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Abstract

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ASSOCIATION OF ORGANOLITHIUM COMPOUNDS AND ITS ROLE IN POLYMERIZATION PROCESSES

In studying the kinetics of lithium-initiated polymerization in hydrocarbon media, a number of works (1–4) established that the rate of polymerization increases more slowly than the concentration of the initiator. It was shown that, in the polymerization of styrene, isoprene, and butadiene under these conditions, the dependence of the rate of the process on the initiator concentration is individual for each monomer (4). On the basis of experimental data, the polymerization rate after a certain induction period can be represented by the following expression:

$$-\frac{d}{dt} = K[\mathrm{M}][\mathrm{LiR}]^{1/n}, \tag{1}$$

where $n > 1$.

The deviation from proportionality between the rate of polymerization and the initiator concentration was explained by deactivation of the active centers upon their mutual association (1,3). Polymerization of the monomer is caused only by nonassociated active centers. Association of low-molecular-weight organolithium compounds is well known (5). Association of the active centers formed in lithium-initiated polymerization of isoprene has also been detected by viscometry (4).

The phenomenon of association makes it possible to understand the reason for the lower rates of initiation compared with the chain-growth reaction in the polymerization of hydrocarbon monomers in nonpolar media. The reaction of addition of a monomer to nonassociated ethyllithium is accompanied by a transition from a less stable carbanion to a more stable one as a result of conjugation (here and below, the term "carbanion" denotes the group R in the compound LiR), and therefore should proceed at a higher rate than the chain-growth reaction. However, the greater association of ethyllithium compared with the active centers formed from it leads to an increase in the number of nonassociated active centers during polymerization and, correspondingly, to an increase in the polymerization rate.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

It seemed of interest to obtain quantitative data characterizing the dependence of the degree of association on the structure of polymer carbanions. For this purpose, over a wide range of ethyllithium concentrations, we studied the dependence of the chain-growth rate in the polymerization of styrene, isoprene, and butadiene on the initiator concentration.

To exclude the initiation stage, special experiments were carried out to study the dependence of the degree of initiation on the degree of polymerization at various initiator concentrations.

1. Initiation of polymerization by ethyllithium

In studying the absorption spectra it was found that, upon the transition of ethyllithium into lithium-polymer carbanions, the absorption region shifts toward longer wavelengths. This made it possible to determine the duration of initiation by studying the change in optical density at a selected wavelength during polymerization. Polymerization was carried out in a quartz cuvette-dilatometer placed in a small thermostat with quartz windows. The polymerization rate was determined from the contr—

···with an increase in the volume of the system, and the optical density was measured on an SF-4 spectrophotometer.

It was shown that, in the polymerization of styrene, isoprene, and butadiene in the concentration range of LiR $\leq 10^{-3}$ mole/liter, the stationary period is already observed at a relatively low degree of polymerization. The dependence of the degree of initiation on the degree of polymerization at a concentration of LiR $\simeq 4 \cdot 10^{-3}$ mole/liter is presented in Figs. 1 and 2. As is evident from the data presented, the rate of initiation increases on going from isoprene to butadiene and styrene. E. N. Kropacheva, B. A. Dolgoplosk, and

Fig. 1. Dependences of the polymerization rate $(1, 3)$ and the percent initiation $(2, 4)$ at initiator concentrations of $4 \cdot 10^{-3}$ mole/liter on the degree of polymerization of styrene $(1, 2)$ at $+8^{\circ}$ and butadiene $(3, 4)$ at $+30^{\circ}$. Initial concentration: styrene 1.2 mole/liter, butadiene 2.6 mole/liter

Fig. 2. Dependences of the polymerization rate $(2, 4)$ and the percent initiation $(1, 3)$ on the degree of polymerization of isoprene at $+30^{\circ}$ and initiator concentrations of $2 \cdot 10^{-3}$ $(1, 2)$ and $1.7 \cdot 10^{-2}$ mole/liter $(3, 4)$. Initial isoprene concentration 2.5 mole/liter

E. M. Kuznetsova (^{6}), in the polymerization of styrene and isoprene in bulk in the region of relatively high ethyllithium concentrations (0.1 mole/liter), showed that the initiation process takes place throughout the entire polymerization process. An analogous phenomenon was observed by us in the polymerization of isoprene in heptane solution at a monomer concentration of 2 mole/liter and an initiator concentration of 0.017 mole/liter. After the monomer had been consumed, at such ethyllithium concentrations a sharp increase in the absorption intensity was observed, apparently due to metalation of the CH_3 group of polyisoprene by unreacted ethyllithium (Figs. 2, 3). In the homopolymerization of styrene and butadiene in a mixture of toluene and tetrahydrofuran (THF), the initiation process by ethyllithium in the concentration range of ethyllithium 10^{-2} mole/liter and monomer 1.5 mole/liter, even at low temperatures of $-70°$, proceeds so rapidly that under these conditions it was not possible, during polymerization, to measure the rate of increase in the optical density of the solution. A sharp increase in the rate of initiation of the polymerization of styrene and isoprene by ethyllithium in the presence of THF additions was also observed in ([6]).

2. Evaluation of the dependence of the degree of association on the structure of polymeric carbanions. The dependence of the rate of chain growth on the concentration of active centers during the polymerization of styrene, isoprene, and butadiene was studied in the concentration range of ethyllithium from 10^{-5} to 10^{-2} mole/liter, since at higher initiator concentrations it is difficult to exclude the influence of the initiation stage. To eliminate traces of possible impurities, the walls of the dilatometer under vacuum were successively washed with a solution of ethyllithium in a hydrocarbon solvent and with solvent. The solvents and monomers used were dosed by recondensing them with ethyllithium. The concentration of active centers was determined from the initiator charge and refined from the molecular weights of the resulting polymers ([1],[3],[4]). Polymerization was carried out until

100% conversion, and the monomer concentration at time t was determined from compression data. The data obtained on the dependence of the chain-growth rate of styrene 1, isoprene 2, and butadiene 3, 4 in toluene and heptane on the initiator concentration are given in Fig. 3. It follows from Fig. 3 that the exponent n in equation (1), which characterizes the degree of association, remains constant over a wide range of initiator concentrations (from 10^{-5} to 10^{-2} mole/l). The value of n depends on the structure of the carbanion: for the active centers of polystyrene n is close to 2, for polyisoprene $n \simeq 3 \div 4$, for polybutadiene $n \simeq 5 \div 6$. The value $n = 2$ for the active centers of polystyrene was also obtained in work [7].

Fig. 3. Dependences of polymerization rates (mole/l • sec) of monomers on initiator concentration at +30 and $[M] = 1$ mole/l. 1 —styrene in toluene solution, 2 —isoprene in heptane solution, 3 —butadiene in toluene solution, 4 —butadiene in heptane solution

On the basis of the dependences obtained, the chain-growth process in lithium-initiated polymerization may be represented by the following scheme:

Fig. 3. Dependences of polymerization rates (mole/l • sec) of monomers on initiator concentration at +30 and [M] = 1 mole/l. 1 —styrene in toluene solution, 2 —isoprene in heptane solution, 3 —butadiene in toluene solution, 4 —butadiene in heptane solution

Figure 2: Fig. 3. Dependences of polymerization rates (mole/l • sec) of monomers on initiator concentration at +30 and [M] = 1 mole/l. 1 —styrene in toluene solution, 2 —isoprene in heptane solution, 3 —butadiene in toluene solution, 4 —butadiene in heptane solution

$$\mathrm{RM}_x\mathrm{Li} + (\mathrm{RM}_x\mathrm{Li})_{i-1} \underset{K_{2i}}{\overset{K_{2i-1}}{\rightleftarrows}} (\mathrm{RM}_x\mathrm{Li})_i;$$

$$i = 2, 3, 4\ldots \qquad (2)$$

$$\mathrm{RM}_x\mathrm{Li} + \mathrm{M} \xrightarrow{K_p} \mathrm{RM}_{x+1}\mathrm{Li}, \qquad (3)$$

on the basis of which the polymerization rate is

$$-\frac{d[M]}{dt} = K_p[M][\mathrm{RM}_x\mathrm{Li}], \qquad (4)$$

where $[\mathrm{RM}_x\mathrm{Li}]$ is determined from the equality

$$[\mathrm{RLi}]_0 = [\mathrm{RM}_x\mathrm{Li}] + \ldots + i\frac{K_3\ldots K_{2i-1}}{K_4\ldots K_{2i}}[\mathrm{RM}_x\mathrm{Li}]^i + \ldots, \qquad (5)$$

obtained using the conditions of thermodynamic equilibrium

$$\frac{d[(\mathrm{RM}_x\mathrm{Li})_i]}{dt} = 0 \quad (\text{including } i = 1). \qquad (6)$$

Taking into account the predominance of n-membered associates of active centers, the chain-growth rate is determined by the dependence

$$-\frac{d[M]}{dt} = K_p[M]\left(\frac{K_4\ldots K_{2n}}{nK_3\ldots K_{2n-1}}[\mathrm{RLi}]_0\right)^{1/n}, \qquad (7)$$

i.e., it completely coincides with the experimental dependence (1).

Table 1 gives the activation-energy values for the chain-growth reaction in the polymerization of styrene, isoprene, and butadiene, obtained by measuring the polymerization rates in the course of the process at different temperatures. It follows from the table data that when the initiator concentration is changed by $\sim 10^3$ times, the activation-energy values change relatively little. Since the activation energy of the process is $E = E_p + Q/n$, where E_p is the activation energy of the elementary act of monomer addition to the unassociated active center, and Q is the thermal effect of association, the small change in activation energies over a wide interval of initiator concentrations indicates the relatively high strength of the associates and the constancy of the composition of the associates.

In addition to the above-mentioned one-stage mechanism of the chain-growth act (reaction (3)), the two-stage mechanism of chain growth considered by us earlier also appears very probable—through the formation of a complex of the monomer with the lithium of the active center and subsequent rearrangement of the complex into an organometallic compound [8,9]. In this case, at relative-

but at low concentrations of complexes and unassociated active centers, as compared with the concentration of associated centers, the kinetic dependences have a form analogous to (7) (K_p is replaced by $K'_p \cdot K_o/(K_d + K'_p)$, where K'_p is the rate constant for rearrangement of the complex, and K_o and K_d are the constants of formation and dissociation of the complex). As noted in (4), one of the reasons for the enrichment of their copolymers with styrene in diene monomers may be the selectivity of the complex-formation process. Some indication of the possibility of complex formation of active centers with the π-electrons of the benzene rings of solvents may be

Table 1

Rates and activation energies of the polymerization processes of styrene, isoprene, and butadiene in hydrocarbon solvents

<table>
<tr><th>Monomer</th><th>Solvent</th><th>$[\text{RLi}]_0 \cdot 10^4$, mol/l</th><th>$\frac{d[\text{M}]}{[\text{M}]dt} \cdot 10^4$, $\text{l}^{-1} \cdot \text{sec}^{-1}$ at 30°</th><th>E, kcal</th></tr>
<tr><td>Styrene</td><td>Toluene</td><td>1.3</td><td>0.93</td><td>13.6$±0.5||Styrene|Toluene|400|40|14.6±0.5||</td></tr>
</table>

the increase in the rate of polymerization of butadiene and isoprene in toluene as compared with polymerization in heptane (Table 1, Fig. 3).

In work (10), the existence of associates of active centers in the process of polymerization of the named monomers is denied. The authors assume that in the system only equilibrium (2) can occur at $i = n$, and do not take into account the subsequent stages of equilibrium with $i = n - 1;\ n - 2;\ \ldots\ 2$. In connection with this, the authors assume that $[\text{KM}_x\text{Li}] = [(\text{RM}_x\text{Li})_{n-1}]$, and obtain that in all cases the order of the reaction with respect to initiator must have the value 1/2, which is not observed experimentally. Denying the presence of association, the authors naturally could not correctly interpret the results they obtained and were forced to introduce into the kinetic scheme formal concepts of initiation and termination in the chain ([2,10]).

From the analysis presented above (equations (2)—(7)), it is seen that the order of the reaction with respect to initiator is determined by the degree of association of the active centers. According to experimental data, the degree of association of active centers depends on the structure of the carbanion and in the systems studied varies from 2 to 6. The strength of the associates is relatively high, since even at concentrations of 10^{-5} mol/l the active centers are predominantly in the associated state.

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1. F. Welch, J. Am. Chem. Soc., **81**, 1345 (1959).
2. A. A. Korotkov, N. N. Chesnokova, L. B. Trukhmanova, Vysokomolek. soed., **1**, 46 (1959).
3. Yu. L. Spirin, D. K. Polyakov, A. R. Gantmakher, S. S. Medvedev, Vysokomolek. soed., **2**, 1082 (1960).
4. Yu. L. Spirin, D. K. Polyakov, A. R. Gantmakher, S. S. Medvedev, DAN, **139**, 899 (1961).
5. G. E. Coates, *Organo-metallic Compounds*, London—N. Y., 1960.
6. E. N. Kropacheva, B. A. Dolgoplosk, E. M. Kuznetsova, DAN, **130**, 1253 (1960).
7. D. I. Worsfold, S. Bywater, Canad. J. Chem., **38**, 1891 (1960).
8. Yu. L. Spirin, A. R. Gantmakher, S. S. Medvedev, Vysokomolek. soed., **1**, 1258 (1959).
9. Yu. L. Spirin, A. A. Arest-Jakubovich et al., J. Polym. Sci., **58**, No. 166, 1181 (1962).
10. A. A. Korotkov, G. V. Rakova, Vysokomolek. soed., **3**, 10, 1483 (1961).

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