Preparation and Properties of Polyallenes III. Polymerization of Allenes Induced by Al-i-Bu$_3$-VOCl$_3$ Catalyst

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Preparation and Properties of Polyallenes. III. Polymerization of Allenes Induced by Al-i-Bu₃-VOCl₃ Catalyst

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Summary

The polymerization activity of several allenes under the influence of Al-i-Bu$_3$-VOCl$_3$, and structure and properties of the solid polymers obtained, have been studied. Allene; butadiene-1, 2; hexadiene-1, 2; 3-methylbutadiene-1, 2; 3-methylpentadiene-1, 2; and pentadiene 2, 3 could be converted into soluble, solid polymers. 2-Methylpentadiene-2, 3; tetramethylallene; and tetraphenylallene did not react under the polymerization conditions applied. The following order of polymerization activity seems to be valid: $CH_2=C=CH_2 > R_1CH=C=CH_2 > R_1R_2C=C=CH_2 \geqslant R_1CH=C=CHR_2 > R_1R_2C=C=CHR_3 \simeq R_1R_2C=C=CR_3R_4$. The polymers of the homologues of allene were obtained as amorphous solids with the exception of poly(3-methylbutadiene-1, 2), which was fairly crystalline.

Based on data obtained by IR and NMR analyses, a polymerization mechanism is proposed for the various types of allenes.

In the preceding papers [1, 2] of this series the polymerization of allene with Ziegler-type catalysts, and structure and properties of the polymers obtained, have been discussed. In this paper, the polymerization activity of several allenes under the influence of Al-i-Bu$_3$-VOCl$_3$ catalyst, and structure and properties of the polyallenes obtained, are described.

INVESTIGATION OF THE POLYMERIZABILITY OF SOME HOMOLOGUES OF ALLENE

The following monomers are investigated for polymerization activity under the influence of the triisobutylaluminum−vanadium oxy-

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trichloride catalyst: butadiene-1, 2; hexadiene-1, 2; 3-methylbutadiene-
1, 2; 3-methylpentadiene-1, 2; pentadiene-2, 3; 2-methylpentadiene-2, 3;
2, 4-dimethylpentadiene-2, 3; and tetraphenyl allene.

The preparation and purification of the allenes are given in de-
tail in the experimental part. It was found that the monomers buta-
diene-1, 2; hexadiene-1, 2; 3-methylbutadiene-1, 2; 3-methylpenta-
diene-1, 2; and pentadiene-2, 3 could be converted into solid polymers,
and that no polymerization products could be isolated from polymeriz-
ation experiments with the other allenes. In these cases the mono-
mers could be recovered practically quantitatively. It was further
found that polymerizations to low molecular weight volatile hydro-
carbons did not take place, nor were there indications that the mono-
mers isomerized under the influence of the catalytic system.

The results of some representative polymerization experiments
are given in Table 1. In these experiments the monomer was dis-
solved in a suitable solvent, after which the indicated quantity of
vanadium oxytrichloride was added. In the majority of cases, this
leads to the formation of a dark-brown turbid solution, but the reac-
tion of butadiene-1, 2 and tetraphenylallene with this catalyst com-
ponent gave an orange-brown and a clear wine-red solution, respec-
tively. When triisobutylaluninum was added, purple-brown turbide
reaction mixtures were obtained which, in those experiments in
which polymerization occurred, gradually became more or less vis-
cous. After the reaction times given in the table, 10–20 ml of iso-
propanol was added, and the polymer was precipitated by pouring the
content of the reaction vessel in an excess of methanol acidified
with hydrochloric acid. The polymers were washed with methanol
several times, and subsequently dried between filter paper and in
vacuo over phosphorus pentoxide, until the weights did not decrease
anymore. The results obtained indicate that the polymerization
activity decreases in the order $CH_2=C=CH_2 > R_1CH=C=CH_2 >$
$R_1R_2C=C-CH_2 \geqslant R_1CH=C=CHR_2 > R_1R_2C=C=CHR_3 \simeq$
$R_1R_2C=C=CR_3R_4$ [R, alkyl (C_1-C_3)]. It should be emphasized that
any comparison of reactivities is only justified for systems of equal
purity. In the experimental part it will be made clear that the quan-
tity of impurities present in the various compounds, although low,
is certainly not the same in all cases. On the other hand, the ratio of
the catalyst over the monomer was chosen relatively large, so that
the deactivating effect of the impurities becomes less important.

PROPERTIES

The polymers of the homologues of allene were obtained as rub-
ber-like solids, with the exception of polypentadiene-2, 3, which was
obtained as a fine powder. The rubber-like polymers gradually
became hard and brittle. In contact with air they deteriorate rapidly.

TABLE 1. Comparison of Polymerizability of Some Allene Hydrocarbons ($VOCl_3$–Al–i–Bu_3 catalyst, normal temperature and pressure)

Monomer			Solvent, ml	$VOCl_3$, mmole	Al/V, molar	Contact time, hr	Polymer, g	Conversion, %	Conversion, % mmole $VOCl_3$	Monomer converted/$VOCl_3$, moles/mole
Formula	Name	g, moles								
$CH_2=C=CH_2$	Allene	2.0 (0.05)	Cyclohexane, 100	0.5	6	2	1.8	90	180	90
$CH_3-CH=C=CH_2$	Butadiene-1,2	3.2 (0.06)	Cyclohexane, 100	0.5	6	2	2.1	66	132	78
$C_3H_7-CH=C=CH_2$	Hexadiene-1,2	3.0 (0.04)	Isooctane, 100	0.5	6	1.5	1.9	63	126	46
CH_3‹$\rangle C=C=CH_2$ (CH_3)	3-Methylbutadiene-1,2	1.5 (0.02)	Isooctane, 50	0.3	5	2	0.21	14	47	10
CH_3‹$\rangle C=C=CH_2$ (C_2H_5)	3-Methylpentadiene-1,2	3.0 (0.04)	Isooctane, 100	1.0	3	2	0.68	23	23	8
$CH_3-CH=C=CH-CH_3$	Pentadiene-2,3	5.0 (0.07)	Isooctane, 50	0.5	8	2	0.24	5	10	7
CH_3‹$\rangle C=C=CH-CH_3$ (CH_3)	2-Methylpentadiene-2,3	3.6 (0.04)	Isooctane, 50	1.0	5	2	0	0	0	0
CH_3‹$\rangle C=C=C\langle$ (CH_3)(CH_3)(CH_3)	2,4-Dimethylpentadiene-2,3	7.0 (0.07)	Isooctane, 25	2.0	4	2	0	0	0	0
$(C_6H_5)_2C=C=C(C_6H_5)_2$	Tetraphenylallene	4.1 (0.01)	Benzene, 25	0.5	4	2	0	0	0	0

Therefore the freshly prepared products were kept under nitrogen in closed ampoules and stored in the refrigerator as soon as possible after their isolation. We did not succeed in obtaining reliable viscosity measurements, as the samples in contact with solvents formed interactable gels in which the polymers were only partly in solution. It might be assumed, however, that, owing to low monomer to catalyst ratios, the polymers which were formed in solution were of rather low molecular weight.

X-ray diffraction diagrams of the polymers displayed exclusively amorphous bands, with the exception of poly(3-methylbutadiene-1, 2), which appeared to be well crystallized. Efforts to induce crystallinity in the amorphous polymers by heat-treatment at about 80°C were unsuccessful.

The infrared spectra of the polymers were recorded at freshly prepared samples. The infrared spectrum of polyallene has been discussed in detail in Part I [1], and showed the vinylidene group to be present as the main unsaturation, next to vinyl and cis. The infrared spectra of the other polymers are discussed below (see Figs. 1 and 2).

Polybutadiene-1, 2

See Fig. 1b. The spectrum indicates the presence of $>C=CH_2$ (890 and 3080 cm^{-1}), CH_3 (1360-1390, 2875, and 2965 cm^{-1}), and CH_2 (1465, 2930 and 2860 cm^{-1}). The $>C=C<^H$ grouping can at best be present in low concentration (825 cm^{-1}).

Polyhexadiene-1, 2

See Fig. 1c. The following groups can be identified: $>C=CH_2$ (900 and 3080 cm^{-1}), $-CH_3$ (2955, 2872, 1460, and 1380 cm^{-1}), and $-CH_2-$ (2930 and 1460 cm^{-1}). There is no indication for the presence of $>C=C<^H$ and vinyl in appreciable concentrations. The presence of cis-CH=CH— is not to be excluded (absorption at 740 cm^{-1}).

Polypentadiene-2, 3

See Fig. 2a. The rather intensive absorption maximum at 835 cm^{-1} indicates the presence of the $R_1R_2C=CHR_3$. The absorptions at 1450 cm^{-1} and between 1360 and 1390 cm^{-1} correspond with the presence of $-CH_2-$ and CH_3- groups.

Poly(3-methylbutadiene-1, 2)

See Fig. 2b. The spectrum indicates the presence of CH_3 and CH_2 (1370, 1435, and 2980 cm^{-1}). In low concentrations, $=CH_2$ (890 and 1380 cm^{-1}) and trans —CH=CH (965 cm^{-1}) may be present. Tetra-

alkyl-substituted ethylene groups cannot be indicated, as these groups in general are invisible in the infrared.

Poly (3 - methylpentadiene -1, 2)

See Fig. 2c. There is no indication that =CH groups occur in the compound. CH_2 and CH_3 groups occur in high concentrations (1450 and 2925 cm^{-1}; 1370, 1450, 2870, and 2960 cm^{-1}). Many CH_2 and CH_3 groups can occur as ethyl groups (1065 cm^{-1}).

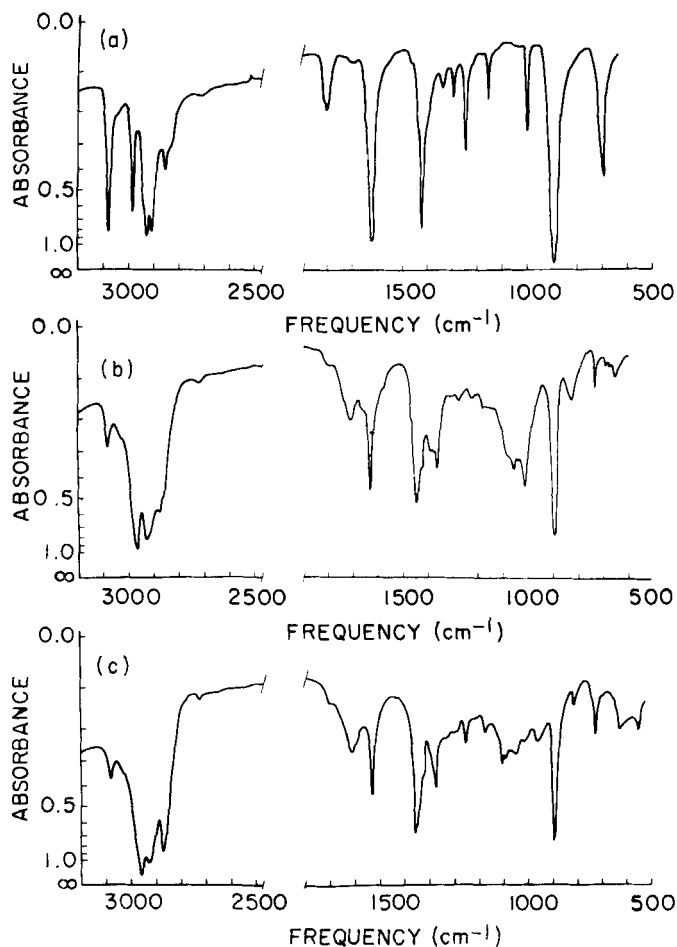FIG. 1. Infrared spectra: (a) polyallene; (b) polybutadiene-1, 2; (c) polyhexadiene-1, 2.

The structure of the polymers has also been investigated by NMR analysis. The NMR spectrum of polyallene appeared to be consistent with the presence of
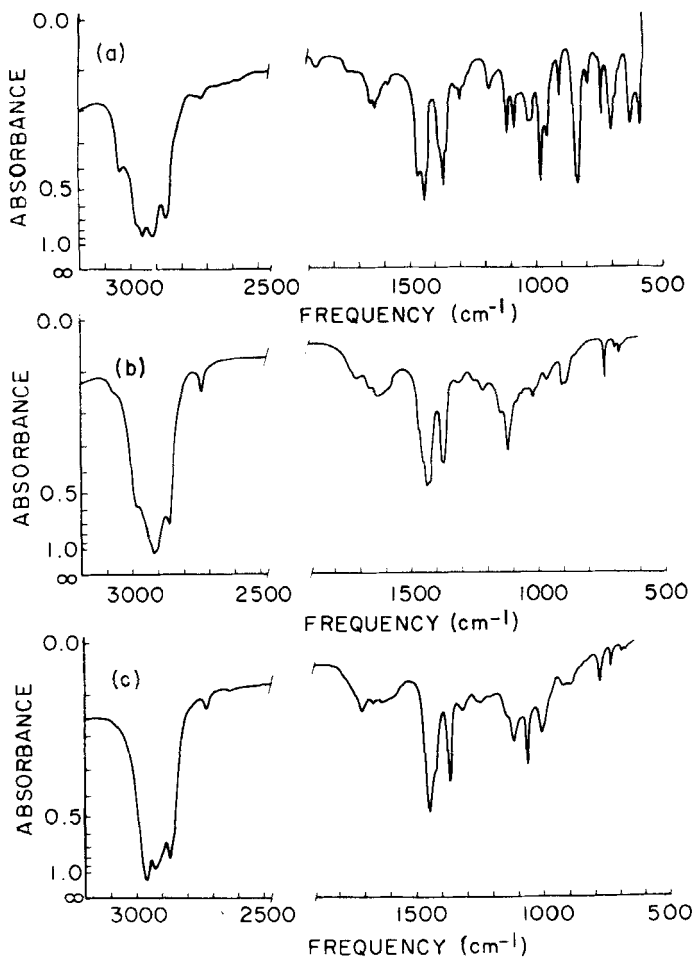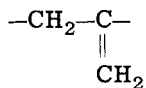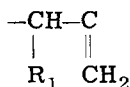
$$-CH_2-\underset{\underset{CH_2}{\|}}{C}-$$

FIG. 2. Infrared spectra: (a) polypentadiene-2, 3; (b) poly(3-methylbutadiene-1, 2); (c) poly(3-methylpentadiene-1, 2).
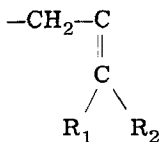
units [1]. In the other cases, measurements (o-dichlorobenzene, 80–100°C) were carried out at samples that had been stored for some months to more than 1 year. Measurements appeared to be hampered by the fact that the polymers were no longer completely soluble; they could be brought to swell only in the best cases. The diagrams showed many unsharp peaks which were not always easily interpretable. In the cases of polybutadiene-1, 2; poly(3-methyl-butadiene-1, 2); and poly(3-methylpentadiene-1, 2), the interpretation of the NMR spectra was, qualitatively, rather consistent with the occurrence of the principal structures as assumed from the infrared analysis.

DISCUSSION

From the analysis it is concluded that in the polymers obtained from the allenes of the types $R_1CH=C=CH_2$, $R_1R_2C=C=CH_2$, and $R_1CH=C=CHR_1$, the dominating structures are, respectively*:

$$
\begin{array}{ccc}
-CH-C & -CH_2-C & -CH-C \\
|\quad\ \| & \| & \|\quad\ \| \\
R_1\ \ CH_2 & C & R_1\ \ C \\
& /\ \ \backslash & /\ \ \backslash \\
& R_1\ \ R_2 & R_1\ \ H \\
(a) & (b) & (c)
\end{array}
$$
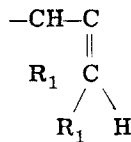
In Ziegler-type polymerizations polymerization is generally assumed to start with a coordination of the transition metal of the catalyst with the double bond to be polymerized of the monomer. Hence, with allenes of the type $R_1CH=C=CH_2$, this coordination is assumed to take place mainly at the nonterminal double bond. It may be favored due to an increased electron density at this bond. In the case of allenes of the type $R_1R_2C=C=CH_2$ the steric influence of both alkyl groups may impede coordination at the nonterminal double bond, in favor of the terminal bond to be coordinated. The polymerization

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*Absence of infrared unsaturation, as indicated by structure (b), is also consistent with a polymerization reaction in which both double bonds are involved. In that case, however, the polymer formed should be expected to gel from solution. This does not agree with our observations.

processes are represented by the following schemes:

For $R_1CH=C=CH_2$ $(R_1 = H, \text{alkyl})$

$$
\begin{array}{ccc}
\overset{\delta^+}{V}\!\!-\!\!\overset{\delta^-}{R} & \xrightarrow{} & V\cdots R \\
\uparrow & & \\
H_2C=C=CHR_1 & & H_2C=C\cdots CHR_1
\end{array}
\qquad
\xrightarrow{}
\qquad
\begin{array}{c}
\overset{\delta^+}{V}\!\!-\!\!\overset{\delta^-}{C}\!\!-\!\!CHRR_1 \\
\parallel \\
CH_2
\end{array}
$$

(Ia)   **(Ib)**   **(Ic)**

or

$$
\begin{array}{ccc}
\overset{\delta^+}{V}\!\!-\!\!\overset{\delta^-}{R} & \xrightarrow{} & V\cdots R \\
\uparrow & & \\
R_1HC=C=CH_2 & & R_1HC\cdots C=CH_2
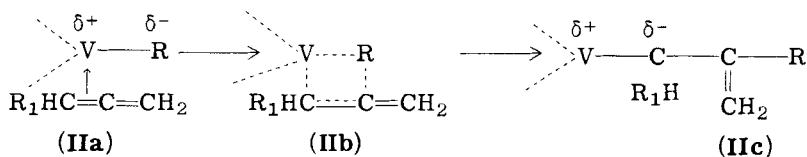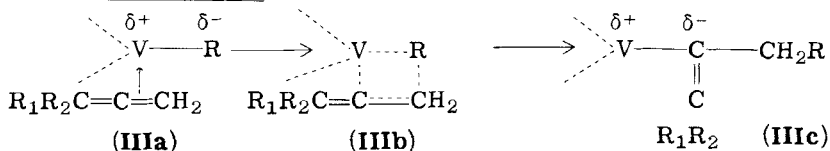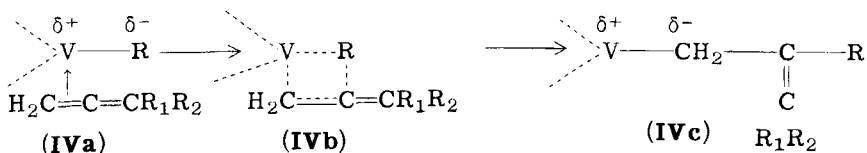\end{array}
\qquad
\xrightarrow{}
\qquad
\begin{array}{c}
\overset{\delta^+}{V}\!\!-\!\!\overset{\delta^-}{C}\!\!-\!\!C\!\!-\!\!R \\
R_1H \quad \parallel \\
CH_2
\end{array}
$$

(IIa)   **(IIb)**   **(IIc)**
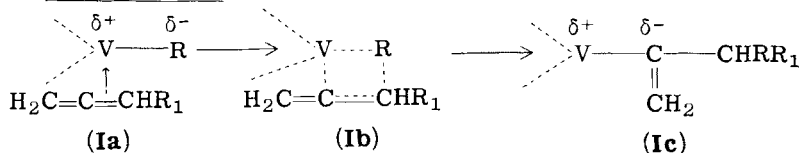
For $R_1R_2C=C=CH_2$ $(R_1, R_2 = \text{alkyl})$

$$
\begin{array}{ccc}
\overset{\delta^+}{V}\!\!-\!\!\overset{\delta^-}{R} & \xrightarrow{} & V\cdots R \\
\uparrow & & \\
R_1R_2C=C=CH_2 & & R_1R_2C=C\cdots CH_2
\end{array}
\qquad
\xrightarrow{}
\qquad
\begin{array}{c}
\overset{\delta^+}{V}\!\!-\!\!\overset{\delta^-}{C}\!\!-\!\!CH_2R \\
\parallel \\
C \\
R_1R_2
\end{array}
$$

(IIIa)   **(IIIb)**   **(IIIc)**

or

$$
\begin{array}{ccc}
\overset{\delta^+}{V}\!\!-\!\!\overset{\delta^-}{R} & \xrightarrow{} & V\cdots R \\
\uparrow & & \\
H_2C=C=CR_1R_2 & & H_2C\cdots C=CR_1R_2
\end{array}
\qquad
\xrightarrow{}
\qquad
\begin{array}{c}
\overset{\delta^+}{V}\!\!-\!\!CH_2\!\!-\!\!\overset{\delta^-}{C}\!\!-\!\!R \\
\parallel \\
C \\
R_1R_2
\end{array}
$$

(IVa)   **(IVb)**   **(IVc)**

If it is assumed that the allenic double bond system must be parallel to the vanadium–carbon bond [3], for each monomer type two orientations must be considered: **(Ia)** and **(IIa)**, and **(IIIa)** and **(IVa)**, respectively. Steric reasons could be in favor of orientations according to **(Ia)** and **(IVa)**, i.e., with the alkyl groups away from the bimetallic complex. The low polymerization activity of pentadiene-2,3 may be understood for steric reasons, because, whatever the orientation of the addition may be, always one alkyl substituent should interact with the growing chain-catalytic complex.

It has to be stressed, however, that the polyadditions may take place according to much more complicated mechanisms, e.g., multi-centred processes in which the whole allenic system is involved.

This possibility has also been mentioned by Jacobs and Johnson in connection with the addition of hydrogen chloride to allenes [4]. Peer assumes such a process to account for the formation of propargyl chloride as a by-product in the reaction between allene and chlorine [5]. In this connection mention should be made of some recent papers in which the synthesis of π-allylpalladium complexes from some allenes and palladium compounds is described [6].

EXPERIMENTAL

For techniques of catalyst transfer and polymerization, and instruments, see [1, 2].

Materials (see also [1])

Allene was obtained by dehalogenation of 2, 3-dihalopropene with zinc. It was purified by fractional distillation [1].

Butadiene-1, 2. 3-Hydroxybutyne-1 was prepared from acetylene and acetaldehyde according to a procedure given for the preparation of 3-hydroxy-3-methylbutyne-1 and 3-hydroxy-3-methylpentyne-1 [7]; b.p. 108–109°C, $n_D^{20} = 1.4266$, yield 27% on acetaldehyde.

3-Chlorobutyne-1 was prepared by reacting 1 mole of 3-hydroxybutyne-1 with 1.05 mole of thionyl chloride in the presence of pyridine [4]; b.p. 69–70°C, $n_D^{20} = 1.4264$, yield 49%.

Butadiene-1, 2 was prepared by adding 3-chloro-butyne-1 to a zinc–copper couple in ethanol [4] at 40–60°C. The escaping gas is purified by passing it through washing bottles containing an ammoniacal Cu(I) solution and water, successively, and distilled slowly (b.p. ca. 10°C). It appeared to contain small amounts of butenes (glc). It was purified further by means of a preparative gas-chromatographic technique (copper tube, diameter 1.3 cm, length 6 m, filled with Supercel C 22, 40-50 mesh, stationary-phase dimethylsulfolan (20 w.%), eluent nitrogen, rate 50 ml/min, temperature –10°C). It appeared to be very pure according to glc and IR analysis.

Hexadiene-1, 2. 3-Hydroxyhexyne-1 was prepared from acetylene and butyraldehyde [8]; yield 31%, b.p. 63–64°C/30 mm, $n_D^{20} = 1.4355$.

3-Chlorohexyne-1, see [8], yield 54%, b.p. 60–61°C/90 mm, $n_D^{20} = 1.4385$.

Hexadiene-1, 2 was prepared from 3-chlorohexyne-1 and Zn–Cu in absolute ethanol [8]. Yield 48%, b.p. 75.3–75.7°C, $n_D^{20} = 1.4286$. IR analysis: no —C≡C—H. Glc (7–8 benzchinolin, 55°C): unknown impurities in trace amounts.

3-Methylbutadiene-1, 2. 3-Hydroxy-3-methylbutyne-1 was obtained by condensation of acetylene and acetone [7]. Yield 67%, b.p. 103–104.5°C, $n_D^{20} = 1.4214$.

3-Chloro-3-methylbutyne-1 was prepared by shaking a mixture of 1 mole of 3-hydroxybutyne-1, 1 mole of calcium chloride and 5

moles of concentrated hydrochloric acid, in the presence of 1 g of hydroquinone [4, 9]. Yield 42%, b.p. 75–76°C, $n_D^{25} = 1.4174$.

3-Methylbutadiene-1, 2 (see [4]). Yield 48%, b.p. 40. 3–40. 5°C, $n_D^{25} = 1.4168$. IR analysis: traces of compounds containing $-C{\equiv}C-H$ may be present. Glc: only trace amounts of impurities.

3 -Methylpentadiene-1, 2. 3-Hydroxy-3-methylpentyne-1 (see [7]). Yield 79%, b.p. 121–123°C, $n_D^{20} = 1.4314$.

3-Chloro-3-methylpentyne-1 (see [4]). Yield 48%, b.p. 46. 5–48°C/ 96 mm, $n_D^{25} = 1.4318$.

3-Methylpentadiene-1, 2. (see [4]). Yield 55%, b.p. 71. 8–72. 1°C, $n_D^{25} = 1.4295$. IR analysis: no indications for impurities. Glc: impurities in only trace amounts.

Pentadiene-2, 3. 4-Hydroxypentyne-2 was prepared by condensation of propynylmagnesium bromide and acetaldehyde [10]. Yield 51%, b.p. 61. 5–63°C/30 mm, $n_D^{20} = 1.4474$.

4-Chloropentyne-2 was obtained by chlorination of 4-hydroxypentyne-2 by means of $SOCl_2$ and pyridine [8]. Yield 33%, b.p. 55–58°C/ 85 mm, $n_D^{20} = 1.4504$.

Pentadiene-2, 3 was prepared according to the prescription given for hexadiene-1, 2 [8]. Yield 23%, b.p. 48. 2–48. 8°C (lit. b.p. 48. 265 [15]), $n_D^{20} = 1.4267$. IR analysis: an unknown impurity in low concentration. Glc: next to the main component ($>$ ca. 96%) three unknown components in very low concentrations.

2-Methylpentadiene-2, 3. 4-Hydroxy-4-methylpentyne-2 was prepared from propynylmagnesium bromide and acetone [10]. Yield 49%, b.p. 81–83°C/100 mm, $n_D^{18} = 1.4435$.

4-Chloro-4-methylpentyne-2 was prepared by introducing dry hydrogen chloride into 4-hydroxy-4-methylpentyne-2, at 5–10°C for 45 min. The excess of hydrogen chloride is removed by evacuating the reaction flask. The aqueous layer is separated and the remaining liquid is distilled. The main fraction boils at 61–63°C/98 mm; $n_D^{18} = 1.4471$. Yield 92%.

2-Methylpentadiene-2, 3 was prepared according to the prescription given for hexadiene-1, 2 [8]. B.p. 71. 2–71. 5°C, $n_D^{20} = 1.4312$, yield 11% (lit. b.p. 72°C/760 mm, $n_D^{20} = 1.425$ [15]). IR analysis: no indications for compounds containing triple bonds or conjugated systems. Glc: some unknown compounds in very low concentrations.

2, 4-Dimethylpentadiene-2, 3 was prepared according to a prescription given in an Eastman Technical Data Report [11]. Into a quartz tube (57 $\times$ 3. 1 cm) filled over a length of 35 cm with quartz pieces, heated in a furnace at 450–460°C, was introduced 70 g (0. 5 mole) of preheated 2, 2, 4-trimethyl-3-hydroxy-3-pentenoic acid–β-lactone in a slow stream, diluted with nitrogen, in 2 hr. The pyrolyzate was collected in a flask cooled at −15°C. The effluent gas is mainly carbon dioxide. The pyrolysate was fractionated in an effective column. The colorless main fraction boiled at 87. 1–87. 6°C. Yield 38 g (80%). $n_D^{20} = 1.4415$ (lit. $n_D^{20} = 1.4405$). IR analysis: a

compound with a $=CH_2$ group is present in small amounts; no ketene is present, no groups containing oxygen. Glc (silanated Apiezon, 70°C): some unknown impurities are present in traces and very small concentrations.

Tetraphenylallene [12, 13] was prepared by heating a mixture of 12. 5 g (0. 064 mole) of diphenylketene, 22. 5 g (0. 052 mole) of triphenylphosphine diphenylmethylene [14], and 15 ml of benzene in a sealed tube at 140°C for 2 hr. When the reaction product is cooled and some precipitate is removed, the solvent is distilled off and the residue is crystallized from acetone. The first crystallizing fraction melts at 155–156°C. The fraction that crystallizes later melts at 163–164°C. It can be purified by repeated recrystallization, giving a perfectly white solid that melts at 165°C. Yield 6 g (33%). %C: 94. 2% (calc. 94. 18%); %H: 5. 9% (calc. 5. 82%). IR analysis: no indications for the presence of triple bonds or conjugated systems.

Acknowledgments

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Zusammenfassung

Die Polymerisation verschiedener Allene unter Einfluss des Al-i-Bu$_3$-VOCl$_3$ Katalysators und die Struktur und Eigenschafte der Polymere sinduntersucht worden. Allen; Butadien-1, 2; Hexadien-1, 2; 3-Methylbutadien-1, 2; 3-Methylpentadien-1, 2; und Pentadien-2, 3 könnten polymerisiert werden zu löslichen festen Polymeren, aber 2-Methylpentadien-2, 3; Tetramethylallen; und Tetraphenylallen zeigten unter diesen Umständen keine Polymerisationsfähigkeit. Es setzt sich heraus, dass die Polymerisationsfähigkeit abnimmt in der Reihefolge: $CH_2=C=CH_2 > R_1CH=C=CH_2 \geqslant R_1CH=C=CHR_2 > R_1R_2C=C=CHR_2 \simeq R_1R_2C=C=CR_3R_4$.

Die Polymere der Allenhomologe sind amorphe feste Körper, mit Ausnahme des Poly (3-Methylbutadien-1, 2) das kristallin ist.

Die Struktur der Polymere und das Polymerisationsmechanismus wird diskutiert.

Résumé

La polymérisation de quelques carbures alléniques par l'initiateur Al-i-Bu$_3$-VOCl$_3$ et la structure et les propriétés des polymères obtenues ont été étudié. L'allène; le 1, 2-hexadiène-1, 2; le 3-méthylbutadiène-1, 2; le 3-methylpentadiène-1, 2; aussi que le pentadiène-2, 3 donnent des polymères solides et solubles. Le 2-méthylpentadiène-2, 3; le tetraméthylallène; et le tetraphénylallène ne sont pas réactifs sous cettes conditions. L'activité de polymérisation décroit dans l'ordre $CH_2=C=CH_2 > R_1CH=C=CH_2 \geqslant R_1CH=C=CHR_2 > R_1R_2C=C=CHR \simeq R_1R_2C=C=CR_3R_4$.

La structure des polymères a été examiné en résonance magnétique nucléaire et par spectrographie infrarouge.

Un mécanisme de polymérisation pour les diverses types de monomères est proposé.