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Abstract

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Polymerization of Ethylene with a Soluble Organometallic Complex Catalyst

$Sn(C_6H_5)_4 + AlCl_3 + VCl_4$

As is known, typical Ziegler catalysts, widely used in the polymerization of ethylene and other vinyl monomers, are insoluble in the reaction medium. In recent years, increasing attention has been directed toward the study and application, in ethylene polymerization reactions, of soluble catalytic systems.

In addition to their considerable theoretical interest, soluble catalytic complexes, as we have already indicated earlier ([1]), are highly promising for practical use. In a soluble catalytic complex, every ionic bond can interact with the monomer, initiating chain growth. In the case of a heterogeneous catalyst, however, only a small fraction of such bonds, on the very surface of the catalyst, proves to be active. As a consequence, the consumption of homogeneous catalyst is significantly lower, i.e., the specific yield of polymer per unit of catalyst is higher than with a heterogeneous catalyst.

Moreover, the solubility of the catalyst makes it possible to obtain a polymer practically free of impurities of unreacted catalyst. This circumstance makes it possible to simplify the process of obtaining polyethylene by eliminating from it one of the most difficult stages—washing the polymer free of catalyst residues, which adversely affect the properties of the finished polymer.

Finally, polymerization of ethylene with soluble catalysts leads to the production of a polymer with a narrow molecular-weight distribution, since during polymerization the amount of catalyst in the reaction medium remains constant. The homogeneity of polyethylene with respect to molecular-weight distribution proves to be a positive factor in some processes of its processing.

The serious advantages of soluble catalytic systems have led to the appearance of a number of works devoted to the study of the polymerization reaction of ethylene with soluble organometallic complex catalysts, among which our attention was attracted by the system first proposed by Carrick et al. ([2]), $Sn(C_6H_5)_4 + AlX_3 + VCl_4$ (X—halogen). The main component of this catalyst —tetraphenyltin—differs from a number of organometallic compounds, in particular from aluminum alkyls, by sufficient stability toward air and moisture. This catalytic system is truly soluble, which is confirmed by the absence of the

Tyndall effect, as well as by the fact that its catalytic activity is retained after filtration through a bacterial filter (1 μ).

Experimental Part

Polymerization of ethylene* was carried out in a flow system at constant pressure close to atmospheric. The reactor (capacity 250 ml), equipped with a stirrer, reflux condenser, thermometer, and special devices for introducing ethylene and the catalyst components, was thermostated at 65°, and was flushed first with dry oxygen-free nitrogen and then with ethylene. After this, a definite amount of solvent was poured into the reactor; cyclohexane was used as the solvent, having first been chromatographically purified from traces of unsaturated hydrocarbons, freed from moisture with molecular sieves, and distilled over phosphorus pentoxide in a stream of dry inert gas. A calculated amount of repeatedly recrystallized tetraphenyltin was then placed in the reactor.

After the solvent had been saturated with ethylene (for 40 min), freshly prepared VCl_4 was charged into the reactor through a burette as a dilute solution in cyclohexane, and a saturated solution of $AlCl_3$ in hot cyclohexane was added. After addition of the last catalyst component, a vigorous polymerization reaction began, but it ended rapidly. The absorption of ethylene during polymerization was monitored from the readings of gas meters installed at the inlet and outlet of the reactor. One hour after the beginning of polymerization, methyl alcohol was introduced. The polymer was filtered off, washed three times with methyl alcohol, and dried to constant weight in a vacuum dryer ("pistol") at the boiling temperature of chloroform ($t_{\text{b.p.}} = 61.2^{\circ}$).

Table 1

Polymerization of ethylene on the catalytic system $Sn(C_6H_5)_4 + AlCl_3 + VCl_4$ in cyclohexane at 65°

No. of experiment	$Sn(C_6H_5)_4$, g	$Sn(C_6H_5)_4$, mmol	$AlCl_3$, g	$AlCl_3$, mmol	VCl_4, g	VCl_4, mmol	Total loading of catalyst, g	Catalyst conc., g/ml	Solvent, ml	Polymer yield, g	Polymer yield, g per 1 g catalyst	η_x^*
13	0.07	0.165	0.035	0.26	0.002	0.01	0.107	0.0011	100	1.3	12.2	2.5
12	0.07	0.165	0.051	0.38	0.002	0.01	0.123	0.0012	100	2.0	16.2	3.2

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* Industrial ethylene, containing 98.5% C_2H_4, was subjected to thorough purification from oxygen and moisture by means of a nickel–chromium catalyst and appropriately activated molecular sieves.

No. of experiment	$Sn(C_6H_5)_4$, g	$Sn(C_6H_5)_4$, mmol	$AlCl_3$, g	$AlCl_3$, mmol	VCl_4, g	VCl_4, mmol	Total loading of catalyst, g	Catalyst conc., g/ml	Solvent, ml	Polymer yield, g	Polymer yield, g per 1 g catalyst	η_x^*
14	0.07	0.165	0.060	0.45	0.002	0.01	0.132	0.0013	100	2.6	19.8	4.1

* The characteristic viscosity of the polymer (η_x) was determined in decalin at 120°.

Table 1 gives the results of several characteristic experiments on the polymerization of ethylene.

In studying the properties of the catalytic system $Sn(C_6H_5)_4 + AlCl_3 + VCl_4$, it was found that the order of mixing of the components does not exert a substantial influence on the course of polymerization. However, the yield of polymer and its molecular weight depend to a considerable extent on the amount of $AlCl_3$ introduced and on the rate at which it is fed into the reaction medium as a solution in boiling cyclohexane. Thus, increasing the amount of $AlCl_3$ increased the polymer yield and, at the same time, its molecular weight (see Table 1). When less than a certain amount of $AlCl_3$ was introduced, polymerization was not observed at all.

The comparatively low specific yields of polyethylene are evidently due to the fact that, under the experimental conditions, oxygen was absent from the reaction medium and the possibility of reactivation of the catalyst was excluded.

In studying the influence of oxygen on the ethylene polymerization reaction, it was shown that the maximum polymer yield was obtained when the oxygen content in ethylene was 0.05-0.1% (^{3}). The influence of oxygen is connected with the following concepts regarding the mechanism of ethylene polymerization with the catalytic system under investigation. It is assumed that the active center of the catalyst is an organic compound of divalent vanadium, RVX ($^{4-6}$). The chain-growth reaction probably proceeds through the formation of a π-complex of the olefin with the transition metal and subsequent insertion

monomer through the V—C bond:

$$X—V—C_6H_5 + CH_2{=}CH_2 \rightarrow X—V—C_6H_5 \rightarrow X—V—CH_2CH_2—C_6H_5$$

$$\uparrow$$

Fig. 1

Figure 1: Fig. 1

Fig. 3

Figure 2: Fig. 3

$CH_2{=}CH_2$

This mechanism is confirmed by the presence of a phenyl residue of the catalyst as the terminal group of the polymer. Thus, in the course of polymerization the V—C bonds are gradually consumed. For the formation of new bonds it is necessary that the arylation reaction of vanadium occur again. But it is known that a hydrocarbon group preferentially combines with the more electropositive metal, and the electronegativity of transition metals is higher in the higher valence state. The effect of oxygen, in all probability, consists in converting vanadium to a higher valence state, in which it is readily arylated by tetraphenyltin; i.e., the system $Sn(C_6H_5)_4 + VCl_4 + AlCl_3$ in the presence of oxygen acts by the mechanism of a redox system.

Fig. 1

The polyethylene obtained by us was studied by means of absorption spectra in the infrared region on an IKS-14 instrument. The analysis was carried out in the laboratory of M. M. Kusakov, to whom the authors express their gratitude. The sample was tested in the form of a film 0.05 and 0.1 mm thick.

In the spectrum (Fig. 1) bands were found indicating the presence of polyethylene chains (1456, 1297, 722, 709 cm^{-1}). The double nature of the 722—709 cm^{-1} band indicates the crystalline state of the polyethylene under study. Not one of the olefinic groupings was detected. Isolated methyl groups CH_3— also were not detected. All this indicates the high linearity of the polyethylene obtained, resembling polymethylene $(CH_2)_n$, usually obtained from diazomethane. For comparison, let us note that polyethylene obtained on a heterogeneous Ziegler-type catalyst, for example on the system $Al(iso\text{-}Bu)_3 + TiCl_4$, contains from 5 to 10 methyl groups per 2000 carbon atoms and about 8 unsaturated groups per 10000 carbon atoms. The high crystallinity of the polyethylene under investigation is also confirmed by X-ray diffraction data, illustrated in Fig. 2 (see insert, p. 366). The thermomechanical curves obtained, shown in Fig. 3, indicate the presence of a region of the high-elastic state and a high flow temperature. This is evidently explained by the high molecular weight of the polyethylene. Also obtained were

Fig. 3

curves of nominal stress versus relative elongation of the polymer. It is difficult to draw definite conclusions about the mechanical properties of the polyethylene studied from these curves, since the films subjected to tensile deformation were not uniform (the conditions of their pressing had not been selected). However, at a temperature of 80° the polyethylene specimens had a relative elongation of $< 700\%$.

Important information on the polymerization process on the catalytic system examined was obtained by us with the aid of the Mossbauer effect; the results of these studies, carried out jointly with the group of L. S. Polak, will be presented in another publication.

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