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Abstract

Full Text

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Some Features of the Polymerization of Butadiene in the Presence of Complex Cobalt Catalysts

Among the various methods for obtaining 1,4-cis-polybutadiene, considerable attention of researchers is attracted by processes of butadiene polymerization based on the use of complex cobalt catalysts(1-7). In the present article we give some results of a study of the polymerization of butadiene, proceeding in benzene solution in the presence of a catalytic system consisting of an alcohol complex of cobalt chloride (CKK) and diisobutylaluminum chloride (DIBA).

The initial task of these investigations was to find the regularities determining the dependence of the polymerization rate, the molecular weights, and the microstructure of the polymers on the concentrations of CKK and DIBA and on their ratio.

Fig. 1. Dependence of the polymerization rate (1) and molecular weight of polybutadiene (2) on the water concentration.
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However, in carrying out these investigations it was established that the polymerization rate and the molecular weight of the polymers formed are strongly affected by the presence of water in such small quantities that its determination and dosing cannot be carried out by ordinary methods. The emergence of a new task—the investigation of this process as a function of the water concentration—caused great experimental difficulties and required a substantial restructuring of the entire research procedure. Only the creation of all-glass apparatus for dosing the starting substances and for carrying out dilatometric experiments made it possible to obtain results satisfactory in reproducibility. A detailed description of this procedure is given in work(8).

All experiments were carried out at 22° and at a butadiene concentration of

Fig. 2

Figure 2: Fig. 2

1.58 mol/l. It was found that the curves of polymer yield versus time are characterized by a certain short period during which the polymerization rate progressively increases, then passes through a maximum, after which it decreases. Therefore, as the principal parameter of the polymerization rate for comparison of experiments carried out under different conditions, the maximum rate in time was chosen.

The molecular weights were determined by the viscometric method at one and the same percent conversion.

The results obtained in studying the influence of individual components of the catalytic system on the polymerization rate of butadiene,

$$V\left(\frac{\%\text{ reduction in volume}}{\text{min.}}\right)$$

and on the molecular weight of the polymers obtained, $\overline{M}$, are presented in Figs. 1-3. Concentrations are expressed in mmol/l.

The data presented show that this influence manifests itself in a very complex manner. The presence of different amounts of water introduces especially significant complications.

The influence of water at constant [CK] and [DIBA] was studied by adding to thoroughly dried benzene (^{8}) portions of benzene with a known water content (Fig. 1).

The dependence of V on $[H_2O]$ is described by a curve with a sharp maximum. Even in the absence of water an appreciable polymerization rate is observed, but only a small amount of very low-molecular-weight polymer is formed.

Fig. 2. *a*—dependence of the polymerization rate on the concentration of the cobalt complex at different water concentrations: $[AlR_2Cl]$ = 17.0 mmol/l; $[H_2O]$: 1—2.5; 2—1.67; 3—0.85 mmol/l. *b*—dependence of the molecular weight of polybutadiene on the concentration of the cobalt complex at $[H_2O]$ = 1.67. 1—$\overline{M} = f[CoCl_2]$; 2—$\lg \overline{M} = f(\lg[CoCl_2 \cdot 10^3])$

Of particular interest, and surprising, is the dependence of the molecular weights of polybutadiene on the water concentration. Whereas the rate curve is characterized by a sharp maximum, the molecular weights of polybutadiene increase steadily throughout the entire range of water concentrations studied as $[H_2O]$ increases. This leads to the idea of the role of water as a certain factor that promotes stabilization of the growing polymer chains.

Fig. 3

Figure 3: Fig. 3

In this connection, one may suppose that, in the absence of water, initiation reactions proceed at a sufficient rate (possibly with the participation of the alcohol contained in the cobalt complex). However, the polymerization chains that arise under these conditions perish at an early stage of their development. The introduction of water limits chain-termination reactions, which leads to an increase in the length of the reaction chains (an increase in $\overline{M}$), i.e., to an increase in the polymerization rate.

At the same time, alongside the chain-stabilization reactions, reactions also occur between water and the components of the catalytic system (formation of inactive complexes, hydrolysis reactions, association, etc.), which lead to binding of water; as a result, the effective concentrations of the catalyst components and of water decrease. As a consequence of these reactions, the polymerization rate decreases.

Thus, as a result of the competition of two factors acting in opposite directions—stabilization of growing chains, on the one hand, and reduction in the number of centers of chain initiation and in the effective $[H_2O]$, on the other—the relative role of which, other conditions being equal, is determined by the initial water concentration, there arises the peculiar dependence of the polymerization rate shown in Fig. 1. Under these conditions, the molecular weight of the polymers should increase with increasing water concentration until the number of active centers becomes so small that polymerization as a whole becomes immeasurably slow.

The nature of the dependence of the polymerization rate and $\overline{M}$ of the polymers on the concentration of the cobalt component of the catalytic system is connected with the influence of reactions leading to a reduction in the number of active centers and in the effective $[H_2O]$ (see Fig. 2). Thus, with increasing [CKK], the polymerization rate at first increases in proportion to [CKK], and then tends toward a limiting value; moreover, the lower the initial $[H_2O]$, the smaller is the threshold value for reaching the limit and the lower is the value of the steady-state rate.

Fig. 3.
a—dependence of the polymerization rate on the concentration of diisobutylaluminum chloride
$[H_2O] = 0.85$; $[CoCl_2 \cdot xC_2H_5OH] = 0.038$; 1—
$V_{max} = f[AlR_2Cl]$; 2—$V_{max} = f[AlR_2Cl]^{1/2}$.
b—dependence of the molecular weight of polybutadiene on the concentration of diisobutylaluminum chloride;
1—$\overline{M} = f[AlR_2Cl]$; 2—$\lg \overline{M} = f(\lg[AlR_2Cl])$.

The molecular weights decrease with increasing [CKK], apparently as a result

of a greater degree of binding of water by the active components of the catalytic system (Fig. 2b). Similar phenomena are also observed when [DIBA] is increased (see Fig. 3).

Naturally, the facts presented are still far from sufficient for a complete substantiation of the assumptions made concerning the nature of the processes of complex cobalt polymerization and their further development. However, one conclusion of this work is that finding the true regularities of processes of this type will hardly be possible without taking into account the significant role played in them by water.

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