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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Study of the Rate of Addition of Ethyllithium to Styrene and Isoprene in the Course of the Polymerization Process

The work of S. E. Bresler et al. established that, in the polymerization of isoprene and divinyl under the influence of butyllithium, polymers with very narrow molecular-weight distributions are formed. In the authors' opinion, the very low polydispersity and the Gaussian character of the molecular-weight distributions are due to the fact that the growth of all molecular chains begins practically simultaneously and continues until the monomer is completely consumed. It follows from this that the initial organometallic compound must add practically at once to the corresponding diene monomer, thereby causing frontal development of the polymerization process.

Such an explanation seems unlikely in view of the different reactivity of the initial lithium alkyls and of the products of their addition to the diene, in which the C—Li bond is conjugated with a double bond. Compounds of the indicated type, as is known, possess considerably higher reactivity ([2,3]).

Fig. 1. 1 —reactor with a capacity of 50 ml; 2 —thermostated jacket; 3 —vessel with a capacity of 70-80 ml for taking samples; 4 —burette for aqueous salt solution; 5 —gas burette; 6, 7 —three-way stopcocks for taking samples; 8 —coil condenser

In the present communication, experimental data are presented on the kinetics of addition of ethyllithium to isoprene and styrene during their polymerization. The choice of ethyllithium as the organometallic compound is explained by the convenience of determining its concentration from ethane. Ethyllithium was synthesized from ethyl chloride and metallic lithium in heptane ([4]).

All experiments were carried out in an atmosphere of pure dry argon. The isoprene, heptane, and tetrahydrofuran used in the work were boiled and distilled

Fig. 2

Figure 2: Fig. 2

over metallic sodium. Styrene was dried over calcium chloride and distilled in vacuum.

Polymerization was carried out in a thermostatted reactor (Fig. 1), previously conditioned at a temperature of 250-300°. At definite time intervals from the beginning of the polymerization process, samples were withdrawn from the reaction vessel to determine the amount of polymer and of lithium ethyl that had not entered into reaction. The polymer was precipitated from the reaction mixture with methyl alcohol, washed, and dried in vacuum to constant weight. The amount of lithium ethyl that had not entered into reaction was determined from the amount of ethane formed when the sample of the reaction mixture (withdrawn into vessel 3) was decomposed with water. For this purpose, after decomposition of the reaction sample with water, the decomposition products were heated in vessel 3 at 80° in order to remove ethane from solution, after which the gas was completely displaced by hot brine into gas burette 5 (Fig. 1). The ethane content was determined by burning the gas over copper oxide in a quartz tube.

Fig. 2. Kinetics of polymerization of styrene under the action of lithium ethyl: kinetics of lithium ethyl consumption (*I*) and kinetics of polymerization (*II*) during polymerization of styrene in bulk at a temperature of +1°; kinetics of lithium ethyl consumption (*III*) and kinetics of polymerization (*IV*) during polymerization of a styrene solution (16%) in heptane in the presence of tetrahydrofuran at a temperature of −20°.

In the case of isoprene polymerization, before combustion the gas was shaken in a pipette with Hempel' s saturated solution of mercuric sulfate in sulfuric acid in order to absorb isoprene vapors.

The molar ratios between lithium ethyl and monomer in all experiments were 1/150 (for isoprene) and 1/100 (for styrene).

Figures 2 and 3 present the experimental data obtained in the polymerization of styrene in bulk at a temperature of +1° (\$±0.5°)*(curves ∗ I ∗ and ∗ II∗, Fig.2)andofisopreneatatemperatureof*24°(±\$0.5°) (curves *I* and *II*, Fig. 3). From the data presented it follows that the addition of lithium ethyl to the monomer occurs gradually over the entire course of the polymerization process.

The polymerization process of styrene and isoprene in the presence of tetrahydrofuran, with which organolithium compounds form complexes, was studied in an analogous manner. The use of a number of complex-forming additives, as is known $^{(5-9)}$, substantially accelerates the polymerization of dienes and affects the structure of the polymer chain formed. Polymerization was carried out in heptane solutions containing 16% styrene and 20% isoprene, at a temperature of −20° in the case of styrene and +25° in the case of isoprene. Polymerization of styrene in heptane solution was carried out directly in the sampling vessel (Fig. 1, 3), since polystyrene is insoluble in heptane, which makes it difficult to withdraw samples from the reactor during the polymerization process.

In Figs. 2 and 3, curves *III* show the consumption of lithium ethyl during the polymerization of styrene and isoprene in the presence of tetrahydrofuran 1 : 5; curves *IV* in Figs. 2 and 3 respectively show the polymer yield. As can be seen, the introduction of tetrahydrofuran leads to a sharp increase in the rate of the primary act of addition of lithium ethyl to the monomer and, correspondingly, in the rate of the entire polymerization process. The "living" polymer chain formed retains the ability for further growth for a long period of time after complete

consumption of ethyllithium and monomer. As shown in Fig. 3 (curves V and VI), the polymerization process resumes at the former rate when a solution of isoprene (20%) in heptane is introduced after 20 (curve V) and 50 min (curve VI) after complete consumption of the initially introduced monomer and ethyllithium.

From the results obtained it follows that the primary acts of addition of ethyllithium to styrene and isoprene proceed gradually during the entire polymerization process. The data presented by us refer to the concentration region of ethyllithium 0.7-1 mole % (relative to monomer). The rates of the primary act of addition and of chain growth may depend substantially on the degree of association of ethyllithium. The latter, as has been established (10), decreases with decreasing concentration of the organometallic compound in solution.

Complex-forming additives (tetrahydrofuran) lead to a considerable acceleration of the primary act of addition of ethyllithium to the monomer and to an acceleration of the entire polymerization process.

Fig. 3. Kinetics of the polymerization of isoprene under the action of ethyllithium. Kinetics of ethyllithium consumption (I) and kinetics of polymerization (II) during polymerization of isoprene in bulk at a temperature of +24°. Kinetics of ethyllithium consumption (III) and kinetics of polymerization (IV) during polymerization of a solution of isoprene (20%) in heptane in the presence of tetrahydrofuran at a temperature of +25°. Kinetics of polymerization of a solution of isoprene (20%) in heptane in the presence of tetrahydrofuran, introduced into the reaction medium after complete consumption of ethyllithium and monomer.

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