Academician A. V. TOPCHIEV and V. N. ANDRONOV

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Academician A. V. TOPCHIEV and V. N. ANDRONOV

POLYMERIZATION OF ISOBUTYLENE IN THE PRESENCE OF MONOFLUOROPHOSPHORIC AND DIFLUOROPHOSPHORIC ACIDS AND A MOLECULAR COMPOUND OF MONOFLUOROPHOSPHORIC ACID WITH BORON FLUORIDE

The most studied among fluorine compounds used as catalysts in the polymerization reaction of olefins are boron fluoride and hydrogen fluoride. The catalytic properties of other fluorine compounds have been studied very little.

During the last decade, a number of methods have been developed for synthesizing new fluorine compounds—monofluorophosphoric and difluorophosphoric acids ([1]-[4]). The catalytic properties of these compounds have not yet been studied.

The authors of the present article studied the polymerization reaction of propylene in the presence of monofluorophosphoric and difluorophosphoric acids. The catalytic properties of a molecular compound of monofluorophosphoric acid with boron fluoride in the polymerization reaction of propylene were also studied ([5]). In the present work, the polymerization reaction of isobutylene was studied in the presence of fluorophosphoric acids and their compounds with boron fluoride. For comparison, the polymerization reaction of isobutylene in the presence of a molecular compound of orthophosphoric acid with boron fluoride was also studied.

The polymerization of isobutylene was carried out in the same apparatus as the polymerization of propylene. Into a reactor filled with a carrier moistened with catalyst, at a definite temperature, isobutylene was fed after preliminary drying in a column with calcium chloride. The polymerization products were cooled and collected in a receiver. The olefin not entering into the reaction was collected in a gasometer.

It was established that isobutylene is readily polymerized both in the presence of monofluorophosphoric and difluorophosphoric acids and in the presence of a molecular compound of monofluorophosphoric acid with boron fluoride. Polymer formation proceeds at a high rate and with high yield.

Fig. 1. Distillation curves of polyisobutylene. I: t = 15°; H_2PO_3F + silica gel; II: t = 100°; H_2PO_3F + silica gel; III: t = 152°; H_2PO_3F + activated carbon; IV: t = 152°; H_2PO_3F + silica gel

Figure 1: Fig. 1. Distillation curves of polyisobutylene. I: t = 15°; H_2PO_3F + silica gel; II: t = 100°; H_2PO_3F + silica gel; III: t = 152°; H_2PO_3F + activated carbon; IV: t = 152°; H_2PO_3F + silica gel

The degree of polymerization of isobutylene is substantially influenced by the nature of the catalyst used, the carrier, the temperature of the experiment, and the duration of catalyst operation.

To clarify the influence of the carrier and the temperature of the experiment on the composition and yield of isobutylene polymers, a series of experiments was carried out on the polymerization of isobutylene in the presence of monofluorophosphoric acid deposited on silica gel and activated carbon, at temperatures of 15, 100, and 152°.

For each experiment, 50 l of isobutylene and 20 ml of monofluorophosphoric acid deposited on 90 ml of carrier were taken. The olefin was fed into the reactor at a rate of 5 l per hour.

The conversion of isobutylene to polymer in all experiments was 100%, with the exception of the experiment on polymerization of isobutylene over monofluorophosphoric acid deposited on silica gel at 152°. The conversion of olefin in this experiment was 93%.

As can be seen from Fig. 1, as the experimental temperature was raised the polymer obtained was considerably lighter, and the content of the diisobutylene dimer and trimer fractions increased at the expense of a decrease in the amount of high-boiling polymers.

Polymers obtained in the presence of monofluorophosphoric acid deposited on silica gel were lighter than polymers obtained in the presence of the same catalyst deposited on activated carbon. The difference in the fractional composition of the polymers was especially noticeable when the experiments were carried out at 152°.

In the polymerization of isobutylene in the presence of monofluorophosphoric acid deposited on activated carbon and on silica gel, as the experimental temperature was raised, a noticeable increase was observed in the amount of the intermediate fraction boiling within the range 106–175°. This increase in the amount of the intermediate fraction is explained by the fact that the main polymerization reaction was accompanied by the isomerization reaction of the diisobutylene fraction.

Fig. 1. Distillation curves of polyisobutylene. *I*: $t = 15°$; H_2PO_3F + silica gel; *II*: $t = 100°$; H_2PO_3F + silica gel; *III*: $t = 152°$; H_2PO_3F + activated carbon; *IV*: $t = 152°$; H_2PO_3F + silica gel

The isomerization of olefinic hydrocarbons is a quite usual phenomenon in polymerization in the presence of certain catalysts (for example, $AlCl_3$, $ZnCl_2$, etc.) and accompanies the polymerization reaction even at the stage of formation of dimeric forms.

The yield of isobutylene polymers when monofluorophosphoric acid deposited on activated carbon was used as the catalyst was considerably higher than the polymer yield obtained when the same amount of catalyst deposited on silica gel was used.

To determine the yield and the duration of operation of the catalyst, isobutylene was passed continuously at a rate of 5 liters per hour through a reactor into which 90 ml of support and 20 ml of catalyst were placed. After 50 liters of gas had been passed through, the conversion of isobutylene was noted, and the polymer was drained from the receiver and distilled in a rectification column.

In experiments carried out at 15° using silica gel as the support, the conversion of isobutylene had already fallen to 62% in experiment No. 4, whereas in the presence of monofluorophosphoric acid deposited on activated carbon, the conversion of isobutylene in experiment No. 10 was 100%. The same pattern was also observed at temperatures of 100 and 152°.

The more rapid decrease in the catalytic activity of monofluorophosphoric acid deposited on silica gel, and the lighter polymers obtained when this support was used (in comparison with H_2PO_3F deposited on activated carbon), is apparently explained by the fact that monofluorophosphoric acid interacts chemically to some extent with silica gel. As a result, the composition of the catalyst changes somewhat, which leads to an increase in the yield of light fractions and a decrease in the catalytic activity of the catalyst.

As the catalyst operated, a considerable decrease was observed in the specific gravity and refractive index of the polymer, and a considerable increase in the content of light fractions in the polymerizate. For example, in experiments carried out in the presence of H_2PO_3F on carbon at 152°, in experiment No. 1 the polymer had $d_4^{20} = 0.7511$, $n_D^{20} = 1.4303$, and contained 27% of the diisobutylene fraction. In experiment No. 10 the polymer had $d_4^{20} = 0.7206$, $n_D^{20} = 1.4219$, and contained 56% of the dimer fraction. In experiment No. 30 an even greater decrease in specific···

weight ($d_4^{20} = 0.7176$) and refractive index ($n_D^{20} = 1.4142$), and an increase in the content of the diisobutylene fraction (up to 69%).

The duration of the acid' s action in the polymerization reaction, and consequently its consumption, is a very important characteristic determining the technical suitability of the catalyst.

The authors of this article studied the duration of action of monofluorophosphoric acid deposited on activated carbon in the polymerization reaction of isobutylene at 152°. The catalyst consumption was rather low and amounted to

Fig. 2. Fractional composition of isobutylene polymers obtained with various catalysts: I: H2PO3F; II: H2PO2F2; III: H3PO4 • BF3; IV: H2PO3F • BF3

Figure 2: Fig. 2. Fractional composition of isobutylene polymers obtained with various catalysts: I: H2PO3F; II: H2PO2F2; III: H3PO4 • BF3; IV: H2PO3F • BF3

1.45% (by weight), with a comparatively high conversion of isobutylene in the last experiment (equal to 56%).

Table 1

Polymerization of isobutylene in the presence of difluorophosphoric acid at 15 and 100°

Experiment temp., °C	Polymer obtained, g	d_4^{20}	n_D^{20}	b.p. 106	106–175	175–183	residue
15	110	0.7648	1.4359	6	4	59	31
100	110	0.7931	1.4452	5	6	15	74

In Table 1 are given data on the polymerization of isobutylene in the presence of difluorophosphoric acid deposited on activated carbon at temperatures of 15 and 100°. For each experiment, 50 l of isobutylene were taken.

From Table 1 it is seen that, in the polymerization of isobutylene in the presence of difluorophosphoric acid deposited on activated carbon, the polymer obtained at 15° was somewhat lighter than the polymer obtained at 100°. At the same time, at 15°, at the beginning of the experiment, rather strong gumming of the catalyst was observed, evidently as a consequence of the formation on the catalyst surface of catalytically weakly active products of olefin addition to the catalyst (apparently of the ester type). At 100° the formation of these products was observed to a lesser degree, since at this temperature the products of olefin addition to the catalyst are not stable. As a result, better contact was ensured between the catalyst surface and isobutylene, and the polymers obtained had a higher specific gravity and contained fewer low-boiling fractions.

Fig. 2. Fractional composition of isobutylene polymers obtained with various catalysts:
$I:$ H_2PO_3F; $II:$ $H_2PO_2F_2$; $III:$ $H_3PO_4 \cdot BF_3$; $IV:$ $H_2PO_3F \cdot BF_3$

The distillation curves of isobutylene polymers obtained in the presence of monofluorophosphoric and difluorophosphoric acids and molecular compounds of orthophosphoric and monofluorophosphoric acids with boron fluoride are presented in Fig. 2, from which it is seen that the degree of polymerization of isobutylene in the presence of the catalysts studied decreases in the following order:

$$H_2PO_3F \cdot BF_3 > H_3PO_4 \cdot BF_3 > HPO_2F_2 > H_2PO_3F.$$

The bromine numbers of the dimer and trimer fractions of isobutylene indicated that the polymers obtained by us consisted mainly of unsaturated compounds.

For the dimer and trimer fractions of isobutylene obtained at 152° in the presence of monofluorophosphoric acid deposited on activated carbon, the chemical composition was studied.

Oxidation of the isobutylene dimer fraction (100–106°) with a 1% solution of $KMnO_4$ established that this fraction consists of two isomers: 2,4,4-trimethylpentene-1 and 1,4,4-trimethylpentene-2.

We have already indicated that, in the polymerization of isobutylene in the presence of monofluorophosphoric acid deposited both on activated carbon and on silica gel, when the experimental temperature was raised to 152°, an increase was observed in the amount of the intermediate fraction boiling within 106–175°. Distillation of this fraction showed that the greater part of it boils within 108–120°. The principal constants of this fraction differ considerably from the constants of Butlerov’ s diisobutylene and are very close to those of 2,3,4-trimethylpentene-2. Consequently, at 152° the polymerization reaction of isobutylene is accompanied by isomerization of the diisobutylene fraction. Spectral analysis by the method of combination scattering of light established that this fraction consists of 2,3,4-trimethylpentene-2.

The chemical composition of the triisobutylene fraction (175–183°) was established by oxidation of this fraction with chromic acid mixture. It was shown that the triisobutylene fraction consists mainly of 1,1-dineopentylethylene and 2,2,4,6,6-pentamethylheptene-3. The presence in this fraction of small amounts of 2,4,4,6,6-pentamethylheptene-1 and 2,4,4,6,6-pentamethylheptene-2 is highly probable.

Institute of Petroleum
Academy of Sciences of the USSR

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