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![Figure 1](image)

1961

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

CHEMISTRY

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POLYMERIZATION OF HEPTENE-1 ON THE CATALYTIC SYSTEM

$Al(\mathbf{iso}\text{-}C_4H_9)_3 + TiCl_4$

To elucidate the mechanism of polymerization of α-olefins on complex organometallic catalysts and to establish the relationship between the structure of the starting hydrocarbons and the properties of the polymers formed, the study of the polymerization of straight-chain olefins C_6—C_8, which give very low-melting polymers, is of considerable interest. It is assumed (^{1}) that the melting temperatures of polyolefins obtained from C_6—C_8 α-olefins lie in the minimum temperature region for this class of polymers owing to steric difficulties in the ordered packing of polymer chains. In the periodical literature, investigation of the polymerization of higher homologs of the α-olefin series is limited to only two papers (^{2,3}), dealing with questions of the polymerization of α-hexene.

Fig. 1. Dependence of the yield of polyheptene on temperature at the ratio $Al(iso\text{-}C_4H_9)_3 : TiCl_4 = 1 : 1$

In the present work, the polymerization of heptene-1 with the catalytic system $Al(iso\text{-}C_4H_9)_3 + TiCl_4$ in the absence of solvent was studied. Preliminary experiments showed that the greatest conversion of monomer is attained at an equimolar ratio of the catalyst components. The influence of polymerization temperature is shown graphically in Fig. 1, from which it follows that the optimal conversion was observed at a temperature of about 60°, which approximately corresponds to the optimal polymerization temperatures of other α-olefins under comparable conditions.

A similar picture is given by the temperature course of the intrinsic viscosity of polyheptene, shown in Fig. 2a. An increase in temperature evidently leads to some destruction of the polymer under the influence of the catalyst, which also causes a decrease in its intrinsic viscosity, which, as in other polymers, also

Fig. 2. Dependence of $[\eta]$ of polyheptene: a —on the polymerization temperature at the ratio $Al(iso\text{-}C_4H_9)_3 : TiCl_4 = 1 : 1$; b —on the ratio $Al(iso\text{-}C_4H_9)_3 : TiCl_4$ at 50°

Figure 2: Fig. 2. Dependence of $[\eta]$ of polyheptene: a —on the polymerization temperature at the ratio $Al(iso\text{-}C_4H_9)_3 : TiCl_4 = 1 : 1$; b —on the ratio $Al(iso\text{-}C_4H_9)_3 : TiCl_4$ at 50°

depends on the ratio between the catalyst components. The greatest values of the intrinsic viscosities are reached within the range of $AlR_3/TiCl_4$ values equal to 1.5—2.5 (see Fig. 2b). $[\eta]$ is the intrinsic viscosity in decalin at 95°.

The molecular weight of polyheptene obtained under optimal conditions and representing a viscous glassy product is, according to ebullioscopic determination, approximately 3500. The melting temperature of polyheptene was —40°. X-ray structural analysis gave an X-ray diffraction pattern characteristic of a completely amorphous substance (see Fig. 3, see insert to p. 557).

The structure of the polymer was studied by means of infrared absorption spectra. Fig. 4 presents the infrared spectrum of polyheptene,

To the article by L. S. Palatnik and N. T. Gladkikh, p. 567

Fig. 2. X-ray diffraction patterns of a copper condensate on substrates at various temperatures (λK_αCu):
a —$t = 130°$ (region I);
b —$t = 175°$ (region II);
c —$t = 215°$ (region III);
d —$t = 245°$ (region III)

Fig. 4. Electron micrographs of silver films of various thicknesses, 75,000× (7)

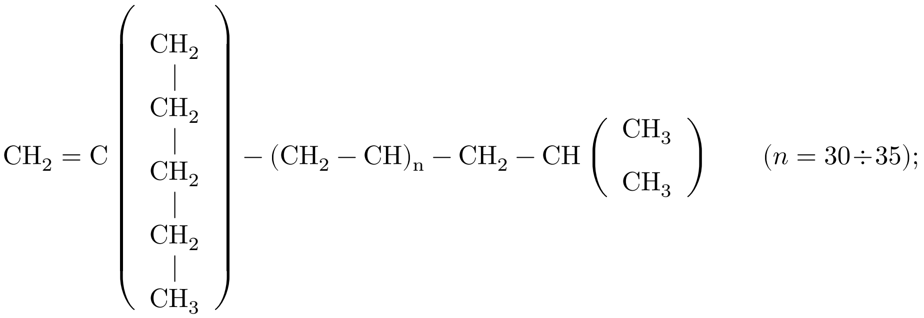
To the article by A. V. Topchiev, B. A. Krentzel, V. V. Dal̓ , and V. D. Opengheim, p. 614

Fig. 3. X-ray diffraction pattern of polyheptene

obtained on an IKS-14 spectrophotometer. The spectrum shows bands with maxima at 1460, 767, and 725 cm^{-1}, corresponding to absorption by CH_2 groups, the last of which corresponds to absorption by a polymethylene chain consisting of at least 4 $-CH_2-$groups. The absorption band at about 890 cm^{-1} corresponds to out-of-plane deformation vibrations of the C—H bond in the system $R_1R_2C{=}CH_2$; the presence of an isopropyl group is indicated by absorption at about 1170, 1145, and a shoulder at 1347 cm^{-1} on the band at 1382 cm^{-1}.

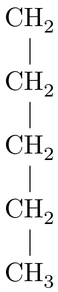
Fig. 2. Dependence of $[\eta]$ of polyheptene: **a** —on the polymerization temperature at the ratio $Al(iso\text{-}C_4H_9)_3 : TiCl_4 = 1 : 1$; **b** —on the ratio $Al(iso\text{-}C_4H_9)_3 : TiCl_4$ at 50°.

Thus, the corresponding characteristic absorption of individual structural groups permits the following structure of the polyheptene molecule to be proposed:



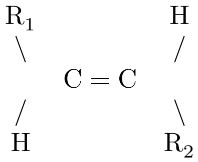
$$\mathrm{CH_2=C}\begin{pmatrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_3}\end{pmatrix}-\mathrm{(CH_2-CH)_n-CH_2-CH}\begin{pmatrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{pmatrix}\qquad (n=30\div35);$$

with, at the CH unit in the chain,



$$\begin{matrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_3}\end{matrix}$$

However, the presence in the spectrum of an absorption band at about 972 cm^{-1}, corresponding to out-of-plane deformation vibrations of C—H bonds of an olefinic group



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indicates the possibility that a double bond is present in the middle of the polymer chain. This question requires further clarification.

Experimental Part

The starting monomer was obtained by pyrolysis at 540-550° of heptyl acetate[4], prepared by acetylation of n-heptanol. After the usual washing and drying, the olefin obtained was freed from traces of alcohol and diene compounds formed

Fig. 4. Infrared absorption spectrum of polyheptene

Figure 3: Fig. 4. Infrared absorption spectrum of polyheptene

incidentally during pyrolysis by boiling for 60 hours over metallic sodium; it was then rectified over metallic sodium on a packed column equivalent in separating capacity to approximately 70 theoretical plates. The pure olefin was characterized by the following constants:

	b.p., °C (at 760 mm Hg)	n_D^{20}	d_4^{20}	MR
Found	93.5	1.3998	0.69696	34.134
Literature data	93.64	1.3998	0.69698	34.059

The monomer was stored under an atmosphere of purified argon over metallic sodium. Molecular-spectral examination showed that the monomer was individual *n*-heptene-1, without impurities. Triisobutylaluminum was used in a heptane solution and, according to analysis for alkyl content,

groups had a concentration of 0.52 g/ml. Titanium tetrachloride used was commercial, chemically pure grade, distilled over fresh copper turnings at 136°, and was used as a solution of concentration 0.1 g/ml in cyclohexane. Polymerization of *n*-heptene-1 was carried out in rotating sealed glass ampoules, $V = 40$ ml, placed in a thermostat. In all experiments bulk polymerization was carried out, without solvent; the total concentration of catalyst in the monomer everywhere amounted to 5% by weight.

For accurate measurement, both the monomer and the catalyst components were dosed by means of a 1-ml microburette with a scale division of 0.01 ml, with two-

Fig. 4. Infrared absorption spectrum of polyheptene

way stopcocks and a bent outlet, entering into a ground-glass four-socket manifold attached to the burette, connected with 4 ampoules. The entire system was evacuated several times and flushed with argon freed of moisture and oxygen. Before filling, the evacuated ampoules were cooled with dry ice, and from the burette the measured quantities of reagents entered them in the following sequence: triisobutylaluminum, the first portion of monomer, titanium tetrachloride, the second portion of monomer.

At the end of the experiment the ampoule was opened, and the contents, in order to decompose the catalyst residue, were treated with methanol acidified with hydrochloric acid. The viscous polymer mass obtained was dissolved in boiling diethyl ether, the solution was filtered, and the polymer was precipitated in the cold with methanol; then dissolution and precipitation of the polymer were repeated, after which the polymer was extracted and dried in a special vacuum apparatus at room temperature to constant weight. The polyheptene treated in this way contained:

Found, %: C 85.89; H 14.11; ash –not detected.
Calculated, %: C 85.67; H 14.23

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Received
29 V 1961

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Note: Figure translations are in progress. See original paper for figures.