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Abstract

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THE INFLUENCE OF WATER ON THE COURSE OF BUTADIENE POLYMERIZATION IN THE PRESENCE OF COMPLEX COBALT CATALYSTS

In a previous paper by Diakonetsku and Medvedev ([1], [2]) it was established that, during the polymerization of butadiene in benzene solution in the presence of the catalytic system $\mathrm{Al}(iso\text{-}\mathrm{C}_4\mathrm{H}_9)_2\mathrm{Cl}$—alcohol complex of CoCl_2, the presence of water gives rise to a number of new specific phenomena directly related to the initial concentrations of water, which sharply alter the entire kinetic picture of the polymerization (extreme values of the polymerization rate, increase in the molecular weights of polybutadiene with increasing $[H_2O]_0$, etc.).

This led to the conclusion that, in order to elucidate the true regularities characterizing the course of these processes, it was necessary to carry out a more complete and precise investigation and, above all, to determine the conditions under which the rate of the processes reaches its maximum value (the region of invariant rates).

To solve this problem, a system was chosen consisting of the pyridine complex of cobalt chloride ($\mathrm{CoCl_2Py_2}$) and diisobutylaluminum chloride [$\mathrm{Al(iso\text{-}}C_4H_9\mathrm{)Cl}$], and a procedure was developed that best ensured the absence of moisture and oxygen in the initial reaction system and by means of which it was possible to carry out precise dosing of the required amounts of added water and catalyst components. This procedure fully ensured the obtaining of reproducible kinetic results. All operations for preparing and dosing the substances participating in the process, as well as for carrying out the experiments, were performed in an all-glass apparatus that had first been carefully evacuated under high vacuum while heated. Butadiene was passed through tetrabromobutane and kept for a specified time over lithium ethyl. Benzene, previously purified by the generally accepted procedure, was boiled for several hours with a liquid sodium-potassium alloy and then treated with lithium ethyl.

A dilatometric method was used to study the kinetics. The catalyst components were introduced by successively breaking thin-walled dosing glass ampoules in the dilatometer. First, water was introduced into the benzene solution containing the monomer in the form of a benzene solution with a known water content; then the aluminum component of the catalyst was introduced into the thermostated solution, and 10 minutes later the cobalt component. The time of introduction of the cobalt component was taken as the start of the reaction. The polymerization temperature was $21 \pm 0.1°$, and the butadiene concentration in all experiments was 1.94 mol/l.

Determination of the initial water concentrations $[H_2O]_0$ corresponding to maximum polymerization rates. Preliminary experiments established that in the absence of water, even at high catalyst concentrations, butadiene polymerization proceeds at a negligibly low rate and with the formation of negligible amounts of a very low-molecular-weight product. The introduction of water into the initial reaction mixture is accompanied by an increase in the polymerization rate. An especially sharp increase in rate is observed at an initial $[H_2O]_0 \approx 0.4$ mmol/l. With a further increase in $[H_2O]$, the rate reaches its maximum value, after which it falls sharply.

To determine the extreme values of the polymerization rates as a function of $[\mathrm{H_2O}]_0$, five series of experiments were carried out, differing from one another in the initial concentrations of the cobalt component [Co], while maintaining a constant ratio between the aluminum and cobalt components $[\mathrm{Al}]/[\mathrm{Co}] = 400$. In the individual series [Co] was: 0.005; 0.008; 0.012; 0.020 and 0.025 mmol/l. The water concentration $[\mathrm{H_2O}]$ in all series was varied from 0.4 to 0.65 mmol/l.

To illustrate the kinetic behavior of the systems studied, Fig. 1 is presented, showing the dependence of polymer yield on time at various $[\mathrm{H_2O}]_0$, obtained in the study of one of the indicated series: [Co]—constant = 0.012 mmol/l. It is seen here that the maximum rate of the process, V_{max}, under the conditions of this series is realized at $[\mathrm{H_2O}]_{\mathrm{max}} = 0.52$ mmol/l. Only in this case (see straight line 4) does the process proceed in a stationary manner. Any deviation from $[\mathrm{H_2O}]_{\mathrm{max}}$, either to the lower or to the higher side, disturbs the stationarity of the process and leads to its premature attenuation.

Fig. 1. Dependence of polymer yield on time at various $[\mathrm{H_2O}]_0$. [Co]-constant = 0.012 mmol/l, $[\mathrm{H_2O}]$ mmol/l: 1 –0.40; 2 –0.45; 3 –0.492; 4 –0.52; 5 –0.55; 6 –0.575; 7 –0.65.

Analogous results were obtained in all the other series. In this case the indicated situation was always preserved: the maximum rate is at the same time the basic condition for the process to proceed in a stationary regime: $V_{\mathrm{max}} = V_{\mathrm{stat}}$.

On the basis of the data obtained (see Table 1), the dependence of the initial polymerization rates, V_{init}, on the water concentration was established at various concentrations of the complex cobalt catalyst (Fig. 2).

All the curves expressing these dependences are characterized by different values of the maxima, the positions of which relative to $[\mathrm{H_2O}]$, as is seen in Fig. 2, upon decreasing the catalyst concentration are shifted slightly, but quite regularly, toward lower water concentrations. It should be noted that special experiments (condition: [Co]—constant, [Al]—variable) established that, under the adopted conditions ($[\mathrm{Al}]/[\mathrm{Co}] > 200$), a change in [Al] practically does not change the

Fig. 2. Dependence of the initial rates of polymerization, V_{init}, and average molecular weights on the concentration of water at different concentrations of the complex cobalt catalyst. [Co] mmol/l: 1—0.025; 2—0.020; 3—0.012; 4—0.008; 5—0.005. [Al]/[Co] = const = 400.

Figure 1: Fig. 2. Dependence of the initial rates of polymerization, V_{init}, and average molecular weights on the concentration of water at different concentrations of the complex cobalt catalyst. [Co] mmol/l: 1—0.025; 2—0.020; 3—0.012; 4—0.008; 5—0.005. [Al]/[Co] = const = 400.

polymerization rate, which agrees with the data obtained in the work of D' yakonesku.

For this reason, all changes in rates associated with changes in the concentration of the complex catalyst should be regarded as the result of changes only in its cobalt component [Co].

It is seen in Fig. 2 that, although the polymerization rates over the entire investigated interval of $[H_2O]_0$ are symbatic with [Co], nevertheless there exists only one definite value of $[H_2O]_{\max}$ at which the function $V = f(\text{Co})$ is single-valued:

$$V_{\max} = K \cdot [\text{Co}].$$

From the data given below it follows that the polymerization rate is proportional to the cobalt concentration to the first power.

[CO], mmol/l	$[H_2O]_{\max}$, mmol/l	$V_{\max}$, %/min	$K \cdot 10^{-2}$
0.025	0.55	2.50	1.00
0.020	0.53	1.80	0.90
0.012	0.50	1.22	1.02
0.008	0.48	0.80	1.00
0.005	0.47	0.45	0.90

Very distinctive phenomena are observed when studying changes in the molecular weights of polybutadiene as a function of $[H_2O]_0$.

Earlier, in the work of Diakonescu, it was shown that the molecular weight of the polymers increases with increasing $[H_2O]_0$; however, the small number of molecular-weight determinations made in that work was not sufficient for a correct description of the form of this dependence.

Fig. 2. Dependence of the initial rates of polymerization, V_{init}, and of the average molecular weights on the concentration of water at different

concentrations of the complex cobalt catalyst.
[Co] mmol/l: 1—0.025; 2—0.020; 3—0.012; 4—0.008; 5—0.005. [Al]/[Co] = const = 400.

As is evident from the data presented in Fig. 2, the molecular weights of the polymers formed increase progressively with the concentration of water up to regions close to $[H_2O]_{max}$, in complete agreement with the increase in the polymerization rate. This fact may serve as a new argument in favor of the previously stated assumption concerning the role of water as a factor promoting the development of reaction (polymerization) chains.

Near the region of V_{max}, the indicated correlation between the process rate and the molecular weight of the polymers disappears; however, the increase in molecular wei-

Table 1

Dependence of the initial polymerization rates and molecular weights on the water concentration at various concentrations of the complex cobalt catalyst

Series No.	[Co], mmol/l	[Al], mmol/l	[Al]/[Co]	$[H_2O]$, mmol/l	initial V, %/min	[η]	Molecular weight	1,4-cis	1,2	1,4-trans
1	0.005	2.0	400	0.40	0.28	2.80	300 000	–	–	–
2	0.005	2.08	415	0.45	0.30	2.96	340 000	96.7	1.7	1.5
3	0.005	2.0	400	0.492	0.42	4.5	585 000	97.5	1.2	1.2
4	0.0051	2.1	412	0.55	0.25	–	–	98.0	1.0	1.0
1	0.0090	3.60	400	0.40	0.36	1.50	120 000	–	–	–
2	0.0084	3.57	425	0.475	0.72	3.10	330 000	–	–	–
3	0.0080	3.18	397	0.492	0.62	4.33	560 000	–	–	–
4	0.0080	3.28	410	0.52	0.65	7.20	1 140 000	98.0	1.0	1.0
5	0.0078	3.22	413	0.55	0.56	–	–	–	–	–
6	0.0080	3.18	397	0.575	0.38	7.75	1 260 000	99.0	1.0	–
7	0.0080	3.17	397	0.65	0.36	–	–	–	–	–
1	0.0120	4.90	408	0.40	0.65	1.17	90 000	–	–	–

Series No.	[Co], mmol/l	[Al], mmol/l	[Al]/[Co]	$[H_2O]$, mmol/l	initial V, %/min	$[\eta]$	Molecular weight	1,4-cis	1,2	1,4-trans
2	0.0120	4.81	401	0.45	0.69	1.90	175 000	95.2	2.5	2.3
3	0.0121	4.80	397	0.492	1.10	2.16	210 000	96.0	2.0	2.0
4	0.0120	4.71	393	0.520	1.25	4.48	570 000	–	–	–
5	0.0118	4.78	398	0.55	0.78	–	–	97.3	1.5	1.2
6	0.0120	4.73	396	0.575	0.70	6.95	1 050 000	99.5	0.5	–
7	0.0120	4.88	406	0.65	0.60	–	–	–	–	–
1	0.021	8.5	405	0.40	0.79	0.96	68 000	92.5	4.5	3.0
2	0.0199	8.0	402	0.45	0.89	1.00	73 000	–	–	–
3	0.0205	8.8	430	0.492	1.20	1.10	87 000	93.5	3.8	2.8
4	0.0200	8.15	406	0.52	1.83	2.4	246 000	–	–	–
5	0.0202	8.20	407	0.54	1.70	3.56	420 000	–	–	–
6	0.0200	7.80	390	0.55	0.95	–	–	91.0	4.7	4.3
7	0.0200	8.10	406	0.65	0.54	–	–	–	–	–
1	0.0266	10.6	398	0.45	0.99	0.84	57 000	–	–	–
2	0.0249	9.90	397	0.492	1.06	–	68 000	–	–	–
3	0.0250	9.30	374	0.52	2.38	2.07	195 000	–	–	–
4	0.0264	10.65	403	0.575	1.88	4.65	600 000	–	–	–
5	0.0250	9.87	395	0.65	0.66	–	–	–	–	–

···sov upon increasing $[H_2O]_0$ continues, passes beyond the limits of $[H_2O]_{max}$, despite the sharp drop in rate in this region, but in this case proceeds not according to a stepwise, but according to a linear law.

Determination of the quantitative relationship between the molecular weights of the polymers and [Co] over the entire range of $[H_2O]_0$ does not appear possible, since small changes in $[H_2O]_0$ cause a sharp increase in molecular weights. In Fig. 2 it is nevertheless evident that in the nonstationary zones before and after V_{max}, an increase in [Co] is accompanied by a decrease in the molecular weight of the polymers. However, all polymers obtained at different [Co], but under conditions corresponding to V_{max}, have identical molecular weights. The molecular weights corresponding to V_{max} are marked in Fig. 2 by small circles. The fact that the molecular weights of polymers formed during the polymerization of butadiene in the presence of complex cobalt catalysts are independent (in the region of V_{max}) is a new characteristic feature of the course of these processes under stationary conditions.

It may be supposed that the main difference between stationary and nonstationary processes of this type is that the former proceed at a constant concentration of effective water, whereas the nonstationary ones are accompanied by unproductive consumption of water.

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1. I. Diakonesku, Dissertation, Moscow Institute of Fine Chemical Technology named after M. V. Lomonosov, 1963.

2. I. Diakonesku, S. S. Medvedev, DAN, 155, No. 4, 890 (1964).

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