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Abstract

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STUDY OF THE RELATIVE REACTIVITY OF 1,3-BUTADIENE AND 1- AND 2-BUTENES IN THE PROCESS OF CATIONIC POLYMERIZATION

Questions of the relative reactivity of monomers in processes of ionic and coordination-ionic polymerization have in recent years attracted much attention. The relative activity of monomers in cationic polymerization has been least studied. Usually, the reactivity of monomers in polymerization processes is evaluated from the values of copolymerization constants.

In the present work, the copolymerization of 1,3-butadiene with 1- and 2-butenes was studied using labeled C^{14} butadiene. This made it possible to obtain more reliable data on the composition of the copolymers formed. Polymerization was carried out in a solution of ethyl chloride (containing up to 7 mol.% toluene, introduced with the catalyst solution) and toluene. The monomer concentration was 20 mol.%, and the catalyst concentration ($AlC_2H_5Cl_2$—H_2O) was 0.1 mol.% relative to monomer. In separate experiments the catalyst $AlC_2H_5Cl_2$—HCl was used.

1,3-Butadiene labeled with C^{14} was synthesized from a mixture of radioactive and inactive 1,3-butadiene tetrabromide ([1]). In obtaining pure butenes, the mixture of C_4 alkenes—the product of dehydration of *n*-butyl alcohol—was subjected to rectification in order to isolate 1-butene ([2]).

cis-2-Butene and trans-2-butene were obtained from fractions enriched in the corresponding isomer. The first was obtained with the use of synthetic zeolites CaA, the second by preparative chromatography ([3], [4]).

Copolymerization was carried out at temperatures of −40 and −78° in two-chamber ampoules with a partition. A monomer mixture was introduced into one chamber, and the solvent and catalyst components into the other. The ampoules were filled in an atmosphere of dry argon. After thermostating, the partition in the ampoule was broken with a glass striker. When a degree of polymerization not exceeding 10–12% was reached, the ampoule was opened and 1–2 ml of methyl alcohol was added to deactivate the catalyst. Unpolymerized monomers and solvent were removed by vacuum treatment. The polymer was dried in vacuum at 40°. The composition of the copolymer was determined from the radioactivity of the polymers using the procedure described in ([5]).

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

The activity of monomeric butadiene was determined from the radioactivity of polybutadiene obtained under the same conditions as the copolymer.

The relative activities of the monomers were calculated from the differential Mayo-Lewis equation. The copolymerization constants were calculated without taking into account the participation of double bonds of the polymer chain in the polymerization process.

The experimental data are given in Figs. 1 and 2. As can be seen from Fig. 1, during polymerization in ethyl chloride the reactivity of 1-butene is substantially lower than the reactivity of 1,3-butadiene. The 2-butenes, characterized by an increased electron density at the double bonds, are close in reactivity to butadiene. cis- and trans-2-butenes are characterized by identical activity in the process of cationic copolymerization with 1,3-butadiene. With decreasing polymerization temperature

ization from −40 to −78°, the relative activity of the monomers does not change. In the copolymerization of 1,3-butadiene with 2-butenes, r_1 and r_2 are less than 1. From the theory of radical copolymerization it is known that this corresponds to the case in which a tendency toward alternation of units in the chain is observed, i.e., the cation of monomer A preferentially reacts with monomer B, and conversely.

The results obtained may be used to elucidate the nature of certain secondary reactions occurring in the cationic homopolymerization of dienes. From the regularities revealed it follows that the growing crotyl cation will preferentially react with the internal double bond of the chain, which is modeled by the structure of 2-butene.

Fig. 1. Dependence of the composition of copolymers of 1,3-butadiene and 1- and 2-butenes on the composition of the monomer mixture. Solvent—ethyl chloride. Catalyst $AlC_2H_5Cl_2$—H_2O.
I—1,3-butadiene—1-butene: $r_1 = 1.81$ (for 1,3-butadiene), $r_2 = 0.15$ (for 1-butene), *a*—at $t = -40°$, *b*—at $t = -78°$;
II—1,3-butadiene—2-butene: $r_1 = 0.45$ (for 1,3-butadiene), $r_2 = 0.15$ (for 2-butene), *v*—1,3-butadiene—cis-2-butene at $t = -40°$, *g*—1,3-butadiene—trans-2-butene at $t = -40°$, *d*—1,3-butadiene—equimolar mixture of 2-butenes at $t = -78°$.

Fig. 2. Dependence of the composition of copolymers of 1,3-butadiene and 1- and 2-butenes on the composition of the monomer mixture. Solvent—toluene.
I—1,3-butadiene—1-butene, $r_1 = 0.19$ (for 1,3-butadiene), $r_2 = 0.26$ (for 1-butene). *a*—at $t = -40°$, catalyst $AlC_2H_5Cl_2$—H_2O, *b*—at $t = -40°$, catalyst $AlC_2H_5Cl_2$—HCl;

II—1,3-butadiene—2-butene, catalyst $AlC_2H_5Cl_2$—H_2O: $r_1 = 0.17$ (for 1,3-butadiene), $r_2 = 0.51$ (for 2-butene), v—1,3-butadiene—cis-2-butene at $t = -40°$, g—1,3-butadiene—trans-2-butene at $t = -40°$.

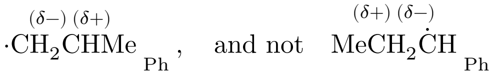
$$\sim CH_2CH{-}CHCH_2CH_2CH{=}CHCH_2^{(+)} \xrightarrow{1} \sim CH_2CH^{(+)} \xrightarrow[+2C_4H_6]{2} \sim CH_2CHCH_2CH^{(+)} \quad \text{etc.}$$

As is known, the unsaturation of diene polymers obtained by cationic polymerization is considerably lower than the theoretical value and in many cases reaches only 40–60% of theory. At low degrees of polymerization, when the probability of reaction of the crotyl cation with a double bond of its own chain predominates, structures of the polyvinylcyclohexene type may arise (reaction 2).

The high activity of the crotyl cation in reactions with 1- and 2-butenes indicates that the stabilizing effect of conjugation in it is apparently small, in contrast to crotyl free radicals and anions.

For radicals of the allylic type this effect, as is known, is equal to 22–24 kcal/mol ([6]). For crotyl anions it is possibly somewhat higher,

which follows from the fact that addition of an alkali metal to styrene leads to the formation of



$$\cdot\overset{(\delta-)}{CH_2}\overset{(\delta+)}{CH}\underset{Ph}{Me}, \quad \text{and not} \quad Me\overset{(\delta+)}{CH_2}\overset{(\delta-)}{\dot{C}H}_{Ph} \qquad (7)$$

Data on the copolymerization of 1,3-butadiene with 1- and 2-butenes in toluene solution are presented in Fig. 2. In this case, the same regularities are observed as were noted for copolymerization in ethyl chloride solution, with the difference that in the indicated system the relative reactivity of 1- and 2-butenes with respect to butadiene increases. As is seen from Fig. 2, the copolymer composition is the same when the catalytic systems $AlC_2H_5Cl_2$—H_2O and $AlC_2H_5Cl_2$—HCl are used. It should be noted, however, that during polymerization in toluene solution, owing to the formation of low-molecular-weight polymer, the relative proportion of "terminal" toluene groups increases; these groups can enter into the polymer composition through alkylation of the aromatic nucleus. Therefore, some correlation of the reported values of the constants is possible, taking this factor into account.

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