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Abstract

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ON THE QUESTION OF THE NATURE OF THE ACTION OF COMPLEX CATALYSTS IN THE POLYMERIZATION REACTION OF VINYL COMPOUNDS

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Complex catalysts, which are products of the interaction of metal halides of the transition decades of Groups 4, 5, and 6 of the periodic system of the elements with alkyls of metals of Groups 1, 2, and 3, and which have an indefinite composition, have been discovered recently ($^{1-4}$), and contradictory opinions have been expressed on the question of the nature of their catalytic action.

Ziegler (^{1}) assigns the reaction under consideration to reactions with a stepwise mechanism, with the formation at each stage of addition of a monomer molecule of a stable organometallic compound, in analogy with his ideas on the mechanism of polymerization by organoalkali compounds (^{5}). He rejects the possibility that the reaction proceeds with the participation of free radicals or by the mechanism of acid catalysts. Natta (^{4,6}) argues for a mechanism of alkaline catalysis with a carbanion as the active center. Finally, Nenitzescu (^{7}) advances considerations in favor of the view that the reaction proceeds through free radicals.

To determine the class of any new catalyst for a polymerization reaction, a convenient method is one based on determining the composition of the copolymer formed in the copolymerization of two monomers of different polarity (^{8}). The most characteristic pair of monomers is styrene–methyl methacrylate, since the resulting copolymers, depending on the reaction mechanism, differ very sharply in composition (^{9}). But neither methyl methacrylate nor acrylonitrile is polymerized by complex catalysts over a wide temperature range (from −80° to 60°), even with an excess of catalyst (up to 10% catalyst by weight of monomers was tested). Polymerization of equimolecular mixtures of styrene with methyl methacrylate or with acrylonitrile likewise does not occur.*

Therefore we studied the monomer pair styrene–7 α-methylstyrene. In all experiments the solvent was toluene; the monomer ratio was close to equimolecular, with their total concentration from 1.7 to 2.5 g-mol/l. The catalysts tested were: ethyllithium, triethylaluminum, titanium tetrachloride, and a complex catalyst (the product of interaction of the latter two). Polymerization was carried out in ampoules with a partition: a solution of the monomers in toluene was introduced into one compartment, and a solution of the catalyst into the other. After filling and sealing, the ampoule was kept at room temperature from half an hour to several hours. When solutions of titanium tetrachloride and triethylaluminum were mixed, the reaction, with formation of a black precipitate, proceeded practically instantaneously. The ampoule was placed in a thermostat and, after the contents had reached the temperature of the latter, the partition was broken and the two solutions were mixed. To stop the reaction, the ampoule was opened, the contents were poured into methyl alcohol, and the polymer was thoroughly washed with it.

* Our results are in full agreement with the data of Kolesnikov (^{12}), who likewise was unable to obtain acrylonitrile polymers with complex catalysts.

The content of α-methylstyrene units in the reprecipitated copolymer was determined by infrared spectroscopy from the absorption band at 1111 cm^{-1}. The accuracy of the measurements was ±5% of the measured value*. The main conditions and results of the experiments are given in Tables 1 and 2.

Pure monomers are polymerized by three of the catalysts tested and are not polymerized by triethylaluminum. Polymerization of α-methylstyrene with ethyllithium proceeds slowly: at 18° over 20 h, 38% of the monomer reacted.

For the case of chain radical copolymerization of styrene and α-methylstyrene, the copolymerization constants are respectively $r_1 = 0.71$ and $r_2 = 0.14$ $^{(10)}$. Consequently, in copolymerization of an equimolecular mixture of monomers, the copolymer formed in the initial stage should contain 60% styrene units and 40% α-methylstyrene.

Table 1

Experiment No.	Catalyst	Initial concentration (g-mol/l): catalyst (1 component)	Initial concentration (g-mol/l): triethylaluminum	Initial concentration (g-mol/l): styrene	Initial concentration (g-mol/l): α-methylstyrene	Duration of experiment (min)	Polymerization temperature (°C)	Polymerization depth (%)	Content of α-methylstyrene units in the copolymer (mol. %)
67	Ethyllithium	0.023	–	1.07	1.37	5	20	21	0
70	Ethyllithium	0.054	–	0.87	0.87	900	–20	17	0
64	Ethyllithium	0.041	–	0.96	1.05	1080	20	52	2
65	Ethyllithium	0.065	–	1.01	1.10	14	20	49	3

Experiment No.	Catalyst	Initial concentration (g-mol/l): catalyst (1 component)	Initial concentration (g-mol/l): triethylaluminum	Initial concentration (g-mol/l): styrene	Initial concentration (g-mol/l): α-methylstyrene	Duration of experiment (min)	Polymerization temperature (°C)	Polymerization depth (%)	Content of α-methylstyrene units in the copolymer (mol. %)
66	Titanium tetrachloride	0.0037	–	1.00	1.09	1	−80	13	70
51	Titanium tetrachloride	0.0121	–	1.00	1.08	3	−80	43	69
68	Titanium tetrachloride + triethylaluminum	0.009	0.010	0.93	1.01	3	−80	24	70
42	Titanium tetrachloride + triethylaluminum	0.016	0.011	0.98	1.07	270	−80	36	77

Experiment No.	Catalyst	Initial concentration (g-mol/l): catalyst (1 component)	Initial concentration (g-mol/l): triethylaluminum	Initial concentration (g-mol/l): styrene	Initial concentration (g-mol/l): α-methylstyrene	Duration of experiment (min)	Polymerization temperature (°C)	Polymerization depth (%)	Content of α-methylstyrene units in the copolymer (mol. %)
53	Titanium tetrachloride + triethylaluminum	0.011	0.007	0.85	0.92	85	−80	39	57

On the basis of the composition of the copolymer formed (see Table 1), complex catalysts should be assigned to the type of acidic catalysts. Their acidic properties, naturally, do not change with the ratio of the initial components of the catalyst (see Table 2).

Table 2

Experiment No.	Number of moles of triethylaluminum per 1 mole of titanium tetrachloride	Initial concentration (g · mol/l): titanium tetrachloride	Initial concentration (g · mol/l): triethylaluminum	Initial concentration (g · mol/l): styrene	Initial concentration (g · mol/l): α-methylstyrene	Duration of polymerization (h)	Polymerization temperature (°C)	Polymerization depth (%)	Content of α-methylstyrene units in the copolymer (mol. %)
44	0.7	0.017	0.012	0.95	1.03	1	−80	1.6	68
58	1.1	0.019	0.021	0.94	1.02	0.2	−80	3.2	76
54	1.7	0.013	0.021	1.01	1.05	1.6	−80	2.9	69
57	3.2	0.018	0.057	0.87	0.87	18	−80	2.1	74

The fact that, in their presence, polymerization of methyl methacrylate and acrylonitrile does not proceed also indicates that complex catalysts belong to the acidic type, whereas with butyllithium and other alkaline catalysts it is possible to obtain polymers of high molecular weight at temperatures considerably below zero (11).

The difference between complex and acidic catalysts should be sought not in the nature of the active center responsible for the growth of the polymer chain, as Natta does (6), but in the structural features of the heterogeneous catalyst.

* Measurements were carried out by E. I. Pokrovskii.

It is highly probable that, in the case of complex catalysts, because of the special features of their crystalline structure, adsorbed monomer molecules react with the active center on the surface of the catalyst. Naturally, the rate of polymerization will prove to be slower for those compounds that are adsorbed only to a very small extent on the catalyst surface, for example isobutylene, pseudobutylene, etc. Conversely, molecules of the simplest unsaturated hydrocarbons (ethylene, propylene, primary butylene), owing to adsorption, are activated and, in such an active state, become capable of reacting at a high rate with active centers on the same catalyst surface. When ordinary acid catalysts are used (aluminum chloride, boron fluoride, etc.), because there is no preliminary activation of the molecules of the listed monomers, the rate of their polymerization is low, and the polymers formed have a low molecular weight.

Such a hypothesis explains all the principal regularities of polymerization by complex catalysts observed by Ziegler, Natta, and by us. It follows from the hypothesis that, for example, in going from triethylaluminum to triisobutylaluminum, or from ethyllithium to isobutyllithium in complex catalysts, the rate of the chain-initiation reaction and, consequently, the overall reaction rate should change appreciably. In polymerization in solutions of hydrocarbons possessing pseudoacidic properties, for example in toluene, the chain-transfer reaction observed during polymerization with basic catalysts should not be of essential importance. The assumptions presented here, and certain others, are the subject of our further investigations.

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