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Abstract

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CHEMISTRY

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THE ROLE OF ELECTRON-DONOR ADDITIVES, WATER, AND ALKYLATING AGENTS IN THE STEREOSPECIFIC POLYMERIZATION OF BUTADIENE UNDER THE INFLUENCE OF A COBALT CATALYTIC SYSTEM

The great interest shown in the study of the "cobalt" catalytic system is associated both with the high stereospecificity of its action in the polymerization of butadiene and with the distinctive regularities observed in this process. Electron-donor additives (ethers, dialkyl sulfides, and tertiary amines), in amounts comparable with the concentration of dialkylaluminum chloride, lead to an increase in the content of 1,2-units in the polymer chain. At the same time, the rate of polymerization and the molecular weight of the polymer decrease sharply (^{1}). An increase in the amount of 1,2-units is also observed when a certain quantity of trialkylaluminum is introduced into the system (^{2}).

Fig. 1 and Fig. 2

Fig. 1. Effect of triisobutylaluminum on the content of 1,2-units in the chain *(1)*, the polymer yield *(2)*, and the intrinsic viscosity *(3)*. [$CoCl_2$] 0.0096 mmol, Al/Co = 150 : 1 (mol), butadiene 12.5 g, butadiene concentration in benzene 1.8 mol/l, polymerization temperature +30°, duration 20 h.

Fig. 2. Effect of KCl and NaCl additives on the content of 1,2-units in the chain $(1, 1')$, intrinsic viscosity $(2, 2')$, and polymer yield $(3, 3')$; $1, 2, 3$—for KCl, $1', 2', 3'$—for NaCl. [$CoCl_2$] 0.0096 mmol, Al/Co = 150 : 1 (mol), butadiene 12.5 g, butadiene concentration in benzene 1.8 mol/l, polymerization temperature +50°, duration 16 h.

We have shown that the introduction of trialkylaluminum into the system also leads to a strong decrease in the intrinsic viscosity of the polymer and in the rate of polymerization (Fig. 1). It should be noted that this system contained about 10 mol.% water relative to R_2AlCl. As the amount of water is decreased, the effect of R_3Al additives becomes still more pronounced. Water in small amounts leads to a strong acceleration of the polymerization process and to an increase in the molecular weight of the polymer (^{3}). The complex character of

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this phenomenon has prompted a number of detailed kinetic studies devoted to elucidating the mechanism of the promoting action of water on the polymerization process (^{4}).

However, at present a number of facts have accumulated indicating that the action of water is not specific and that an analogous influence is exerted by certain alcohols, allyl halides, aluminum chloride, etc. (^{3}). It appears possible to consider, from a unified point of view, the nature of the influence of these factors on the process of stereospecific polymerization.

Figure 3

Fig. 3. Effect of additions of dibutyl sulfide on the yield of metallic cobalt when the system $\mathrm{R_2AlCl - CoCl_2}$ is aged in the absence of monomer. $[\mathrm{CoCl_2}] = 0.26$ mmol/l, Al/Co $= 150 : 1$ (mol), interaction time 3 h, temp. 20°.

As is known (^{5}), solutions of dialkylaluminum chloride should be regarded as a system in which certain amounts of alkylaluminum dichloride and trialkylaluminum are always present:

$$2\mathrm{R_2AlCl} \rightleftarrows \mathrm{RAlCl_2} + \mathrm{R_3Al}.$$

Electron-donor impurities are complexed first of all with the alkylaluminum dichloride, shifting the equilibrium toward trialkylaluminum. Therefore, the influence of electron donors on the polymerization process is analogous to the influence of additions of trialkylaluminum. We have shown that potassium chloride and sodium chloride, which form (^{5}) complexes with alkylaluminum dichloride, also have a similar effect (Fig. 2).

The introduction into the $\mathrm{R_2AlCl - CoCl_2}$ system of small amounts of electron-donor impurities increases its reducing properties; this is illustrated by the increase in the yield of metallic cobalt when the system is aged in benzene in the absence of monomer (Fig. 3). The presence of a maximum on the curve (Fig. 3) is due to the fact that, after exhaustion of the alkylaluminum dichloride, complexes of trialkylaluminum with the electron donor arise; these, as the experimental data have shown, are characterized by lower reducing properties. The reducing properties of the system also increase in the presence of potassium chloride. In the presence of butadiene, the reduction of cobalt chloride is not accompanied by precipitation of metallic cobalt, apparently owing to the formation of π-crotyl derivatives of cobalt.

If alkylaluminum dichloride is additionally introduced into the catalytic system consisting of $\mathrm{R_2AlCl - CoCl_2}$ (in a molar ratio of $150 : 1$), then electron-donor impurities in corresponding amounts do not affect the polymerization process at all (see Table 1).

The considerations expressed concerning the role of electron-donor impurities in the polymerization process agree with the fact that, in the case of the systems $\mathrm{RAlCl_2 - CoCl_2}$, $\mathrm{RAlCl_2 - MeX_n}$, small amounts of electron-donor impurities

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prove necessary for cis-polymerization (6–8). In this case the electron-donor impurities bind aluminum chloride, thereby inhibiting cationic processes and shifting the equilibrium toward dialkylaluminum chloride.

The possibility of disproportionation of alkylaluminum halides under the action of complexing agents was shown earlier by Ziegler (9).

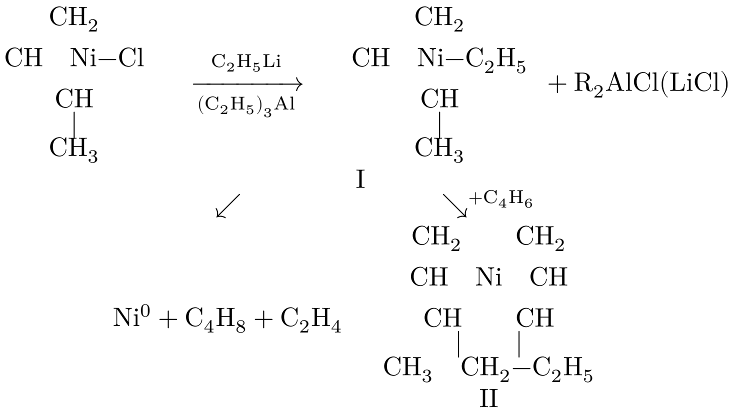
We studied the chemical significance of the influence of KCl and R_3Al using as an example the interaction of triethylaluminum and ethyllithium with π-crotylnickel chloride, proceeding from the fact that the latter models a growing chain of cis-polybutadiene (10). It is known that the reaction of metal alkyls of groups I–III with nickel halides and halides of other metals leads to reduction of the latter to the metallic state as a result of decomposition of transition-metal organometallic compounds

$$2R_3Al + NiCl_2 \rightarrow 2R_2AlCl + R{-}Ni{-}R$$

$$R{-}Ni{-}R \rightarrow R_{-H} + R_{+H} + Ni$$

π-Allyl complexes of the indicated metals are sufficiently stable at ordinary temperatures (11).

In studying the reactions of crotylnickel chloride with triethylaluminum and ethyllithium in dilute benzene solution (0.14 mole/liter, ratio Ni : Li(Al) = 1), it was found that in the absence of monomer, at room temperature, rapid decomposition occurs with formation mainly of disproportionation products (ethylene and butenes). The yield of these products in the case of ethyllithium after 2 hours is 66%.



In the presence of butadiene, the decomposition rate of product (I) is substantially lower, owing to the possible formation of a stable bis-π-crotyl nickel derivative (product II).

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Thus, an increase in the reducing properties of the system leads to an increase in the probability of irreversible chain termination with reduction of nickel to the metallic state, or with conversion into a bis-π-crotylnickel state inactive for polymerization (10).

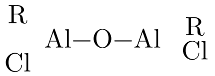
It is known that, as alkyl groups in trialkylaluminum are replaced by halogen atoms, alkoxy groups, etc., the reactivity of organoaluminum compounds with respect to the C—Al bond decreases (5).

When some amount of $AlCl_3$ and $RAlCl_2$ is introduced into solutions of R_2AlCl, a shift of equilibrium is observed toward a decrease in the concentration of R_3Al. When small amounts of water are added, trialkylaluminum reacts with it first of all, which also leads to a decrease in the reducing properties of the system. Redistribution reactions involving aluminum chloride, alkylaluminum dichloride, or alumoxane proceed primarily with R_3Al. Bromine and allyl halides act in an analogous manner.

It therefore appears possible to outline the following general picture of the process:

$AlCl_3$; $RAlCl_2$; Br_2; H_2O;

$CH_2{=}CH{-}CH_2Hal$;



$$\overset{R}{\underset{Cl}{}}Al{-}O{-}Al\overset{R}{\underset{Cl}{}}$$

$$\left\{\begin{array}{l}\text{Increase in the amount of 1,4-cis units}\\ \text{Increase in the molecular weight of the polymer}\\ \text{Increase in the rate of polymerization}\end{array}\right.$$

Table 1

Effect of alkylaluminum dichloride on the polymerization of butadiene in the presence of complex-forming additives

Butadiene 12.5 g, concentration of butadiene in benzene 1.8 mol/l

Complex-forming additive	Concentration, mmol: additive	Concentration, mmol: $(i\text{-}C_4H_9)_2AlCl$	Concentration, mmol: $i\text{-}C_4H_9AlCl_2$	Content of units in the polymer chain, %: 1,4-cis	Content of units in the polymer chain, %: 1,4-trans	Content of units in the polymer chain, %: 1,2	Intrinsic viscosity [η]
–	0	1.42	0	92	4	4	2.16
–	0	1.42	1.61	92	4	4	4.46
KCl	1.42	1.42	0	75	8	17	0.70
KCl	1.42	1.42	1.61	92	4	3	–
KCl	2.84	1.42	0	64	8	28	0.30
KCl	2.84	1.42	1.61	89	6	5	1.86

Complex-forming additive	Concentration, mmol: additive	Concentration, mmol: $(i\text{-}C_4H_9)_2AlCl$	Concentration, mmol: $C_4H_9AlCl_2$	Content of units in the polymer chain, %: 1,4-cis	Content of units in the polymer chain, %: 1,4-trans	Content of units in the polymer chain, %: 1,2	Intrinsic viscosity $[\eta]$
$(C_4H_9)_2S$	0.86	1.42	0	69	7	24	0.76
$(C_4H_9)_2S$	0.86	1.42	1.61	91	5	4	2.18
$(C_4H_9)_2S$	1.72	1.42	0	66	5	29	0.61
$(C_4H_9)_2S$	1.72	1.42	1.61	80	6	14	1.21

$$2R_2AlCl \rightleftarrows RAlCl_2 + R_3Al$$

$$\begin{matrix} R_3Al;\ RSR;\ ROR \\ R_3N;\ KCl;\ NaCl \end{matrix} \left\{ \begin{matrix} \text{Increase in the amount of 1,2-units} \\ \text{Decrease in the molecular weight of the polymer} \\ \text{Decrease in the rate of polymerization} \end{matrix} \right.$$

The effect of water is apparently associated not only with a shift of the indicated equilibrium, but also with its direct participation in the formation of the catalytic complex, since in its complete absence the polymerization process practically does not proceed. It may be assumed that the "stamp" leading to the cis structure of the chain contains cobalt, the outer shell of which is isoelectronic with the shell of monovalent nickel in crotylnickel chloride. The reduction reaction of this complex under the influence of trialkylaluminum in the presence of butadiene should lead to bis-π-crotylcobalt chloride

[[unclear: structural formula with Co, CH, CH_2, CH_3, and two Cl substituents]] $\xrightarrow{R_3Al}$ [[unclear: struc

Compounds with monovalent cobalt, as is known, cause the formation of 1,2-polybutadiene (^{12}).

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