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Abstract

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Complex Formation and Chain Structure in the Polymerization of Divinyl with Butyllithium

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In a number of works ([1–3]) it was established that, in the catalytic polymerization of monoolefins and dienes, the chain structure is to a considerable extent determined by the nature of the catalytic complex participating in the polymerization process. It was thereby shown that the initial catalytic complex is directly related to each elementary act of chain growth.

The preparation of organolithium compounds in an isolated pure form is associated with great experimental difficulties. Along with the formation of organometallic compounds, the possibility is not excluded of the formation of a complex mixture of products of their oxidation. In order to clarify the influence of these oxidation products on the chain structure in the polymerization of butadiene, it seemed advisable to investigate the effect of oxygen.

As a result of the investigation carried out, we established that, in the polymerization of divinyl by organolithium compounds, the introduction into the system of comparatively small amounts of oxygen leads to a substantial increase in the number of 1,2 units in polybutadiene at the expense of a decrease in 1,4 units. Additions of alcohol and phenol have an analogous effect on the structure of the polymer chain (Table 1).

The data obtained are of fundamental interest in that they indicate the necessity of protecting the system from the entry of oxygen when the task is to synthesize divinyl polymers with a maximum content of 1,4 units in the chain. The influence of oxygen on the structure of polybutadiene is apparently due to the formation of oxygen-containing products that form complexes with organolithium compounds.

Dialkyl monosulfides exert an analogous effect; their influence was studied by us in detail. The effect of additions of dimethyl, dipropyl, and diisopropyl sulfides on the chain structure of polybutadiene during polymerization in the absence of oxygen was studied.

The experimental data obtained in the polymerization of butadiene by butyllithium in the presence of dialkyl sulfides showed that they substantially increase

the content of 1,2 units in the chain. In the case of dimethyl sulfide, the content of 1,2 units increases from 12 to 68% (Table 2).

From these data it is evident that the influence of the dialkyl sulfide decreases with increasing alkyl radical. Earlier ([4]), using butyllithium as an example, we showed the capacity of organolithium compounds to form complexes with dimethyl sulfide. The precipitated insoluble complex had the composition

$$C_4H_9Li \cdot S \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

In general form such compounds can be written as $RMe \cdot S\left(\begin{matrix} R' \\ R'' \end{matrix}\right)$, where Me is an alkali metal, and R, R^1, and R″ are alkyl radicals. Although in the process

Table 1

Polymerization of divinyl with butyllithium at 50° in a petroleum ether solution in the presence of additions of oxygen, alcohol, and phenol

Experiment no.	Name of additive	Concentration of butyllithium, mol. % relative to monomer	Concentration of additive, mol. % relative to monomer	% of 1,2 units in polybutadiene
1	No additive	0.040	–	12
2	No additive	0.055	–	11
3	No additive	0.056	–	10
4	No additive	0.060	–	10
1	Oxygen	0.050	0.018	32
2	Oxygen	0.050	0.037	21
3	Oxygen	0.057	0.037	43
4	Oxygen	0.057	0.037	33
5	Oxygen	0.060	0.011	26
6	Oxygen	0.130	0.011	29
1	Lithium benzylate*	1.36	5.30	39
2	Lithium benzylate*	1.36	5.30	37
1	Lithium pheno-late*	0.15	5.79	35

Experiment no.	Name of additive	Concentration of butyllithium, mol. % relative to monomer	Concentration of additive, mol. % relative to monomer	% of 1,2 units in polybutadiene
2	Lithium phenolate*	0.15	5.79	33

* The benzylate and phenolate are indicated, since the reaction of butyllithium with hydroxyl-containing additives leads to the formation of these substances even before their introduction into the monomer system.

Table 2

Polymerization of divinyl with butyllithium at 50° with additions of dialkyl sulfides in a petroleum ether solution

Experiment no.	Name of additive	Concentration of butyllithium, mol. % relative to monomer	Concentration of additive, mol. % relative to monomer	% of 1,2 units in polybutadiene
1	No additive	0.040	–	12
2	No additive	0.060	–	10
3	No additive	0.30	–	11
4	No additive	0.30	–	12
1	Dimethyl sulfide	0.14	61.74	62
2	Dimethyl sulfide	0.19	82.0	68
1	Dipropyl sulfide	0.66	0.202	29
2	Dipropyl sulfide	0.22	2.49	31
1	Diisopropyl sulfide	0.28	57.3	28
	Diisopropyl sulfide	0.28	57.3	25

polymerization, complexes of a more complex composition than that isolated by us may probably participate; the influence of complex-forming additives on the structure of the chain can be represented on the basis of Ziegler' s ideas[5] about the polymerization process as a successive organometallic synthesis. For the present case this scheme may be represented as follows:

$$\mathrm{R{-}CH_2Me} + \mathrm{S}\begin{matrix}\mathrm{R_1}\\ \mathrm{R_{11}}\end{matrix} \longrightarrow \mathrm{R{-}CH_2{-}Me \cdot S}\begin{matrix}\mathrm{R_1}\\ \mathrm{R_{11}}\end{matrix}$$

$$\mathrm{R{-}CH_2Me \cdot S}\begin{matrix}\mathrm{R_1}\\ \mathrm{R_{11}}\end{matrix} + \mathrm{C_4H_6} \longrightarrow \mathrm{R{-}CH_2(C_4H_6)Me \cdot S}\begin{matrix}\mathrm{R_1}\\ \mathrm{R_{11}}\end{matrix}$$

In view of the fact that the complex-forming additive is directly bound to the metal of the organometallic compound, it affects the character of the carbon-metal bond throughout the entire process of chain formation and thereby affects the structure of the polymer.

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