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Abstract

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STATIONARY AND NONSTATIONARY PROCESSES OF BUTADIENE POLYMERIZATION CATALYZED BY THE SYSTEM $R_2AlCl—CoCl_2(Py)_2$*

In studying the polymerization of butadiene in the presence of the catalytic system—the pyridine complex of cobalt chloride + diisobutylaluminum chloride (^{1})—it was established that, depending on the initial concentration of water, polymerization proceeds by two mechanisms: stationary and nonstationary.

Stationary processes, all other conditions being equal, are realized only at one definite initial concentration of water: $[H_2O]_0 = [H_2O]_{st}$. Any deviation from this condition leads to nonstationary processes. In connection with the results obtained, it was assumed that stationary processes proceed at a constant water concentration, whereas nonstationary processes are accompanied by irreversible consumption of water.

In order to confirm this assumption, on the basis of a previously developed precise dilatometric method (^{1}), a study was carried out of changes in the rates of polymerization caused by the addition of water during the course of the polymerization process. The experiments were carried out, as in previous work, in benzene solution at a constant temperature of 21° and a constant initial butadiene concentration of 1.54 mol/l.

The experiments whose results are illustrated in Fig. 1 were carried out at the same initial concentrations of the cobalt $[Co]_0$ and aluminum $[Al]_0$ components of the catalyst.

The stationary process (condition: $[H_2O]_0 = [H_2O]_{st}$) in Fig. 1 is characterized by straight line D. Curves A (condition: $[H_2O]_0 > [H_2O]_{st}$) and B (condition: $[H_2O]_0 < [H_2O]_{st}$) describe nonstationary processes.

If, during the course of process B, water is added in such an amount that the total amount of water introduced into the system is equal to the amount of water introduced at the beginning of process A, then the polymerization rate increases sharply and remains constant for a long time (process C). However, the polymerization rate under these changed conditions ($V_C = 0.24\%/\text{min}$) is

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

not only less than the initial rate of process A ($V_A = 0.65\%/\text{min}$), but also less than the initial rate of the original process B ($V_B = 0.44\%/\text{min}$).

These results indicate that, under conditions of nonstationary polymerization, there occur not only reactions of irreversible binding of water, which lower its effective concentration, but also reactions leading to deactivation of the catalytic system (destruction of the initial active centers of the catalyst)**. Both of these reactions are the principal factors, causing the premature decay of the nonstationary polymerization process.

In this connection, it could be expected that the addition of water during stationary polymerization should cause not an increase in the rate, as occurs under nonstationary conditions, but a decrease in the rate of polymerization. That this is in fact the case is illustrated in Fig. 1 by process E.

The irreversible binding of water by the components of the complex catalyst and its destruction are processes that occur over time, and the period of this time is commensurate with the time interval of the polymerization.

Fig. 1. Effect of added water on the rate of polymerization. Initial concentration $[Co]_0 = 0.01$ mmole/l, $[Al]_0/[Co]_0 = 400$; A –water introduced only at $t = 0$, $[H_2O]_0 = 0.59$ mmole/l; B –the same at $[H_2O]_0 = 0.35$ mmole/l; C –after additional introduction $[H_2O] = 0.23$ mmole/l; D –stationary process $[H_2O]_0 = 0.5$ mmole/l; E –the same after addition during the process of $[H_2O] = 0.4$ mmole/l.

Fig. 2. Effect of added water at various stages of the nonstationary process. Process A –initial conditions: $[Co]_0 = 0.005$ mmole/l; $[H_2O]_0 = 0.25$ mmole/l. Added $[H_2O] = 0.23$ mmole/l: B –after 10 min; C –after 35 min. D –corresponding stationary process $[H_2O]_0 = 0.48$ mmole/l.

Figure 2 presents the results of experiments with addition of water at various stages of polymerization. If, during the course of the nonstationary process A, water is added in such an amount that the total concentration of water in

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* Py–pyridine.

** As the initial concentration of water is increased, when the polymerization rate decreases, the molecular weight of the polymer formed steadily increases. This indicates that in this case only the number of initial centers causing chain initiation decreases. The average length of the growing chains, on the contrary, increases (see work ([1])).

the system would be equal to the initial water concentration of the stationary process D, then the rate of process A increases; moreover, the values of the rates stimulated by identical concentrations of added water are smaller the longer the time interval from the beginning of the processes to the introduction of additional amounts of water. When water is introduced at 140 min, when the rate of the initial process approaches zero, no changes are observed, since at this stage of the process the initial active centers have been almost completely destroyed.

It is highly probable that the unproductive binding of water in polymerization processes is due to its interaction with the aluminum component of the initial catalyst, the concentration of which, under the experimental conditions adopted, is 2.5 orders of magnitude higher than $[Co]_0$. For this purpose, a study was carried out of the effect of the time of aging of the reaction solution of R_2AlCl in the presence of corresponding amounts of water and butadiene on

the polymerization rate before introduction of the cobalt component (the time of the beginning of the process). Experiments showed that, in nonstationary polymerization, the holding time of this mixture substantially affects the polymerization rate. In polymerization under stationary conditions, however, the holding time, as is seen from Fig. 3, does not cause changes in the rate, and the stationarity of the process is not disturbed.

This means that the effective concentration of water remains constant.

Fig. 3

Fig. 4

Fig. 3. Effect of the holding time of the reaction mixture before introduction of the cobalt component on the polymerization rate. Stationary process **A** –initial conditions: $[\mathrm{Co}]_0 = 0.020$ mmol/l; $[\mathrm{H_2O}]_0 = 0.52$ mmol/l; $[\mathrm{Al}]_0 = 8$ mmol/l. Holding time: **1** –10 min, **2** –60 min, **3** –60 min, **4** –90 min. Nonstationary processes **B** and **C** –($[\mathrm{H_2O}]_0 > [\mathrm{H_2O}]_{\mathrm{st}}$). Initial conditions: $[\mathrm{Co}]_0 = 0.020$ mmol/l; $[\mathrm{Al}]_0 = 9.45$ mmol/l; $[\mathrm{H_2O}]_0 = 0.65$ mmol/l. Holding time: process **B** –10 min, process **C** –90 min.

Fig. 4. Dependence of polymer yield on the initial monomer concentration. Initial conditions: $[\mathrm{Co}]_0 = 1.85 \cdot 10^{-5}$ mol/l; $[\mathrm{H_2O}]_0 = 5 \cdot 10^{-4}$ mol/l; $[\mathrm{Al}]_0 = 7.4 \cdot 10^{-3}$ mol/l. Processes: **A** –$[\mathrm{C_4H_6}]_0 = 0.780$ mol/l; **B** –$[\mathrm{C_4H_6}]_0 = 1.540$ mol/l; **C** –$[\mathrm{C_4H_6}]_0 = 2.30$ mol/l; **D** –$[\mathrm{C_4H_6}]_0 = 3.04$ mol/l; **E** –polymer yield over time in percent under conditions **A**, **B**, **C**, **D**.

Numerous experiments, both in earlier work (^{1}) and in the present work, showed that in the stationary process there is a proportional dependence of the polymer yield (%) on time, i.e., independence of the rate from the monomer concentration, which changes over time as a result of polymerization. However, studies carried out at different initial concentrations of butadiene, $[\mathrm{M}]_0$ (Fig. 4), established that the rate of the process, at a constant concentration of active centers (V_{st}), strictly obeys the equation:

$$-\frac{d[\mathrm{M}]}{dt} = k[\mathrm{M}]_0, \tag{1}$$

whence the polymer yield is $\Delta[M] = [M]_0 - [M]$, $\Delta[M] = k[M]_0 t$, or, in percent, $100\,\Delta[M]/[M]_0 = kt$.

It should be noted that relation (1) in the stationary process ($[M]_0 = 1.54$ mole/l) is maintained until the monomer concentration in the reaction system has reached 1.02 mole/l, which corresponds to approximately 35% polymerization; after this the rate begins to decrease, approaching zero at complete polymerization. However, the onset of these deviations is caused not only by a change in the monomer concentration, but also by a change in the physical properties of the system (increase in viscosity, shielding of active centers by the polymer being formed, etc.). This follows from the fact (Fig. 4, straight line A) that at an initial monomer concentration of 0.78 mole/l the polymerization proceeds at a constant rate, despite the fact that during the process $[M]$ falls to 0.48 mole/l, which is appreciably less than the corresponding value in deep polymerization, when deviations from relation (1) are observed.

It may be thought that similar phenomena are also represented in nonstationary processes, for, as was shown earlier, the principal factors determining the change in rate are: 1) nonproductive consumption of water and 2) destruction of the initial active centers, and not a change in the monomer concentration.

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