E. V. ZABOLOTSKAYA, V. A. KHODZHEMIROV, A. R. GANTMAKHER

and Academician S. S. MEDVEDEV

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Abstract

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E. V. ZABOLOTSKAYA, V. A. KHODZHEMIROV, A. R. GANTMAKHER and Academician S. S. MEDVEDEV

SEPARATE AND JOINT POLYMERIZATION OF ISOPRENE UNDER THE ACTION OF α-$TiCl_3 \cdot Al(C_2H_5)_3$

The mechanism of polymerization in the presence of combined catalysts has not yet been sufficiently studied. Most work aimed at elucidating the mechanism of these processes has been devoted to studies of the separate and joint polymerization of ethylene with propylene. To reveal the regularities of polymerization, it is essential to broaden the range of systems studied; in particular, the use of monomers of different structure is of interest.

We studied the polymerization of isoprene, both separately and jointly with styrene, under the action of titanium trichloride and triethylaluminum. In order to prevent precipitation of the polymer from solution, the reaction was carried out in benzene.

Fig. 1. Dependence of the polymerization rate on the concentration of isoprene. 1 —experimental points, 2 —points calculated from equation (9).

A dilatometric method was used to carry out the polymerization. Purification of the initial substances differed little from that described earlier, but additional drying of isoprene and benzene with lithium ethyl and purification of isoprene through sulfone were introduced. The dosing of the components was basically carried out analogously to that indicated earlier ([1]).

The principal kinetic dependences for both separate and joint polymerization were determined at 75°; the degree of conversion did not exceed 10 wt.%.

Processing of the polymers for determination of viscosity, molecular weights, and compositions was carried out in an atmosphere of dry argon. Weight-average molecular weights (M_w) were measured by the light-scattering method, and number-average molecular weights (M_n) by osmometry. The compositions of the joint polymers were determined by infrared spectroscopy.*

In studying separate polymerization, the dependence of the polymerization rate on the concentrations of titanium trichloride, monomer, and temperature was investigated. The molecular weights of the polymers obtained were also determined.

A proportional dependence was found between the rate of the process and the amount of titanium trichloride per unit volume. In accordance with this, it may be considered that the number of active centers is determined by the concentration of $TiCl_3 \cdot Al(C_2H_5)_3$ complexes on the surface of titanium trichloride. It should be noted that all the work was carried out with one batch of titanium trichloride with an average grain size of 1.5-2 μ.

It was established that the proportional dependence of the polymerization rate on monomer concentration, observed in the polymerization of olefins ([2–4]) and styrene ([1]), did not occur in the polymerization of isoprene. The rate of polymerization increased more slowly than the concentration of isoprene (Fig. 1).

* The molecular weights of the polymers were determined by N. V. Makletsova and A. P. Golovina, to whom the authors express their gratitude, as well as to N. V. Desyatova for the spectrometric measurements.

It may be assumed that the polymerization process, as was considered earlier ([1,4]), proceeds on the surface of the catalyst through the stage of complex formation of the monomer with the titanium component of the catalyst, with subsequent insertion of the polarized molecule along the Al–C bond:

$$[\text{scheme}] + CH_2{=}CHR \underset{K''}{\overset{K'}{\rightleftarrows}} [\text{scheme}] \tag{1}$$

\end{equation}

$$[\text{scheme}] \xrightarrow{K} [\text{scheme}] \tag{2}$$

\end{equation}

A similar mechanism was proposed earlier by other authors as well ([5–7]). Assuming that initiation has essentially no effect on the rate of polymerization and that the size of the molecular polymer chains is limited by chain-transfer reactions, which are accompanied by regeneration of the active center, the rate of polymerization of styrene (V_A) and the rate of polymerization of isoprene (V_B) can be expressed as follows:

$$V_A = K_{AA}[A]\sigma_A^*, \tag{3}$$

where K_{AA} is the rate constant for the reaction of an adsorbed styrene molecule A with a styrene end group in the polymer chain; $[A]$ is the concentration of styrene end groups in the polymer chains (in separate polymerization, equal to 1); σ_A is the fraction of active centers $TiCl_3 \cdot AlR_3$ occupied by styrene molecules on the catalyst surface corresponding to one mole of $TiCl_3$.

From the stationarity conditions, σ_A can be expressed by the equation:

$$\sigma_A = \frac{K'_A(A)}{K''_A + K_{AA} + K'_A(A)}, \tag{4}$$

where K'_A and K''_A are the rate constants of adsorption and desorption of styrene, respectively; (A) is the concentration of styrene in the bulk. Since the rate of styrene polymerization is proportional to the monomer concentration, $K'_A(A) \ll K''_A + K_{AA}$, and

$$V_A = K_{AA}\frac{K'_A}{K''_A + K_{AA}}(A) = K_{AA}K_A(A). \tag{5}$$

From the experimental data $K_{AA}K_A = 1 \cdot 10^{-2}$ l/mol $\cdot$ min. Using completely analogous notation with the subscript B for isoprene, we express the rate of polymerization of isoprene V_B:

$$V_B = K_{BB}[B]\sigma_B \tag{6}$$

($[B]$ in the separate polymerization of isoprene is equal to 1.)

$$\sigma_B = \frac{K'_B(B)}{K''_B + K_{BB} + K'_B(B)}. \tag{7}$$

In the region of low isoprene concentrations, $K'_B(B) \ll K''_B + K_{BB}$, then

$$V_B = \frac{K_{BB}K'_B(B)}{K''_B + K_{BB}} = K_{BB}K_B(B). \tag{8}$$

* All values of rates, σ, and rate constants are referred to the catalyst surface corresponding to 1 mole of $TiCl_3$. The values of the true rate constants can be obtained by dividing the constants obtained by the number of moles of $TiCl_3 \cdot AlR_3$ complexes per 1 mole of $TiCl_3$.

From the linear equation (9), transformed from equations (6) and (7),

$$\frac{1}{V_\mathrm{B}} = \frac{K'_\mathrm{B} + K_\mathrm{BB}}{K'_\mathrm{B}}\frac{1}{K_\mathrm{BB}}\frac{1}{(\mathrm{B})} + \frac{1}{K_\mathrm{BB}} \tag{9}$$

and using the values of V_B and (B) given in Fig. 1, the values $K_\mathrm{BB} = 4.15 \cdot 10^{-2}$ min^{-1} and $K_\mathrm{B} = \frac{K'_\mathrm{B}}{K''_\mathrm{B}+K_\mathrm{BB}} = 0.65$ l/mol, as well as $K_\mathrm{BB}K_\mathrm{B} = 2.7 \cdot 10^{-2}$ l/mol $\cdot$ min, were determined. In Fig. 1, in addition to the experimental points, the calculated values of V_B for low isoprene concentrations are plotted.

From the data on the study of the dependence of the rate of isoprene polymerization on temperature in the interval from 60 to 95°, the overall activation energy was determined to be 13 kcal/mol.

In studying the molecular weights of polyisoprene it was found that the ratio M_w/M_n is close to 1 (Table 1), i.e., as in the case of polymerization

Table 1

Molecular weights of polymers. (Molecular weight of polystyrene of the order of 1000000 ([1]))

$[C_5H_8]$, mol/l	$[C_8H_8]$, mol/l	$[Al(C_2H_5)_3]\cdot 10^2$, mol/l	$TiCl_3\cdot 10^2$, mol/l	$V\cdot 10^3$, mol/l·min	Isoprene in starting mixture, mol.%	$[\eta]$	Mol. wt. · 10^{-3} M_w	Mol. wt. · 10^{-3} M_n
0.97	–	3.62	3.83	–	100	2.15	500	500
3.03	–	3.72	3.82	–	100	2.25	700	690
1.35	0.66	3.84	3.17	11.8	67.2	2.30	–	600
0.95	1.01	3.58	3.22	5.2	48.5	2.00	–	375
0.41	3.60	4.26	5.86	–	13.0	2.00	–	385

of isoprene with $TiCl_4\cdot AlR_3$ ([8]), the polymer obtained possesses monodispersity. In addition, it is seen that the molecular weight of polyisoprene, analogously to the molecular weight of polystyrene ([1]) obtained with the same combined catalyst, depends little on the monomer concentration. In the study of joint polymerization, the compositions of the copolymers* and the dependence of the polymerization rate on the composition of the initial mixture were determined.

From Fig. 2, which presents data characterizing the dependence of the composition of the copolymers on the composition of the initial mixture, it is seen that the copolymer compositions, compared with the initial composition, are considerably enriched in isoprene.

The rate of incorporation of isoprene and styrene into the copolymer in this system is determined by the equations:

$$-\frac{dA}{dt} = K_{\mathrm{AA}}\sigma_{\mathrm{A}}[A](1-\sigma_{\mathrm{B}}) + K_{\mathrm{BA}}\sigma_{\mathrm{A}}[B](1-\sigma_{\mathrm{B}}), \tag{10}$$

$$-\frac{dB}{dt} = K_{\mathrm{BB}}\sigma_{\mathrm{B}}[B] + K_{\mathrm{AB}}\sigma_{\mathrm{B}}[A]. \tag{11}$$

Here the values of the copolymerization constants r_A and r_B, calculated from the data on copolymer compositions by means of the usual differential form of the composition equation, correspond to the following ratio of constants and are equal to:

$$r_A = \frac{K_{\mathrm{A}} K_{\mathrm{AA}}}{K_{\mathrm{B}} K_{\mathrm{AB}}} = 0.1; \qquad r_B = \frac{K_{\mathrm{B}} K_{\mathrm{BB}}}{K_{\mathrm{A}} K_{\mathrm{BA}}} = 6.$$

From Fig. 3, which shows the change in the rate of joint polymerization as a function of the composition of the initial mixture, it is seen that the rate of joint polymerization is considerably lower than the rates of separate polymerization of isoprene and styrene. An especially sharp inhibiting action of isoprene is observed when it is added in small amounts to styrene.

* The complete solubility of copolymers enriched in styrene in butanone (in which polyisoprene is insoluble), and of copolymers enriched in isoprene in octane (in which polystyrene is insoluble), indicated the absence of homopolymerization under these conditions.

The inhibiting effect is due to the lowering of the rate of reaction (2) when a styrene molecule is replaced by an isoprene molecule in the terminal unit of the growing chain. The values obtained from the experimental data for the ratio of the corresponding rate constants of reaction (2)—addition of a styrene molecule to a terminal styrene group (K_{AA}) and of isoprene (K_{BA}),

$$r_1 = \frac{K_{AA}}{K_{BA}} = 2.2^*,$$

and of addition of an isoprene molecule to a terminal isoprene group (K_{BB}) and of styrene (K_{AB}),

$$r_2 = \frac{K_{BB}}{K_{AB}} = 0.27,$$

are in agreement with this assumption.

Fig. 2. Dependence of the copolymer composition on the composition of the initial mixture

Fig. 3. Dependence of the rate of joint polymerization on the composition of the initial mixture: V'—rate at a total monomer concentration of 2 mol/l, reduced to the same amount of titanium trichloride per liter

It is interesting to note that the molecular weights change in parallel with the change in the polymerization rate at different compositions of the initial mixture, as is evident from comparison of the data in Table 1 and the curve in Fig. 3.

Physicochemical Institute
named after L. Ya. Karpov

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* From the values given above $r_B = \dfrac{K_B K_{BB}}{K_A K_{BA}} = 6$ and $K_B K_{BB} = 2.7 \cdot 10^{-2}$ l/mol·min

$$\text{one obtains } K_A K_{BA} = 0.45 \cdot 10^{-2} \text{ l/mol} \cdot \text{min}.$$

From the obtained value and from the product

$$K_A K_{AA} = 1 \cdot 10^{-2} \text{ l/mol} \cdot \text{min}$$

one obtains the ratio

$$\frac{K_{AA}}{K_{BA}} = \frac{K_A K_{AA}}{K_A K_{BA}} = \frac{1 \cdot 10^{-2}}{0.45 \cdot 10^{-2}} = 2.2.$$

From the value

$$r_A = \frac{K_A K_{AA}}{K_B K_{AB}} = 0.1$$

and

$$K_A K_{AA} = 1 \cdot 10^{-2} \text{ l/mol} \cdot \text{min},$$

one obtains

$$K_B K_{AB} = 0.1 \text{ l/mol} \cdot \text{min}$$

and the ratio

$$\frac{K_{BB}}{K_{AB}} = \frac{K_B K_{BB}}{K_B K_{AB}} = \frac{2.7 \cdot 10^{-2}}{0.1} = 0.27.$$

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