-propylene copolymer at about -120°C [14] and arises from the presence of $(-\text{CH}_2-)_4$ groupings. Therefore, this structure is not present in polyallene.

DISCUSSION

Initiation Reactions and Activity of the Catalysts

The polymerization of allene appears to depend greatly on reaction conditions such as the type of organoaluminum compound, the ratio of the catalyst components, the reaction time, and the temperature. This may arise mainly from differences in composition and/or concentration of the actual sites of polymerization at the varying conditions of the polymerization experiments.

Generally, reactions between the components of Ziegler-type catalysts to form the catalytic active species are accompanied by a reduction of the transition metal compound. It is assumed that this reduction takes place via the formation of unstable organo-transition metal compounds. In the case of organoaluminum-vanadium catalyst, it has been found that for a given alkyl group the power of the aluminum compound to reduce vanadium compounds such as

*We do not think that the other explanation for the width of the peak—an extremely broad molecular weight distribution—is applicable to this case.

VOCl_3 and VCl_4 decreases at decreasing degree of alkylation of the aluminum compound: $\text{AlR}_3 > \text{AlR}_2\text{X} > \text{AlRX}_2$ (R, alkyl; X, halogen) [16–19]. With all three types of organoaluminum compounds, species with both tri- and divalent vanadium have been demonstrated, the percentages being dependent on reaction conditions such as concentration of the aluminum compound and ratio of the catalyst components. It has been shown further that soluble as well as insoluble reaction products may be formed in which vanadium is in a complexed form with organoaluminum halide. Formation of a soluble V–Al complex is preferred when organoaluminum halide, especially RAlX_2 , and a high Al/V mole ratio (e.g. > 9) are applied. This type of catalyst has been studied in detail in the system $\text{Sn}(\text{C}_6\text{H}_5)_4\text{--AlBu}_3\text{--VCl}_4$, in which it has a stable, pink color. It has a very high activity to polymerize ethylene. It is assumed that the catalytically active species is a low (presumably II) valence organovanadium compound that is stabilized and kept in solution by organoaluminum halide [19–23]. On the other hand, insoluble, colloidal, dark-colored precipitates are formed by preference, when aluminum alkyls with higher alkyl substitution, e.g., AlR_3 , and lower Al/V ratios are applied [17, 20, 21].

With regard to the polymerization activity of these systems, it has been shown that the activity to polymerize ethylene and ethylene (co)propylene is in the order $\text{RAlCl}_2 > \text{R}_2\text{AlX} > \text{AlR}_3$ [21, 24]. From our polymerization experiments with allene it is concluded that the polymerization activity has the opposite order $\text{AlR}_3 > \text{AlR}_2\text{X} > \text{AlRX}_2$ (p. 4). In some orientating experiments, the catalyst combinations of Table 1 have also been studied on their activity to polymerize ethylene. All combinations were active, and in consistence with the results of de Liefde Meyer and van der Kerk, reported above [21], highest activity was observed with $\text{EtAlBr}_2\text{--VOCl}_3$ catalysts, especially when high Al/V ratios (> 30) were applied. Under these conditions practically clear solutions were obtained, in which, however, allene could not be polymerized.

These data indicate that in Ziegler catalysts containing vanadium, different initiators—e.g., different as regards physical state, valency, and arrangement of groups around the vanadium—may be operative. The soluble organovanadium compound mentioned above, if formed by preference when monoalkylaluminum dihalides and high Al/V ratios are applied, is very active in the polymerization of ethylene. Apparently, allene is not to be polymerized with this catalyst. When higher alkylated aluminum alkyls (AlR_3 , AlRX_2) are applied, less stable, colloidal, low-valence vanadium–aluminum complexes will be formed predominantly. The polymerization of ethylene—be it less effective—may be initiated also by this type of catalyst. Such catalysts could be responsible for the polymerization of allene.

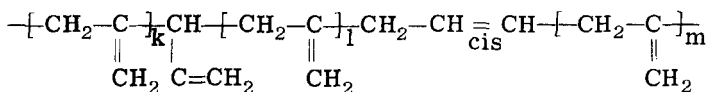
It has been shown that this very type of catalyst is strongly liable to alteration [16, 17, 24]. Junghanns et al. [24] assume that, in these

systems, the initially formed active catalyst is transformed into an inactive species. A rapid loss in activity was also observed during the polymerization of allene (Fig. 2). In these experiments the catalyst was prepared in the presence of monomer, but polymerization activity decreased also when the catalyst components were mixed in the absence of allene and the monomer was added after a certain time of aging. The decrease in activity during polymerization must also be due to a lowered transport of monomer to the reaction mass as a result of the increasing viscosity of the system. This factor is certainly important in those experiments in which high conversions were obtained.

The low activity of trimethylaluminum (Table 1) may be caused by an increased stability of metal-carbon bond in the methylvanadium compound formed, as has been found in the case of methyl-titanium compounds [17, 25-27]. In the polymerization of ethylene with an $\text{AlMe}_3\text{-TiCl}_4$ catalyst, the stability toward disproportionation of the Me-Ti bond causes an induction period during which, by insertion of ethylene into the Ti-C bond, higher alkyl-Ti compounds are formed, which rapidly disproportionate and restore the catalytic activity [25, 27]. It was observed in our experiments that the solutions obtained by mixing methylaluminum compounds and VOCl_3 in cyclohexane all showed a rather stable, red color (Table 1). The ultimate low yield of polyallene suggests that the addition of an allene molecular to a methyl-transition metal bond proceeds with much more difficulty than with an ethylene molecule.

Polymerization Mechanism

From the physicochemical measurements it is assumed that the polyallene chain consists essentially of monomer units having vinylidene structure, linked together by units with vinyl and *cis* structures:



In general, little variation was observed in the ratios of the respective infrared absorbance intensities (KBr disks), and no correlation was found between the structure of the polymer and polymerization conditions. In a typical sample, the quantity of vinylidene groups was determined as 80 mole % of the total unsaturation.*

In accordance with views held by Carick et al. [19, 28] and others

*Extinction at 880 cm^{-1} of 0.1 wt. % polyallene dissolved in *o*-dichlorobenzene at 125°C ; molar extinction of $\text{>C}=\text{CH}_2$ measured for 2-methylnonene-1 and 2-methylnonadecene-1. Total unsaturation = 1 double bond per monomer unit.

were obtained, however, when this gas was led through effective washing towers containing, e.g., solutions of silver nitrate in glycerol.

Nitrogen was purified by passing it through a tower containing an active copper catalyst (BTS catalyst, BASF) at 70°C and through drying towers with silica and Anhydron, successively.

Cyclohexane (May and Baker) was treated with oleum (60%) for 1 hr, washed until neutral, dried, and distilled. This treatment was repeated until no aromatics could be detected by ultraviolet spectroscopy.

Heptane (May and Baker) was treated with concentrated H_2SO_4 , washed to neutral, dried over $CaCl_2$ and distilled over Na.

Vanadium oxytrichloride was originally prepared by refluxing a mixture of V_2O_5 and $SOCl_2$. After 6 hr reaction time, the yellow $VOCl_3$ was distilled off (b.p. 124.8–125°C) [35] and collected in ampoules under nitrogen. Lateron (Stauffer) in commercial quality was used.

Triethyl- and trimethylaluminum were obtained from the Ethyl Co., triisobutylaluminum from Texas Alkyls and Schering-Bergkamen, and trihexylaluminum and diisobutylaluminum chloride from Texas Alkyls. The other alkylaluminum halides were prepared from higher alkylated organoaluminum compounds and aluminum trihalide [36, 37].

Instruments

Perkin-Elmer Spectrophotometer No. 221; NMR spectrometer Varian A 60. The shear modulus and damping were measured by means of the Nonius torsion pendulum [38]. For each temperature, measurements were done at three frequencies. The values at 1 cycle/sec were determined by interpolation (for temperatures < 100°C), or by extrapolation (for temperatures > 100°C).

Techniques of Catalyst Transfer and Polymerization

As the catalysts are sensitive to oxygen and moisture, catalyst transfer and polymerization reactions were carried out under nitrogen, by means of well-established techniques (see, e.g., [39]) using a dry-box, hypodermic syringes, and needles flasks that can previously be filled with nitrogen. Connections between needles and flasks were made through flat rubber membranes and serum caps.

Polymerizations

Polymerizations were performed in round-bottomed flasks of 500 and 1000 ml for the larger-scale experiments, and in pressure bottles of about 200 ml for the experiments on a smaller scale. The round-bottom flasks are provided with gas inlet and outlet tubes, and can also be provided with a thermometer. The polymerizations were carried out with shaking. It was tried to keep the temperature constant during the experiment by external cooling. As a result of

rapid heat evolution and bad movement of the reaction mass at high conversions, this could only be attained at experiments with low conversions. In the other experiments the temperature may have become rather high locally, and a rise of the thermometer temperature of 5–10°C was possible.

Extractions

It appeared impossible to obtain reliable information on the solubility of the polymers when a hot-extraction apparatus of the conventional type was used. This must be ascribed to the great swelling tendency of the polymer, by which the filter clogs and a sufficient draining of the polymer mass by the solvent is impeded. Much better results were obtained when an extraction apparatus was used in which the dissolution step and filtration step can be performed separately (see Fig. 10). The general procedure for an extraction

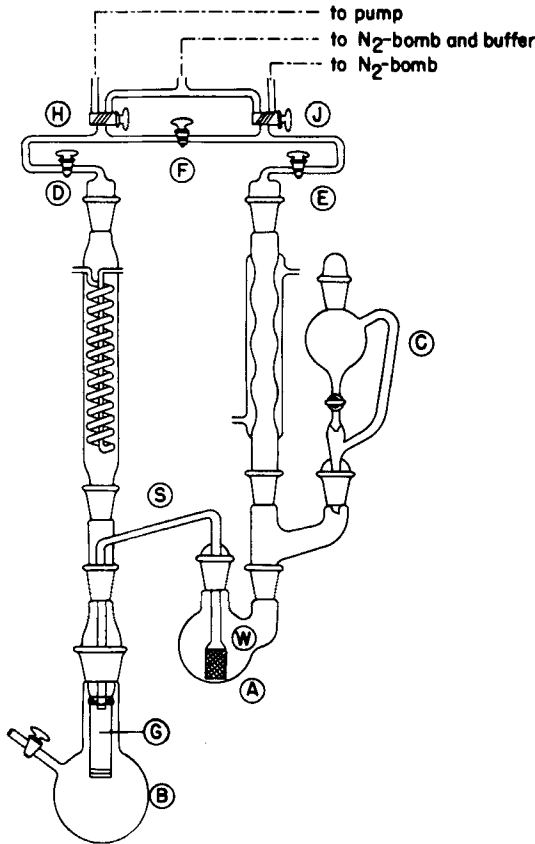


FIG. 10. Extraction apparatus.

is as follows. Round-bottomed flasks A (volume 250 ml) and B (500 ml), and dropping funnel C (250 ml) are filled with the polymer (750–250 mg) and 200 ml of extraction solvent, 50 ml of solvent, and 250 ml of solvent, respectively. To avoid oxidation during the extraction, the whole apparatus is evacuated and filled with nitrogen (three times) by an appropriate manipulation of stopcocks D, E, F, H, and J.

The solvent in A and B is heated to reflux, and boiling is maintained until the polymer in A has been dissolved or has become wholly transparent ($\frac{1}{2}$ to 2 hr). The hot polymer solution in A is forced over into B by building up nitrogen pressure in A, and separated from undissolved polymer by passing a wad of glass wool (W) in the siphon (S) and a G_1 -filter in B. The extraction procedure is repeated twice by introducing into A a new amount of solvent from C, etc. The dissolved part of the polymer (in B) is isolated by cooling the solution or distilling off the solvent, and treating the polymer thoroughly with methanol (containing antioxidant). It is dried in vacuo over P_2O_5 and kept in closed ampoules.

Acknowledgments

The authors express their thanks to the Managing Board of Mobil Oil Nederland, who sponsored part of the work reported here, for permission to publish this paper. They are indebted to Ir. J. Heijboer, Mr. H. J. Huldy, Dr. J. H. L. Zwiers (Analytical Institute TNO), and Dr. E. Talman for their assistance in the characterization of the polymers.

They acknowledge valuable discussions on this investigation with Prof. Dr. E. C. Kooyman (Laboratory for Organic Chemistry, University of Leiden).

REFERENCES

- [1] R. Havinga, thesis, Leiden, 1964.
- [2] W. P. Baker, *J. Polmer Sci.*, **A1**, 655 (1963).
- [3] S. Otsuka, K. Mori, and F. Imaizumi, *J. Am. Chem. Soc.*, **87**, 3017 (1965).
- [4] K. Griesbaum, *Angew. Chem.*, **78**, 966 (1966).
- [5] R. Havinga, A. Schors, and J. W. Visser, *J. Macromol. Sci.*, **A2(1)**, 21 (1968).
- [6] R. Havinga and A. Schors, *J. Macromol. Sci.*, **A2(1)**, 31 (1968).
- [7] U. S. Pat. 3,151,104 (1964); *CA* **62**, 1760 (1965).
- [8] H. A. Focke, *Kolloid-Z.*, **180**, 118 (1962).
- [9] M. S. Karasch, A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, **17**, 207 (1952).
- [10] K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).
- [11] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, and J. Wiley, New York, 1962.

- [12] K. Nakanishi, *Infrared Absorption Spectroscopy*, Holden-Day, San Francisco, Nankodo Company, Ltd., Tokyo, 1962.
- [13] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 1959.
- [14] H. D. Heinze et al., *Kautschuk Gummi*, **14**, WT208 (1961).
- [15] K. A. Wolf, *Z. Electrochem.*, **65**, 604 (1959).
- [16] G. Bier, *Angew. Chem.*, **73**, 186 (1961).
- [17] G. Bier, A. Gumboldt, and G. Schleitzer, *Makromol. Chem.*, **58**, 43 (1962).
- [18] W. L. Carrick, A. G. Chasar, and J. J. Smith, *Abstracts of Papers*, 134th A.C.S Meeting, Sept. 1958, p. 2T.
- [19] W. L. Carrick, A. G. Chasar, and J. J. Smith, *J. Am. Chem. Soc.*, **82**, 5319 (1960).
- [20] W. L. Carrick, W. T. Reichle, M. W. Kluber, E. F. Bonner, and J. J. Smith, *Abstracts of Papers*, 133rd A.C.S. Meeting, April 1958, p. 19R; J. J. Smith, E. F. Bonner, F. M. Rugg, L. H. Wartman, and W. L. Carrick, *ibid.*
- [21] H. J. de Liefde Meyer and G. J. M. van der Kerk, *Rec. Trav. Chim.*, **85**, 1021 (1966).
- [22] G. W. Phillips and W. L. Carrick, *J. Am. Chem. Soc.*, **84**, 920 (1962).
- [23] G. W. Phillips and W. L. Carrick, *J. Polymer Sci.*, **59**, 401 (1962).
- [24] E. Junghanns, A. Gumboldt, and G. Bier, *Makromol. Chem.*, **58**, 18 (1962).
- [25] H. N. Friedlander and K. Oita, *Ind. Eng. Chem.*, **48**, 1885 (1957).
- [26] C. van Heerden, *J. Polymer Sci.*, **37**, 47 (1959).
- [27] C. Beerman, *Angew. Chem.*, **71**, 195 (1959).
- [28] F. J. Karol and W. L. Carrick, *J. Am. Chem. Soc.*, **83**, 2654 (1961).
- [29] D. S. Breslow and N. R. Newburg, *J. Am. Chem. Soc.*, **81**, 81 (1959).
- [30] D. B. Ludlum, A. W. Anderson, and C. E. Ashby, *J. Am. Chem. Soc.*, **80**, 1380 (1958).
- [31] E. D. Fischer, *Chem. Soc. (London) Spec. Publ.*, **13**, 73 (1959).
- [32] P. Cossee, *J. Catalysis*, **3**, 80 (1964); *Tetrahedron Letters*, **17**, 7 (1960).
- [33] A. Kempkes, dissertation, Aachen, 1959.
- [34] Brit. Pat. 875.195 (1961).
- [35] G. Brauer, *Handbuch der präparativen anorganischen Chemie*, F. Enke, Stuttgart, 1954, p. 949.
- [36] M. Grosse and A. Mavity, *J. Org. Chem.*, **5**, 119 (1940).
- [37] R. Havinga and Y. Y. Tan, *Rec. Trav. Chim.*, **79**, 56 (1960).
- [38] P. Dekking, dissertation, Leiden, 1961, p. 30.
- [39] W. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Wiley (Interscience), New York, 1961.

Accepted by editor November 17, 1967
 Submitted for publication January 2, 1968

Zusammenfassung

Die Polymerisation von Allen mit organischen Aluminium-Vanadiumoxytrichlorid Katalysatoren in aliphatische Kohlenwasserstoffe ist untersucht worden. Die Polymerisationsfähigkeit nimmt ab in den Reihenfolge: $\text{AlR}_3 > \text{AlR}_2\text{X} > \text{AlRX}_2$ (R, Aethyl oder iso-Butyl; X, Halogen). Trimethylaluminium ist sehr wenig aktiv. Für das System $\text{Al-i-Bu}_3\text{-VOCl}_3$ sind die Einflüsse von Al/V Verhältnis, Reaktionszeit und Temperatur auf die Polymerisation untersucht worden.

Die Polyallene sind hoch-kristalline Körper, die zwischen 115 und 125°C schmelzen. Die Struktur der Polymere ist aufgeklärt mit Hilfe der IR- und NMR-analyse. Die Aktivität des Katalysators rührt von Reaktionen zwischen die Aluminiumverbindungen und das Vanadinoxchlorid her.

Weiterhin wird ein Polymerisationsmechanismus vorgeschlagen.

Résumé

La polymérisation d'allène en solution hydrocarburique sous l'influence des catalyseurs contenant des composés alkylaluminium et l'oxychlorure de vanadium. L'activité des catalyseurs décroît dans l'ordre suivant: $\text{AlR}_3 > \text{AlR}_2\text{X} > \text{AlRX}_2$ (R, éthyle ou isobutyle; X, halogène). Le $\text{Al}(\text{Me})_3$ est très peu réactif. Pour l'initiateur $\text{Al-i-Bu}_3\text{-VOCl}_3$ on a étudié l'influence du rapport molaire Al/V, le temps de réaction et la température sur la polymérisation.

Les polyallènes sont des composés hautement cristallines, fondant entre 115 et 125°C. La structure des polymères obtenues a été examinée en résonance magnétique nucléaire et par spectrographie infrarouge.

Le mécanisme de polymérisation est discuté.