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Abstract

Full Text

Chemistry

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Study of the Kinetics of Isoprene Polymerization under the Action of a Complex Catalyst

(Presented by Academician V. A. Kargin, April 16, 1958)

In elucidating the details of the mechanism of polymerization under the influence of complexes of organoaluminum compounds with titanium chlorides, data on the kinetics of polymerization may be of great interest. Up to the present time the rate of polymerization of propylene has been studied ([1,2]); however, interpretation of the kinetic data is made difficult by the fact that the polymer is practically insoluble in the reaction medium and coats the catalyst particles, as a result of which the rate of the process may depend on the diffusion of monomer through the polymer to the active center.

In the present work, the polymerization of isoprene, which gives polymers soluble in the monomer, in saturated hydrocarbons, and in benzene, was studied. The rate of the polymerization reaction was measured from the heat effect in a calorimeter consisting of a Dewar vessel (capacity 3.5 l) with a lid, placed in an air thermostat in which a temperature approximately equal to the reaction temperature was maintained. The calorimetric liquid was a low-viscosity spindle oil, preliminarily heated to the reaction temperature (about 32°). The ampoule holder was brought outside and connected to a vibration device. The reaction ampoule was divided by a thin partition into two vessels of 45-50 cm^3 each. Into one of them the previously purified monomer and solvent were distilled (total amount 35 cm^3); into the other, the catalyst components were introduced from Schlenk vessels. The change in temperature in the calorimeter was determined with a Beckmann thermometer to an accuracy of 0.01°. After the temperature in the calorimeter with the ampoule placed in it had become established, i.e., over 30-40 min did not change by more than 0.01-0.02°, the shaking device was switched on and the striker broke the partition. Intensive shaking of the ampoule was continued throughout the entire experiment, owing to which both the contents of the ampoule and the calorimetric liquid were mixed. The reaction rate was determined from the rate of heat evolution, i.e., from the rate of rise of the temperature in the calorimeter. With a total temperature rise of 0.1-0.5°, the isothermal character of the reaction is practically preserved. At the same time, such a rise makes it possible to follow the kinetics of the reaction with sufficient accuracy. The adiabatic character of the calorimeter and the absence of significant mechanical heat sources were checked in separate experiments.

Fig. 1

Figure 1: Fig. 1

Figure 1 gives a series of kinetic curves for the polymerization of isoprene under the action of titanium tetrachloride and triisobutylaluminum (ratio of catalyst components 1 : 1) with preliminary formation of the active complex in one of the compartments of the ampoule. First of all, we note that the polymerization rate is maximal immediately after the monomer is combined with the catalyst. A noticeable slowing of the reaction, as a rule, occurs at fairly low degrees of conversion (10–20%) and cannot be explained by the decrease in the concentration of monomer. Nor can it be explained by coating of the catalyst particles with polymer, since the

the polymer is soluble. The cause may be a chemical change of the catalyst surface or poisoning of it by side products of the polymerization reaction.

Distinctive results were obtained when the catalyst components were introduced separately into the reaction medium (one of the components was introduced with the monomer). In this case the course of the reaction changes sharply. During the first 30–40 min the polymerization proceeds very slowly, and heat evolution is practically not observed. Moreover, during this period there is some heat absorption, apparently connected with the process of formation of the catalytic complex (Fig. 2). After the induction period an almost linear rise in temperature begins, accompanied by the corresponding accumulation of polymer. However, even at this stage the polymerization proceeds more slowly than with the same amount of catalyst prepared beforehand. One more important detail, occurring when the catalyst components are introduced separately, should be noted. In this case the reaction mixture is a transparent reddish-brown liquid, which thickens as the reaction proceeds. Only a strong Tyndall effect, arising when the ampoule is illuminated by a narrow beam of light, indicates that the catalyst is not dissolved in the medium, but forms a very finely dispersed colloid.

Fig. 1. Kinetic curves when a ready catalyst mixture is introduced into the reaction medium. **1** –without solvents, each catalyst component 0.00012 mole; **2** –without solvent, each catalyst component 0.00048 mole; **3** –50% solution in isopentane, each catalyst component 0.00012 mole; **4** –50% solution in benzene, each catalyst component 0.00012 mole.

A detailed interpretation of the features of polymerization with separate introduction of the catalyst components requires additional experiments; however, the large role of the interaction of isoprene with the catalyst component introduced into it is already evident. In particular, the presence of interaction is indicated by the appearance of a yellow coloration of the monomer when even a very small amount of $TiCl_4$ is introduced into it. It would be a mistake to assume that only the catalyst component initially introduced into the monomer reacts with the monomer; the second component, which was in a separate com-

Fig. 2

Figure 2: Fig. 2

partment of the ampoule, after rupture of the partition, not yet being bound in the complex, can evidently react with the monomer.

Fig. 2. Kinetic curve when triisobutylaluminum is introduced together with the monomer. Polymerization without solvent; each catalyst component 0.00012 mole.

Thus, the formation of the active complex must be preceded by dissociation of the complexes of its components with isoprene. This process takes place in the presence of a considerable excess of monomer and therefore occupies a significant interval of time. The reaction of formation of the catalytic complex itself is exothermic. In the present case, however, it is associated with the endothermic reaction of decomposition of the initial complexes of the catalyst components with the monomer, as a result of which the overall reaction may prove to be even slightly endothermic (Fig. 2).

In light of the foregoing, the reason for the exceptionally fine dispersion of the catalyst when its components are introduced separately also becomes clear. Indeed, in the usual method of preparing the catalyst, a very large number of crystallization centers are immediately formed in a small volume; they grow very vigorously and merge with one another into a macroscopic precipitate.

In the present case, however, as is clear from what has been said above, the process proceeds considerably more calmly and on a large scale. Of particular importance here is the fact that formation of the catalyst takes place in the presence of the monomer. Owing to this, immediately after the formation of particles of the active catalyst, growth of polymer molecules begins on their surface; these molecules screen the particles from one another, as a result of which further aggregation is hindered.

It is interesting to note that in the polymerization of isoprene dissolved in benzene, a previously prepared coarsely dispersed catalyst is soon reduced to a colloidal state, and the mixture outwardly becomes the same as when the catalyst components are introduced separately. This dispersing action of benzene is evidently connected with its complex-forming properties. In this case the polymerization is sharply slowed down (Figs. 1, 4), which corresponds to the general tendency toward a decrease in the activity of a colloidal catalyst.

Along with the kinetics, we, together with I. Ya. Poddubnyi and N. N. Chesnokova, studied the molecular-weight distributions of polyisoprenes obtained under the action of the complex catalyst and isolated at different degrees of conversion ([3]). It was established that the average molecular weights and molecular-weight distributions over wide ranges are practically independent of the degree of conversion. There, a hypothesis was also advanced concerning the mechanism

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of chain-growth limitation, leading to comparatively narrow and symmetrical molecular-weight distributions.

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