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Table 1

1964

SovietRxiv

Abstract

Full Text

CHEMISTRY

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POLYMERIZATION OF CERTAIN OLEFINIC AND VINYL MONOMERS ON DIETHYLBUTEN-1-YL-1-ALUMINUM IN THE PRESENCE OF TITANIUM HALIDES

Conventional Ziegler–Natta catalysts, effective in the polymerization of nonpolar or weakly polar monomers, prove inactive or only slightly active when attempts are made to polymerize polar monomers and, conversely, active catalytic systems for the polymerization of polar monomers are only slightly active in the polymerization of nonpolar monomers ([1–4]). It has been pointed out that this difference in catalyst activity is due to the different reducing ability of the catalytic systems used. To obtain polymers from polar monomers it is necessary to use catalytic systems that include an organoaluminum compound with reduced reducing ability ([1,2,5]). The literature ([6]) describes the preparation and gives certain properties of the products of addition of acetylene to aluminum trialkyls that contain a multiple bond. The first compound of a new type of aluminum trialkyls with a double bond directly adjacent to aluminum is diethylbuten-1-yl-1-aluminum (DEBA).

Table 1

Polymerization of olefinic and vinyl monomers on the catalytic system diethylbuten-1-yl-1-aluminum—titanium chloride*

Monomer type	Monomer amount, g	Solvent (benzene), g	Catalytic system: diethylbutenylaluminum, g	Catalytic system: titanium tetrachloride, g	Modifying additive: type	Modifying additive: amount, g	T, °C	Time, h	Yield of crystalline polymer, g	Appearance	$[\eta]$	Content of atactic configuration (heptane-washed), %	Elemental composition, %
Ethylene **	—	400	11.2	1.89	—	—	60	4	240	White powder	4(2.2)	2.3(2)	—
Propylene	160	680	11.2	1.54	—	—	45	15	110	White powder	2.8(1.5)	9(7)	—
»	160	680	11.2	1.54	Triethylamine	8	45	15	traces	—	—	—	—
Styrene	10	18	2	2.2	—	—	45	15	3.5	Gray block	—	14(8)	—
»	10	18	2	2.2	—	—	90	2	3	Gray block	4.7(2.1)	10(8)	—
Vinyl chloride	400	300	30	5.5	—	—	45	15	39	Gray powder	0.12	—	Cl 52.1–52.9
»	400	300	30	5.5	Triethylamine	11	45	15	24	Gray powder	0.06	—	C 40.3–40.6
»	400	300	30	5.5	Triethylamine	22	45	15	2.5	Gray powder	0.07	—	H 4.9–4.95
Methyl methacrylate ***	10	—	1	—	—	—	45	15	4.2	White block	0.04	—	C 59.8

* The characteristics of polymers obtained on the ordinary Ziegler–Natta catalytic system are given in parentheses.
** $TiCl_3$ was used instead of $TiCl_4$.
*** The yield of amorphous polymer is indicated.

It seemed of interest to us to study the catalytic ability of this compound in the polymerization of certain monomers. The synthesis of DEBA was carried

Fig. 2. Thermomechanical curves of polyolefin hydrocarbons and polyvinyl chloride. I—polypropylene; II—polyethylene; III—polystyrene; IV—polyvinyl chloride.

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out according to ([6]). The completion of the reaction of triethylaluminum with acetylene was determined by the indicator method ([7]), because DEBA is incapable of interacting with methyl violet. In this respect it behaves analogously to alkylaluminum oxy derivatives ([3,7]).

Table 1 presents the results of experiments on the polymerization of ethylene, propylene, styrene, vinyl chloride, and methyl methacrylate (the process was carried out by the method described in ([8])) in the presence of DEBA. It is seen that the individually taken organoaluminum compound is capable of polymerizing, among the selected monomers, only methyl methacrylate. The resulting polymethyl methacrylate was a white powder and, according to analysis, contained 59.8% carbon. It dissolved at room temperature in chloroform, to a limited extent in acetone, and was almost insoluble in dimethylformamide. The limiting viscosity number at 25° in a chloroform solution proved to be $[\eta] = 0.04$.

The X-ray diffraction pattern of the polymethyl methacrylate obtained is shown in Fig. 1a and is characteristic of an amorphous polymer product. Other monomers used, such as ethylene, propylene, styrene, and vinyl chloride, polymerized in the presence of a cocatalytic additive—titanium chloride. The polymerization process was characterized by the following features.

Fig. 2. Thermomechanical curves of polyolefin hydrocarbons and polyvinyl chloride. *I*—polypropylene; *II*—polyethylene; *III*—polystyrene; *IV*—polyvinyl chloride.

1. The polymerization of ethylene and propylene proceeded with high yields and satisfactory process rates. In particular, for propylene the polymerization rate in the presence of DEBA proved to be of the same order as the polymerization rate under the action of ordinary Ziegler—Natta catalysts (although somewhat lower: at 45°, $K_{\text{red}} = 1.75 \cdot 10^{-3}$ l/min • g $TiCl_3$ in the case of DEBA versus $K_{\text{red}} = 3.6 \cdot 10^{-3}$ l/min • g $TiCl_3$ for triethylaluminum). Correspondingly, the yield of polypropylene was also somewhat lower (110 g versus 140 g on the conventional Ziegler—Natta system).

Lower yields (240 g versus 300 g) were also obtained for polyethylene. An analogous, but sharper, dependence was observed in the polymerization of styrene (3.5 g of polymer in the case of DEBA versus 8 g for $(C_2H_5)_3Al$). Polymerization of vinyl chloride proceeded with yields (up to 10%) that are usual for a process occurring in the presence of a Ziegler catalytic system modified by donor agents ([1]).

Fig. 3. Curves of the reducing ability of some organoaluminum compounds: 1 $-\mathrm{Al(C_2H_5)_3}$, 2 $-\mathrm{(C_2H_5)_2AlCl}$, 3 $-\mathrm{(C_2H_5)AlCH{=}CH{-}C_2H_5}$

Figure 2: Fig. 3. Curves of the reducing ability of some organoaluminum compounds: 1 $-\mathrm{Al(C_2H_5)_3}$, 2 $-\mathrm{(C_2H_5)_2AlCl}$, 3 $-\mathrm{(C_2H_5)AlCH{=}CH{-}C_2H_5}$

2. All the polymers obtained from olefin monomers, as well as from vinyl chloride, were crystalline (Fig. 1 b, c, d, e; see insert, p. 1329). However, for polystyrene the degree of crystallinity proved to be somewhat lower. The intensity of X-ray scattering from the angle of irradiation was approximately 2 times less than that of a reference isotactic polystyrene sample. The crystalline structure of the polymers obtained was also manifested in the thermomechanical curves (Fig. 2), which are characteristic of products with a regular structure (compare with ([1,8–10])). This is also indicated by the data on fractional composition (Table 1).

3. Polymers of olefin hydrocarbons have a higher degree of polymerization in comparison with polymers formed in the presence of the system $\mathrm{(C_2H_5)_3Al + TiCl}_n$. The totality of the results obtained makes it poss—

makes it possible to conclude that the catalytic system based on DEBA in combination with titanium chlorides possesses distinctive catalytic properties, allowing the polymerization of both polar and nonpolar monomers. Such behavior of DEBA may be due to a decrease in its electrophilic properties (in comparison with triethylaluminum), as was the case when using $\mathrm{(C_2H_5)_2Al{-}OC_2H_5}$ or $\mathrm{(C_2H_5)_3Al}$ with additions of donor agents. The similarity to the latter is indicated by experimental facts according to which the addition of an amine or ether in an amount of up to one mole per mole of DEBA considerably lowered the yield of polyolefin hydrocarbons, corresponding to inhibition of the polymerization process in the presence of an excess of a nucleophilic compound ([9], [11]), and also by an increase in molecular weight, for example, in the case of propylene polymerization ([11], [12]) when Ziegler-Natta catalysts modified with nucleophilic additives were used.

Fig. 3. Curves of the reducing ability of some organoaluminum compounds: 1 $-\mathrm{Al(C_2H_5)_3}$, 2 $-\mathrm{(C_2H_5)_2AlCl}$, 3 $-\mathrm{(C_2H_5)AlCH = CH{-}C_2H_5}$

The results obtained are readily explained from the standpoint of the participation, in the stereospecific synthesis of polymers, of surface electron defects of the heterogeneous component of the complex catalyst ([5]), which, depending on the nature of the organoaluminum component, alter the catalytic activity of the polymerization centers.

The reason for this should be sought in the structure of the aluminum-alkyl component. In the cited work ([6]) it was pointed out that DEBA differs markedly in its properties from aluminum trialkyls. In particular, the alkenyl group at the aluminum atom exerts an effect analogous to that of a halogen atom, an alkoxy group, or an amino group, as a result of which the reactivity of the

Fig. 4

Figure 3: Fig. 4

other two Al—C bonds is decreased and, consequently, the ability to polymerize polar monomers appears. DEBA, like oxo derivatives of aluminum alkyls, is not titrated by nucleophilic agents (as was indicated above). For the same reason, the etherate of the unsaturated organoaluminum compound is insufficiently stable and may decompose into its components under high vacuum.

The indicated properties of DEBA, which contains three metal—carbon bonds (similarity to triethylaluminum), of which one is qualitatively different (similarity to the above-mentioned derivatives of $(C_2H_5)_3Al$), are reflected in the reducing ability of this compound, which plays the principal role in heterogeneous polymerization on Ziegler-Natta complex catalysts. In the series of increasing reducing ability of aluminum alkyls (3), DEBA occupies a position between diethylaluminum chloride and triethylaluminum (Fig. 3), which determines the possibility of polymerization of α-olefin monomers. However, along with the common properties, there is also an essential difference in the properties of the unsaturated organoaluminum compound in comparison with monosubstituted derivatives of triethylaluminum. Diethylaluminum chloride and diethylaluminum ethoxide are readily oxidized and cause homogeneous polymerization of vinyl chloride at $t = -30°$ (yields, respectively, 38.5 and 64 g per 1 mole of catalyst), whereas DEBA is oxidized with greater difficulty and polymerization under analogous conditions proceeds with low yields (10 g of polymer per 1 mole of catalyst).

It must also be noted that the oxidation-reduction system DEBA—cumene hydroperoxide behaves in homogeneous polymeri-

zation of vinyl chloride in the same way as the triethylaluminum-ether-cumene hydroperoxide complex (and not as the diethylaluminum ethoxide-cumene hydroperoxide system). This fact indicates that oxidation in this case corresponds to oxidation of the organoaluminum compound in which the vacant orbitals of the aluminum atom are sufficiently saturated. As for the reactivity of the individual bonds of DEBA, the metal-carbon bond (of the ethyl group) is more active than the metal-carbon bond (of the butenyl group). This is supported by the fact that, upon titration of it with water (alcohol), not even traces of butene-1 were found in the reaction of the first Al-C bond. In the gases corresponding to the reaction of the second and third Al-C bonds, both ethane and butene-1 were found. This is also evidenced by the reactions of DEBA at elevated temperatures, which proceed mainly through interaction of the double bonds of the alkenyl group and the Al-C bond (of the ethyl group), with cleavage of the latter (6).

Fig. 4. Dependence of the molecular weight of diethylbuten-1-yl-1-aluminum on time. **I** —sample kept under nitrogen; **II** —the same in vacuum.

It is interesting to note that during storage the molecular weight (Fig. 4) and the viscosity of the product increased, with a simultaneous deterioration of its catalytic activity in the polymerization reaction. Thorough evacuation, although it slowed down the processes indicated above, did not eliminate them. Apparently, if one disregards the insufficiently high purity of DEBA (90–92%), the observed phenomena may be interpreted as reactions involving butenyl and ethyl groups, accompanied by the formation of more complex structures. The possibility of such reactions occurring at elevated temperatures has already been pointed out ([6]). Whereas DEBA rapidly reacted with alcohol, the solid crystalline product obtained upon its prolonged aging was insoluble in benzine (benzene) and was decomposed by alcohol only at elevated temperatures (50–70°), the reaction proceeding very slowly. Mass-spectrometric analysis of the gases showed that, if during alcoholysis of the original DEBA there are approximately 2 equiv. of ethane and 1 equiv. of butene-1 per 1 atom of aluminum, then in the gases from decomposition of its solid modification butene was almost completely absent, while the ethane content decreased threefold.

Thus, the properties of DEBA include both the properties of triethylaluminum and those of its oxy- and halogen derivatives. This distinctive character of the properties of an unsaturated organoaluminum compound leads to the fact that catalytic systems involving it, while active in olefin polymerization, are at the same time capable of inducing polymerization of polar monomers.

Received
20 XI 1963

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