

MECHANISM OF THE PROPAGATION STEP IN THE ANIONIC POLYMERIZATION OF STYRENE*

Miroslav KAŠPAR and Jiří TREKOVAL

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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The paper is dealing with an investigation of the kinetic dependences of the propagation step in the anionic coordination polymerization of styrene in benzene at 303 K with "living" oligostyryllithium as initiator at the onset of the reaction. A short but distinct induction period was found, indicating a preceding slow reaction leading to the formation of a reactive intermediate, which behaves as the initiator of the reaction. Using results obtained in the first paper of this series¹, a new mechanism of propagation has been suggested, the mathematical solution of which is correlated with experimental data.

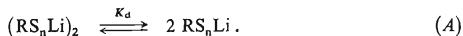
It has been reported in the first paper of the series¹ that in the range of high monomer and initiator concentrations the polymerization rate depends on concentrations of the initial compounds according to the expression

$$v_p = k[(RS_nLi)_2] \cdot [S]_0 \cdot [S], \quad (1)$$

while at low concentrations the dependence is of a different type:

$$v_p = k'[S] \sqrt{K_d} [(RS_nLi)_2], \quad (2)$$

where $[S]$ and $[S]_0$ respectively are the instantaneous and initial concentrations of the monomer, $[(RS_nLi)_2]$ is the concentration of pairs of the "living" chains of oligostyryllithium, and K_d is the equilibrium dissociation constant



Here, the role of the initiator is played by a simple oligomeric chain; the reaction order is therefore one half with respect to the initial concentration of the initiator, and unity with respect to the initial concentration of the monomer, as has also been found by Hsieh² for the reaction in toluene and in cyclohexane. The mechanism of the reaction controlled by the kinetic relation (1) must necessarily be more involved; the system exhibits some sort of memory of the initial concentration of styrene, maybe due to the slow association equilibrium of the dimer of the "living" chain with a molecule of the monomer, as has already been discussed in the literature^{3,4}, and

* Part III in the series Anionic Polymerization of Styrene; Part II: This Journal 43, 2583 (1978).

it is only the latter complex that would operate as the initiation centre proper. The association equilibrium must be slow, because in the case of quick equilibrium the instantaneous concentration of the initiating complex would be controlled by the instantaneous concentration of the monomer, which in turn would change the exponential conversion curves of the monomer into hyperbolae of a second-order reaction. One is justified to assume the possibility of formation of a complex between the organolithium compound and styrene, as even rather weak electron-donors, such as 1-hexene take part in the complexation⁵.

Mathematical treatment of a kinetic model of the polymerization of styrene and dienes has been reported by Cubbon and Margerison⁶, and by Reich⁷; in both cases, the authors consider complete polymerization, including the initiation step. Moreover, in ref.⁶ the equilibrium reaction (*A*) is also considered, but correlation with experimental data fails in the range of monomer concentrations higher than 0.5 mol/l. In ref.⁷ no correlation has been performed.

The slow preceding complexation equilibrium must give rise to an induction period, or at least to a sigmoidal curvature of conversion curves of the monomer in the reaction. It is also obvious⁸ that the conversion curve depends on the way in which active sites are generated. For all these reasons, further measurements of the kinetics of the propagation reaction of styrene were carried out in order to examine the reaction course at the beginning of the coordinates.

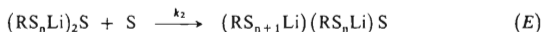
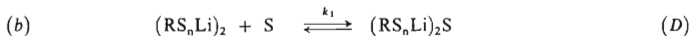
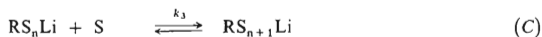
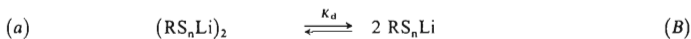
EXPERIMENTAL

The chemicals were prepared and purified as in ref.^{1,9}. The polymerizations and chromatographic analyses were carried out similarly to the preceding paper¹, with the difference that the use samples were taken from the reacting mixture for the GPC analysis automatically owing to the use of a modified gas chromatograph, where the sample (15 μ l) was introduced into a stream of the carrier gas by means of a piston with calibrated aperture in adjustable time intervals. A 10% *p*-xylene added to the monomer was used as the internal standard.

RESULTS AND DISCUSSION

The reaction was carried out in benzene solution; the initiator (*I*) was a "living" oligomer (sec-butyldistyryllithium and sec-butyltetrastryryllithium), and the difference between the reactivities of both "living" oligomers lay within the limits of experimental error (c. 5%). Deviations in the dependence of the overall kinetics from that observed earlier also lay within the limits of experimental error, which suggests good reproducibility of the measurements. The shape of conversion curves near the beginning of the coordinates can be seen in Fig. 1. The reaction exhibits an induction period as expected, but the rate at low *t* is non-zero and varies with initial concentrations of the reaction components more slowly than the rate in the exponential part of the conversion curve. At low initial concentrations of styrene ($[S]_0 < 0.3$ mol/l and $[I]_0 < 0.05$ mol/l), both rates are approximately the same, and the conversion curve is purely exponential. In this range too the reaction orders change from one half to unity with respect to the initial concentration of the initiator, and from unity to two with respect to the initial concentration of the monomer.

The proposed mechanism is based on the superposition of two limiting reactions



By denoting $\sum_n \sum_m [(\text{RS}_n\text{Li})(\text{RS}_m\text{Li})\text{S}] = [\text{Q}]$, which is the overall concentration of the complex, and similarly $\sum_n \sum_m [(\text{RS}_n\text{Li})(\text{RS}_m\text{Li})] = [\text{I}]$, we obtain

$$-\frac{d[\text{S}]}{dt} = k_3[\text{S}] \sqrt{K_d[\text{I}]} + k_1[\text{I}][\text{S}] - k_{-1}[\text{Q}] + k_2[\text{S}][\text{Q}], \quad (3)$$

$$\frac{d[\text{Q}]}{dt} = k_1[\text{I}][\text{S}] - k_{-1}[\text{Q}], \quad (4)$$

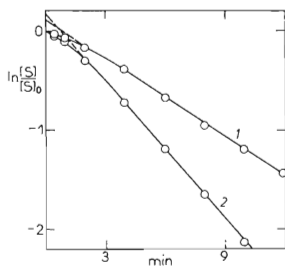


FIG. 1

Conversion Curves of Propagation of Styrene at 30°C

Initial monomer concentration, $[\text{S}]_0$, 1.0 mol/l, initial initiator concentration, $[\text{I}]_0$ (mol/l): 1 0.01, 2 0.02.

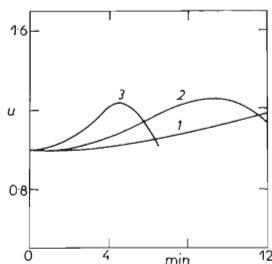


FIG. 2

Dependence of Function 16 on Time

Product $[\text{S}]_0 [\text{I}]_0$ (mol² l⁻²): 1 0.01, 2 0.02, 3 0.05.

assuming that K_d is small. Since the loss of the monomer caused by reaction (D) is very small compared with the other reactions, the second and third terms of the right-hand side of reaction (3) may be neglected. The system is nonlinear and very complicated, however; the loss of the initiator due to the complexation must therefore be neglected, and it must be put that $[I] = [I]_0$. By differentiating Eq. (3) and substituting (4), we obtain

$$d\left(\frac{d[S]}{dt}\right)/dt + k_{-1} \frac{1}{[S]} \frac{d[S]}{dt} + k_1[I]_0 k_2[S] = -k_{-1}k_3 \sqrt{K_d}[I]_0. \quad (5)$$

The initial conditions of the equation are $[S]_0$ and

$$\frac{d[S]}{dt} = -k_3[S]_0 \sqrt{K_d}[I]_0 \quad (6)$$

or, more exactly for the vicinity of the beginning of the coordinates,

$$\frac{d[S]}{dt} = -k_3[S]_0 \sqrt{K_d}[I]_0 - k_1[I]_0 [S]_0. \quad (7)$$

Eq. (5) is not integrable, and its approximate solution in the form of the Taylor series has a very complicated and virtually inapplicable form. The convergency of the series was also very slow, Eq. (5) has therefore been rearranged to

$$\frac{d^2f}{dt^2} + k_{-1} \frac{df}{dt} + k_1[I]_0 k_2[S]_0 e^f = -k_{-1}k_3 \sqrt{K_d}[I]_0 \quad (8)$$

by substitution

$$[S] = [S]_0 e^f, \quad \frac{d[S]}{dt} = [S]_0 \frac{df}{dt} e^f. \quad (9)$$

If we express f as a function of time $f(t)$ in the form of Mac Laurin's series,

$$f(t) = a_0 + a_1 t + \frac{1}{2} a_2 t^2 + \dots + \frac{1}{n!} a_n t^n + \dots, \quad (10)$$

where $a_0 = 0$ with respect to (9), then

$$e^f = e^{a_1 t} \cdot e^{0.5 a_2 t^2} \cdot \dots \cdot e^{((1/n!) a_n t^n)}. \quad (11)$$

By substituting the expansion of the individual factors in Eq. (11), we obtain

$$e^t = \prod_{n=1}^{\infty} \left(1 + \sum_{m=1}^{\infty} \frac{\left(\frac{1}{n!} a_n\right)^m t^{mn}}{m!} \right); \quad (12)$$

by substituting Eq. (10) and the respective derivatives into Eq. (8), by substituting (12) and comparing coefficients for the same powers of t we obtain a system of algebraic equations, from which a_n can be determined after substitution of the initial conditions:

$$\begin{aligned} a_0 &= 0, \\ a_1 &= \left(\frac{d[S]}{dt} \right)_0 / [S]_0, \\ a_2 + k_{-1}a_1 + A &= -k_{-1}k_3 \sqrt{K_d[I]_0}, \\ a_3 + k_{-1}a_2 + Aa_1 &= 0, \\ a_4 + k_{-1}a_3 + A(a_1^2 + a_2) &= 0, \\ a_5 + k_{-1}a_4 + A(a_1^3 + 3a_1a_2 + a_3) &= 0, \end{aligned} \quad (13)$$

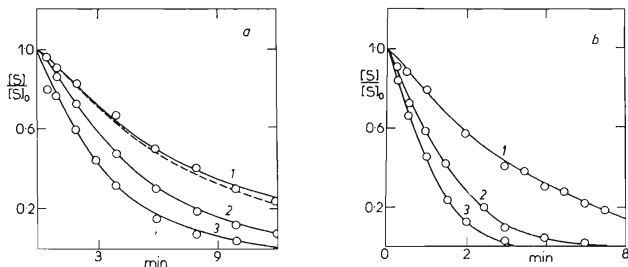


FIG. 3

Comparison of Calculated Conversion Curves with Experimentally Determined Points

a $[S]_0$ (mol/l): 1, 2 1.0, 3 0.5; $[I]_0$ (mol/l): 1 0.01, 2 0.02, 3 0.05. Broken curve calculated for $u = 1$.

b $[S]_0$ (mol/l): 1 0.37, 2 1.0, 3 1.0; $[I]_0$ (mol/l): 1 0.06, 2 0.09, 3 0.19.

where $A = k_1 k_2 [I]_0 [S]_0$. The substitution of Eq. (7) allows the expansion coefficients to be determined:

$$\begin{aligned}
 a_1 &= -k_3 \sqrt{K_d} [I]_0 - k_1 [I]_0, \\
 a_2 &= k_{-1} k_1 [I]_0 - A, \\
 a_3 &= -k_{-1}^2 I_1 [I]_0 + k_{-1} A, \\
 a_4 &= k_{-1}^3 k_1 [I]_0 - k_{-1}^2 A + A^2, \\
 a_5 &= -k_{-1}^4 k_1 [I]_0 + k_{-1}^3 A - 2A^2 k_{-1}, \\
 a_6 &= -k_{-1}^5 k_1 [I]_0 + k_{-1}^4 A + 3A^2 k_{-1}^2 - 4A^3, \\
 a_7 &= -k_{-1}^6 k_1 [I]_0 + k_{-1}^5 A - 4A^2 k_{-1}^3 + 16A^3 k_{-1}, \\
 a_8 &= k_{-1}^7 k_1 [I]_0 - k_{-1}^6 A + 5A^2 k_{-1}^4 - 44A^3 k_{-1}^2 + 34A^4.
 \end{aligned} \tag{14}$$

The terms with $(k_1 [I]_0)^n$, where $n \geq 2$, were neglected in the calculation. After substitution into Eq. (10) and arrangement with respect to the increasing power of k_{-1} , and using the Mac Laurin expansion of the exponential,

$$[S] = [S]_0 \exp \{ -R(e^{-k_{-1}t} + k_{-1}t - 1) - St \} \cdot u, \tag{15}$$

where

$$R = k_1 [I]_0 (k_2 [S]_0 - k_{-1}) / k_{-1}^2, \quad S = k_1 [I]_0 + k_3 \sqrt{K_d} [I]_0,$$

and where u is the correction function for the third and fourth terms on the right-hand side of Eqs (14),

$$\begin{aligned}
 u = \exp \{ U^2 0.6^{-1/2} (e^{-0.6k_{-1}t} + 0.6k_{-1}t - 1)^2 - U^3 0.58^{-1/3} (e^{-0.58k_{-1}t} + \\
 + 0.58k_{-1}t - 1)^3 \},
 \end{aligned} \tag{16}$$

where $U = k_1 k_2 [I]_0 [S]_0 / k_{-1}^2$. For high t , where $e^{-k_{-1}t} \ll 1$, Eq. (15) assumes a simpler form

$$\ln \frac{[S]}{[S]_0} = R - (Uk_{-1} + k_3 \sqrt{K_d} [I]_0) t; \tag{17}$$

R is an intercept on the y -axis in Fig. 1, delimited by a broken straight line and the beginning of the coordinates. Substitution into Eqs (15) and (16) and comparison

with experimental data yielded the following constants:

$$k_1 = 1.15 \pm 0.07 \text{ mol}^{-1} \text{ l min}^{-1},$$

$$k_{-1} = 1.11 \pm 0.05 \text{ min}^{-1},$$

$$k_2 = 7.63 \pm 0.38 \text{ mol}^{-1} \text{ l min}^{-1},$$

$$k_3 K_d^{1/2} = 0.506 \pm 0.025 \text{ mol}^{-1/2} \text{ l}^{1/2} \text{ min}^{-1}.$$

The constants were substituted into Eq. (16), and a correction plot of the function $u = u_{(t)}$ was made; an example is in Fig. 2. Fig. 3 shows graphic correlations of the calculated conversion curves according to Eq. (15) with experimental points. The broken curve in Fig. 3 is the calculated conversion curve with the neglected correction function $u(u = 1)$. The effect of the function u is evidently weak, and therefore there is no need to make this correction function more precise by introducing other terms (the fifth term on the right-hand side of Eq. (14) for a_8 and the following). The agreement between the calculated and experimental values was verified on 24

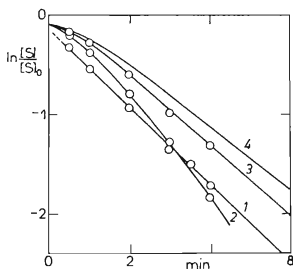


FIG. 4

Dependence of the Conversion Curves of Propagation of Styrene on the Age of Active Sites

$[S]_0$ 0.5 mol/l, $[I]_0$ 0.05 mol/l. 1 initiation with sec-butyllithium, 2, 3 initiation with sec-butyiltristyryllithium 5 min 2 or 15 min 3 old, 4 calculated theoretical conversion curve using Eq. (15).

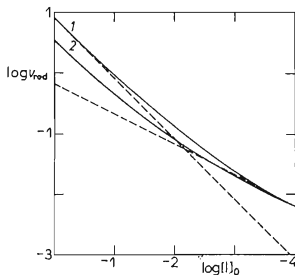


FIG. 5

Theoretical Dependence of the Reduced Rate of Propagation on the Initiator Concentration According to Eq. (17)

Monomer concentration (mol/l): 1 1.0, 2 0.3.

conversion curves and appeared not worse than $\pm 3\%$, with the exception of the reaction proceeding at a comparable initial concentration of the monomer and initiator. For instance, for $[I]_0 = 0.06 \text{ mol/l}$, and $[S]_0 = 0.18 \text{ mol/l}$, the error for $t \geq 10 \text{ min}$ already amounts to 15%. This is due to the neglected loss of the initiator due to complexation and to the neglected loss of the monomer caused by reaction *D*, which at a high $[I]_0/[S]_0$ may be considerable.

Sec-butyllithium is often reported as used directly in generating "living" chains in the reaction^{1,2}. Here, however, further loss of the monomer occurs due to the initiation reaction; more important still, one cannot assume that initiation produces directly dimeric pairs of oligostyryllithium. For this reason, application of the suggested mechanism is not suitable in this case. The dimerization of the chains requires a certain minimal time, as demonstrated in Fig. 4, which documents the dependence existing between the age of oligostyryllithium and the type of the conversion curve. Reactions *D* and *E* become operative already after five minutes, but the rate is still very high (curve 2, Fig. 4), probably with respect to the fraction of the dissociated oligostyryllithium. After some time equilibrium *B* is established in the solution of the initiator, and the conversion curve (2 and 3, Fig. 4) begins to approach the theoretical one (4, Fig. 4). The change in the reaction orders observed in ref.¹ is documented by Fig. 5, showing the theoretical dependence of the reduced rate, v_{red} , on concentrations of the initial compounds. v_{red} is defined by

$$v_{red} = - \lim_{t \rightarrow \infty} \frac{1}{[S]} \frac{d[S]}{dt}; \quad (18)$$

in other words, it is identical with the slope of the straight parts of the conversion curves in Fig. 1. For low concentrations of the initiator curves 1 and 2 in Fig. 5 coincide, i.e. v_{red} is no more dependent on the monomer concentration; hence, according to Eq. (18), the reaction order is unity with respect to the initial monomer concentration, while at high concentration of the initiator it is close to two. The reaction order with respect to the initial concentration of the initiator varies from one half to unity, as shown by broken lines in Fig. 5.

CONCLUSION

The proposed mechanism explains rather adequately the propagation reaction of styrene in a wide concentration range of the initial compounds. In the low concentration range there is a good agreement with data of other authors. For instance, the value determined in ref.⁶ was $k_3 K_d^{1/2} = 0.42 \text{ l}^{1/2} \text{ min}^{-1}$, while here it is $0.506 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ min}^{-1}$. In suggesting the mechanisms, the highest possible simplicity was attempted, and the assumptions were made so as not to contradict the basic facts known about the properties of organolithium compounds. The structure of the com-

plex of the dimeric chain of oligostyryllithium with a molecule of the monomer is not easy to predict. Bearing in mind the number of π -electrons and the properties of lithium, the structure of the type of a tetragonal bipyramid seems to be the likeliest one, having in its apexes lithium atoms with the coordination number four and with a base consisting of two sp^2 hybridized orbitals of α and β atoms of the carbon atom of styrene and two sp^2 hybridized carbanions from the oligostyryllithium dimer; thus, the basic skeleton would contain a sextet of π -electrons. The high reactivity towards the monomer could be explained by the potential instability given by very strong electron repulsion, and thus by an effort to raise the number of conjugated double bonds and to reduce the delocalization energy by accepting another styrene molecule into conjugation, even if a less stable π -octet is formed; the latter can of course be stabilized by closing one σ -bond, which results in addition. It is of course very difficult to prove these additions experimentally because of the low concentration and short lifetime of the complex due to its high reactivity.

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