CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR B. A. DOLGOPLOSK, E. I. TINYAKOVA

1964

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR B. A. DOLGOPLOSK, E. I. TINYAKOVA

ON SOME REGULARITIES OF THE PROCESS OF IONIC POLYMERIZATION

It is known that in the radical copolymerization of two monomers A and B, which differ greatly in reactivity, the addition to B of small amounts of the more reactive monomer A leads to inhibition of the polymerization process of monomer B. Thus, for example, small amounts of styrene inhibit the process of polymerization of vinyl acetate ([1]), small amounts of butadiene inhibit the polymerization of vinyl chloride ([2,3]), etc. The inhibition effect is due to the fact that the benzyl- or allyl-type radicals formed from monomer A are insufficiently active for interaction with the weakly active monomer B (vinyl acetate). It may be expected that in the radical copolymerization of equimolecular mixtures of monomers A and B the following picture should be observed (see Fig. 1).

At first (stage *I*) the process should proceed mainly with the participation of the more active monomer A. When the concentration of A becomes sufficiently small, a retardation of polymerization will be observed, corresponding to a decrease in the mole fraction of A in the mixture, and after complete exhaustion of A, polymerization of monomer B will begin (stage *II*).

Fig. 1

In stages *I* and *II*, copolymers will be obtained whose compositions approach those of homopolymers of A and B. It should be noted that the homopolymerization of B (vinyl acetate) proceeds at a higher rate than the homopolymerization of A, although monomer B is considerably less reactive than A. The more reactive the monomer, the more slowly the chain-growth reaction proceeds in homopolymerization. This, as has been noted ([4,5]), is connected with the fact that the conjugation effect reduces the reactivity of the radical to a greater extent than it increases the reactivity of the monomer. Therefore, for a number of monomers the following relationship is given:

schematic series of monomers and cations

Figure 2: schematic series of monomers and cations

⟶ increase in the reactivity of monomers
⟵ increase in the reactivity of radicals
⟵ increase in the rate of homopolymerization

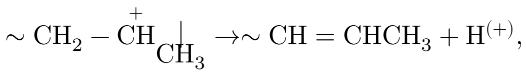
An analogous dependence should be observed in the hypothetical case of free-ionic polymerization. This picture may be distorted to one degree or another in ionic polymerization, in connection with the possible role of counterions, and especially strongly in coordination-ionic systems. It may be expected, however, that certain regularities following from consideration of the question on the basis of the reactivity of the monomers and of the corresponding active centers of the growing chain should manifest themselves in these cases.

Cationic Systems

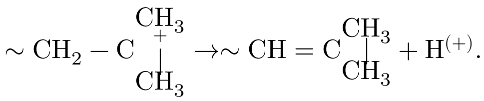
Let us arrange a series of olefins and dienes, and the active centers corresponding to them, according to their relative reactivity in cationic polymerization:

If the rate of homopolymerization is concordant with the reactivity of the active center, then in the series of olefins ethylene should polymerize by the cationic mechanism at the highest rate, and α-olefins, including isobutylene, at a lower rate, since in this series the activity of the growing cation decreases. In fact, however, homopolymerization of isobutylene proceeds considerably faster than that of ethylene and other α-olefins, with the formation of high-molecular-weight polymers. This is apparently explained by the fact that, in the case of more reactive cations, the chain-termination process proceeds more rapidly, for example by elimination (transfer) of a proton:

$$\sim \mathrm{CH_2} - \overset{+}{\mathrm{C}}\mathrm{H_2} \rightarrow \sim \mathrm{CH} = \mathrm{CH_2} + \mathrm{H}^{(+)}, \qquad (1)$$



$$\sim \mathrm{CH_2} - \underset{\mathrm{CH_3}}{\overset{+}{\mathrm{C}}\mathrm{H}} \rightarrow \sim \mathrm{CH} = \mathrm{CHCH_3} + \mathrm{H}^{(+)}, \qquad (2)$$

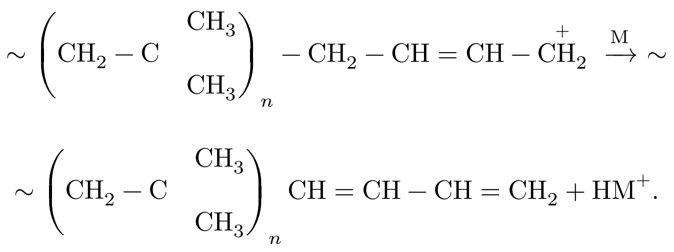


$$\sim \mathrm{CH_2} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\overset{+}{\mathrm{C}}}} \rightarrow \sim \mathrm{CH} = \mathrm{C}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix} + \mathrm{H}^{(+)}. \qquad (3)$$

Although isoprene and 2,3-dimethylbutadiene are more active monomers in cationic polymerization than butadiene, the active centers corresponding to them are more stable because of the positive inductive effect of the alkyl groups.

It should be noted that the unsaturation of the polymer chain in the cationic polymerization of butadiene amounts to only 40-60% of theory (^{6,7}), which indicates a high probability of attack by the crotyl cation on an internal double bond of the polymer chain. The absence of any great selectivity of action in the reaction of the growing chain (cation) with the monomer and with the double bonds of the polymer chain, as we have already noted earlier (^{8}), indicates that the stabilizing effect of conjugation in the case of crotyl cations is considerably lower than for the corresponding anions and free radicals. This is also indicated by the closeness of the copolymerization constants of dienes and α-olefins in cationic polymerization (^{9}).

It follows from the foregoing that, under cationic initiation, small amounts of isobutylene or vinyl alkyl ethers should inhibit the polymerization process of less active monomers, for example propylene, butadiene, or styrene; small amounts of 2,3-dimethylbutadiene should retard the polymerization process of butadiene. The inhibiting effect of small amounts of a more active monomer on the process of cationic polymerization was shown in work (10). It is known that, in the cationic polymerization of isobutylene in the presence of dienes, a strong decrease in the molecular weight of the polymer is always observed. The decrease in the length of the polymer chain is apparently due to the ease with which the proton-transfer reaction proceeds, owing to the higher activity of the crotyl cation and the energetic favorability of the reaction, accompanied by the formation at the chain end of a conjugated system of double bonds:



$$\sim \left(\mathrm{CH_2 - C} \begin{matrix} \mathrm{CH_3} \\ \\ \mathrm{CH_3} \end{matrix} \right)_n - \mathrm{CH_2 - CH = CH -} \overset{+}{\mathrm{CH_2}} \xrightarrow{\mathrm{M}} \sim$$

$$\sim \left(\mathrm{CH_2 - C} \begin{matrix} \mathrm{CH_3} \\ \\ \mathrm{CH_3} \end{matrix} \right)_n \mathrm{CH = CH - CH = CH_2 + HM^+}.$$

In the series butadiene, isoprene, 2,3-dimethylbutadiene, this reaction is more favorable for butadiene, whose cation is the most active, which is in agreement with the experimental facts. In the indicated series, during copolymerization with isobutylene, the influence of the diene on the molecular weight of the copolymer decreases.

In coordination-cationic systems of the type $(\mathrm{A})^{\delta-} \ldots \mathrm{R}^{\delta+}$, the presence of an "anion" at the reaction center leads to a weakening of the activity of the "cation" and thereby to a decrease in the probability of chain termination.

1. initial energy state of the system

$$\underline{\sim \mathrm{CH_2 - CH = CH - CH_2}^{+}}$$

free-cationic process

$$2.\quad \underset{\text{coordination-cationic system}}{\underline{\sim \mathrm{CH_2-CH=CH-\overset{\delta+}{CH_2}\dots[A]^{\delta-}}}}\ \Bigg\}\ \underset{\text{final state of the system}}{\underline{\sim \mathrm{CH=CH-CH=CH_2+H^+}}}$$

The formation of a conjugated system of double bonds at the chain ends during the polymerization of butadiene under the influence of a "cobalt" catalytic system was shown by us earlier (11). On this basis, the mechanism of the "regulating" action of ethylene and other olefins in the stereospecific polymerization of butadiene under the influence of a "cobalt" catalytic system may be considered (12). In the polymerization of butadiene under the influence of the indicated system, ethylene and other olefins lead to a decrease in the molecular weight of polybutadiene and to a shift of the molecular-weight distribution toward lower-molecular-weight fractions. Ethylene is a considerably less reactive monomer than butadiene, and therefore during copolymerization it enters the chain only to a slight extent. However, after entering the chain, owing to the high activity of the resulting "cation," the process of chain stabilization by proton transfer readily proceeds.

It is of interest to note the following fact. The system $R_3Al + TiCl_4$ is highly effective for the homopolymerization of dienes and cyclo-

pentadiene ([13]), but the addition to the diene of very small amounts of cyclopentadiene ($\sim 0.01\%$) causes inhibition of the diene polymerization process, i.e., in this case the same effect is observed as is exerted by traces of butadiene or styrene in the radical polymerization of vinyl acetate or ethylene. This means that cyclopentadiene is a considerably more active monomer than butadiene, but the end of a growing chain containing a cyclopentadiene unit is insufficiently active for reaction with the principal monomer—butadiene. For this pair of monomers, the polymerization kinetics as a function of mixture composition should have the same character as in the examples given above for radical polymerization.

What has been said apparently also holds for mixtures of conjugated dienes with ethylene or α-olefins, since in the indicated systems a small amount of the more active monomer—the diene—substantially slows the polymerization process of the olefin ([14]).

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Received
16 X 1963

CITED LITERATURE

1. C. Walling, *J. Am. Chem. Soc.*, **71**, 1930 (1949).
2. A. D. Abkin, in *Collection: Problems of Chemical Kinetics, Catalysis, and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 338.
3. T. V. Tkachenko, P. M. Khomikovskii et al., *ZhFKh*, **31**, 242 (1957).
4. T. Alfrei, D. Zh. Borre, G. Mark, *Copolymerization*, IL, 1953.
5. Kh. S. Bagdasar' yan, *Theory of Radical Polymerization*, Publishing House of the Academy of Sciences of the USSR, 1959.
6. W. S. Richardson, *J. Polym. Sci.*, **13**, 229 (1954).
7. E. I. Tinyakova, T. G. Zhuravleva et al., *DAN*, **144**, 592 (1962).
8. B. A. Dolgoplosk, E. I. Tinyakova, *DAN*, **146**, 362 (1962).
9. J. H. Immergut, G. Kollmann, A. Malatesta, *Makromol. Chem.*, **41**, 9 (1960).
10. E. B. Lyudvig, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **1**, 1333 (1959).
11. E. I. Tinyakova, B. A. Dolgoplosk et al., *DAN*, **152**, No. 6 (1963).
12. J. Natta, L. Porri, L. Fiore, *Bull. of Inventions*, No. 3, 59 (1960); patent No. 126061 (1959).
13. G. Gaylord, G. Mark, *Linear and Stereoregular Polymers*, IL, 1962.
14. L. M. Lanovskaya, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **2**, 1391 (1960).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.