THE MECHANISM OF THE ANIONIC COORDINATION POLYMERIZATION OF ISOPRENE

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The polymerization kinetics of isoprene (2-methyl-1,3-butadiene) in benzene with butyllithium as the initiator was investigated by the gas chromatographic method. After completion of the initial period of the reaction, its order with respect to the initial concentration of initiator is negative at the concentrations of the latter between 0·01 and 0·25 mol/l, and positive at higher concentrations. A reaction scheme has been suggested with respect to the "cross" association of butyllithium and of the "living" oligoisoprene.

In an earlier paper[1], negative formal reaction orders were found with respect to the initial concentration of initiator $[I]_0$ in the polymerization reaction of isoprene* in the presence of butyl- and hexyllithium within a certain concentration range. A similar dependence was established by Hsieh[2] for butadiene and isoprene in toluene and cyclohexane, and by Spirin and coworkers[3] for isoprene in toluene with ethyllithium as initiator. Sinn and coworkers[4] found a negative order for the polymerization of isoprene with butyllithium as initiator (without solvent). The range of change in the reaction order reported by these authors is similar; it may be assumed, therefore, that the solvent used does not influence this anomaly to any considerable extent. Reich and Stivala[5] tried to demonstrate the polymerization mechanism of dienes, but they did not elucidate the cause of negative orders ascertained for the polymerization. It seems that for a complex characterization of the polymerization mechanism one must take into account the "cross" association of living polyisoprene and butyllithium, which is probably responsible for the negative reaction orders. Morton and coworkers[6,7] demonstrated the complex formation in the ratio

$$(RM_nLi)_2 + (EtLi)_6 \overset{K_k}{\rightleftarrows} 2\ RM_nLi\cdot(EtLi)_3$$

3 : 1, and established that the equilibrium constant of complexation, K_k, was 6·5. Unlike earlier results, other researchers[8,9] observed a change in the reaction order from unity to zero with increasing concentration of butyllithium. Korotkov and coworkers[9] found a second order with respect to the initial monomer concentration, $[M]_0$. In the case of the initiation reaction alone the conditions are still more complex: Lundborg and Sinn[10,11] found that the reaction order varied with respect to the initiator concentration, and that with $[I]_0$ increasing above 10^{-3} mol/l the original order, which was 0·33, decreased to 0·17. On the other hand, Hsieh[2] showed that the rate of initiation of the polymerization of butadiene and isoprene is proportional to the concentration of alkyllithium (sec-BuLi, tert-BuLi, iso-BuLi, BuLi and isopropyllithium) in hydrocarbons. Johnson, Worsfold and Bywater[12,13] found some kind of the induction period of ini-

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* The name "isoprene", commonly used in technology, is applied to 2-methyl-1,3-butadiene.

tiation, and the asymptote of kinetic curves for infinite time reached a 70% conversion at most; the polymerization rate in the linear part of the kinetic curves was proportional to $[I]_0^{2/3}$. A conclusion may also be drawn from ref.[13] that if 50% of butyllithium are transformed by the initiation reaction into a "living" polymer, the rate of propagation is smaller than if the reaction is carried out with the same amount of pure living polyisoprene. This finding may be explained through the formation of an inactive associate between the living polyisoprene and butyllithium.

For the polymerization of isoprene with tert-butyllithium, Roovers and Bywater[14] give a non-constant order with respect to the initial concentration of isoprene; this order decreases from unity to zero with increasing $[M]_0$. Brown[15] tries to explain the decrease in the reaction order with increasing initial concentrations of the reaction components through the participation of a preceding association equilibrium between the hexameric associate and the monomer molecule; it is highly probable, namely, that a π-donor like isoprene considerably participates in the formation of the solvate shell of the alkyllithium associate. With respect to the practical investigation of kinetics a question becomes important to what extent the monomer bound on the initiator associate is amenable to analytical determination. The results will probably differ depending on whether samples of the reaction mixture are analyzed without deactivation (UV spectra of the monomer) or after deactivation (GLC). If samples of the reaction mixture are deactivated with water or alcohols, all six molecules of the alkyllithium associate are of course not hydrolyzed simultaneously: the degree of its association decreases first, and very reactive lower associates may partly be added to the molecule of the coordinated molecule before their total hydrolysis takes place[16]. Such a possibility is suggested by the finding that the highest orders of polymerization determined by GLC were close to unity[1,2], while values obtained by employing the spectral method were considerably lower[13].

This study has as its objective an experimental check-up of the assumption outlined above and a quantitative interpretation of the results obtained, in terms of a kinetic scheme of the reaction, which would satisfactorily explain the apparently controversial earlier data.

EXPERIMENTAL

The preparation and purification of chemicals were the same as described in earlier papers[1,16]; the polymerizations were carried out similarly to refs[1,16] (benzene, 300 K), with deactivation (if necessary) of samples using water or alcohol. Samples employed in GLC analyses without termination[1] were taken from the reactor by using a special device and introduced directly into a stream of carrier gas in a gas chromatograph. There, at the evaporator temperature 200°C and after the dilution of gasified samples 10^3—10^4 times with the carrier gas, bimolecular reactions could be prevented, and monomolecular reactions supported. It was also verified that alkyllithium remaining in the evaporator did not cause the isoprene to polymerize (no loss of isoprene higher than 2% occurred after the injection of mixtures of isoprene and alkyllithium immediately on mixing; hence, the reaction stops after dilution with the gas carrier), and that no depolymerization took place during the analysis, because the analytical method used showed the reaction to proceed until complete consumption of the monomer.

RESULTS AND DISCUSSION

The Range of Low Alkyllithium Concentrations

In the ranges of initial concentrations of initiator ($[I]_0$) $10^{-3} - 1 \,.\, 10^{-1}$ mol/l and monomer ($[M]_0$) 0·25 – 1·0 mol/l, no difference was found between the extents of the reaction (monomer to polymer conversion), if samples were analyzed without deactivation or with the deactivation of the reaction mixture with water or ethanol. Only for the value at the upper boundary of the $[BuLi]_0$ range given above there was a deviation of some 4% of the monomer, and two inflexion points could be distinctly seen on the kinetic curve. The reaction exhibited a distinct induction period, and the reaction order calculated from the slopes of the kinetic curves in their linear part (75–90% conversion) was approximately –0·5 in the centre of the concentration range just mentioned. The reaction order with respect to $[M]_0$ was insignificantly higher than unity. With $[I]_0$ increasing up to 0·04 mol/l, the induction period remains unchanged (approx. 10 min); at higher concentrations it quickly becomes shorter. The initial rate cannot be determined with exactitude (being too low), but it is proportional to $[I]_0^{1/2}$ or $[I]_0^{1/3}$. Using reported data, the following scheme may be suggested[1-15]:

dissociation

$$(RLi)_6 \overset{K_1}{\rightleftarrows} 3\,(RLi)_2 \tag{A}$$

initiation

$$(RLi)_2 + M \xrightarrow{k_i} RMLi + RLi \tag{B}$$

propagation

$$RM_nLi + M \xrightarrow{k_p} RM_{n+1}Li \tag{C}$$

association

$$2\,RM_nLi \overset{1/K_2}{\rightleftarrows} (RM_nLi)_2 \tag{D}$$

cross-association

$$(RM_n)_2 + (RLi)_6 \overset{K_k}{\rightleftarrows} 2\,(RLi)_3.RM_nLi\,. \tag{E}$$

If H denotes the associate of the initiation alkyllithium $(RLi)_6$, D is the associate of the "living" chain $(RM_nLi)_2$, Q is the cross-associate $(RLi)_3.RM_nLi$ and x is the number of mol of the "living" chain arising by the initiation reaction, it may be written

$$\frac{dx}{dt} = k_i[M][(RLi)_2] \doteq k_i[M]\, K_1^{1/3}[H]^{1/3}\,, \tag{1}$$

because according to reported data[2,15], K_1 and K_2 are small. The loss of the monomer is described by the equation

$$-\frac{d[M]}{dt} = \frac{dx}{dt} + k_p[M]\, K_2^{1/2}[D]^{1/2}\,, \tag{2}$$

because the monomer is consumed by the initiation and by the propagation reaction. The equilibrium E gives

$$[D][H]\, K_k = [Q]^2\,; \tag{3}$$

under conditions for the total analytical lithium concentration, and for low K_1, K_2

$$[I]_0 = 6[H] + 2[D] + 4[Q]\,, \tag{4}$$

$$x \quad = 2[D] + [Q] \tag{5}$$

we obtain by substitution into (*3*)

$$[Q] = \frac{(2x + [I]_0) - \sqrt{[(2x + [I]_0)^2 - 4(3-12/K_k)\,(x[I]_0 - x^2)]}}{2\,.\,(3-12/K_k)}\,. \tag{6}$$

If x is small, or if K_k lies between 3 and 6 (ref.[6] for ethyllithium gives $K_k = 6{\cdot}5$), it may be written approximately that

$$[D] \approx \tfrac{3}{2}x^2/(2x + [I]_0)\,, \tag{7}$$

$$[H] \approx \tfrac{1}{6}([I]_0 - x^2)/(2x + [I]_0)\,. \tag{8}$$

The comparatively complicated expression for $[H]^{1/3}$ does not in fact differ from the equation for the straight line

$$[H]^{1/3} \approx (\tfrac{1}{6}[I]_0)^{1/3}\,(1 - x/[I]_0) \tag{9}$$

by more than 5% up to x equal to $0{\cdot}7[I]_0$. After substitution from Eqs (*7*) and (*9*), Eqs (*1*) and (*2*) may be expressed as

$$\frac{\mathrm{d}x}{\mathrm{d}t} \doteq C_1[\mathrm{M}]\,[\mathrm{I}]_0^{1/3}\left(1 - \frac{x}{[\mathrm{I}]_0}\right), \tag{10}$$

$$-\frac{\mathrm{d}[\mathrm{M}]}{[\mathrm{M}]\,\mathrm{d}t} \doteq \frac{\mathrm{d}x}{[\mathrm{M}]\,\mathrm{d}t} + C_2[\mathrm{I}]_0^{1/2}\,\frac{x}{[\mathrm{I}]_0 + x}, \tag{11}$$

where C_1, C_2 are constants, and approximations according to the model $(1 + 2q)^{1/2} \approx 1 + q$ are used.

The mechanism may be contemplated for two limiting cases:

a) $[\mathrm{M}]_0 \gg [\mathrm{I}]_0$; competition between reactions *B* and *C* may be neglected, *i.e.* it may be put that $[\mathrm{M}] = [\mathrm{M}]_0 - x$, and the first term on the right-hand side of Eq. (*11*) may be neglected. Integration of Eq. (*10*) gives

$$x = \frac{[\mathrm{M}]_0\,(\mathrm{e}^{r_1 t} - 1)}{[\mathrm{M}]_0\,\mathrm{e}^{r_1 t}/[\mathrm{I}]_0 - 1}, \tag{12}$$

where $r_1 = C_1([\mathrm{M}]_0 - [\mathrm{I}]_0)\,[\mathrm{I}]_0^{-2/3}$, $C_1 = k_i \,.\, \sqrt{(K_1/6)}$, $C_2 = k_p\,\sqrt{(3K_2/2)}$. By substitution for x into Eq. (*11*) and integration, we obtain at $[\mathrm{I}]_0/[\mathrm{M}]_0 \ll 1$ the expression

$$[\mathrm{M}]/[\mathrm{M}]_0 \doteq \{\mathrm{e}^{r_1 t}/(2\mathrm{e}^{r_1 t} - 1)^{1/2}\}^{-A_1}, \tag{13}$$

where

$$A_1 = C_2/C_1 \,.\, [\mathrm{M}]_0\,[\mathrm{I}]_0^{7/6}/([\mathrm{M}]_0^2 - [\mathrm{I}]_0^2)\,.$$

b) For a high $[\mathrm{I}]_0/[\mathrm{M}]_0$ close to unity, the propagation reaction is more strongly operative (r_1 decreases), x is very small and may be neglected with respect to $[\mathrm{I}]_0$ in Eqs (*10*) and (*11*). The system is then solved by substituting the expression

$$[\mathrm{M}] = [\mathrm{M}]_0\,(\cosh r_2 t + A_2 \sinh r_2 t)^{-2} \tag{14}$$

into Eq. (*10*), from which we obtain by integration that

$$x = \frac{[\mathrm{M}]_0\,C_1[\mathrm{I}]_0^{1/3}}{r_2}\,\frac{\sinh r_2 t}{(\cosh r_2 t + A_2 \sinh r_2 t)}; \tag{15}$$

by substituting into Eq. (*11*) and differentiating, the coefficients are determined by comparing the respective terms at hyperbolic functions:

$$r_2 = \sqrt{\{0{\cdot}25 C_1^2[\mathrm{I}]_0^{2/3} + 0{\cdot}5[\mathrm{M}]_0\,C_1 C_2[\mathrm{I}]\}^{-1/6}}\,,$$

$$A_2 = (1 + 2C_2[\mathrm{M}]_0/C_1[\mathrm{I}]_0^{5/6})^{-1/2}\,.$$

Function (*14*) for various A_2 is shown in Fig. 1. With increasing A_2 the induction period becomes shorter, and for small C_1 the polymerization order with respect to the initial concentration of the initiator is approximately —1/12, $C_1 \approx 0{\cdot}032\ \mathrm{l}^{1/3}\ \mathrm{mol}^{-1/3}\ \mathrm{h}^{-1}$; $C_2 \approx 35{\cdot}0\ \mathrm{mol}^{-1/2}\ .\ \mathrm{l}^{1/2}\ \mathrm{h}^{-1}$. Only C_1C_2 may be determined with exactitude as $1{\cdot}10 \pm 0{\cdot}05\ \mathrm{mol}^{-5/6}\ \mathrm{l}^{5/6}\ \mathrm{h}^{-2}$. Kinetic curves according to Eq. (*14*) are compared in Fig. 2 with experimental points. A similar fit has been observed for all kinetic curves in the given interval of the initial concentrations of the initiator with the exception of the highest concentration.

Using both solutions, (*a*) and (*b*), we calculated the corresponding rates for a 15% conversion of the monomer. The reaction rates thus calculated and plotted depending on the initial concentration of initiator are compared with experimental values in Fig. 3. The data taken for comparison exhibit a good approximate fit; moreover, the dependences resemble that of the polymerization rate of isoprene with ethyllithium as initiator, *cf.* ref.[3]. It may be said that on the whole the results also fit those in ref.[2], where of course the absolute rates are much higher, because the reaction was carried out in toluene at 50°C. Since the comparison performed in Fig. 3 revealed departures from continuity of the dependence in the range of higher concentrations of initiator, this range was investigated in greater detail.

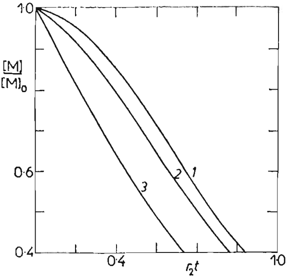

FIG. 1

Function (*14*)
Parameter A_2: *1* 0, *2* 0·1, *3* 0·4.

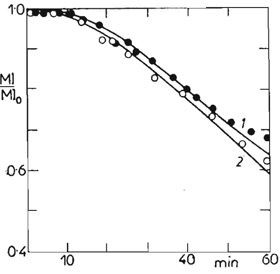

FIG. 2

The Dependence of the Relative Isoprene Concentration on Time in the Polymerization Initiated with Butyllithium at 300 K $[\mathrm{M}]_0 = 0{\cdot}5$ mol/l. $[\mathrm{I}]_0$ in mol/l: *1* 0·025, *2* 0·0125

Curves: dependence calculated using (*14*). Points: experimental values.

The Range of High Alkyllithium Concentrations

In the range of the initial concentration of initiator 0·25 – 1·0 mol/l the conversion of the monomer depends on the procedure employed for analysis in the deactivation of samples of the reaction mixture. Analyses after the deactivation with ethanol yield results different from those obtained by the deactivation with water. The cause may consist in the different resistivity of the complex of the monomer with the hexameric associate of the initiator[15,16] towards various agents. For this reason, deactivation was abandoned, and it was assumed that during the GLC analysis the complex reacts owing to heating (200°C) in the evaporator of the gas chromatograph, *i.e.* that one molecule of the initiator is added to a molecule of the coordinated monomer. The conversion of the monomer determined in this arrangement is considerably higher. This assumption was actually confirmed (Fig. 4), and a further rise in the temperature of the evaporator does not lead to any significant changes in conversion. A discontinuity or an inflex appears on the conversion curves, in the range of the monomer conversion which approximately equals the concentration of the hexameric associate of the initiator (Figs 5*a*,*b*). According to the initial rate, the

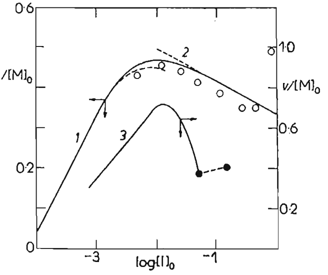

FIG. 3

The Dependence of the Polymerization Rate of Isoprene (in mol l^{-1} h^{-1}) on the Initial Concentration of Butyllithium (mol/l) at a 15% Conversion

1 Theoretical dependence calculated using solution (*a*), *2* theoretical dependence calculated using solution (*b*), *3* dependence in ref.[3]; ○ experimental data of this study for $[M]_0$ 0·5 mol/l.

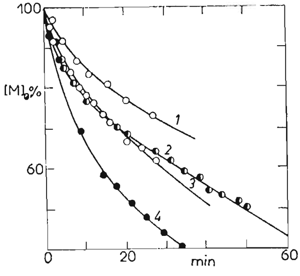

FIG. 4

Kinetic Curves of the Polymerization of Isoprene Initiated with Butyllithium

$[M]_0 = 0·5$ mol/l. $[I]_0$: *1*, *2*, 0·5 mol/l, *3*, *4*, 1·0 mol/l. GLC of the reaction mixture: *1*, *3* deactivation of samples with water, *2*, *4* without the deactivation of samples.

polymerization in this case is roughly first-order with respect to the initial concentration of initiator; the reaction order with respect to the initial monomer concentration is lower than unity in the range of lower monomer concentrations (the reaction was carried out until $[I]_0/[M]_0 = 10 : 1$). Taking into account the reaction[15]:

$$(\mathrm{RLi})_6 + \mathrm{M} \underset{k_2}{\overset{k_1}{\rightleftarrows}} (\mathrm{RLi})_6.\mathrm{M} \xrightarrow{k_1'} \mathrm{RMLi} + 5\ \mathrm{RLi} \qquad (F)$$

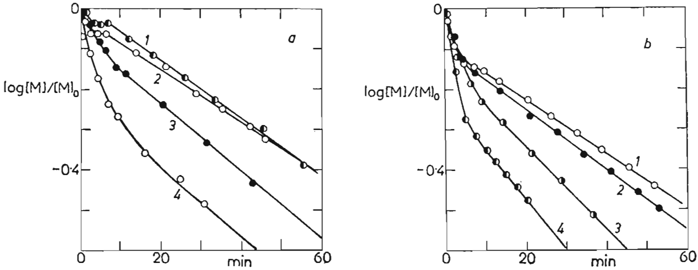

FIG. 5

Kinetic Curves of the Polymerization of Isoprene Initiated with Butyllithium

(*a*) $[M]_0 = 1{\cdot}0$ mol/l. $[I]_0$ (mol/l): *1* 0·1; 2 0·25; *3* 0·5; *4* 1·0. (*b*) $[I]_0 = 0{\cdot}5$ mol/l. $[M]_0$ (mol/l): *1* 1·5; 2 0·75; *3* 0·5; *4* 0·25.

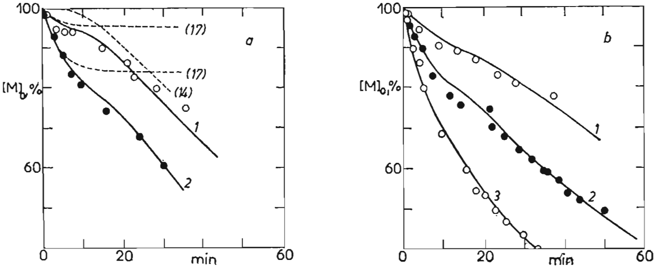

FIG. 6

Comparison of the Calculated Kinetic Curves of the Polymerization of Isoprene (solid curves) with Experimental Data

(*a*) $[M]_0 = 1{\cdot}0$ mol/l. $[I]_0$ (mol/l): *1* 0·25; 2 1·0. Broken curve: teoretical dependence using (*14*) or (*17*) respectively. (*b*) $[M]_0 = 0{\cdot}5$ mol/l. $[I]_0$ (mol/l): *1* 0·125; *2* 0·5; *3* 1·0.

it holds assuming $[\mathrm{M}]_0 \gg [\mathrm{I}]_0$ and only for the beginning, where the loss of reaction components due to initiation and propagation still does not exist, that

$$\frac{\mathrm{d}[\mathrm{Z}]}{\mathrm{d}t} = k_1[\mathrm{M}]_0\left(\tfrac{1}{6}[\mathrm{I}]_0 - [\mathrm{Z}]\right) - (k_2 + k_1')\,[\mathrm{Z}]\,, \qquad (16)$$

where Z stands for the complex $(\mathrm{RLi})_6.\mathrm{M}$. Integration gives

$$[\mathrm{Z}] = \frac{k_1[\mathrm{M}]_0[\mathrm{H}]_0}{k_1[\mathrm{M}]_0 + k_i' + k_2}\left(1 - \exp - (k_1[\mathrm{M}]_0 + k_2 + k_1')\,t\right). \qquad (17)$$

The constants k_1, k_i', k_2 were determined from the initial rates and the acceleration of initiation: $k_1 \approx 15{\cdot}0\ \mathrm{l\,mol^{-1}\,h^{-1}}$; $k_i' \approx 0{\cdot}24\ \mathrm{h^{-1}}$; $k_2 \approx 1{\cdot}0\ \mathrm{h^{-1}}$. An amount of the monomer corresponding to the amount of complex Z was subtracted from theoretical curves obtained according to solution (*b*) by numerical treatment, taking into account the increase in the "living" oligomer due to reaction *F*. The agreement between kinetic curves thus constructed and experimental points (Figs 6*a*,*b*) is a convincing argument in favour of the procedure suggested in this study.

REFERENCES

1. Kašpar M., Trekoval J.: This Journal *42*, 1969 (1977).
2. Hsieh H. L.: J. Polym. Sci. *A3*, 153 (1965).
3. Spirin Yu. L., Polyakov D. K., Gantmacher A. R., Medvedev S. S.: J. Polym. Sci. *53*, 233 (1961).
4. Sinn H., Lundborg C., Onsager O. T.: Makromol. Chem. *70*, 222 (1964).
5. Reich L., Stivala S. S.: Makromol. Chem. *53*, 173 (1962).
6. Morton M., Pett R. A., Fetters L. J.: Macromolecules *3*, 333 (1970).
7. Morton M., Fetters L. J.: J. Polym. Sci. *A2*, 3311 (1964).
8. Minoux J., Francois B.: Makromol. Chem. *46*, 519 (1961).
9. Korotkov A. A., Chesnokova N. N., Trukhmanova L. B.: Vysokomol. Soedin. *1*, 46 (1959).
10. Lundborg C., Sinn H.: Makromol. Chem. *41*, 242 (1960).
11. Lundborg C., Sinn H.: Makromol. Chem. *47*, 86 (1961).
12. Johnson A. F., Worsfold D. J.: J. Polym. Sci. *A3*, 449 (1965).
13. Worsfold D. J., Bywater S.: Can. J. Chem. *42*, 2884 (1964).
14. Bywater S., Roovers J. E. L.: Macromolecules *8*, 251 (1975).
15. Brown T. L.: Advan. Organometal. Chem. *3*, 365 (1965).
16. Kašpar M., Trekoval J.: This Journal *43*, 2853 (1978).

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