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Abstract

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NEW DATA ON THE MECHANISM OF ETHYLENE POLYMERIZATION WITH THE SOLUBLE CATALYTIC SYSTEM

$—Sn(C_6H_5)_4 + AlBr_3 + VCl_4$

(Presented by Academician V. A. Kargin, April 5, 1963)

As is known from previous communications ($^{1-3}$), the soluble catalytic system $Sn(C_6H_5)_4 + AlBr_3 + VCl_4$ makes it possible to polymerize ethylene with the formation of highly crystalline linear polyethylene characterized by a narrow molecular-weight distribution. It was proposed (^{4}) that the mechanism of the active action of this catalytic system consists in the arylation of vanadium chloride by tetraphenyltin, with the formation of vanadium-organic compounds responsible for the initiation and growth of the polymer chain. The role of aluminum bromide was unclear, and to it was ascribed the obscure property of imparting to the catalytic system the ability to dissolve in hydrocarbons and of preventing deep reduction of vanadium tetrachloride.

Our experimental study of the ethylene polymerization reaction in cyclohexane solution with the indicated catalytic system showed that the activity of the catalyst in polymerization depends substantially on the molar ratio of $AlBr_3$ and $Sn(C_6H_5)_4$. At an equimolecular ratio of these components, the catalyst proves to be practically inactive. If, however, the catalytic system included two or more (up to six) moles of $AlBr_3$ per mole of $Sn(C_6H_5)_4$, the catalyst was active. The activity of the catalyst changed hardly at all as the amount of $AlBr_3$ was increased. In all experiments in which the ratio $AlBr_3 : Sn(C_6H_5)_4$ was > 2, the color of the reaction medium was characteristic of a system containing free $AlBr_3$ (raspberry).

Table 1

Molar ratio* $AlBr_3 : Sn(C_6H_5)_4$	Color of the catalytic complex	Yield of polyethylene, g/g $Sn(C_6H_5)_4$
1 : 1	Reddish-brown	2.5
1.5 : 1	»	10.0
2 : 1	Light brown	27.5

Molar ratio* $AlBr_3 : Sn(C_6H_5)_4$	Color of the catalytic complex	Yield of polyethylene, g/g $Sn(C_6H_5)_4$
3 : 1	Raspberry**	22.5
4 : 1	»	25.0
5 : 1	»	22.5
6 : 1	»	25.0

* The amount of VCl_4 in all experiments was 0.04 mmole.
** Aluminum bromide with vanadium chloride in cyclohexane solution forms a raspberry-colored complex.

Table 1 gives data characterizing the yield of polyethylene as a function of the ratios of $AlBr_3$ and $Sn(C_6H_5)_4$ at a temperature of 65° in cyclohexane medium.

On the basis of these experimental data it may be assumed that the following reaction of interaction of aluminum bromide with tetraphenyltin is most probable:

$$Sn(C_6H_5)_4 + 2AlBr_3 \rightarrow 2AlC_6H_5Br_2 + Sn(C_6H_5)_2Br_2.$$

A larger excess of $AlBr_3$ remains unreacted:

$$Sn(C_6H_5)_4 + 3AlBr_3 \rightarrow 2AlC_6H_5Br_2 + Sn(C_6H_5)_2Br_2 + AlBr_3$$

and so on.

In those cases in which there was an excess of aluminum bromide (exceeding the ratio $AlBr_3 : Sn(C_6H_5)_4 = 2$), less time was required for the formation of the active catalyst. Possibly, $AlBr_3$ catalyzes the cleavage of phenyl radicals from $Sn(C_6H_5)_4$.

The organoaluminum compound formed subsequently reacts with vanadium chloride with the formation of a soluble complex, the structure of which is still unclear.

For the formation of the active catalytic complex, as experiments on ethylene polymerization show, a very small amount of vanadium chloride is required. This can be explained by the fact that the catalytic complex is soluble and therefore each ionic bond in it is accessible to the monomer. The solubility of the catalytic system is ensured by the weak reducing ability of $AlC_6H_5Br_2$ with respect to VCl_4.

An increase in the amount of vanadium chloride introduced into the catalytic system apparently promotes the dearylation reaction of the organoaluminum compound, which leads to a decrease in the activity of the catalytic system.

This proposition is illustrated by the data of Table 2, obtained at a molar ratio $AlBr_3 : Sn(C_6H_5)_4 = 2 : 1$ and a temperature of 65°.

Table 2

Vanadium chloride, mmol	Color of the catalytic complex	Yield of polyethylene, g/g $Sn(C_6H_5)_4$
$1.2 \cdot 10^{-7}$	Marsh-colored	25.0
0.001	”	22.5
0.002	”	27.5
0.004	Light brown	30.0
0.008	”	22.5
0.014	”	27.5
0.02	”	20.0
0.04	”	27.5
0.06	”	30.0
0.08	Raspberry-colored	5.0
0.10	”	3.0
0.5	”	1.0

We isolated an unstable product of the interaction of tetraphenyltin and aluminum bromide, which changes in air. It was qualitatively shown that this product is an organoaluminum compound, which agrees with the literature data on exchange reactions of tetraphenyltin (5).

On the other hand, the formation of such an organoaluminum compound was proved by direct determination with the aid of the Mössbauer effect*. A Mössbauer spectrum was first obtained for a solution of tetraphenyltin in cyclohexane (0.625 g per 100 ml). The magnitude of the measured chemical shift corresponded completely to the reference sample. The absence of chemical interaction between tetraphenyltin and vanadium chloride was confirmed by the fact that the Mössbauer spectrum recorded for a solution of this mixture in cyclohexane was completely identical to the spectrum for tetraphenyltin. By contrast, the Mössbauer spectrum for the catalytic system $Sn(C_6H_5)_4 + 2AlBr_3$ showed a clearly expressed quadrupole splitting of the spectral lines, characteristic of the formation of a bromine-substituted organotin compound, to which the formula $Sn(C_6H_5)_2Br_2$ can most probably be assigned.

Thus, it seems to us that the mechanism of ethylene polymerization with the catalytic system $Sn(C_6H_5)_4 + AlBr_3 + VCl_4$ includes, as the first stage, the interaction of $Sn(C_6H_5)_4$ and $AlBr_3$:

$$Sn(C_6H_5)_4 + 2AlBr_3 \rightarrow 2AlC_6H_5Br_2 + Sn(C_6H_5)_2Br_2$$

In the second stage, an active catalytic complex is formed between $AlC_6H_5Br_2$

and VCl_4. The transition metal here provides free *d*-orbitals for the formation of a π-complex with the olefin.

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* The Mössbauer spectra were recorded in the laboratory of L. S. Polak, and their detailed consideration will be the subject of a separate publication.

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

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