Academician of the Academy of Sciences of the Azerbaijan SSR M. A. Dalin, I. I. Pisman, A. A. Bakhshi-Zade, and A. A. Buniyat-Zade

Copolymers obtained from monoolefins are valuable materials both as elastomers and as plastics.

1960

SovietRxiv

Abstract

Full Text

Chemistry

Academician of the Academy of Sciences of the Azerbaijan SSR M. A. Dalin, I. I. Pisman, A. A. Bakhshi-Zade, and A. A. Buniyat-Zade

Copolymerization of Ethylene with Propylene and α-Butylene on a Chromium Oxide Catalyst

Copolymers obtained from monoolefins are valuable materials both as elastomers and as plastics.

D. Natta ([1]) synthesized copolymers of ethylene with propylene on organometallic catalysts in the presence of heavy-metal chlorides (titanium or vanadium). A copolymer containing 50% ethylene and propylene, in elasticity, surpassed butadiene-styrene rubber and approached natural rubber. A. Clark, J. Hogan, R. Banks, and B. Lanning ([2]) studied the copolymerization of ethylene with propylene, α-butylene, and other α-olefins on a chromium oxide catalyst. The copolymer obtained from a gaseous mixture of 10 wt.% propylene and 90 wt.% ethylene had a molecular weight and melting point lower than those of polyethylene synthesized under the same conditions. In their work Clark and co-workers give a graph of the dependence of the molecular weight of the copolymer on the reaction temperature. It is indicated that an ethylene–propylene copolymer is more flexible than polyethylene. The authors do not give other properties. Taking into account the importance of copolymers as elastic plastics, we set ourselves the task of synthesizing copolymers of ethylene with propylene and α-butylene and of studying their properties in greater detail. The present article summarizes the first results of this work.

The copolymerization experiments were carried out in a Vishnevskii mercury-free stirrer ([3]) with a capacity of 2000 ml. Extraction gasoline, previously subjected to contact purification with an activated chromium catalyst, was used as the solvent. In all experiments the amount of solvent was 1000 g, of catalyst 5–6 g, and of calcium carbide 1 g.

The catalyst was prepared by a known method ([4]), by impregnating the support with chromic anhydride and subsequent activation with air at 550°. As the support for the chromium catalyst, an industrial aluminosilicate was used, containing approximately 90% SiO_2, 7–8% Al_2O_3, and small amounts of Fe, Ca, and Mg oxides. The pore volume of the aluminosilicate was 62%, and the specific surface area 220–350 m^2/g. The monomers used were the ethylene and propylene fractions of pyrolysis gas. The composition of the ethylene fraction, in volume percent, was: ethylene 99.2–99.6; methane 0.1–0.2; ethane 0.3–0.4; carbon oxides 0.0050 and oxygen up to 0.0005. Sulfur compounds and carbon dioxide were practically absent. The moisture content in the gas did not exceed 10 mg/m^3.

The composition of the propylene fraction of pyrolysis gas, in volume percent, was: propylene 90; propane 8; ethane 0.7-1; C_4 hydrocarbons about 0.1; dienes up to 0.03. The amount of sulfur compounds did not exceed 1 mg/m^3.

The butylenes were obtained by dehydration of *n*-butyl alcohol over aluminum oxide grade A-1, at 360°. The mixture contained 2-3% isobutylene and 97-98% normal butylenes. According to the literature data ([5]), a mixture of butylenes obtained under the indicated conditions contains 75% butene-1 and 22-23% butene-2.

The butylene fraction, in the course of preparation, was dried over fine-pored silica gel and calcium hydride. The amount of residual moisture in the butylenes was not determined.

The gas mixtures were prepared in thoroughly dried metal cylinders. The experiments were usually carried out until the pressure drop in the autoclave ceased. The autoclave was then cooled, the pressure was released, and the copolymer was removed. The copolymer, together with the catalyst, was heated in a vessel with ligroin and then filtered off from the catalyst on a paper filter. The polymer was then washed with ethyl alcohol, dried, and subjected to analysis.

Table 1

Properties of polyethylene and copolymers of ethylene with propylene and α-butylene

Material	Characteristic viscosity (decalin, 135°C)	Melting temperature, °C	Solubility in boiling *n*-heptane, %	Mechanical properties: $\frac{\Delta l}{l}$, %	Mechanical properties: P, kg/cm^2
Polyethylene	1.8	127–130	10	300–490	250–300
Copolymer of ethylene with propylene	1.5	120–122	65	700–1000	190–220
Copolymer of ethylene with α-butylene	1.7	124–126	40	500–800	250–290

Note. $\frac{\Delta l}{l}$ is the relative elongation upon cold drawing; P is the tensile strength.

Table 1 gives the properties of polyethylene, of a copolymer of ethylene with propylene containing 12.6 wt.% propylene and 87.4 wt.% ethylene, and of a copolymer of ethylene with α-butylene containing 7% butylene and 93% ethylene. All samples were obtained at temperatures of 110° and a pressure of 40 atm.

As can be seen from the data in Table 1, the copolymers of ethylene with propylene and α-butylene differ from polyethylene in melting temperatures, solubility in *n*-heptane, and also in relative elongation upon cold drawing.

It is noteworthy that the copolymer of ethylene with propylene is more flexible but less strong than polyethylene. The copolymer of ethylene with α-butylene approaches polyethylene in strength, but surpasses it in elasticity.

Received
5 II 1960

CITED LITERATURE

1. G. Natta, G. Grespi, *Chimica e Industr.*, **41**, No. 2, 123 (1959).
2. A. Clark, I. Hogan et al., *Ind. and Eng. Chem.*, **48**, No. 7, 1152 (1956).
3. B. Korndorf, *High-Pressure Technique*, Moscow, 1952.
4. Belgian Patent No. 530617, January 24, 1955.
5. V. G. Zizin, M. R. Musaev, *ZhP Kh*, vol. 5, 803 (1956).

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