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Figure 1

Figure 1: Figure 1

Abstract

Full Text

Chemistry

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EFFECT OF ELECTRON-DONOR ADDITIVES ON THE CHAIN STRUCTURE IN THE STEREOSPECIFIC POLYMERIZATION OF BUTADIENE

We previously found (*1*) that, in the polymerization of butadiene under the action of the catalytic system TiJ_4-(iso-$C_4H_9)_3Al$, a substantial change in the microstructure of the polymer chain is observed in the presence of small amounts of simple ethers.

In the present work, using dibutyl sulfide and triethylamine as examples, it is shown that thioethers and tertiary amines exert an analogous influence.

Fig. 1. Effect of butyl sulfide and triethylamine on the microstructure of the polybutadiene chain. 1, 2 —content of 1,4-trans units, respectively, for dibutyl sulfide and triethylamine. 1′, 2′ —the same for 1,4-cis units.

Small amounts of simple ethers lead to a strong retardation of polymerization, and the preservation of the necessary rate of the process was achieved by substantially increasing the concentration of the components of the catalytic system.

In assessing the influence of simple ethers on the ratio of cis and trans structures, it was necessary to introduce corrections taking into account the effect of the change in catalyst concentration on the chain structure. Dibutyl sulfide and triethylamine, in the amounts tested, affect the polymerization rate less than simple ethers, and therefore it seemed possible to vary the catalyst concentration within limits that do not affect the microstructure of the polymer. Polymerization of butadiene was carried out at a temperature of +30° in benzene solution. The concentration of monomer in benzene was 26.5 mole %.

The curves illustrating the effect of dibutyl sulfide and triethylamine on the microstructure of polybutadiene are presented in Fig. 1.

Analogously to simple ethers, these compounds cause an increase in the amount of 1,4-trans units with a corresponding decrease in the amount of 1,4-cis units.

It is still unclear whether, in these systems, cis structures can be quantitatively converted into trans structures, or whether the process proceeds only to a limit determined by the equilibrium of the indicated structures at the given temperature. The latter is characteristic of the free-radical and free-cationic mechanisms of chain growth. It is known (*2*) that, under the influence of certain chemical agents, in particular nitrogen dioxide, sulfur, thio acids, and some organic disulfides, mutual transitions of cis-trans units are observed in the finished polymer chain.

The experiments we carried out showed that cis-polybutadiene undergoes no changes in the presence of the components of the catalytic system $[Ti]_4$ + $[(iso\text{-}C_4H_9)_3Al]$ and electron-donor additives. It follows from this that the formation of trans units occurs only in the course of polymerization, with the direct participation of a complex containing the electron-donor additive.

It should be noted that the process of butadiene polymerization in the presence of electron-donor additives is not accompanied by a decrease in the solubility or unsaturation of the polymers formed.

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