EFFECT OF THE STRUCTURE OF ALKYLLITHIUM ON THE POLYMERIZATION KINETICS OF ISOPRENE

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The kinetics of polymerization of isoprene in benzene initiated with ethyl-, propyl-, butyl-, hexyl-, oct 1-, 2-butyl-, 3-hexyl-, 2-octyl- and 6-methylheptyllithium was investigated. With the exception of ethyllithium, a distinct initial induction period decreasing steeply with increasing concentration of the initiator was observed for all n-alkyllithium initiators. No induction period was observed with the other initiators. The reaction orders decreased at the highest concentrations for most of the initiators, sometimes even to negative values. In the case of ethyl-, 2-butyl- and octyl-lithium this phenomenon has not been observed in the range investigated.

In ref.[1], an anomalous phenomenon in the kinetics of the anionic coordination polymerization of isoprene in a nonpolar medium has been reported and discussed. With increasing concentration of the initiator the reaction rate in a certain concentration range ceases to increase; on the contrary, a decrease sets in, so that the initiator behaves as if it were an inhibitor.

Although the phenomenon has already been reported in earlier papers[2,3], it still was not certain to what extent it was reproducible, independent of certain experimental conditions and of a concrete alkyllithium initiator. Using the finding[4] that the phenomenon may be produced also in another concentration range by adding the Lewis bases, such as triethylamine, and by including association equilibria into the reaction mechanism, the occurrence of negative reaction rates could be characterized quantitatively[5].

A related problem consists in the existence of an induction period of the reaction reported by many authors[6,7], but not confirmed in many further cases[8], which cannot be explained satisfactorily using the present-day theoretical knowledge of the course of polymerization reations.

Since the majority of the existing papers deal only with two or three usual organolithium initiators, an attempt has been made in this study to compare the reaction capacity of several initiators with respect to the discussed anomalies, *i.e.* the negative reaction rates and induction period. For the future, more initiators and a theoretical evaluation of the results are envisaged.

EXPERIMENTAL

Chemicals

Isoprene was purified by distillation with sodium metal and rectification (20 TP column) with calcium hydride in argon, and stored over calcium hydride in argon. Benzene and hexane (GLC internal standard) were predried with calcium hydride and distilled in a column with a solution of butyllithium in benzene or hexane, to achieve perfect removal of compounds able to react with organolithium initiators. Both compounds were stored over potassium metal.

Initiators

Ethyllithium was prepared from ethyl bromide according to ref.[1], the other initiators were obtained by reacting 0·1 mol of the respective chloride with 5 g of lithium suspension in 100 ml of dry benzene at room temperature, in a protective argon atmosphere with vigorous stirring for 5—10 h. 3-Hexyl chloride, hexyl chloride and octyl chloride were prepared by reacting the respective alcohol with phosphorus pentachloride; 2-octyl and 6-methyl heptyl chloride were obtained by reacting the alcohol with thionyl chloride. After shaking with water and pre-drying with calcium chloride, all products were rectified in a column with c. 20 TP over calcium hydride in an argon atmosphere.

Polymerization

A reactor, 100 ml in volume and provided with a double jacket was used, allowing the reaction mixture to be thermostated to 300 K. The reactor contents were vigorously stirred; argon was introduced into the mixture, and in the bottom of the reactor a glass ground joint was sealed in, ensuring direct contact with an automatic system of sampling for the GLC analysis. The reaction components were dosed against a stream of dry argon by means of syringes provided with a sea-led-in burette, in the following order: benzene, monomer, initiator. The total volume of the reaction mixture was 24 ml.

Gas Chromatography

The gas chromatograph was of our own construction, allowing the sample to be injected in regular time intervals directly into the column, to prevent side reactions in the gas phase. Check tests were performed in advance, thus ruling out the possibility of an additional polymerization in the apparatus. The volume of the samples was 15 µl. The column was 2 m long, with an inner diameter of 10 mm, packed with Carbowax 20M on Chromosorb N-AW, with a catharometer manufactured by W. Giede, GDR, used as the detector. The column temperature was 80°C, the pressure of the carrier gas (hydrogen) was 0·1 MPa. A Perkin–Elmer, type 56 recorder was employed.

Evaluation of Results

The monomer used in the reactions was prepared in advance as a 4M solution in benzene with 20% hexane with respect to the monomer added; this guaranteed a constant content of the internal standard in all measurements. For the calibration purposes, similar mixtures with a different monomer: hexane ratio were prepared. It was found that in the concentration range investigated (0·6—1M) the calibration curve did not differ from the straight line by more than 2%, related

to the ratio of the peak heights monomer: hexane. For each reaction, 20—30 samples up to 20 to 40% conversion were analyzed; the initial reaction rate was determined by means of regression analysis with a TI-58 desk computer, and the induction period was determined by using the method of intersection of two regression straight lines. The time of sampling of the reaction mixture was read off from the displacement of the chart, where the moment of injection was recorded by a pulse.

RESULTS AND DISCUSSION

The reactions were carried out in benzene solution at 300 K. First, a series of reactions was performed with a variable starting monomer concentration, in order to find out in what concentration range the induction period will be most distinct. The suitable concentrations varied about $0.8 - 1.5$ mol/l monomer; at higher concentrations the induction period was reduced below the detection limit (1 min), while at lower ones the error of determination increased due to nonconstant conditions of the GLC analysis (pressure fluctuations of the carrier gas) in long-lasting polymerizations. For instance, for $0.04M$ butyllithium, the following periods were recorded: for the isoprene concentrations 0.8 and 1.0 mol/l, 13 min; for 1.5 mol/l, 5 min; 2.0 mol/l, 2 min, and for the monomer concentration 3.0 mol/l, less than 1 min. The other measured initiators obeyed similar dependences, with the exception of octyllithium, where the induction period, though distinct, could not be calculated quantitatively because of the low reaction rate and thus a gradual transition between the two straight lines situated at an angle close to 180°.

An example of conversion curves with the induction period is given in Fig. 1. It can be seen that the induction is not due to a slow initiation reaction (the initial consumption of the monomer is correlated with the starting amount of the initiator): the initiator is obviously added already within the first minutes of the reaction,
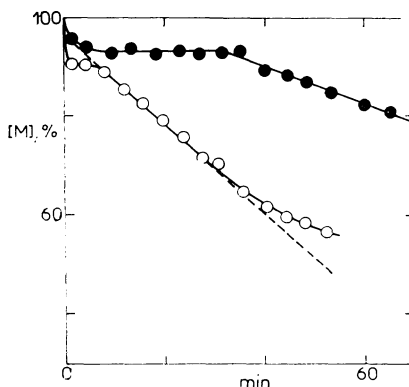

FIG. 1

Kinetic curves of the polymerization of isoprene in benzene at 300 K. Initiation: ○ $0.15M$ propyllithium, ● $0.01M$ hexyllithium. Initial concentration of isoprene, $[M]_0$, 1.0 mol/l

after which the polymerization ceases, in agreement with our theory reported in ref.[5]. The theory assumes the initiator to exist in the form of a hexamer, which seems to corroborate hypotheses forwarded by some authors[9] that 2- and 3-alkyllithium is associated in benzene as a tetramer at most, because 2-butyl, 3-hexyl 2-octyl and 6-methylheptyllithium have no induction period within the whole concentration range. Tetramers of the organic metal probably react *via* a different mechanism, because in the reaction

$$(RLi)_n + M \; \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \; (RLi)_n.M \; \overset{k_i}{\longrightarrow} \; RMLi + (n-1)\,RLi$$
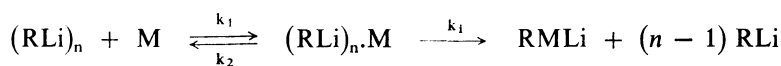
k_i is high compared with k_1, so that the intermediate $(RLi)_n.M$ does not play any essential role.

The higher value of k_i/k_1 is probably also the cause underlying the anomalous behaviour of ethyllithium; in the concentration range of the initiator $0.02-0.2$ mol/l and of the monomer, $0.05-1.0$ mol/l, no induction period was found in this case, and no change was observed in the reaction order. The reaction rate in the whole range may be expressed as

$$v_0 = k[M]_0 \sqrt{[I]_0} \, ,$$

where $k = 0.020\ l^{0.5}\ mol^{-0.5}\ min^{-1}$, $[M]_0$ and $[I]_0$ are the starting concentrations of monomer and initiator.

Although ethyllithium forms a hexamer in benzene, similarly to butyllithium, and in spite of similar rate constants (in the range where the reaction rate does not decrease yet, the analogous constant for butyllithium was $0.022\ l^{0.5}\ mol^{-0.5}\ min^{-1}$), the findings obtained do not allow us to offer an unambiguous cause for the phenomenon: this would require knowledge of all the rate constants of partial reactions of the reaction mechanism[5].

In the case of ethyllithium, no characteristic colour of the reaction mixture appeared during the reaction, unlike the other initiators (the weakest for butyllithium, more intensive for hexyllithium and strongly yellow for propyllithium), where the colour disappeared roughly after the end of the induction period. For octyllithium and 6-methylheptyllithium the colour was less intensive, but still visible; for all these initiators it depended on the starting concentration of the initiator, and the maximum varied about $[I]_0$ 0.05 mol/l. No colour arose with 2- and 3-alkyllithium. This is related to the induction period, but exact spectrophotometric measurements are of course needed. Table I shows the effect of the initiator concentration on the induction period, τ; the two variables are approximately inversely proportionate. Figs 2a, 2b show the dependence of the initial polymerization rate (after the end of the induction) on the initiator concentration. While for 2-butyllithium and octyllithium the reaction rate within the whole concentration range was constant (1.60)

with respect to the initial initiator concentration, for the other initiators a bend always appeared on the curve at higher initiator concentrations, and the reaction

TABLE I

Dependence of the initial concentrations of initiator ($[I]_0$) on the induction (τ). Starting concentration of monomer $[M]_0 = 1$ mol/l

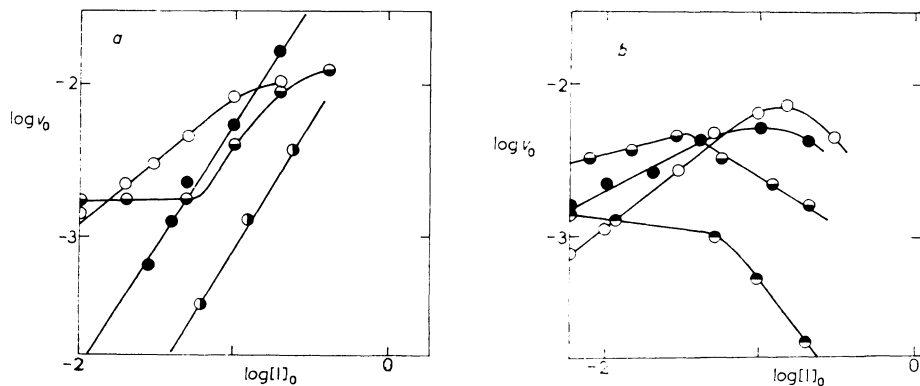| $[I]_0$ mol l^{-1}	τ, min		
	propyllithium	butyllithium	hexyllithium
0·006	—	90	—
0·010	65	33	35·7
0·020	—	20	19
0·030	18	—	—
0·040	—	13	—
0·050	11	—	10
0·10	5·5	11	4·5
0·15	4	—	—
0·2	—	7·5	2
0·3	2	—	—

FIG. 2

Reaction of isoprene in benzene ($[M]_0 = 1$ mol l^{-1}) with initiators (I) at 300 K. Dependence of the initial reaction rate ($v_0 = $ d[M] dt, mol l^{-1} min^{-1}) on $[I]_0$ (mol . l^{-1}). I: (a) ○ 3-hexyllithium, ◑ octyllithium, ● 2-butyllithium; ◔ hexyllithium; (b) ○ propyllithium, ● butyllithium, ◔ 2-octyllithium, ◓ 6-methylpentyllithium

rate dropped even to negative values. In the low concentration range the reaction orders with respect to the initiator concentrations were 0·7 for propyllithium, 0·5 for butyllithium (for the latter, the order increases with increasing $[I]_0/[M]_0$ up to unity, ref.[1]), 0·7 for 3-hexyllithium, 1·5 for 2-octyllithium. 6-Methylheptyllithium had a negative reaction order within the whole range under investigation, hexyllithium had two bends on the curve; the same initiator also had an inflex on a similar dependence in ref.[1], where of course the conversion of the initiator was determined (as hydrocarbon after the hydrolysis).

The fact that all reactions were carried out under absolutely identical conditions rules out an interpretation of the different behaviour of various initiators based on the different reaction arrangement or on the method of analysis of the reaction mixture used. The possibility of a different reaction mechanism for each initiator is also unlikely. Since a small structural change in the alkyl chain of the initiator brings about a great change in the reaction course (octyl, 2-octyl and 6-methylheptyllithium), these differences may be interpreted only by assuming various values of the rate constants of partial processes of a comparatively complex uniform mechanism[5], taking into account the degrees of association of the particular initiators, which will be dealt with in a forthcoming paper.

From the viewpoint of application of the individual initiators, the dependences shown in Figs 2a, 2b allow us to choose an adequate one for certain required molecular masses of the polymers. Even a very active initiator, such as 2-butyllithium, is much less active in the low concentration range (due to the high reaction order) than butyllithium as regards the reaction rate, and thus commercial efficiency.

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