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Abstract

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CATALYSTS BASED ON MAGNESIUM HALOALKYLS AND TITANIUM TETRACHLORIDE FOR THE SYNTHESIS OF AMORPHOUS AND CRYSTALLINE POLYMERS FROM α-OLEFINS AND DIENES

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The preparation of polymers from aliphatic compounds of the ethylene series by initiating polymerization with free radicals is possible only for the first member of this series—ethylene. The interaction of free radicals with ethylene homologues leads to the formation of low-molecular-weight products as a result of termination reactions at the first stages of development of the process ([1]). Ziegler and co-workers used the reaction between organoaluminum compounds and titanium tetrachloride to initiate the polymerization of ethylene ([2]). Further investigations in this field ([3]) led to the discovery of the possibility of initiating the polymerization of olefins, accompanied by the formation of uniformly constructed (isotactic) polymers. Later it was shown that the organoaluminum compounds in the Ziegler catalyst can be replaced by other organometallic derivatives, in particular by sodium and lithium compounds. For example, the systems C_2H_5Na—$TiCl_4$ or C_4H_9Li—$TiCl_3$ also induce the polymerization of ethylene ([4,5]). The mechanism of these reactions cannot yet be regarded as established. It is known that the reaction between the components of the Ziegler catalyst is of an oxidation–reduction character and leads to the formation of titanium derivatives of lower valence states ([6]). Along with this, the formation of hydrocarbons, for example ethane and ethylene, is observed when triethylaluminum is used. Very similar phenomena are also observed in the interaction between salts of heavy metals and organomagnesium compounds.

N. V. Kondyrev and D. A. Fomina ([7]), to whom the first work in this field belongs, showed that the reaction between magnesium haloalkyls and salts of various metals (iron, copper, cobalt, nickel, chromium, molybdenum) leads to the formation of: (a) equivalent amounts of saturated and unsaturated hydrocarbons corresponding to the alkyl of the organomagnesium compound, and (b) reduced forms of heavy metals. Further study of these reactions ([8–10]) led to the conclusion that they proceed through the stage of formation of unstable organic

compounds of heavy metals, the decomposition of which is most often regarded as a free-radical process. On this basis it seemed likely that the reaction between organomagnesium halide compounds and titanium tetrachloride would make it possible to arrive at results analogous to those achieved by Ziegler and Natta with organoaluminum compounds. It must be pointed out that in reactions of the type under consideration, complex-forming agents (ethers, sulfides, oxygen), which can exert a substantial influence on the course of the polymerization process and on the structure of the chain, play a significant role. As is known, magnesium-

organic compounds give strong complexes with ether, which are destroyed only under conditions of prolonged thermal treatment at 150°. We have established that the interaction of organomagnesium compounds of the type R—MgHal with $TiCl_4$ leads to the formation of catalytic complexes that effectively initiate the polymerization of monomers only under the condition of preliminary complete liberation of the magnesium derivatives from ether, as was shown for magnesium chloroethyl, magnesium bromoethyl, and magnesium bromooctyl. In the experimental respect it is convenient to use organomagnesium compounds in the form of dispersions in paraffin. To obtain the latter, the process of destroying the ether complex is carried out in a paraffin medium, which leads to the formation of a fine dispersion, very stable to moisture and not losing its activity for a long time when stored in air.

The effectiveness of the R—MgHal—$TiCl_4$ system for initiating the polymerization process was demonstrated by us with ethylene, propylene, styrene, and isoprene. Ethylene polymerization proceeds without the application of pressure or external heating. The reaction begins almost immediately after ethylene starts to be passed through a suspension of the organomagnesium compound in benzene containing a small amount of titanium tetrachloride. The polyethylene obtained in this way has $[\eta] = 2.55$ (measured in decalin at 135°), m.p. 130—138°, tensile strength 335 kg/cm^2, and relative elongation 730%. These values are analogous to those possessed by polyethylene obtained with the aid of the usual Ziegler catalyst. Of great interest are the data established by us in the polymerization of propylene. In one of Natta' s papers ([11]) it is stated that replacement of organoaluminum compounds in the Ziegler catalyst by organomagnesium compounds excludes the possibility of obtaining isotactic polymers from α-olefins.

As we have shown, in the polymerization of propylene in the presence of magnesium chloroethyl and titanium tetrachloride, approximately equal amounts of amorphous and crystalline (isotactic) forms of the polymer are formed. The amorphous form, soluble in ether, has a glass-transition temperature of −35° and $[\eta] = 0.57$ (in benzene). Along with it, a fraction insoluble in boiling hexane was isolated, the crystallinity of which was proved by spectroscopic and X-ray structural analysis.

Different forms of polymers were also isolated in the case of isoprene polymerization. When the polymerization of the latter was carried out under the influence

of the same components, the following were obtained: 1) a fraction soluble in benzene, containing 87% cis-1,4 units, and 2) an insoluble form containing, according to IR spectrum data, only trans-1,4 units*.

The simultaneous production of cis-1,4-polyisoprene and trans-1,4-polyisoprene, or of amorphous and isotactic polypropylene, is a direct indication that catalytic complexes of different types coexist in the system, leading to the formation of a polymer structure specific to the given complex.

Experimental Part

Synthesis of magnesium haloalkyls. To obtain organomagnesium compounds free of ether, the procedure described by Grignard ([12]) was used, according to which the solvent was distilled off from the ethereal solution of the organic magnesium derivative and the residue was subjected to 30-hour heating at 150–160° in vacuum (10 mm). The resulting white porous mass was ground in a stream of dry nitrogen. To obtain a dispersion of the organomagnesium compound in paraffin,

* Spectroscopic and X-ray studies of the polymers were carried out by E. I. Pokrovskii and L. A. Volkova.

the latter was introduced into the reaction flask after distillation of the bulk of the solvent.

Polymerization of ethylene. Into a suspension of magnesium chloroethyl and $TiCl_4$ in a gasoline fraction (b.p. 90–110°), with vigorous stirring, thoroughly dried ethylene was bubbled. The initial temperature was 20°. By the end of the process the temperature had risen to 50°. Termination of the polymerization process at a definite stage is achieved by adding alcohol.

Polymerization of propylene. The reaction was carried out in a 1.5-liter autoclave equipped with a stirrer, with a charge of 500 ml of benzine and the necessary amount of magnesium chloroethyl and $TiCl_4$. Pressure 6–9 atm. Duration of the reaction at 80°: 1 hour. Polymer yield 115 g.

Polymerization of isoprene. Into a 4-liter autoclave with a stirrer were charged: 1 l of benzine, magnesium chloroethyl, $TiCl_4$, and 0.5 l of isoprene. Duration of the reaction: 1 hour at 70–80°. Polymer yield 200 g. The fraction soluble in benzene (63% of the total amount) contains 87% cis-1,4 units, 5% trans-1,4 units, 3% 1,2 units, and 5% 3,4 units. The insoluble polymer (37%) is 100% 1,4-trans-polyisoprene.

Polymerization of styrene. 20 g of styrene was vigorously stirred with a solution of 0.4 g $TiCl_4$ in 60 ml of benzine, containing 0.5 g of magnesium chloroethyl as a suspension, at 60° for 1 hour. The polymer yield was quantitative.

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