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Abstract

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COPOLYMERIZATION OF BUTADIENE WITH ISOPRENE UNDER THE INFLUENCE OF COMPLEXES OF BUTYLLITHIUM WITH TRIETHYLAMINE AND TETRAHYDROFURAN

Earlier (^{1}), data were published on the joint polymerization of butadiene and isoprene in the presence of complex catalysts based on cobalt and titanium salts. In the present communication we give the results of a study of the copolymerization process of butadiene and isoprene in the presence of complexes of butyllithium with triethylamine and tetrahydrofuran. The anionic character of polymerization under the influence of such complexes has been established in a number of examples ($^{2-4}$). Copolymerization of butadiene with isoprene was carried out at a molar ratio catalyst : monomer = 1 : 300. Triethylamine and tetrahydrofuran were introduced in an amount of 70 moles per 1 mole of butyllithium. The solution of butyllithium in n-heptane was prepared and analyzed by the usual method (^{5}).

Polymerization was carried out in an ampoule with a partition, placed in a water thermostat at 20°. The catalyst and complex-forming agent were placed in one compartment of the ampoule; in the other, on a distributing comb, the monomers were dosed with an accuracy of 2 rel. %. All work was carried out in an atmosphere of argon, with careful removal of traces of oxygen and moisture from the apparatus and the components of the reaction mixture. Polymerization was interrupted at a low degree of conversion by rapidly cooling the ampoule to $-70°$, after which the ampoule was opened, 2-3 ml of ethyl alcohol was added to decompose the catalyst, and unreacted monomers and solvents were distilled off. The degree of polymerization was determined from the weight of the polymer dried in vacuum. To determine the composition of the copolymer, butadiene labeled with C^{14} was used; it was obtained from a mixture of radioactive and inactive butadiene tetrabromide (^{6}). The activity of the monomeric butadiene was determined from the radioactivity of polybutadiene (^{7}). Measurements of the radioactivity of the polymers were made in films in a layer of complete absorption of the radiation of the isotope C^{14}, using an end-window counter BFL-25 with a mica window 1.3 mg/cm^{2} thick (measurement error 2%).

The copolymerization constants were calculated from the Fineman–Ross equation (8), using the method of least squares. Because of the large difference in the values of the copolymerization constants of the two monomers, the error

Table 1

Dependence of the composition of butadiene-isoprene copolymers on the composition of the monomer mixture

Catalyst	Butadiene content in the monomer mixture, mol. %	Degree of polymerization	Content of butadiene units in the copolymer according to radioactivity, mol. %	Copolymerization constants: for butadiene	Copolymerization constants: for isoprene
$Li(n\text{-}C_4H_9)+N(C_2H_5)_3$	20.2	15.3	54.4	3.6	0.11
$Li(n\text{-}C_4H_9)+N(C_2H_5)_3$	30	9.4	63	3.6	0.11
$Li(n\text{-}C_4H_9)+N(C_2H_5)_3$	40.3	5.6	71.2	3.6	0.11
$Li(n\text{-}C_4H_9)+N(C_2H_5)_3$	50	7.75	85	3.6	0.11
$Li(n\text{-}C_4H_9)+N(C_2H_5)_3$	75	28.3	91.1	3.6	0.11
$Li(n\text{-}C_4H_9)+(CH_2)_4O$	20	5.4	57.1	4.5	0.13
$Li(n\text{-}C_4H_9)+(CH_2)_4O$	32.8	17.5	69	4.5	0.13
$Li(n\text{-}C_4H_9)+(CH_2)_4O$	49.7	30	83.6	4.5	0.13
$Li(n\text{-}C_4H_9)+(CH_2)_4O$	75	24.5	91	4.5	0.13

the determination of constants was 25%. In the case when the polymer yield exceeded 10%, in the calculations and in plotting the curves a correction was introduced to the initial monomer concentrations according to formula (9):

$$M_{\text{corr}} = M + \frac{M-m}{2} \cdot k,$$

where M is the molar fraction of the monomer in the initial mixture, m is its molar content in the copolymer, and k is the degree of polymerization.

Fig. 1. Dependence of the composition of the butadiene-isoprene copolymer on the composition of the monomer mixture. 1—for the catalyst $Li(n\text{-}C_4H_9) + (CH_2)_4O$; 2—for the catalyst $Li(n\text{-}C_4H_9) + N(C_2H_5)_3$; 3—for the catalyst $Li(n\text{-}C_4H_9)$ in hexane (according to data of ([10]))

Figure 1: Fig. 1. Dependence of the composition of the butadiene-isoprene copolymer on the composition of the monomer mixture. 1—for the catalyst $Li(n\text{-}C_4H_9) + (CH_2)_4O$; 2—for the catalyst $Li(n\text{-}C_4H_9) + N(C_2H_5)_3$; 3—for the catalyst $Li(n\text{-}C_4H_9)$ in hexane (according to data of ([10]))

The experimental results are given in Table 1 and in Fig. 1. The copolymerization constants of butadiene and isoprene in hexane solution under the action of butyllithium, obtained by G. V. Rakova and A. A. Korotkov ([10]), are 3.4 for butadiene and 0.47 for isoprene (the calculation was carried out by the integral equation of Mayo and Lewis ([11])). If the Fineman-Ross equation is applied to the data of that work, values $r_1 = 2.8$ (for butadiene) and $r_2 = 0.43$ (for isoprene) are obtained. Thus, the relative activity of butadiene in copolymerization with isoprene in the presence of butyllithium increases for the series of solvents: hexane—triethylamine—tetrahydrofuran (respectively 2.8; 3.6; 4.5). The results obtained are in agreement with ideas concerning an increase in the polarization of the C(−)—Li(+) bond under the influence of complex-forming electron-donor reagents ([2,3]). An increase in the negative charge on the active center leads to a decrease in the activity of isoprene in comparison with butadiene, since the electron density on the double bonds of isoprene is higher owing to the presence of the methyl group.

Fig. 1. Dependence of the composition of the butadiene-isoprene copolymer on the composition of the monomer mixture. 1—for the catalyst $Li(n\text{-}C_4H_9) + (CH_2)_4O$; 2—for the catalyst $Li(n\text{-}C_4H_9) + N(C_2H_5)_3$; 3—for the catalyst $Li(n\text{-}C_4H_9)$ in hexane (according to data of ([10])).

Earlier we established ([1]) that the copolymerization constants of butadiene (r_1) and isoprene (r_2) are, respectively, 1.0 and 1.0 for the catalytic system R_3Al—$TiCl_4$, and 2.3 and 1.15 for the catalytic system R_2AlCl—$CoCl_2$. It follows from this that, with respect to the ratio of monomer activities, Ziegler catalytic systems differ substantially from anionic ones.

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