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

M.KAŠPAR and J.TREKOVAL
Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

Received July 10th, 1975

Kinetic relationships involved in the propagation step of the anionic coordination polymerization of styrene in benzene were investigated using gas chromatography as the analytical method. At concentrations of the "living" chains higher than 10^{-2} mol/l there occurred deviations from the one-half reaction order with respect to the active centres, and from the first order with respect to the monomer concentration. These anomalies were attributed to the influence of a competitive third-order reaction. The reaction orders appeared to be concentration-dependent; the reaction order with respect to the concentration of the active centres changed from one half to unity, while the reaction order with respect to the starting monomer concentration changed from unity to two.

The mechanism of the propagation step of the anionic coordination polymerization of vinyl monomers in nonpolar media is often explained in the literature by means of the scheme[1]

$$(RS_nLi)_2 \xrightleftharpoons{K_d} 2\,RS_nLi \qquad RS_nLi + S \rightarrow RS_{n+1}Li\,, \tag{A}$$

where RS_nLi is the "living" polymer chain containing n monomer units, S is monomer or its constitutional unit, and K_d is the dissociation constant.

The reaction order with respect to the total concentration of the active centres, *i.e.* "living chains", that follows from the preceding dissociation equilibrium in the first reaction step is one half; this has been confirmed by some authors[2,3]. On the other hand, Welch[4] found that the reaction order was unity, while other authors[5] give different values. The association of the "living" polystyryllithium has been investigated[6,7] viscometrically, and the formation of a chain dimer in nonpolar solvents has been confirmed.

Brown[8] regards the mechanism outlined above as energetically disadvantageous and suggests a scheme according to which a π-complex of the associated organometallic compound with the monomer would be formed in the first step of the reaction. Such hypothesis is also favoured by the great complexation power of organolithium compounds with the π-donors, even with

---

* Part I in the series Anionic Polymerization of Styrene.

very weak ones, such as 1-hexine[9]. By employing a quantum mechanical calculation of the formation of such complex, Yonezawa[10] offered a very satisfactory explanation of the results of the copolymerization of styrene with *p*-methylstyrene.

Since in all papers published so far[1-5] the concentrations of the active centres lay below $2 . 10^{-2}$ mol/l, we concentrated our attention on the course of the reaction within the concentration of the active centres higher than 10^{-2} mol/l.

EXPERIMENTAL

Chemicals. The monomer was purified by distillation with sodium metal and rectification over calcium hydride in argon. The solvents and GLC standards used in the experiments were shaken with conc. sulphuric acid, 10% solution of potassium hydroxide and water and on drying distilled over a Na/K alloy over which they were also stored. Sec-butyllithium was prepared by reacting 1·2 mol of 2-butylchloride (distilled in presence of CaH_2) with 20 g of lithium powder in 0·8 l of benzene with intensive stirring in dry argon for five hours; the concentration of the solution of the organometallic compound as determined titrimetrically was 1·35 mol/l. Hexyllithium was prepared similarly from 0·5 mol of hexyl chloride and 10 g of lithium in 0·4 l of dry benzene; the concentration of the solution of the product was 1·05 mol/l. "Living" oligomers used for initiation were prepared similarly to ref.[2].

Polymerization. An internal GLC standard (10%) was added to the monomer and the mixture was diluted with dry benzene to a solution of styrene in a concentration of 5 mol/l, from which aliquot portions were taken for the reaction. The reaction was carried out in argon in a thermostated apparatus (equipped for intensive stirring and for sample-taking) dried by washing with a solution of the initiator. The volume of the reacting mixture was 10—20 ml. The samples taken during the reaction (c. 0·3 ml) were immediately mixed with 0·05 ml of water, and the amount of unreacted reaction components in them was determined by gas chromatography.

Gas chromatography. 2·5 m column, Carbowax 20M packing on silanized chromosorb N, catharometer as detector. Styrene was determined at a column temperature of 160°C, evaporator temperature 200°C and carrier gas (hydrogen) pressure 100 kPa, which corresponds to a flow rate of c. 50 ml/min. Butane was determined at a column temperature of 80°C, carrier gas pressure 50 kPa and evaporator temperature 200°C. The chromatograms were evaluated by calibration with mixtures of the monomer with the internal standard (*p*-xylene, cyclohexane) having a known ratio of the components.

RESULTS AND DISCUSSION

The polymerization was carried out in benzene solution with the "living" oligomer (sec-butyldistyryllithium) used as initiator at the beginning; the monomer loss (S) in the reaction was determined by gas chromatography. The conversion curves thus obtained (Fig. 1) prove that the reaction is first-order with respect to the instantaneous monomer concentration. The dependence of the initial reaction rate on the concentration of the active centres or on the starting monomer concentration was used in the determination of the respective reaction orders (Fig. 2*a*, *b*); the reaction is not affected by the GLC internal standard (*p*-xylene, cyclohexane, Fig. 2*a*) used.

The rate of initiation with sec-butyllithium is higher by an order of magnitude than the rate of propagation[2], so that both reaction steps are well separated from each

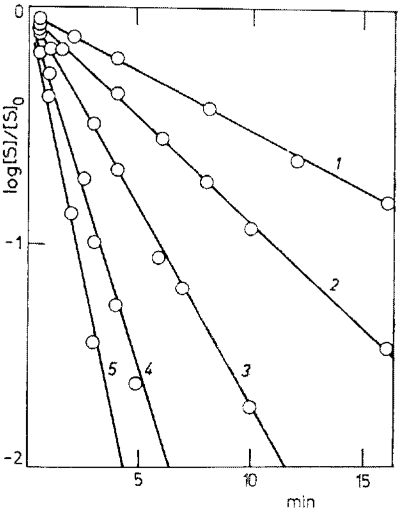

FIG. 1

Polymerization of Styrene (S) Initiated with Sec-butyldistyryllithium at 25°C

$[S]_0$: 1·0 mol/l. Concentration of active centres; mol/l: *1* 0·02; *2* 0·03; *3* 0·06; *4* 0·1; *5* 0·2.

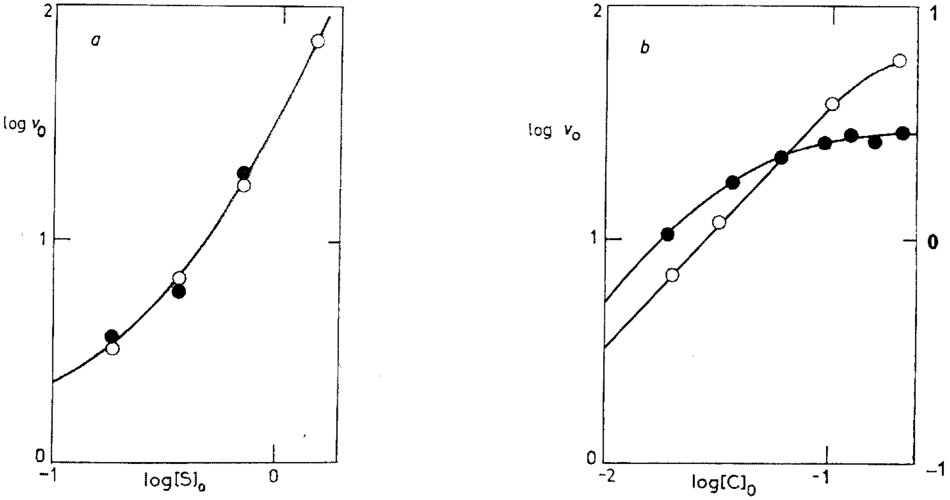

FIG. 2

Dependence of the Initial Polymerization Rate of Styrene (v_0 in mol/l h) at 25°C (*a*) on the Starting Concentration of Styrene ($[S]_0$ in mol/1] and (*b*) on the Concentration of Active Centres ($[C]_0$ in mol/l)

a Starting concentration of sec-butyldistyryllithium 0·06 mol/l. Internal standard GLC: ○ *p*-xylene, ● cyclohexane. *b* $[S]_0$: 1·0 mol/l. Initiation: ○ sec-butyldistyryllithium, ● hexyllithium–hexyldistyryllithium in a 1/1 molar ratio. ○ left scale, ● right scale.

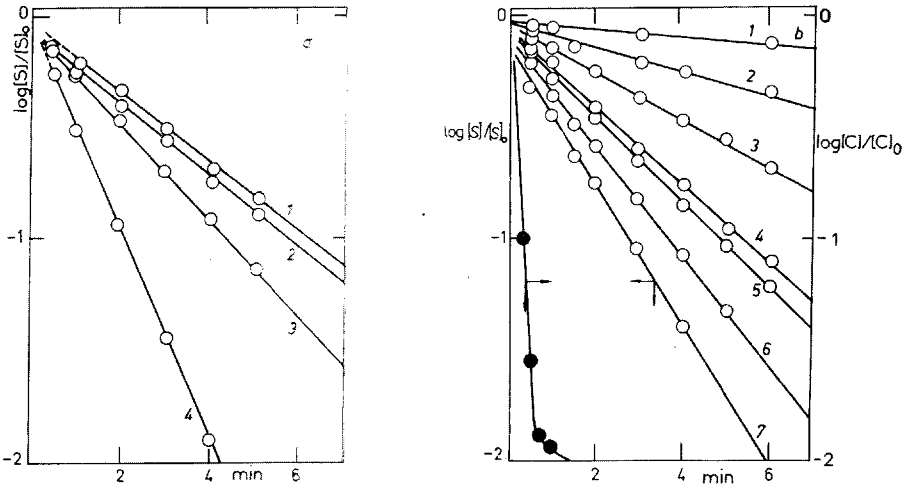

FIG. 3

Polymerization of Styrene (S) Initiated with Sec-butyllithium at 30°C

a Concentration of active centres 0·03 mol/l, S_0 mol/l: *1* 0·5; *2* 0·25; *3* 1·0; *4* 2·0. *b* $[S]_0$: 0·5 mol/l. Concentration of active centres ($[C]_0$) mol/l: *1* 0·005; *2* 0·01; *3* 0·025; *4* 0·04; *5* 0·05; *6* 0·075; *7* 0·1. Conversion curve of the initiator consumption at $[C]_0$ 0·1 mol/l represented by ●.

TABLE I

Reaction Order with Respect to the Concentration of Active Centres (C) and to the Starting Monomer Concentration for the Polymerization of Styrene (S) Initiated with Sec-butyllithium at 30°C

$[S]_0$ mol/l	$[C]_0 . 10^2$ mol/l	Reaction order	$[C]_0 . 10^2$ mol/l	$[S]_0$ mol/l	Reaction order
	with respect to $[C]_0$			with respect to $[S]_0$	
2·0	4—10	0·95	1·0	0·3 —1·0	1·0
1·2	2— 8	1·00	2·0	0·3 —0·6	1·0
1·0	2—20[a]	1·05	2·0	0·6 —1·2	1·0
1·0	1— 8	1·00[c]	3·0[d]	0·25—0·5	1·0
0·6	2— 8	0·88	3·0[d]	0·5 —2·0	1·5—1·6
0·5	1—10[c]	0·78	6·0	0·18—0·85	1·0—2·0[b]
0·3	2— 8	0·80	8·0	0·3 —0·5	1·0
0·3	0·5—1	0·57	8·0	0·5 —2·0	1·0—2·0
			10·0[d]	0·25—2·0	1·0—2·0

[a,b] Initiation with sec-butyldistyryllithium, 25°C. [a] Fig. 2*b*, [b] Fig. 2*a*. [c] Fig. 4*a*, [d] Fig. 4*b*.

other. The possibility of using this organometallic compound in generating the active centres directly in the reaction mixture was confirmed: under the given conditions, the log $[S]/[S]_0$ *vs* time dependences are characterized by straight lines (Fig. 3*a*, *b*), though they do not pass through the origin ($[S]/[S]_0 = 1$) owing to the consumption of one part of the monomer by the initiation reaction. Fig. 3*b* shows a comparison of the conversion curves of the polymer with the curve of the initiator loss measured by gas chromatography as a relative loss of butane in the reaction after the termination of the reaction mixture with water. The reaction order is a function of the concentration of the active centres (Fig. 4*a*, Table I) and of the starting monomer concentration (Fig. 4*b*, Table I). The reaction order with respect to the starting monomer concentration within a range of 0·3 to 2·0 mol/l increases with increasing monomer concentration from unity to two. It was also found that at a starting monomer concentration lower than 0·3 mol/l the order remains constant and equal to unity. The suspected effect of viscosity of the medium was refuted by repeated measurements in various apparatuses having different coefficients of thermal conductivity, which gave identical results. A similar effect was found with the reaction carried out in the heptane–benzene mixture 1 : 1, although the absolute reaction rates and viscosity of solution were lower in this case.

With sec-butyllithium and sec-butyldistyryllithium as initiators the reaction order

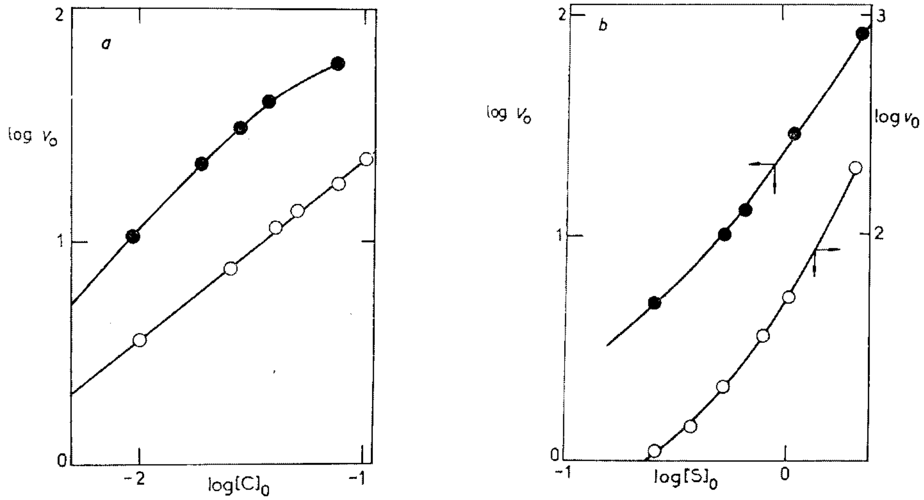

FIG. 4

Dependence of the Initial Polymerization Rate of Styrene (v_0 in mol/l h) Initiated with Sec-butyllithium at 30°C (*a*) on the Concentration of Active Centres ($[C]_0$ in mol/l) and (*b*) on the Starting Monomer Concentration ($[S]_0$ in mol/l)

a $[S]_0$, mol/l; ○ 0·5, ● 1·0. *b* $[C]_0$, mol/l: ● 0·03, ○ 0·1.

with respect to the concentration of the active centres always exhibits a slight decrease at highest concentrations (Figs 2*b*, 4*a*); owing to the high reaction rates in this concentration range the phenomenon could not be studied in detail by using the experimental arrangement described here. To explain the phenomenon, a supplementary series of experiments was carried out with hexyllithium–hexyldistyryllithium in a molar ratio of 1 : 1 as initiator (hexyllithium was chosen because of its low rate of initiation). The decrease in the reaction rate could be observed already at much lower concentrations of the active centres that with sec-butyllithium or sec-butyldistyryllithium, and at a concentration of the active centres higher than 0·1 mol/l the reaction order was virtually zero (Fig. 2*b*); the higher reaction rate at low concentrations of the active centres in this case can obviously be attributed to the perceptible role of hexyllithium as initiator. The decrease in the order with respect to the concentration of the active centres in the range of higher initiator concentrations can be explained by the existence of traces of unreacted initiator, which probably causes inactivation of the growing chains (*cf.*[4,11]). In the concentration range of initiator higher than 10^{-2} mol/l there occurs a deviation from the kinetics adequate to the suggested mechanism (*A*). A decrease in the concentration both of the living chains and of the monomer renders the phenomenon less distinct. In principle, the deviations of the reaction orders can be explained by taking into account the competitive reaction described tentatively by

$$v'_p = k[(RS_nLi)_2] \cdot [S]_0 \cdot [S] \,. \qquad (1)$$

The dependence of the reaction rate (v'_p) on the initial monomer concentration is of the second power, while that on the instantaneous monomer concentration is linear. It is evident that at higher concentration of the reaction components the rate of this reaction will prevail over the reaction rate for which it holds

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

according to mechanism (*A*).

Since the formation of the dimer of the "living" chain has been unequivocally confirmed in the literature, an undissociated dimer must react in the rate-controlling reaction step, in accordance with Brown's view[8]. The participation of the complex in the reaction is also corroborated by the overall reaction rate, which is three, and at the same time by the fact that a trimolecular course of the reaction is not possible because of the low concentrations of the individual components, active centres in particular, and because of the high steric requirements of the addition.

REFERENCES

1. Cubbon R. C. P., Margerison D.: Polymer *6*, 103 (1965).
2. Hsieh H. L.: J. Polym. Sci., Part A, *3*, 173 (1965).
3. Worsfold D. J., Bywater S.: Can. J. Chem. *38*, 1891 (1960).
4. Welch F. J.: J. Amer. Chem. Soc. *81*, 1345 (1959).
5. Spirin Yu. L., Gantmacher A. R., Medvedev S. S.: Dokl. Akad. Nauk SSSR *146*, 368 (1962).
6. Morton M., Fetters L. J., Pett R. A., Meier J. F.: Macromolecules *3*, 327 (1970).
7. Bywater S., Worsfold D. J.: Macromolecules *5*, 393 (1972).
8. Brown T. L.: J. Organometal. Chem. *5*, 191 (1966).
9. Makowski H. S., Lynn H.: J. Macromol. Sci., Chem. *2*, 683 (1968).
10. Yonezawa T., O'Driscoll J. F., Higashimura T.: J. Polym. Sci., Part A, *3*, 2215 (1965).
11. Spirin Yu. L., Polyakov D. K., Gantmacher A. R., Medvedev S. S.: J. Polym. Sci. *53*, 233 (1961).

Translated by L. Kopecká.