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Figure 1. Kinetics of polymerization of vinyl butyl ether in toluene solution under the influence of $CoCl_2 \cdot n$BuOH (concentration of vinyl butyl ether 0.75 mol/l, concentration of $CoCl_2 \cdot n$BuOH = 0.001 mol/l)

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Abstract

Full Text

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STUDY OF THE CATIONIC ACTIVITY OF THE COMPONENTS OF THE "COBALT" SYSTEM AND OF THE NATURE OF THE END GROUPS OF THE POLYMER CHAIN

The "cobalt" catalytic system, consisting of dialkylaluminum halides and various cobalt compounds, possesses high stereospecificity in the polymerization of butadiene (^{1}-^{3}). Using the polymerization of vinyl alkyl ethers (^{4}), isobutylene, dienes, and other monomers (^{5}) as examples, it has been shown that dialkylaluminum chloride under certain conditions proves to be an effective initiator of cationic polymerization.

In the present communication it is shown that the second component of the "cobalt" system—cobalt chloride—is also an initiator of the process of cationic polymerization. The cationic activity of $CoCl_2$ was studied using the polymerization of vinyl butyl ether as an example. It was established that the process of its polymerization proceeds in a solution of toluene or ethyl chloride both with anhydrous $CoCl_2$ (in a heterogeneous medium) and with the butanol complex ($CoCl_2 \cdot n$BuOH), soluble in hydrocarbon media.

Fig. 1. Kinetics of polymerization of vinyl butyl ether in a toluene solution under the influence of $CoCl_2 \cdot n$BuOH (concentration of vinyl butyl ether 0.75 mol/l, concentration of $CoCl_2 \cdot n$BuOH = 0.001 mol/l)

Figure 1 presents the results obtained in studying the kinetics of polymerization of vinyl butyl ether under the influence of the butanol complex of $CoCl_2$ at 10-30°. The activation energy of polymerization, calculated on the basis of these data, is 9.6 kcal/mol (Fig. 2).

Thus, both components of the "cobalt" catalytic system used for the stereospecific polymerization of butadiene are initiators of the process of cationic polymerization. These results to a certain extent confirm the considerations expressed earlier concerning the coordination–cationic mechanism of action of the system ([6],[7]).

It should be noted that the pyridine complex of cobalt chloride does not cause polymerization of vinyl butyl ether. This may be connected both with the greater strength of the $\mathrm{CoCl_2 \cdot \mathit{n}Py}$ complex and with the inhibiting action of pyridine on the process of free-cationic polymerization.

It was of interest to study the nature of the end groups in cis-polybutadiene obtained under the influence of the catalytic system $\mathrm{R_2AlCl}$—$\mathrm{CoCl_2}$.

It is known that poly-α-olefins obtained under the influence of Ziegler–Natta catalysts contain vinylidene groups at the chain end, formed, as is believed, as a result of chain termination and transfer to the monomer or upon dissociation of the catalytic complex by transfer of a hydride ion ([8]).

Chain termination during the polymerization of dienes on complex catalysts may proceed in an analogous manner. In this case the reactions should lead to the appearance of conjugated double bonds at the end of the chain (equations 1-2).

For the anion-coordination mechanism of chain growth:

$$
\begin{aligned}
(1a)\ & |\mathrm{Cat}|^{+}\,\overline{\mathrm{CH}}_2 - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} \sim + \\
& + \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH} = \mathrm{CH_2} \rightarrow |\mathrm{Cat}|^{+}\overline{\mathrm{CH}}_2 - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_3} + \\
& + \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} \sim
\end{aligned}
$$

For the cation-coordination mechanism of chain growth:

$$
\begin{aligned}
(1b)\ & |\mathrm{Cat}|^{-}\overset{+}{\mathrm{C}}\mathrm{H_2} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} \sim + \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH} = \mathrm{CH_2} \rightarrow \\
& \rightarrow |\mathrm{Cat}|^{-}\overset{+}{\mathrm{C}}\mathrm{H_2}\mathrm{CH} = \mathrm{CH} - \mathrm{CH_3} + \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} \sim \\
& \sim (2)\ |\mathrm{Cat}|^{-} - \overset{+}{\mathrm{C}}\mathrm{H_2} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} - \mathrm{CH_2} = \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} \sim\rightarrow \\
& \rightarrow |\mathrm{Cat}|\,\mathrm{H} + \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} \sim
\end{aligned}
$$

Compounds containing conjugated double bonds react quantitatively with maleic anhydride. This reaction, which underlies the method for the quantitative determination of conjugated dienes (9), was used by us to determine the presence of conjugated double bonds in the polybutadiene obtained.

The accuracy of determining maleic anhydride under various conditions, including in the presence of natural rubber, was checked beforehand, and conditions for complete hydrolysis of maleic anhydride were selected. From the data given in Table 1 it is evident that maleic anhydride is determined completely in the presence of natural rubber.

Fig. 2. Temperature dependence of the polymerization rate

Figure 2: Fig. 2. Temperature dependence of the polymerization rate

To increase the relative proportion of conjugated double bonds in the polymer chain, in order to improve the accuracy of the analysis, a polymer with low molecular weight was obtained. Proceeding from the established relationship (10,11):

$$\text{Mol. wt.} = \frac{k_1[\mathrm{M}]}{k_2\sqrt{[\mathrm{Co}]}},$$

where Mol. wt. is the molecular weight of the polymer, [M] is the concentration of monomer, and [Co] is the concentration of cobalt salt, the polymerization was carried out at a very low butadiene content and a high concentration of $CoCl_2$.

Fig. 2. Temperature dependence of the polymerization rate

The polymerization process was carried out at a temperature of 50° in a glass reactor equipped with a magnetic stirrer and a thermostating jacket. Butadiene was periodically introduced into the reaction medium from the gas phase, and its concentration in the solution throughout the process did not exceed 1-1.5%. The concentration of $CoCl_2 \cdot n\mathrm{BuOH}$ was about 1.5-1.25% (by weight) relative to the monomer; the ratio

$$\frac{\text{iso-Bu}_2\text{AlCl}}{\text{CoCl}_2 \cdot n\text{BuOH}} = 30:1$$

(mol.). The polymerization process lasted 30-40 min. The total polymer content in the solution at the end of the process was 5-7%.

To stop the process, after the completion of polymerization methanol acidified with HCl was introduced into the reactor. Neozone D was added to the filtered polymer solution; the solution was washed with water to remove the remaining $CoCl_2$ completely, after which the polymer was thoroughly dried in vacuum.

Two series of experiments were carried out, in each of which the polymer was averaged. The molecular weight of the product obtained, determined ebullioscopically, was 3600 ± 200.

To increase the accuracy of the analysis, polymer samples for the reactions with maleic anhydride were taken sufficiently large that 0.10-0.15 g of maleic anhydride was consumed in the reaction. From the data in Table 1 it is seen that, with a polymer sample of 4-5 g, 0.12-0.16 g of maleic anhydride is consumed in the reaction with conjugated double bonds, which indicates sufficient reliability of the data obtained.

Table 1

Interaction of maleic anhydride with the polymer

Type of polymer	Polymer sample, g	Sample of maleic anhydride for analysis, g	Maleic anhydride found after the reaction, g	Maleic anhydride bound to the polymer, g	Number of monomer units per 1 conjugated double-bond system
Butadiene “cobalt”	4.54	0.212	0.086	0.126	68
Butadiene “cobalt”	5.45	0.282	0.113	0.168	59
Natural rubber	–	0.1136	0.110	–	–

It follows from this that, on average, each polymer molecule contains one grouping with conjugated double bonds.

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