Academician A. V. TOPCHIEV, B. A. KRENTSEL, I. M. TOLCHINSKY

and G. V. GARNISHEVSKAYA

1957

SovietRxiv

Abstract

Full Text

Chemistry

Academician A. V. TOPCHIEV, B. A. KRENTSEL, I. M. TOLCHINSKY
and G. V. GARNISHEVSKAYA

ON THE PREPARATION OF CRYSTALLINE POLYPROPYLENE BY POLYMERIZATION OF PROPYLENE ON AN ORGANOMETALLIC CATALYST

Recently the chemistry of polymeric compounds has been enriched by new methods of polymerization—stereospecific polymerization, which makes it possible to obtain stereoregular crystalline poly-α-olefins. In the works of Natta and coworkers [1], who discovered this method, extensive data are given characterizing the structure and properties of stereoregular (called by them isotactic) polymers. However, the articles published on this question contain almost no data concerning the conditions for the synthesis of such polymers. Among the new types of compounds, polypropylene, which possesses a number of valuable properties, is of great interest. In connection with this, it seemed of interest to elucidate the conditions for obtaining crystalline polypropylene.

Experimental Part

The starting propylene was obtained by dehydration (over aluminum oxide at 350°) of isopropyl alcohol and contained 99.2% C_3H_6 and 0.8% $N_2 + O_2$; in a number of experiments a propylene-propane fraction of petroleum gas was used, containing C_3H_6 85.1%, O_2 0.2%, N_2 0.8%, CO_2 0.2% (the remainder C_3H_8 and a small admixture of C_2H_4 and n-C_4H_8).

Triethylaluminum in combination with titanium tetrachloride was used as the polymerization catalyst. The triethylaluminum was prepared by the previously described method [2]. Polymerization was carried out both at atmospheric and at elevated pressures. The apparatus for polymerization at atmospheric pressure is shown in Fig. 1.

Propylene from the cylinder (1), through a gas meter (2) and a rheometer (3), entered the system for purification from oxygen and other impurities. The purification system consisted of an electric furnace (4) with a copper packing, in which a temperature of about 350° was maintained, and also of three scrubbers (5, 6, 7), filled respectively with granular caustic soda, ascarite, and activated aluminum oxide; when working with the technical propylene-propane fraction,

Fig. 1. Diagram of the apparatus for polymerization of propylene at atmospheric pressure

Figure 1: Fig. 1. Diagram of the apparatus for polymerization of propylene at atmospheric pressure

before the scrubbers an absorber filled with 68% H_2SO_4 was connected in order to free the gas from the admixture of $n\text{-}C_4H_8$.

From the purifier the gas, through a forcontact bottle (8) with a solution of triethylaluminum (or bypassing it), entered the reactor (9). The reactor was a glass vessel of 500 ml capacity, equipped with a high-speed stirrer, a reflux condenser, and a thermometer. With the aid of a thermostating jacket, a definite temperature was maintained in the reactor.

Into the reactor, previously evacuated and purged with nitrogen from a cylinder (12) through an ordinary purification system (13—17), a solvent was charged; the solvent used was previously treated ···

“kalosha” gasoline with $d_4^{20} = 0.7254$ and a boiling point in the range 85–115°. The required amount of catalyst was charged into the same reactor with the aid of special devices (not shown in the diagram). The unreacted gas was discharged to the atmosphere through a reflux condenser and a Tishchenko bottle (10), filled with a high-boiling hydrocarbon, and a gas meter (11).

After completion of the experiment, the reactor was cooled to +10°, and the contents were treated with absolute methanol under stirring in order to decompose the remaining catalyst. The precipitated polypropylene was filtered off and washed repeatedly with methanol and water. The polypropylene was then dried at 60–70° to constant weight and subjected to further studies.

Fig. 1. Diagram of the apparatus for polymerization of propylene at atmospheric pressure

Experiments under slight pressure (4-6 atm.) were carried out in a 1-liter autoclave made of stainless steel and equipped with a paddle stirrer ($n = 180$ rpm).

Preliminary experiments showed that, in polymerization both at atmospheric pressure and at elevated pressure, the best results are obtained at temperatures close to 50°.

As can be seen from Table 1, practically identical results were obtained when working with pure and technical-grade propylene.

Increasing the pressure to 5-6 atm. made it possible to increase substantially the degree of conversion of propylene and to obtain a polymer yield of up to 150 g per liter of reaction volume in approximately the same reaction time. A sample of polypropylene obtained at atmospheric pressure under the indicated conditions (Table 1) was investigated in the laboratory of M. V. Vol’ kenshtein.*

The X-ray diffraction pattern of the polypropylene (without investigation of texture) showed the presence of sharp rings characteristic of a crystalline material. The microphotogram—the blackening curve—showed no visible differences from that reported by Natta. However, the "percent crystallinity" could not be determined by this method.

Investigation of the infrared absorption spectrum of polypropylene over a wide temperature range showed the presence of bands characteristic of the amorphous portion of the material, which increase sharply upon melting.

The melting temperature proved to be practically identical to that reported by Natta. A quantitative estimate, based on determination of the relative intensity of the "amorphous" absorption bands, indicates that this polypropylene sample is approximately 75% crystalline material.

In order to determine the influence of the molar ratios between the catalyst components on the intrinsic viscosity of polypropylene, a series of experiments was carried out in which the ratio $Al(C_2H_5)_3 : TiCl_4$ was varied. With an increase in this ratio, the intrinsic viscosity (determined in decalin at a temperature of 150°) increases, and the melting temperature of polypropylene correspondingly rises to 160–165°.

Table 1

Results of the polymerization of propylene at atmospheric pressure

Starting material	$Al(C_2H_5)_3$, mol.	$TiCl_4$, mol.	Amount of catalyst, g per 100 g of substance	Benzene added, l	Unreacted propylene remaining, l	Duration of reaction, h	Propylene conversion, %	Intrinsic viscosity
Propylene, alcohol grade	5	1	5	70	55	3.0	21.4	0.90
Technical propylene fraction	5	1	5	68	54	3.0	20.5	0.86

---

* We express our gratitude to L. A. Volkova and E. I. Pokrovsky, who carried out the investigation.

Received
25 III 1957

CITED LITERATURE

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

2. A. V. Topchiev, B. A. Krentsel, N. F. Bogomolova, Yu. Ya. Goldfarb, *DAN*, **111**, No. 1 (1956).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.