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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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THE EFFECT OF ELECTRON-DONOR ADDITIVES ON THE MICROSTRUCTURE OF THE CHAIN IN THE STEREOSPECIFIC POLYMERIZATION OF BUTADIENE IN THE PRESENCE OF "COBALT" CATALYTIC SYSTEMS

It is known that, in the polymerization of dienes under the influence of lithium or organolithium compounds, impurities of electron-donor character (ethers, amines, thioethers), which form complexes with the polymerization initiator, lead to a sharp increase in the amount of 1,2- (or 3,4-) units, with a corresponding decrease in the amount of 1,4-units (*1–5*).

Using the catalytic system TiJ_4—(iso-$C_4H_9)_3Al$ as an example, we showed (*6, 7*) that, in terms of the character of the influence of electron-donor components on the microstructure of the chain, Ziegler systems differ substantially from typical anionic systems. In the present case, these components lead to a transition of 1,4-cis structures into 1,4-trans structures.

Fig. 1. Effect of thioethers on the microstructure of the polybutadiene chain. 1, 2 —content of 1,4-cis units for dibutyl sulfide and diethyl sulfide, respectively; $1'$, $2'$ —the same for 1,2-units; $1''$, $2''$ —the same for 1,4-trans units.

Fig. 2. Effect of dibutyl sulfide on the molecular weight of polybutadiene.

However, these features are not characteristic of all stereospecific coordination-ionic systems.

A number of studies (*8-10*) have shown that the most stereoregular polybutadiene, containing about 95% 1,4-cis units, is obtained when using catalytic systems containing cobalt compounds and dialkylaluminum chloride.

We studied the effect of dialkyl sulfides, simple ethers, and tertiary amines on the chain microstructure during the polymerization of butadiene under the influence of a catalytic system consisting of hydrocarbon-soluble ···

···donors of the cobalt chloride complex with ethyl alcohol and diisobutylaluminum chloride.

The polymerization of butadiene was carried out in benzene solution at a temperature of 30°. The concentration of cobalt chloride was 0.01 wt. % relative to the monomer. Quantitative evaluation of the polymer microstructure was performed from IR-spectroscopic data, using the absorption bands at 912 and 966 cm^{-1}.

As is evident from the curves presented in Fig. 1, the introduction of dialkyl sulfides into the system leads to a substantial change in the microstructure of the polybutadiene chain.

It is characteristic that the decrease in the content of 1,4-cis units is accompanied by a corresponding increase in the amount of 1,2-units. The amount of 1,4-trans units remains unchanged.

Simple ethers and tertiary amines exert an analogous effect on the microstructure of the chain during the polymerization of butadiene under the action of the "cobalt" system. However, even in small amounts these compounds (above 0.1 mole per 1 mole of diisobutylaluminum chloride) sharply reduce the polymerization rate.

The introduction into the system of impurities of electron-donor character also leads to a considerable decrease in the molecular weight of the polymers, as illustrated in Fig. 2 using dibutyl sulfide as an example (Fig. 2).

As follows from Figs. 1 and 2, a definite correlation is observed between changes in the chain microstructure and in the molecular weight of the polymer.

The experimental data presented illustrate the influence of electron-donor impurities on the chain microstructure and the specificity of their action as a function of the nature of the catalytic systems employed.

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