Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Guyot, A. and Vialle, J.(1970) 'Isoprene Polymerization by Butyllithium in Cyclohexane. I. Initiation Reaction', Journal of Macromolecular Science, Part A, 4: 1, 79 — 105
To link to this Article: DOI: 10.1080/00222337008060967
URL: http://dx.doi.org/10.1080/00222337008060967

J. MACROMOL. SCI.–CHEM., A4(1), pp. 79-105, January, 1970

Isoprene Polymerization by Butyllithium in Cyclohexane. I. Initiation Reaction

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SUMMARY

Kinetic studies, using a gas chromatographic method, of the consumption of n-, sec-, and t-butyllithium during the polymerization of isoprene in cyclohexane show in the three cases a sigmoidal curve. When the concentration of polyisoprenyllithium increases, the initiation rate goes through a maximum with n-butyllithium but continuously increases in the two other cases. The three corresponding lithium-butoxides have a drastic effect on the initiation rate. Thus, the addition of n-butoxide strongly increases the initial rate, but the rate further decreases except in the case of sec-butyllithium. The behavior of the sec-butoxide is roughly the same, but more limited, while the t-butoxide causes a slight initial promotion in the case of n-BuLi and sec-BuLi but decreases the initiation rate in the case of t-BuLi. These results are discussed in terms of association of organolithium molecules and ion pairs reactivity.

INTRODUCTION

Some preliminary results have been reported [1] on the kinetics of initiation and propagation of isoprene polymerization in cyclohexane initiated by either n- or sec-butyllithium. These results agree with an extensive previous study by Hsieh [2] showing that sec-butyllithium is much more efficient than n-butyllithium; however, they have established further that the process is much more complex than reported by Hsieh. With both these initiators, the shape of the kinetic curves, either for the initiation or the propagation reaction, is the same, sigmoidal; the behavior of both initiators is thus fundamentally the same. It has been shown also that lithina, which may result from traces of moisture, depresses the initiation rate but hardly affects the propagation rate. Related to this last point, Roovers and Bywater [3] have shown that both lithium n- and t-butoxide decrease the initiation and propagation rates in the polymerization of styrene in benzene initiated by n-butyllithium. Also Worsfold and Bywater [4] reported that n-butoxide suppressed the induction period in the isoprene polymerization in cyclohexane initiated by n-butyllithium. More recently Roovers and Bywater [5] confirmed this effect in the case of the t-butoxide and the sec-butyllithium in hexane solution, and they have shown further that the propagation rate is depressed.

The chromatographic method that we used allowed us to study simultaneously the initiation and the propagation reactions. We wish to report here the results of a complete study of the initiation reaction during the overall process of isoprene polymerization in cyclohexane initiated by n-, by sec-, or by t-butyllithium in the absence of or in the presence of each of the three corresponding lithium butoxides. A second paper will deal with the propagation reaction.

EXPERIMENTAL

Materials

Commercial pure-grade cyclohexane is refluxed on sodium, distilled, and condensed through a molecular sieve (Union Carbide 5A) column under argon atmosphere. Pentane and hexane, which are used as internal concentration references, are treated similarly.

Isoprene, supplied by the Institut Français du Pétrole, is refluxed for a few hours in the presence of sodium wire, then distilled to eliminate its polymerization inhibitor, and condensed through a 5A molecular sieve column, which also retains traces of n-pentane.

The three butyllithiums are commercial products (Alpha Inorganic, Inc.), generally in concentrated hexane solutions, which are diluted with purified cyclohexane to obtain the required concentrations. The desired amount of pentane is then added as internal standard.

The lithium butoxides are prepared in situ by reaction of a part of the butyllithium with the suitable butyl alcohol. The alcohol is dried by refluxing on sodium and then distilled under dry, purified argon. A commercial lithium sec-butoxide (Alpha Inorganic, Inc.) has also been used.

Polymerization Procedure

The autoclave is a glass pressure bottle fitted with a stainless-steel flat cover equipped with various stainless-steel taps, a worm for thermostatic fluid, O-ring joints, and a bar magnet for stirring.

After preheating, the apparatus is assembled and evacuated to 10^{-2} Torr. A diluted solution of butyllithium is introduced to react with impurities adsorbed on the walls. This solution is then carried off by argon pressure and vacuum is achieved again.

Cyclohexane is charged first, followed by the butyllithium solution. Eventually, butyl alcohol or lithium butoxide solution is added. After the desired temperature is reached, the solution is titrated as described below and isoprene is introduced.

At the end of the polymerization, residual butyllithium is destroyed with methanol and the polymer is precipitated in a large excess of methanol, washed with methanol, dried, and weighed at room temperature.

Kinetic Studies

The principle and some applications of our chromatographic method have already been published [6]. Some progress has been made since.

Kinetics of butyllithium consumption (initiation) and isoprene consumption (propagation) are obtained simultaneously by gas chromatographic analysis of samples picked up at suitable time intervals from the liquid and gaseous phases in the autoclave which contain pentane and hexane as internal concentration references from butyllithium and isoprene solutions, respectively. The samples from the liquid phase are picked up via a double syringe, already described [6], which permits simultaneous pumping of the reacting solution and an ethyl alcohol solution in cyclohexane. The two solutions are pushed simultaneously into a small tube closed by a soft PVC stopper; the automatic mixing insures the destruction of residual butyllithium to give the corresponding butane without contact with oxygen. From the tube, conventional gas chromatographic analyses are carried out after a storage time which may last about 2 days without any change.

From known solutions of butane and pentane in cyclohexane, calibration curves are drawn (Fig. 1). The precise temperatures or relative volumes of the gas and liquid phases are not critical. Butane may be present in the

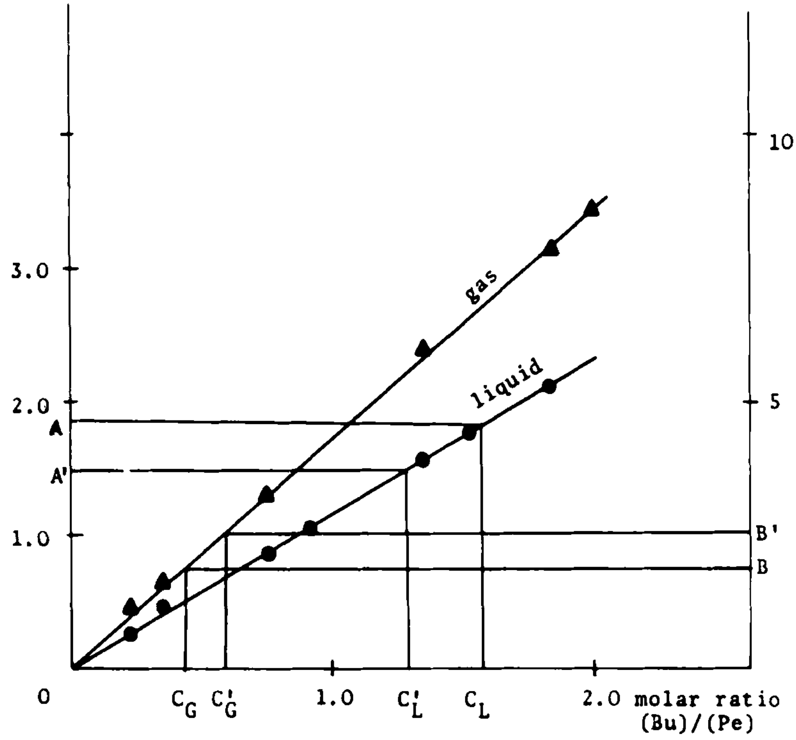

Fig. 1. Calibration curve for BuLi titration (for the significance of A, A'. . . C_L', see the text).

liquid and gas phases from destruction of butyllithium by adventitious moisture or added alcohols. The butane titrated from the liquid phase is representative of the precedent butane plus the residual butyllithium. Thus, the actual concentration of the butyllithium solution is obtained from the difference between the liquid and the gas phase determinations. Of course, during the polymerization the composition of the gas phase does not change.

If the monomer solution is not well purified, impurities such as moisture or oxygen traces are expected to react immediately with butyllithium. Then, if the initiation reaction is not instantaneous, the amount of impurities may be deduced from analysis of samples picked up just after the introduction of the isoprene solution. The experimental chromatographic ratio change from A to A' for the gas phase and from B to B' for the

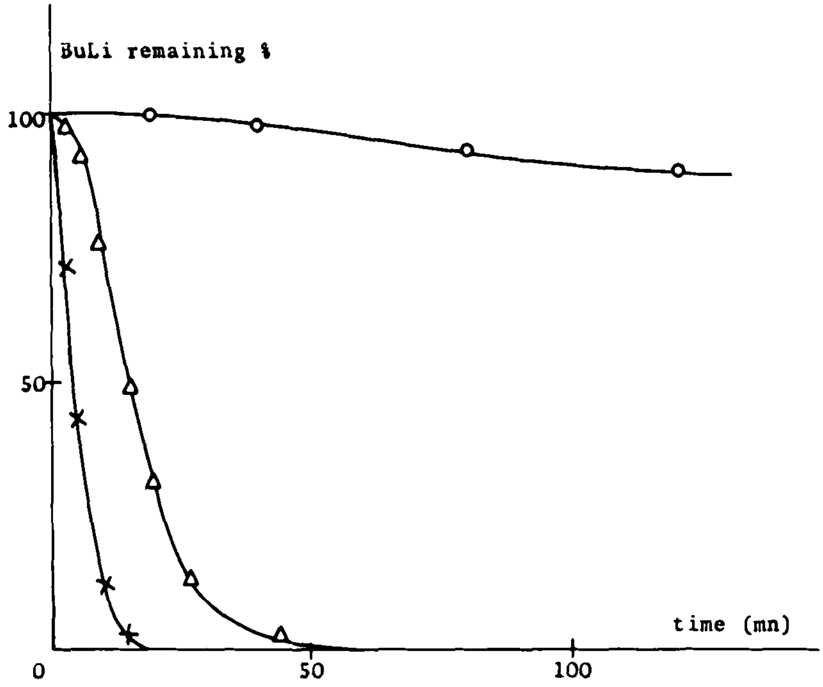

Fig. 2. Consumption of the various butyllithiums, mole/liter.
X $[\text{sec-BuLi}]_0 = 2.31 \times 10^{-3}$ $[M]_0 = 0.71$
△ $[\text{t-BuLi}]_0 = 2.62 \times 10^{-3}$ $[M]_0 = 0.89$
○ $[\text{n-BuLi}]_0 = 2.92 \times 10^{-3}$ $[M]_0 = 0.80$

liquid phase is shown in Fig. 1. Oxygen gives lithium butoxide and thus decreases the amount of butane from the liquid phase (from C_L to C_L'). Moisture gives butane and increases its amount in the gas phase (from C_G to C_G'). In the same way, butyl alcohol, added for the purpose of causing formation of lithium butoxide, may be controlled.

For the monomer analysis, with hexane as internal concentration standard, a calibration curve for the ratios isoprene/hexane was also drawn.

Polymer Analysis

Excellent controls of the kinetic number average molecular weight, calculated as the ratio of monomer to butyllithium consumption, were obtained using Mechrolab vapor pressure (Model 301) or membrane (Model 502) osmometers, and also from GPC [7].

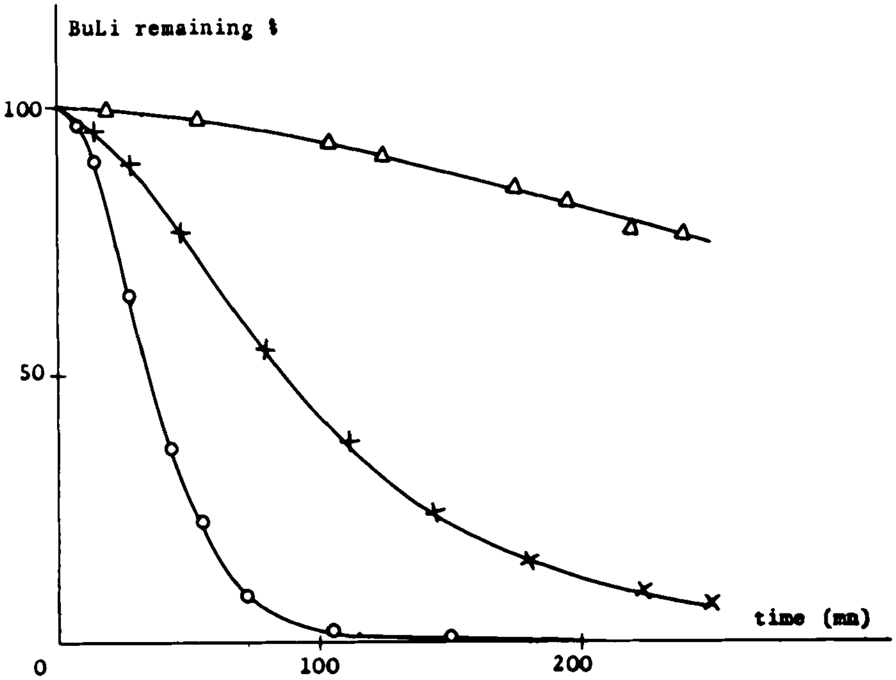

Fig. 3. sec-BuLi consumption for high initiator concentrations, mole/liter.
△ $[\text{sec-BuLi}]_0 = 11.92 \times 10^{-3}$ $[M]_0 = 0.045$
X $[\text{sec-BuLi}]_0 = 9.56 \times 10^{-3}$ $[M]_0 = 0.127$
○ $[\text{sec-BuLi}]_0 = 8.70 \times 10^{-3}$ $[M]_0 = 0.328$

RESULTS

Behavior of the Three Butyllithiums

Figure 2 illustrates the kinetics of butyllithium (BuLi) consumption at 25°C with similar initial concentrations of monomer $[M]_0$ and initiator $[\text{BuLi}]_0$ indicated in the legend. In agreement with Hsieh [2], sec-BuLi is a little more efficient than t-BuLi and much more efficient than n-BuLi. The typical sigmoidal shape of the curves, already reported [1] for n- and sec-BuLi, is clearly visible for the t-BuLi curve. Under these conditions, the process is too rapid with sec-butyllithium, and the initial acceleration is not noticeable, but, as shown in Fig. 3, the induction period is obvious

Table 1. Multistep Consumption of n-Butyllithium

Step no.	Temperature, °C	Monomer addition, mole/liter	sec-BuLi addition, 10^3 moles/liter	Residual BuLi, 10^3 moles/liter	Total polyisoprenyl Li formed, 10^3 moles/liter
0	–	–	–	8.05	–
1	50	0.114	0	6.61	1.44
2	50	0.134	0	5.83	2.22
3	70	0.168	0	5.13	2.92
4	69	0.333	0	4.20	3.85
5	25	0.200	0	4.05	4.00
6	25	0.205	2.95	4.05	6.95
7	25	0.465	0	3.94	7.06

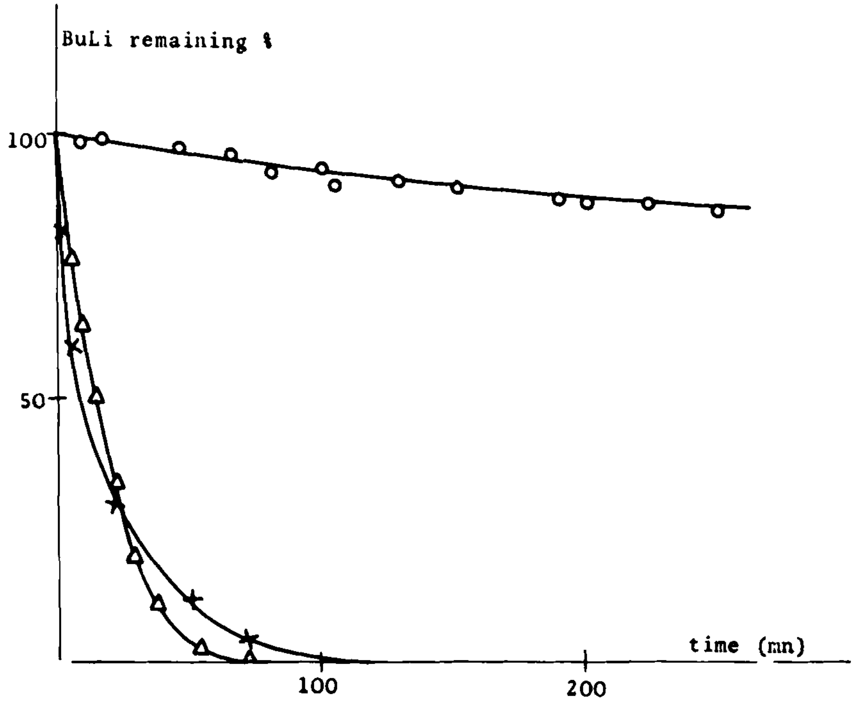

Fig. 4. Butyllithium consumption in the presence of polyisoprenyllithium, mole/liter.

○ $[\text{n-BuLi}]_0 = 4.00 \times 10^{-3}$ $[\text{M}]_0 = 0.44$, $[\text{PILi}]_0 = 2.45 \times 10^{-3}$

X $[\text{sec-BuLi}]_0 = 2.70 \times 10^{-3}$ $[\text{M}]_0 = 0.205$, $[\text{PILi}]_0 = 3.00 \times 10^{-3}$

△ $[\text{t-BuLi}]_0 = 5.55 \times 10^{-3}$ $[\text{M}]_0 = 0.135$, $[\text{PILi}]_0 = 1.75 \times 10^{-3}$

if the ratio $[\text{sec-BuLi}]_0/[\text{M}]_0$ is high enough. With n-BuLi it is impossible to obtain the complete consumption of the n-BuLi when the initial isoprene concentration is kept low. Even further additions of isoprene, although carried out at temperatures as high as 70°C, cause only a slight increase in butyllithium consumption. If sec-BuLi is further added with a small charge of monomer, rapid consumption takes place, corresponding quite well with the amount of sec-BuLi added. The results of this series of experiments are reported in Table 1. As the concentration of polyisoprenyllithium increases, the yield of the initiation reaction decreases even if high temperatures are used, and it seems impossible to reach total consumption. Thus, in cyclohexane, the seeded technique, such as described by Morton et al. [8] for studies in hexane solutions, is not reliable.

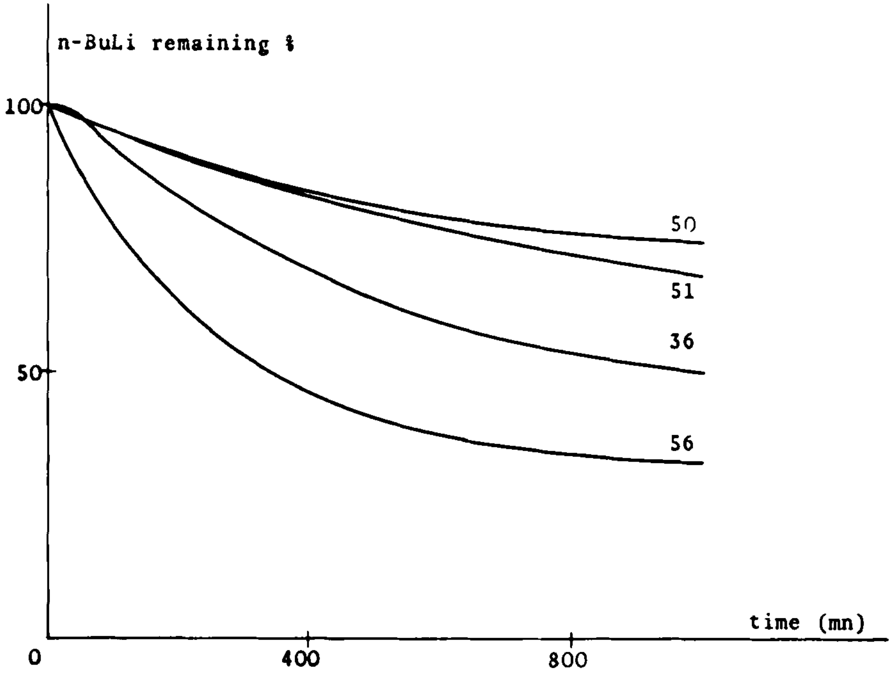

Fig. 5. Consumption of n-BuLi in the presence of various lithium butoxides (the numbers refer to runs listed in Table 2).

When each of the three butyllithiums is used in the presence of polyisoprenyllithium (PILi) prepared in a preliminary step from sec- or t-butyllithium, the induction period is always suppressed. Typical results are illustrated in Fig. 4. Thus, autocatalysis is suppressed if a sufficient amount of PILi is present.

Effect of Lithium Butoxides

As our work was in progress, Roovers and Bywater [5] reported that t-BuOLi markedly increased the initial rate of initiation with sec-BuLi but that the maximum rate was scarcely affected. These results are in agreement with ours, but we have observed that the effects of the added butoxides are not always the same. They can decrease or increase the initiation rate, and the extent of their effect depends on the peculiar system of butyllithium and lithium butoxide. Precise results are illustrated by the kinetic curves in Figs. 5, 6, and 7; the experiments were carried out at 25°C. The

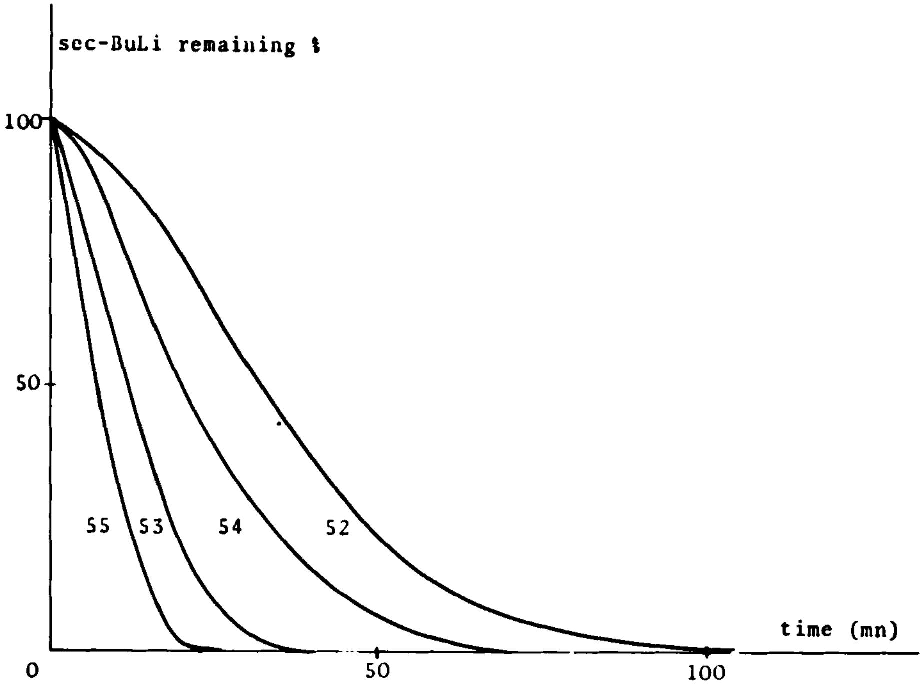

Fig. 6. Consumption of sec-BuLi in the presence of lithium butoxides (see Table 3 for the initial conditions of the numbered runs).

initial concentrations of the different reactants are given on Tables 2, 3, and 4, respectively. In the case of n-BuLi (Fig. 5), each of the three butoxides increases the initial rate, but n-BuOLi is much more efficient in this respect. Further, the initiation rate decreases and the final n-BuLi consumption is lower than without butoxide except with n-BuOLi; however, even in this latter case, complete initiation is not reached.

With sec-BuLi (Fig. 6) each butoxide increases the initial rate with an efficiency which seems to be in the order t-BuOLi < sec-BuOLi < n-BuOLi. As reported by Roovers and Bywater [5], the maximum rate is little affected by t-BuOLi, but we can see here that it is increased by the other butoxides. With n-BuOLi, the duration of the initiation reaction is reduced by a factor of 5 and thus the system n-BuOLi-sec-BuLi is the best one for preparing monodisperse stereoregular polyisoprene.

The results obtained with t-BuLi (Fig. 7) are much more complex; n-BuOLi causes a rapid increase in the initial rate, but after a short time it

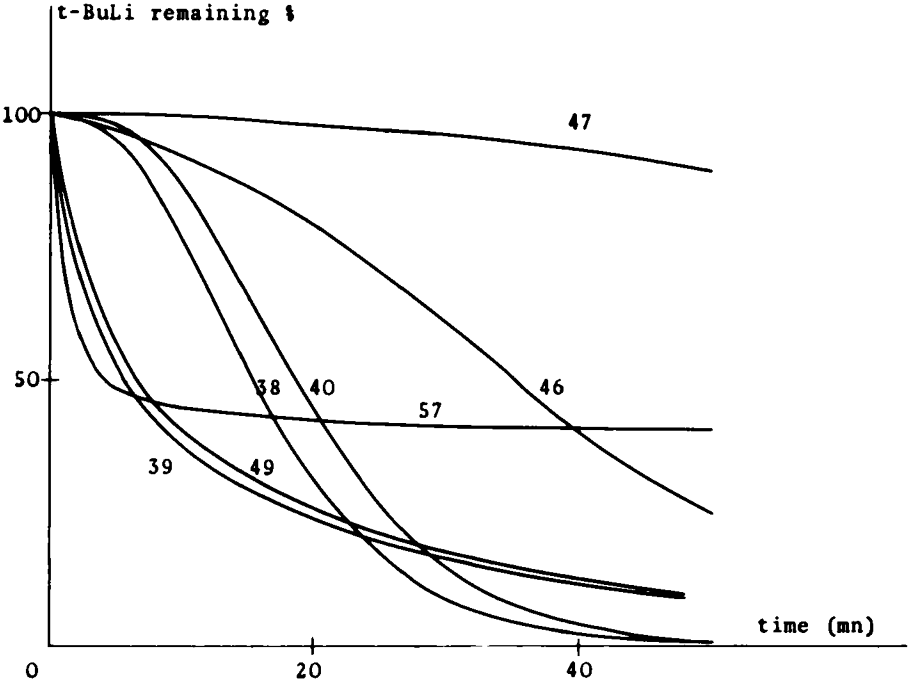

Fig. 7. Consumption of t-BuLi in the presence of lithium butoxides (see Table 4 for the initial conditions of the numbered runs).

practically quenches the reaction before completion. Sec-BuOLi causes a great increase in the initial rate, but then the rate decreases slowly and a longer time is necessary for total initiation. At moderate concentration t-BuOLi causes a slight increase in the initial rate, but then the rate decreases rapidly and markedly. At a higher t-BuOLi/t-BuLi ratio, the rate is slower during the entire reaction. However, except in the presence of n-BuOLi, after a relatively long time initiation is complete.

Kinetic Studies

The sigmoidal shape of the kinetic curves indicates that the initiation rate depends not only on the reactants, monomer and butyllithium, but also on the product, polyisoprenyllithium (PILi). It depends also on the presence, the amount, and the nature of lithium butoxide, and finally, as quoted in our preceding paper [1], on the presence and the amount of lithina.

Table 2. Initial Concentrations for Experiments with n-Butyllithium

Run no.	$(\text{Isoprene})_0$ mole/liter	$(\text{n-BuLi})_0$ X 10^3 moles/liter	(n-BuOLi) X 10^3 moles/liter	(sec-BuOLi) X 10^3 moles/liter	(t-BuOLi) X 10^3 moles/liter	(n-BuLi) consumed X 10^3 moles/liter
36	0.895	2.62	0.095	0	0	152.1
50	0.725	3.32	0.195	2.17	0	1.60
51	0.615	3.30	0	0	2.76	1.70
56	0.600	2.41	4.20	0	0	1.64

Table 3. Initial Concentrations for Experiments with sec-Butyllithium

Run no.	$(\text{Isoprene})_0$ mole/liter	$(\text{sec-BuLi})_0$ $\times 10^3$ moles/liter	(n-BuOLi) $\times 10^3$ moles/liter	(sec-BuOLi) $\times 10^3$ moles/liter	(t-BuOLi) $\times 10^3$ moles/liter
52	0.356	5.85	0	0	0
53	0.287	4.39	0	6.05	0
54	0.350	5.60	0	0	5.82
55	0.345	6.15	5.95	0	0

Table 4. Initial Concentrations for Experiments with t-Butyllithium

Run no.	$(\text{Isoprene})_0$ mole/liter	$(\text{t-BuLi})_0$ × 10^3 moles/liter	(n-BuOLi) × 10^3 moles/liter	(sec-BuOLi) × 10^3 moles/liter	(t-BuOLi) × 10^3 moles/liter
38	0.80	2.98	0	0	0
40	0.78	2.68	0	0	0
46	0.76	2.47	0	0	2.50
47	0.77	1.87	0	0	3.09
48	0.85	2.74	0	0	1.48
57	0.72	2.50	3.64[a]	0	0
39	0.73	2.28	0	2.93[b]	0
49	0.75	2.03	0	2.75[c]	0

[a] In this experiment the initiation was not complete. It was limited to 67% of the t-BuLi introduced, when the monomer consumption was completed.

[b] Commerical sec-BuOLi.

[c] sec-BuOLi from sec-BuOH.

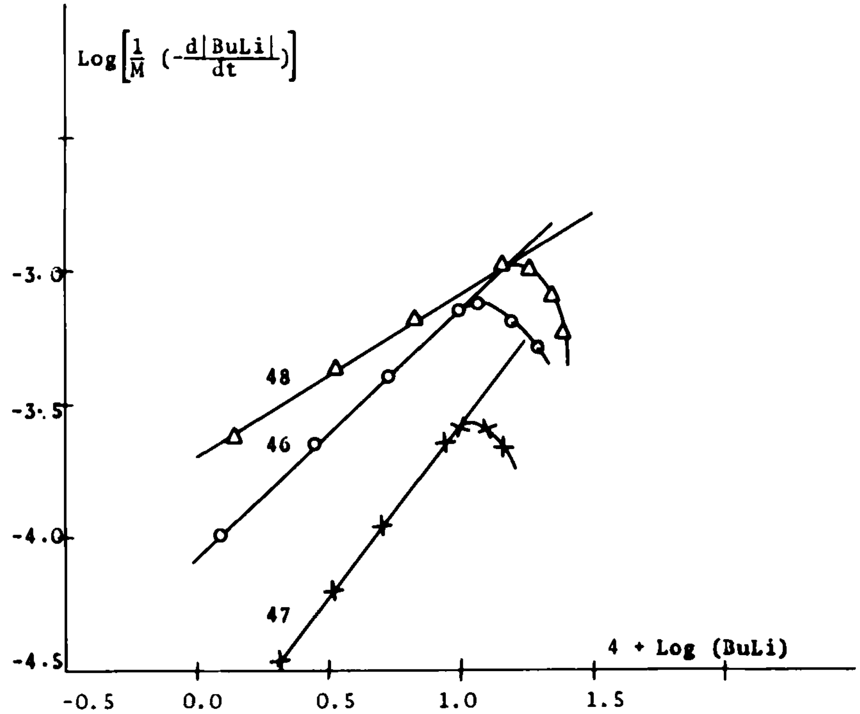

Fig. 8. Influence of t-BuOLi concentration on the apparent order of the initiation reaction versus the t-BuLi concentration, mole/liter.

△ $[\text{t-BuLi}]_0 = 2.74 \times 10^{-3}$ $[\text{M}]_0 = 0.85$, $[\text{t-BuOLi}] = 1.48 \times 10^{-3}$
○ $[\text{t-BuLi}]_0 = 2.47 \times 10^{-3}$ $[\text{M}]_0 = 0.76$, $[\text{t-BuOLi}] = 2.50 \times 10^{-3}$
X $[\text{t-BuLi}]_0 = 1.87 \times 10^{-3}$ $[\text{M}]_0 = 0.77$, $[\text{t-BuOLi}] = 3.09 \times 10^{-3}$

Even in the absence of lithina and butoxide, which often may be present as adventitious impurities, no simple kinetic law is expected to be valid during the entire process, and determination of the separate order versus any of the reactants is a very difficult task. For instance, the determination of the order versus monomer concentration requires that the rates be measured in different experiments at points chosen so that the concentrations of the same BuLi and PILi are exactly the same. This has been carried out by Roovers and Bywater [5] in the case of sec-BuLi for initial conditions where PILi is not present. They observed a first-order versus monomer concentration. Although gas chromatographic measurements are very sensitive, they always involve errors of about 1 or 2%. That precision is not sufficient to allow accurate determination of the initial rate; however, our results are roughly in agreement with the law observed by Roovers and Bywater, and we thus admit this law and there is no obvious reason that it would not be valid during the entire process.

Admitting the first-order versus monomer concentration, and omitting the effect of PILi, it is possible to try to obtain an apparent order versus BuLi concentration, on plotting log (-dBuLi/dt) (1/M) against log BuLi. Such a plot gives straight lines in a number of cases, but these straight lines are valid only for the part of the process which follows the initial acceleration period. With sec-BuLi, a number of experiments give slopes of 0.66 as an average value, in agreement with the results of Roovers and Bywater [5] for the apparent order at the maximum value of the rate. The values of the slopes obtained with t-BuLi are more disperse, between 0.2 and 0.75. With n-BuLi it is generally impossible to draw straight lines. In the presence of butoxides the values of the slopes change markedly except with sec-BuLi. For instance, it is possible to obtain straight lines, in the case of n-BuLi, whose slopes are near 2 with n-BuOLi and t-BuOLi and near 0.5 with sec-BuOLi. The results with t-BuLi are more complex: high slope (about 5) with n-BuOLi, slope decreasing from 2.5 during the process with sec-BuOLi, and slope increasing with the amount of t-BuOLi as shown in Fig. 8.

In any case, because they represent only limited parts of the processes and depend on a number of factors, these apparent orders are probably of little significance and cannot be interpreted safely.

In their study of the initial part of the process initiated by sec-BuLi, Roovers and Bywater [5] observed a first-order versus butyllithium concentration. Such a result clearly demonstrates that the initiation reaction involves the major part of the butyllithium species present, associated as well as dissociated. Because the association number is not a fixed one and depends on the concentration, as shown by the molecular weight measurements of n-BuLi in diluted solutions [9], it represents only an average, and different species of associated particles are present. Thus, the first order observed by Roovers and Bywater is probably valid for all these species, and we may assume that it is valid for all kinds of associated particles containing not only butyllithium molecules but others such as lithium butoxide or PILi. This assumption allows us to study the influence of PILi on the initiation rate, using plots of $-(d[\mathrm{BuLi}]/dt)\ (1/[\mathrm{M}])\ (1/[\mathrm{BuLi}])$ versus $[\mathrm{PILi}]/[\mathrm{BuLi}]_0$. Such plots are drawn in Figs. 9-15.

Considering the experiments without added lithium butoxide, it may be seen in Fig. 9 that in the three cases the apparent rate constant increases very much at the very beginning of the process; after about 3%

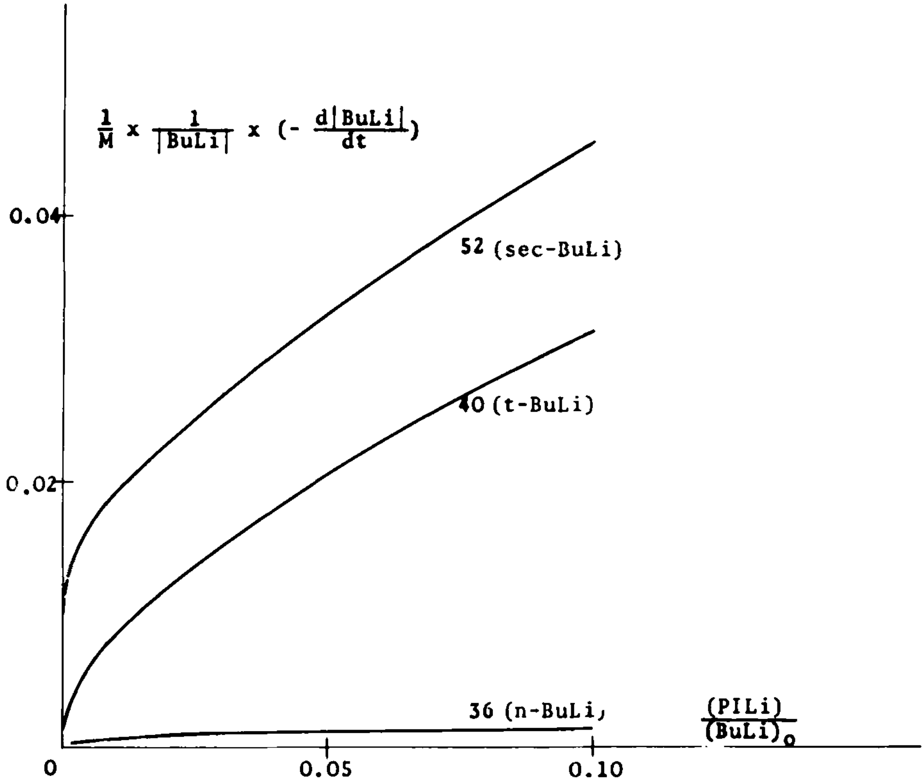

Fig. 9. Influence of PILi on the beginning of the initiation reaction without butoxide (the numbers refer to experiments listed in Tables 2, 3, and 4).

conversion, the rate seems to be constant in the case of n-BuLi and increases steadily in the two other cases. However, as shown in Fig. 10, the behavior may be different if further stages of the reaction are considered. With sec-BuLi, the apparent rate constant is reproducible, although the initial ratio of isoprene/BuLi varies between 13 and 61, as shown in Table 5. Such a result strongly supports the assumption of the first-order versus butyllithium concentration and indicates further that the distribution of the associated species does not depend very much on the initial concentrations of the reactants. With t-BuLi, the increase in the apparent rate constant is much more pronounced, but the validity of the assumption is more questionable. However, it should be noted that the three experiments reported involve changes in initial BuLi concentration from 1 to 12 and in the isoprene-to-BuLi ratio from 9 to 300. A surprising result is obtained with n-BuLi;

Table 5. Initial Concentrations for Experiments without Lithium Butoxides

Run no.	M, mole/liter	n-BuLi $\times 10^3$ moles/liter	sec-BuLi $\times 10^3$ moles/liter	t-BuLi $\times 10^3$ moles/liter	Initial M/BuLi
20	0.328	0	8.70	0	37.7
24	0.127	0	9.56	0	13.3
52	0.356	0	5.85	0	60.8
31	0.150	0	0	17.3	8.7
32	0.066	0	0	1.70	38.8
40	0.783	0	0	2.68	292
36	0.895	2.62	0	0	342
37	0.570	3.20	0	0	178

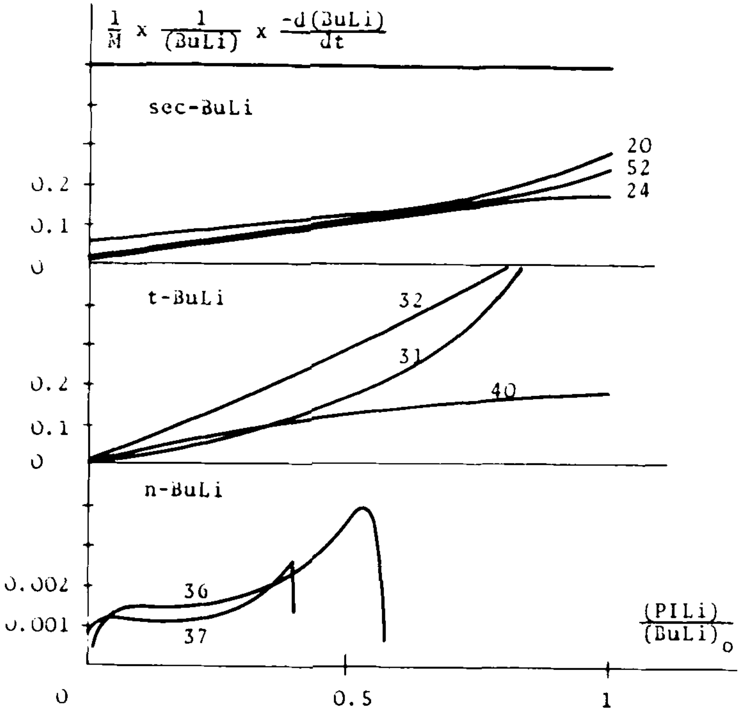

Fig. 10. Influence of PILi on the initiation rate without lithium butoxide (numbers refer to runs listed in Table 5).

after a quasi-steady value, the rate goes through a sharp maximum and then decreases abruptly to negligible values. Then it is not possible to obtain complete consumption of the initiator. The practical limit of the reaction depends on the initial monomer-to-n-BuLi ratio and increases with it. But when the limit is reached, it cannot be passed by further addition of even a great amount of monomer. This result probably indicates that the remaining butyllithium molecules are engaged in very stable and inactive particles.

When lithium butoxides are added to a solution of n-BuLi, the initiation rate is very much increased at the beginning of the reaction, and, as quoted before, n-BuOLi is the most efficient followed by sec-BuOLi and t-BuOLi. But, as shown in Fig. 11, the apparent rate constant decreases continuously during the process and may become lower than that observed with pure n-BuLi. In all the experiments carried out, the monomer is consumed

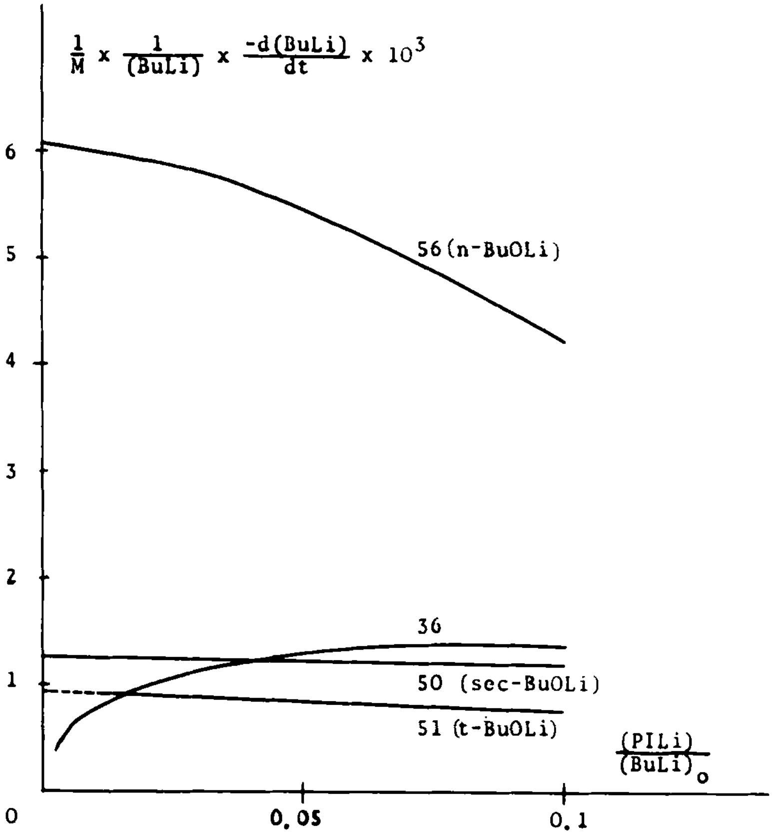

Fig. 11. Influence of PILi on the beginning of the initiation reaction with n-BuLi in the presence of lithium butoxides (numbers refer to experiments listed in Table 2).

before a limit of the consumption of the initiator is reached; however, this consumption is never total and the maximum value reached in the presence of n-BuOLi is about 70% (run 56, Table 2). The results obtained with sec-BuLi are shown on Figs. 12 and 13. Here, the initiation is always complete and the apparent rate constant increases continuously during the entire initiation process, and especially at the end. The efficiency in the increase of the rate constant is again n-BuOLi > sec-BuOLi > t-BuOLi. This order is valid also in the case of t-BuLi, as shown in Fig. 14, but with n-BuOLi and sec-BuOLi, the rate decreases during the process. As already quoted,

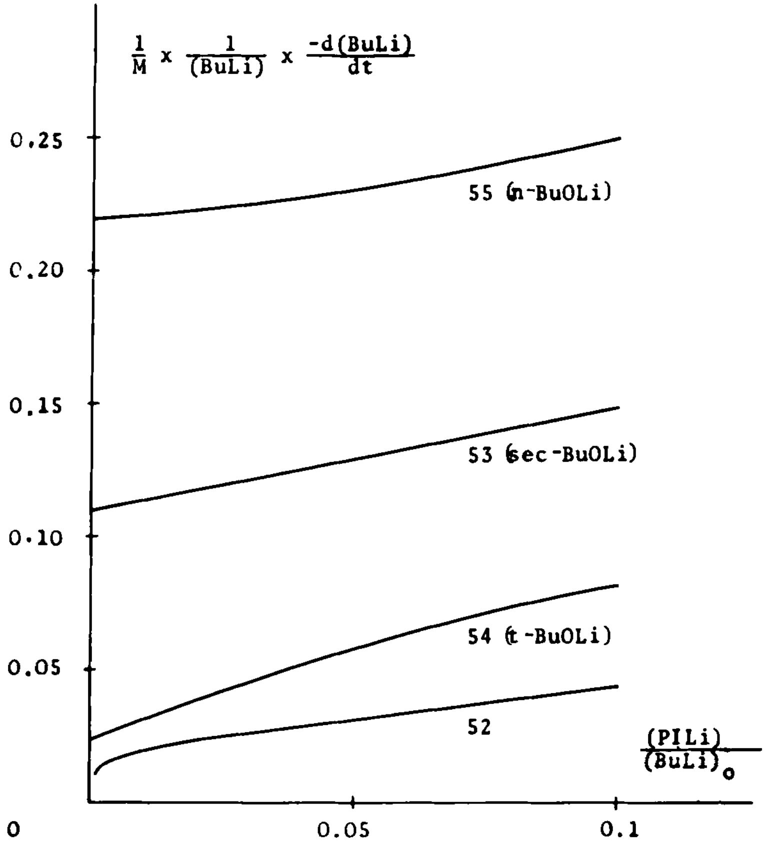

Fig. 12. Influence of PILi on the beginning of the initiation reaction with sec-BuLi in the presence of lithium butoxides (numbers refer to experiments listed in Table 3).

t-BuOLi decreases the initiation rate observed with t-BuLi only, and the effect depends chiefly on the relative concentration of t-BuOLi, as shown in Fig. 15.

All these results show that PILi may be associated with the different butyllithium molecules and may also be present in mixed particles including butyllithium and lithium butoxides. Its effect may be to decrease or to increase the reactivity of the mixed particles with respect tot he initiation reaction, depending on the nature of the alkyl groups attached to the lithium or oxygen atoms.

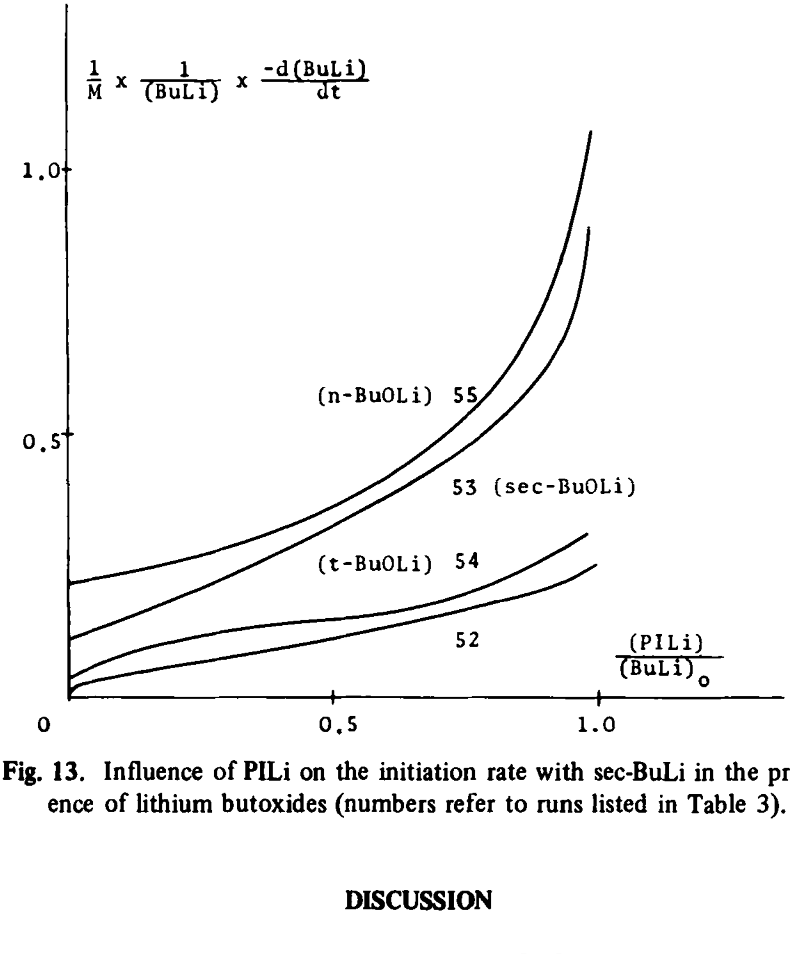

Fig. 13. Influence of PILi on the initiation rate with sec-BuLi in the presence of lithium butoxides (numbers refer to runs listed in Table 3).

DISCUSSION

As pointed out by Szwarc in a recent book [10], the organolithium derivatives are electron-deficient compounds and they form, in hydrocarbon solvents, tightly bonded agglomerates of a few monomeric molecules such as tetramers or hexamers. In these compounds, the lithium atoms are bonded with three carbon atoms, and the bonds are not covalent but rather ionic with charge delocalization. On the other hand, the results of Roovers and Bywater [5] clearly proved that the tetramers of sec-BuLi are directly involved in the initiation reaction when the solvent is cyclohexane. In our presentation of the results we have supposed that such a situation would be valid during the entire process. However, the phenomena are undoubtedly

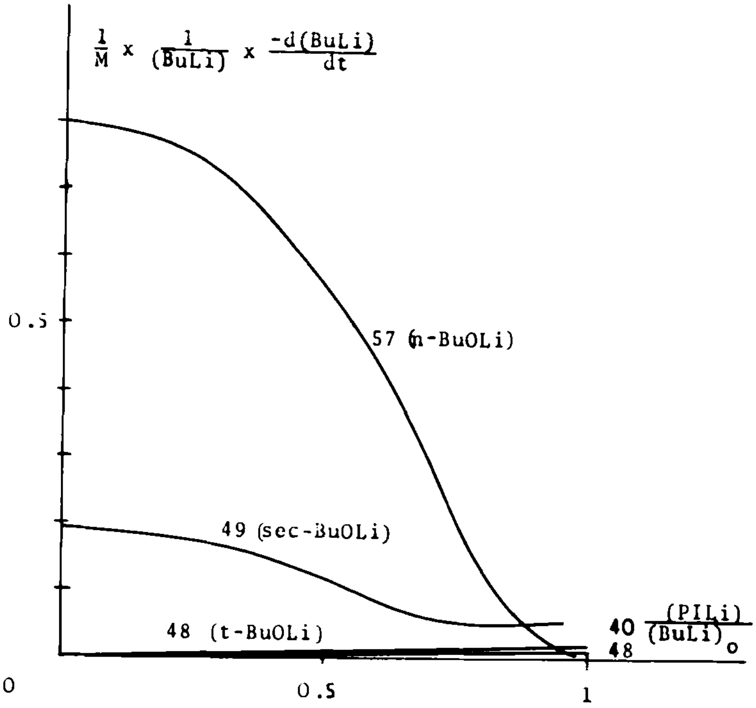

Fig. 14. Influence of PILi on the initiation rate by t-BuLi in the presence of lithium butoxides (numbers refer to runs listed in Table 4).

more complex. Exchange of the alkyl groups actually takes place through dissociation of the agglomerates, and reassociation [11]. Ionic species with localized carbanions are possible also, as suggested by Szwarc and also by Makowski and Lynn [12]. They may be formed during the first step of the initiation reaction

$$Li_4Bu_4 + I \longrightarrow (Li_4Bu_3)^+, {}^-IBu$$

The cation of such a contact ion pair is probably less stable than the initial agglomerate, because it is an unsymmetrical particle. Then it dissociates, giving

$$(Li_4Bu_3)^+, {}^-IBu \longrightarrow (Li_2Bu_2) + (Li_2Bu)^+, {}^-IBu$$

The new contact ion pair may be dissociated again, giving a highly reactive

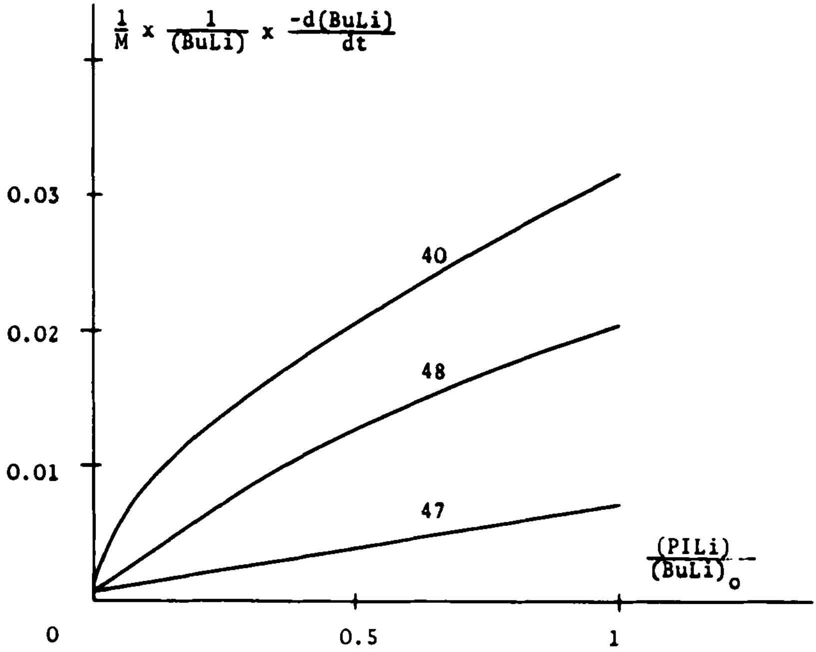

Fig. 15. Influence of PILi on the initiation rate with t-BuLi in the presence of t-BuOLi (numbers refer to runs listed in Table 4).

monomeric unit, which undergoes the initiation reaction. It may also be reacted directly with the monomer, giving a double ion pair or a symmetric ionic particle with charge localization. As suggested by Szwarc [10], the acceleration of the initiation is probably caused by the attack of the initial tetramers by the ion pairs generated from the dissociation. For instance,

$$(Li^+)_2, (^-IBu)_2 + (Li_4Bu_4) \longrightarrow (Li_4Bu_3)^+, {}^-IBu$$
$$+ (Li_2Bu)^+, {}^-IBu$$

Because the propagation takes place simultaneously and because of the various equilibria of association-dissociation, a number of particles are created, which may be symmetrical or not, with or without charge localization. Two major ways are then possible for the initiator reaction: (a) direct attack of an agglomerate of butyllithium or mixed butyl- and polyisoprenyllithium with or without charge delocalization, or (b) insertion of monomer into a Li^+, ^-Bu ion pair formed through a dissociative process.

The overall initiation rate depends on the stability of the agglomerates versus both chemical reaction and dissociative processes. Probably the stability is the highest when the degree of association of the particles is higher. It is possible, then, to explain the initial behavior of the n-BuLi, which is chiefly hexameric, while the sec-BuLi and t-BuLi are tetrameric only. Another important parameter is probably the exchange rate between the mixed particles and the initial ones. Roovers and Bywater [5] have shown that the exchange rate between sec-BuLi and PILi is rapid in cyclohexane. This situation is probably valid in the case of t-BuLi, but it may not be the case with n-BuLi. Then, the fact that there is a limit to the reaction shows that some kind of mixed particles are probably very inactive versus initiation and that exchange is very slow. The acceleration of the reaction is limited so that the attack of the initial agglomerates by ion pair is not very efficient, and the dependence of the reaction limit on the initial monomer-to-initiator ratio proves that the attack of the initial hexamers by the monomer is probably the determining process of the initiation.

The lithium butoxides are also agglomerated in particles; t-BuOLi is a hexamer in cyclohexane solution [13], and n-butoxide, of lower solubility, is considered to be associated in high linear polymer [14]. It has been shown that n-butyllithium greatly increases the solubility of lithium n-butoxide [13]; butyllithium is then probably at the end of a polymeric chain of the butoxide, and in this position it may be very reactive versus initiation. Such a structure may explain quite well the high reactivity of the initial mixed species of lithium n-butoxide and the various alkyllithiums. A comparison of the corresponding curves in Figs. 11 (run 56), 13 (run 55), and 14 (run 57) shows that the efficiency of n-butoxide is highest in the case of t-BuLi, followed by sec-BuLi, and lowest in the case of n-BuLi, with a factor of about 100 compared with the two other BuLi. Such a factor reflects the effect of the stability of the initial BuLi agglomerate; thus, the placement of BuLi at the end of the chains of polymeric n-BuOLi probably requires the dissociation of the initial BuLi particles. The order of reactivity of the mixtures n-BuOLi-sec-BuLi and n-BuOLi-t-BuLi in the initiation reaction is different from that observed when the butoxide is not present. The reason for this is not obvious and the ractivity may depend either on the attack of the BuLi particle by n-BuOLi (or the reverse) or on the proper reactivity of the mixed species versus the monomer.

The shape of both t-BuOLi and sec-BuOLi particles is different from that of n-BuOLi; the corresponding particles are much more similar to those of BuLi, say, a core of Li and O atoms shielded by aliphatic groups. It is possible that their co-association with BuLi particles may take place without disruption of the initial agglomerates in a manner similar to that observed by Brown et al. [15, 16] in the case of ethyllithium and lithium ethoxide. Such a situation may account for the lower efficiency of sec-BuOLi in the promotion of the initial initiation rate, as compared with n-BuOLi. The shielding effect is expected to be more important in the case of t-BuOLi, and, indeed, its promoting action is lower and, in the case of t-BuLi, is a retardation rather than a promotion.

Further, when PILi is present the situation is again more complex because, compared with the initial rate, the initiation rate may increase or decrease with the yield of PILi. Then, ternary mixed particles are created with various reactivities, depending on the nature and the amount of the components, and the accelerating effect due to the presence of PILi may be overcome by the fact that some ternary particles may be less reactive than the linear ones containing only BuLi and BuOLi. Alternatively, there may be a preferential association between PILi and BuOLi which increases the concentration of pure BuLi agglomerates of low reactivity.

In our opinion, it is not possible to discuss the results further without better knowledge of the structure and properties of mixed binary and ternary particles. Determinations of the association degrees, the exchange rates, and the degree of charge localization of the various ionic species are highly desirable.

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Accepted by editor July 22, 1969
Received for publication July 29, 1969