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Fig. 1

Figure 1: Fig. 1

Abstract

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On the Mechanism of Radiation Polymerization of Isobutylene and Styrene in the Presence of Solid Additives

(Presented by Academician S. S. Medvedev, 25 III 1964)

It was established earlier (^{1}) that the rate of polymerization of isobutylene at $-78°$ under the action of γ-rays increases sharply when zinc oxide and other substances (silicon oxide, magnesium oxide, various salts, etc.) are added to the system. An increase in the rate was also observed when the surface area of the reaction vessel was increased in the case of radiation polymerization of styrene in ethyl chloride at $-78°$ (^{2}).

To clarify the role of solid additives in the development of ionic carbonium polymerization, the separate and joint polymerization of isobutylene and styrene in bulk under the action of γ-rays at various temperatures was investigated. Finely dispersed glass powder and zinc oxide were used as additives.

Fig. 1. Kinetics of polymerization of styrene (1—3) and isobutylene (4—9) in bulk in the presence of solid additives. Dose rate 70 and 14 $(6, 9)$ rad/sec. Styrene: 1 —without additive, 2 —with glass, 3 —with ZnO. Isobutylene: $4, 7$ —without additive; $5, 8$ —with glass, $6, 9$ —with ZnO.

The experiments were carried out using a Co^{60} source at the L. Ya. Karpov Physico-Chemical Institute with an activity of 20000 g-eq. of radium (^{3}). Isobutylene, preliminarily dried by freezing out the moisture and subsequent filtration at $-78°$, was distilled on a column (20 theoretical plates). The fraction boiling at $-6.9°$ was collected. The purification of styrene was described earlier (^{4}). After distillation, the monomers were additionally dried with calcium hydride at room temperature and recondensed in vacuum. Zinc oxide (chemically pure grade) was preliminarily calcined at 400° for 4 h. The glass powder was treated with aqua regia, repeatedly washed with distilled water, and dried. Before the experiment, the zinc oxide and glass powder were calcined in the reaction vessel at 300° in vacuum (10^{-4}—10^{-5} mm Hg) for 8 h. The amount of

Fig. 2. Kinetics of polymerization of isobutylene on zinc oxide at 0° without irradiation

Figure 2: Fig. 2. Kinetics of polymerization of isobutylene on zinc oxide at 0° without irradiation

zinc oxide and glass powder introduced was, by volume, equal to the volume of the liquid phase.

The kinetics of the separate polymerization of isobutylene and styrene were studied by means of a dilatometric method. Experiments on copolymerization were carried out in ampoules. The construction of the dilatometer and the procedure for carrying out the experiments are described in Ref. (4).

As was shown earlier, the polymerization of isobutylene at −78° under the action of γ-rays proceeds by a carbonium mechanism (4-6). The results of various authors (1), as well as our data (Fig. 1), on the accelerating effect of zinc oxide and powdered glass on the radiation polymerization of isobutylene at −78° indicate the substantial role of these additives in the development of the ionic polymerization reaction at low temperatures.

New information on the importance of solid additives for carrying out the ionic polymerization process was obtained by us in studying polymerization at 0°. It was established that the yield of polyisobutylene increases sharply when zinc oxide is added to the monomer and increases in the presence of powdered glass not only at −78°, but also at 0°. An analogous effect of zinc oxide was also found in the polymerization of styrene at 0°. The introduction of glass powder does not affect the rate of polymerization of styrene under these conditions (Fig. 1).

Fig. 2. Kinetics of polymerization of isobutylene on zinc oxide at 0° without irradiation

Of interest are the data we obtained on the tendency of isobutylene to polymerize in the presence of zinc oxide at 0° without γ-irradiation. As can be seen from Fig. 2, polymerization in this case proceeds at a fairly high rate, increasing with time. The molecular weight of the polymer formed in this process is 20,000. No reaction is observed in the absence of irradiation at −78° or when zinc oxide is replaced by glass powder.

S. V. Lebedev showed that isobutylene polymerizes in the presence of floridin with the formation of a low-molecular-weight product (7). These experiments illustrate the catalytic action of zinc oxide and floridin at ordinary temperatures, on the surface of which the polymerization process develops.

At present it is difficult to explain the increase in the reaction rate with time observed in our experiments (Fig. 2)—a fact unusual for isobutylene.

It is seen from Fig. 3 that copolymers of isobutylene and styrene obtained at 0°

Fig. 3 and Fig. 4: plots of copolymer composition and polymerization rate versus initial mixture composition.

Figure 3: Fig. 3 and Fig. 4: plots of copolymer composition and polymerization rate versus initial mixture composition.

under the action of γ-rays without solid additives, as well as with the addition of glass powder, are enriched in the styrene component, which indicates a radical mechanism of the reaction in these cases. In carbonium polymerization of these monomers under the action of catalysts of the Lewis acid type (⁀8) or under the influence of γ-rays at $-78°$ in ethyl chloride (⁀4), the polymers are enriched in the isobutylene component. At 0°, polymerization in the presence of zinc oxide also leads to the formation of copolymers enriched in the isobutylene component (Fig. 3), which testifies to an ionic mechanism of the reaction under these conditions. The constants of copolymerization of isobutylene (1) and styrene (2) at 0°, calculated on the basis of data on the composition of the copolymers (Fig. 3), have the following values.

With addition of zinc oxide: $r_1 = 3.3$; $r_2 = 0.2$.

Without additive or with the addition of glass powder: $r_1 = 0.5$; $r_2 = 3.7$.

From Fig. 4, which presents curves of the dependence of the rate of copolymerization of isobutylene and styrene at 0° (γ-rays) on the composition of the initial mixture, it is seen that, when the reaction is carried out in the presence of zinc oxide, the addition of small amounts of isobutylene to styrene leads to a considerable decrease in the reaction rate. The decrease in rate is due to the occur–

by renewal in the system of the less active carbonium ion of isobutylene, with which the rate of interaction of the styrene molecule is lower than with its own, more active styrene carbonium ion.

The addition of small amounts of styrene to isobutylene, for the same reasons, should also lead to a decrease in the polymerization rate. Therefore the rates of copolymerization of these monomers are always lower than the rates of their separate polymerization. However, the inhibiting effect of styrene on isobutylene as a result of the copolymerization reaction should not be manifested as strongly as is the case under consideration (Fig. 4, experiments in the presence of ZnO). Undoubtedly, a certain role in the lowering of the rate of polymerization of isobutylene by styrene is played by the "sponge" effect. It was shown that the addition of small amounts of ethylbenzene lowers the rate of polymerization of isobutylene.

Fig. 3. Dependence of the copolymer composition on the composition of the initial mixture for the isobutylene–styrene system. Polymerization in bulk at 0°: *a* –without additive; *b* –in the presence of glass; *v* –in the presence of zinc oxide

Fig. 4. Dependence of the rate of copolymerization of isobutylene and styrene in bulk on the initial composition of the monomer mixture. *a* —without additive, *b* —in the presence of glass, *v* —in the presence of zinc oxide. Temperature 0°, dose rate 70 rad/sec

It had previously been established that in radiation carbonium polymerization (−78°) styrene polymerizes faster than isobutylene (^{4}), which is in agreement with the reactivity of these monomers and of their carbonium ions. At 0° in the presence of zinc oxide a reversal of the rates occurs, because under these conditions styrene is partly polymerized by a radical mechanism, while the radiation yield of radicals for styrene is small.

The curves describing the dependence of the rate of joint polymerization of isobutylene and styrene on the composition of the initial mixture, both without additives and in the case of glass powder, have a different form (Fig. 4). The kinetic dependences we found in these cases may be connected with the fact that at 0° styrene, in the absence of zinc oxide, unlike isobutylene, polymerizes by a radical mechanism, as was convincingly shown earlier (^{6}). The joint polymerization of styrene and isobutylene under the conditions considered, as follows from the data on the composition of the copolymers (Fig. 3), also proceeds by a radical mechanism. The rate of joint

the rate of radical polymerization should continuously decrease as the concentration of isobutylene in the mixture increases, owing to the low rate of interaction of isobutylene with styryl and, still more, with allyl radicals arising in the system.

Thus, it has been established that, under the action of ionizing radiation, the copolymerization of isobutylene and styrene proceeds by an ionic mechanism not only at −78° (4), but also at 0° in the presence of zinc oxide. An increase has also been found in the rate of the separate polymerization at 0° of isobutylene and styrene on zinc oxide, and of isobutylene in the presence of glass powder. These results confirm the previously expressed suggestion (9) concerning the significant role of the surface in the development of ionic radiation polymerization. At low temperatures, conditions favorable for the development of ionic polymerization are created even in the absence of solid additives; at higher temperatures, however, realization of the ionic process is possible only in the presence of additives that increase the lifetime of the carbonium ions formed, which apparently occurs in the case of polymerization with zinc oxide.

The body of available data (10) makes it possible to consider that the development of the ionic polymerization of isobutylene and styrene is associated with the interaction of monomer molecules with a proton formed in the chemisorbed layer as a result of the transfer of an electron from atomic hydrogen to zinc oxide.

The exceptional role of the proton in these reactions follows from the work (6), in which a considerable increase in the rate of polymerization of isobutylene in the presence of ethyl chloride was shown.

More detailed information on the action of alkyl halides will be published subsequently.

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