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. II. Propagation Reaction', Journal of Macromolecular Science, Part A, 4: 1, 107 — 125
To link to this Article: DOI: 10.1080/00222337008060968
URL: http://dx.doi.org/10.1080/00222337008060968

J. MACROMOL. SCI.–CHEM., A4(1), pp. 107-125, January 1970

Isoprene Polymerization by Butyllithium in Cyclohexane. II. Propagation Reaction

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SUMMARY

The kinetics of the propagation reaction in the polymerization of isoprene initiated by n-, sec-, or t-butyllithium, in the absence or in the presence of the three corresponding lithium butoxides, are studied in the two possible major cases. In the first case, the propagation takes place without simultaneous initiation; the reaction is then first-order versus the monomer concentration and one-sixth-order versus the polyisoprenyllithium concentration. The lithium butoxides decrease the propagation rate, but the effect is not very dependent on the nature of the butoxide. In the second case, the presence of the initiator decreases the propagation rate in a manner which depends on the concentrations of the reactants and on the nature of the initiator. The effect of the lithium butoxide is not simply additive. Depending on the relative concentrations, a synergistic effect may be observed. It is suggested that the active species are chiefly ion pairs of unassociated polyisoprenyllithium. Ion pairs from associated molecules may have limited activity.

INTRODUCTION

The preceding paper [1] dealt with the kinetics of the initiation reaction during the polymerization of isoprene with n-, sec-, or t-butyllithium (BuLi) as catalyst, in cyclohexane as solvent. It was shown how polyisoprenyllithium (PILi) and the various lithium butoxides accelerate or, in a few cases, decrease the initiation rate, and the results were discussed in terms of mixed associated particles containing the different species present. We concluded that these particles are directly active in the initiation reaction, which does not necessarily involve the dissociated butyllithium molecules.

The present paper deals with the same problems, in connection with the propagation reaction. The experimental methods have been fully described in the preceding paper, so that we may recall only that the kinetics of isoprene consumption are followed by gas chromatographic analysis, hexane being the internal concentration reference, and that the same analysis simultaneously measures the butyllithium consumption from the residual butane produced on hydrolysis, pentane being the reference. We have to consider two cases: Case I, the propagation reaction is the sole reaction, when the initiation reaction has been completed; or case II, the two reactions take place simultaneously. In the latter case, the monomer consumption is corrected from the contribution of the initiation reaction, taking into account a first-order versus monomer concentration. Some preliminary results have been published [2]. It has been shown that in case I, the reaction is first-order versus monomer concentration and follows a fractional one-fourth-order versus the PILi concentration, in agreement with a number of authors [3-5], and that in case II the presence of sec-butyllithium causes a sharp decrease in the propagation rate and increases up to about one-fourth the apparent order versus PILi. Some results on the decreases in propagation rate upon addition of lithium butoxides have been published by Roovers and Bywater [6, 7].

RESULTS

The initial concentrations of the more significant runs are given in Table 1, and the corresponding kinetics curves are illustrated in Figs. 1-4. All these curves show the well-known sigmoidal shape, which means that at the beginning of the process initiation takes place and increases the active PILi concentration, thus causing acceleration of the propagation, and that at the end of the process the decrease in monomer concentration is responsible for the decreasing rate. In the case of sec-BuLi and t-BuLi initiation, the maximum rate corresponds rougly to the end of the initiation reaction, indicated by arrows in Figs. 2-4. In the case of n-BuLi, the consumption of the monomer is always complete before total consumption of the initiator. A rapid examination of the curves shows that the three

Table 1. Feed of Initial Concentration of the Reactants

Run no.	$[M]_0$ mole/liter	[n-BuLi] × 10^3 moles/liter	[sec-BuLi] × 10^3 moles/liter	[t-BuLi] × 10^3 moles/liter	[n-BuOLi] × 10^3 moles/liter	[sec-BuOLi] × 10^3 moles/liter	[t-BuOLi] × 10^3 moles/liter	$\frac{[\text{BuOLi}]}{[\text{BuLi}]_0}$ moles/liter
36	0.895	2.62	–	–	–	–	–	0.037
40	0.78	–	–	2.68	–	–	–	–
46	0.76	–	–	2.47	–	–	2.70	1.09
47	0.77	–	–	1.87	–	–	3.46	1.85
48	0.85	–	–	2.74	–	–	1.87	0.68
49	0.75	–	–	2.03	–	2.75	–	1.35
50	0.73	3.32	–	–	0.196	2.17	–	0.71
51	0.61	3.06	–	–	–	–	2.57	0.84
52	0.356	–	5.83	–	–	–	–	–
53	0.287	–	4.39	–	–	6.05	–	1.38
54	0.330	–	5.6	–	–	–	5.82	1.04
55	0.344	–	6.15	–	5.95	–	–	0.96
56	0.60	2.41	–	–	4.20	–	–	1.75
57	0.72	–	–	2.50	3.64	–	–	1.45

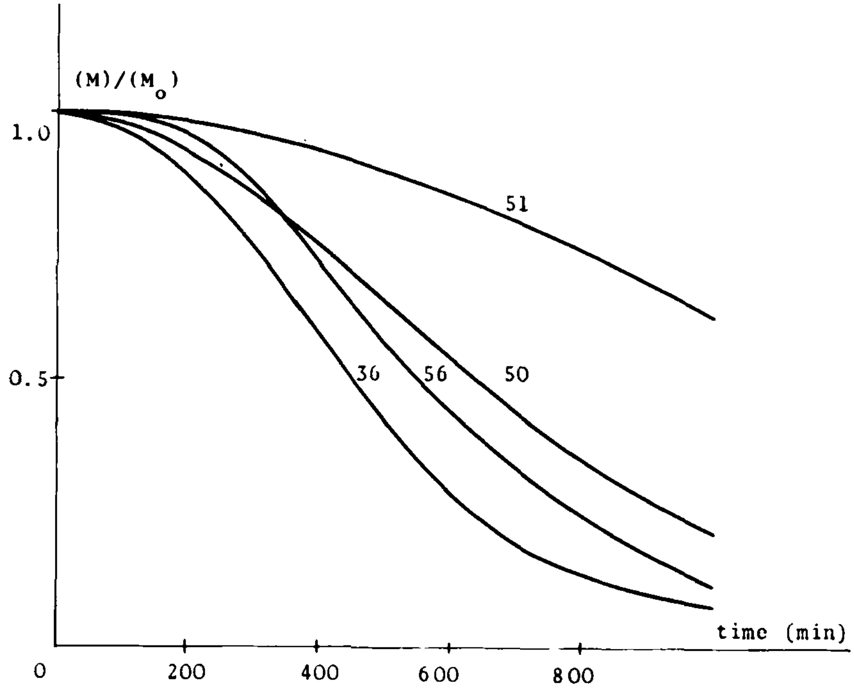

Fig. 1. Isoprene consumption in the presence of lithium butoxides, the initiator being n-BuLi. Numbers refer to run numbers in Table 1: (36) no BuOLi, (50) sec-BuOLi, (51) t-BuOLi, (56) n-BuOLi.

lithium butoxides decrease the propagation rate in all cases; but precise interpretation requires taking into account the effect of the butoxide on the initiation rate, chiefly in the case of n-BuLi. The best way is to distinguish between the two major cases.

Case I

The propagation takes place without simultaneous initiation. The results refer, then, to the parts of the curves to the right of the arrows in Figs. 2-4. It has been verified here that the reaction is first-order versus monomer concentration whether butoxides are present or not. The apparent order versus PILi is obtained from plots of log (1/M)(-dM/dt) against log PILi. Such plots, corresponding to experiments carried out at 25 and 50°C, without added butoxide, are illustrated in Fig. 5. In the two cases the best straight lines have a slope close to 0.16, which corresponds to a

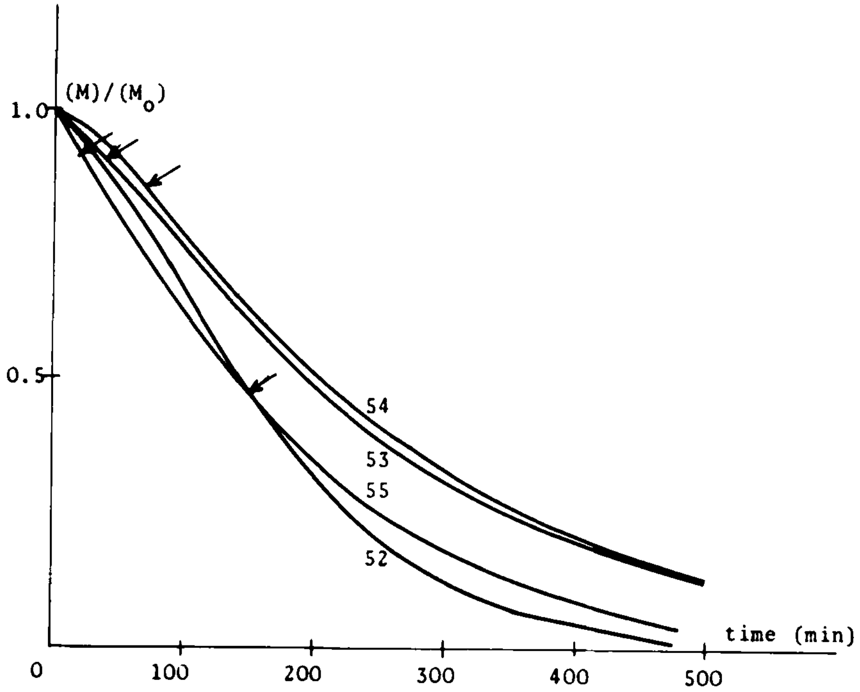

Fig. 2. Isoprene consumption in the presence of lithium butoxides, the initiator being sec-BuLi. Numbers refer to run numbers in Table 1: (52) no BuOLi, (53) sec-BuOLi, (54) t-BuOLi, (55) n-BuOLi.

one-sixth order in place of the one-fourth order previously reported. From these results, it is possible to determine an apparent activation energy of 26 kcal/mole for the propagation reaction. This value is only slightly higher than that reported by Morton et al. [8] (22.6 kcal/mole) for experiments carried out in hexane. Using our value, it is possible to calculate the corresponding values of the rate at 30°C and then to compare them with the results of other authors, as shown in Fig. 6. The agreement is good, but our experimental points are generally a little higher than the others. The difference may be due either to a solvent effect or to incomplete initiation when n-BuLi has been used; this is more apparent for the Morton results [8].

The addition of lithium butoxide causes a decrease in the propagation rate; this effect is illustrated in Fig. 7, which corresponds to an experiment in which, at the end of the initiation reaction (curve 2), sec-BuOLi has

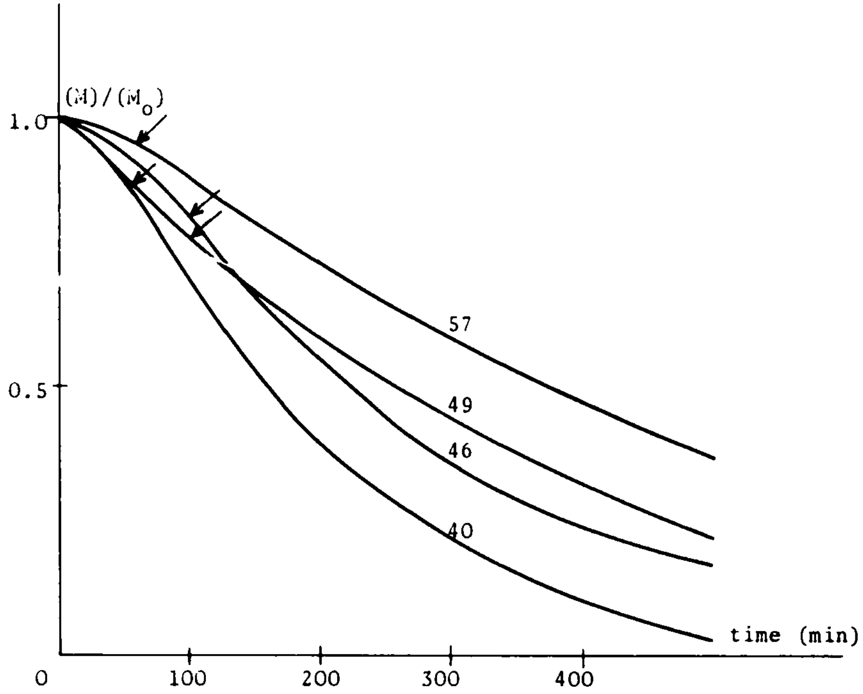

Fig. 3. Isoprene consumption in the presence of lithium butoxides, the initiator being t-BuLi. Numbers refer to run numbers in Table 1: (40) no BuOLi, (46) t-BuOLi, (49) sec-BuOLi, (57) n-BuOLi.

been added. The propagation rate is divided by a factor of about 3. The measurement of the rates in a number of experiments where various BuOLi have been added at the beginning of experiments, the initator being sec-BuLi or t-BuLi, shows that, after the end of the initiation reaction, the rate is lower than that which may be calculated using the one-sixth-order line in Fig. 5 for the corresponding PILi concentration. As shown in Fig. 8, the ratio of the experimental rate, R_{ex}, to the calculated one, R_0 seems not to be very dependent on the nature of the butoxide but decreases when the relative amount of butoxide increases.

Case II

The propagation and the initiation occur simultaneously. It has been reported that ethyllithium [9] or sec-butyllithium [2] causes a decrease in the propagation rate. The direct proof of this is illustrated in Fig. 9.

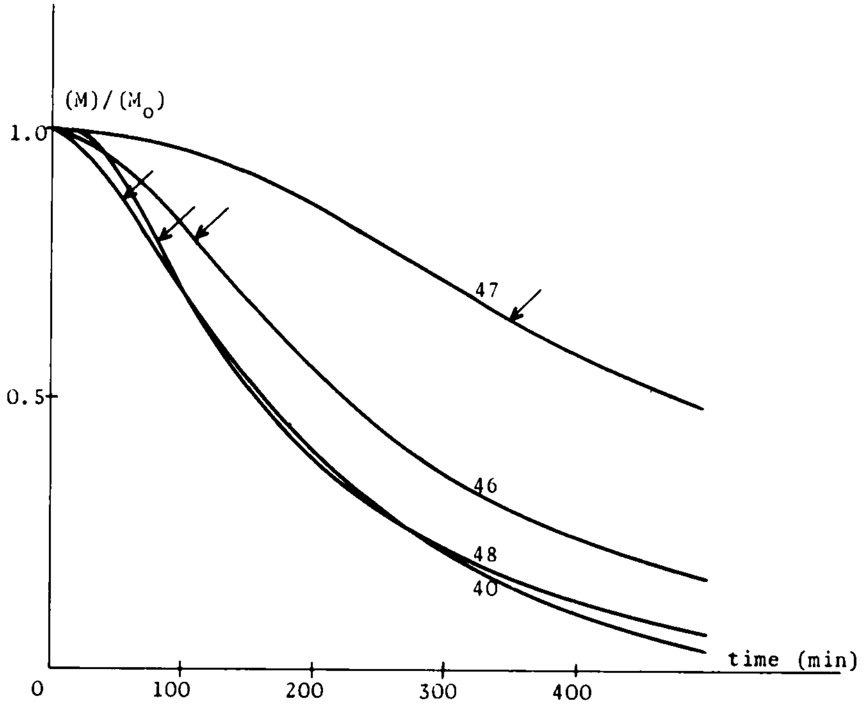

Fig. 4. Isoprene consumption in the presence of t-BuOLi, the initator being t-BuLi. Numbers refer to run numbers in Table 1.

In the corresponding experiment a polymerization was initiated by low-molecular-weight PILi. After addition of isoprene, the polymerization was carried on with only propagation for about 40 min and then t-BuLi was added. It is obvious that, although initiation takes place again and thus new active chains are formed, the propagation rate is lower. In Fig. 10 are illustrated the results of several experiments by double logarithmic plots of the propagation rate against PILi during the initiation period with t-BuLi. It appears that there is no definitive order because the plots are curved; however, it may be seen that very small amounts of residual t-BuLi cause a large decrease in the experimental propagation rate (R_{ex}) compared with the calculated value (R_0) given by the straight line corresponding to the one-sixth order observed in case I. From the data in Fig. 10, it is possible to build, as shown in Fig. 11, a set of curves giving the ratio R_{ex}/R_0 as a function of [t-BuLi] for constant values of [PILi]. All the curves present the same shape and, after a rapid initial decrease,

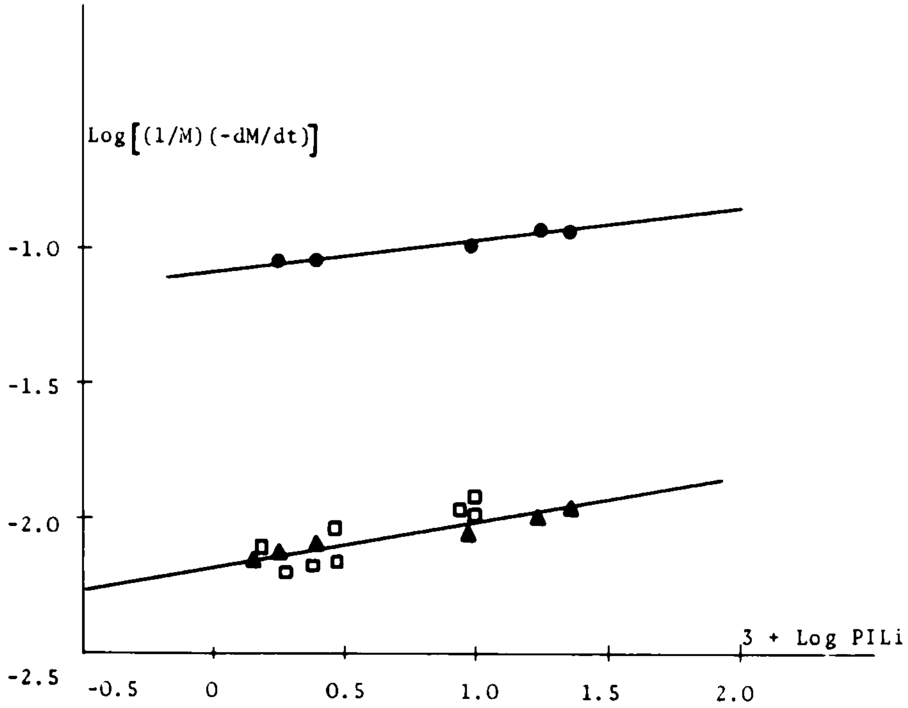

Fig. 5. Dependence of propagation rate on PILi concentration. Experiments at 25°C with sec-BuLi (□); experiments with t-BuLi at 25°C (▲) or 50°C(●).

take a "plateau" value at a level fixed by the value of [PILi]. The dotted lines correspond to fixed values of the ratio [BuLi]/[PLi]. One observes a sharp minimum for the low values of the ratio, which becomes more and more flat for the higher values. The general behavior is that the decrease in the rate is more pronounced with the small concentrations of the reactants. Similar results about the depressive effect of sec-BuLi are shown in Figs. 12 and 13. The general shapes of the sets of curves are not very different except that the plateau values are obtained for higher values of BuLi concentration and are less dependent on the PILi concentrations; also, the shapes of the dotted lines corresponding to fixed values of the ratio BuLi/PLi are changed. In order to compare quantitatively the depressive effects of the three butyllithiums, we have plotted in Fig. 14 the ratio R_{ex}/R_0 versus [PILi] for a fixed [BuLi] = 1 X 10^{-3} mole/liter. For

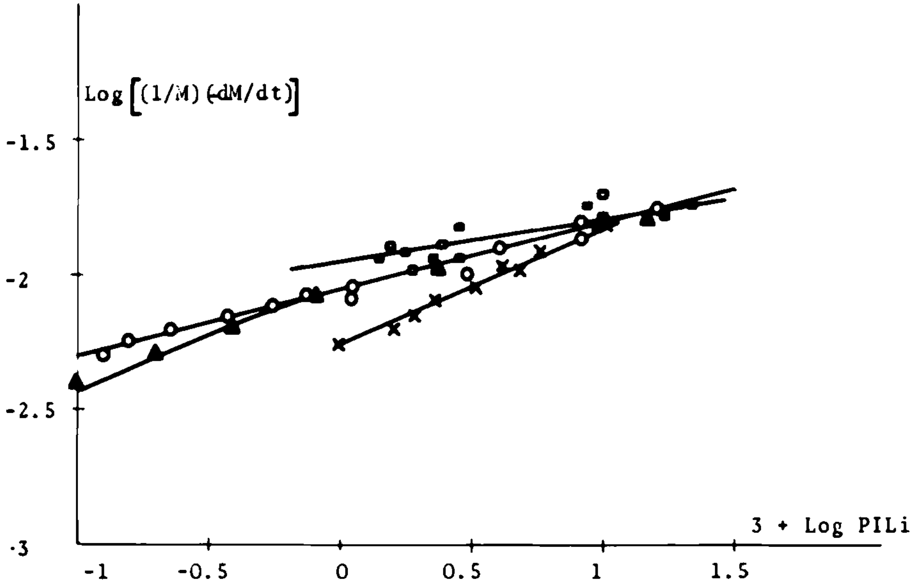

Fig. 6. Dependence of propagation rate on PILi concentration at 30°C. ○, Worsfold and Bywater results in cyclohexane with n-BuLi [3] ; ▲, Sinn et al. results in heptane with n-BuLi [14] ; X, Morton et al. results in hexane with n-BuLi [8] ; □ our calculated results in cyclohexane with sec-Bu-Li and t-BuLi.

the higher values of [PILi], the effects of the three BuLi are practically the same. For moderate values of PILi, sec-BuLi is the most efficient, but its depressive effect remains limited for very low [PILi], while the effects of t-BuLi and chiefly n-BuLi increase very much and tend to become a complete inhibition. Other values of BuLi exhibited the same behavior. When lithium butoxide is present, its depressive effect is observed again in addition to that of the BuLi. Figure 15 illustrates this fact in the case of polymerizations initiated with t-BuLi, by plots of the rate ratio against the initiation yield. The dotted lines are calculated from the set of curves of Fig. 11 for hypothetical experiments with the same initial BuLi and monomer concentrations. The experimental curves are lowest when the BuOLi concentrations are the highest; for t-BuLi and sec-BuOLi, the depression seems not to be very dependent on the butoxide species. The experiment with n-BuOLi is represented by one point only, because in

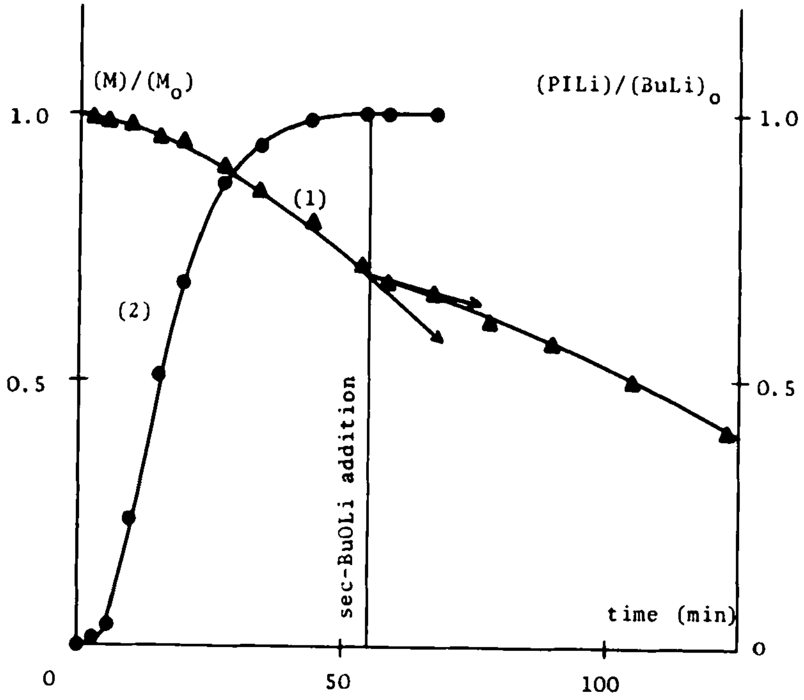

Fig. 7. Influence of added sec-BuLi on propagation; isoprene remaining (1), t-BuLi consumed (2).

this case the initiation is very rapid at the beginning but practically stops before completion; the position of the point shows that, for corresponding concentrations (Table 1), the effect of the n-BuOLi is less important than those of the two other butoxides.

It is interesting to try to separate the proper effect of the butoxide from that of the initiator. The latter may be calculated as R_c/R_0 by interpolation from the set of curves of Fig. 11, 12, or 13. The former would be R_{ex}/R_c and thus we have

$$R_{ex}/R_0 = [R_{ex}/R_c]\ [R_c/R_0]$$

Plots of R_{ex}/R_c are shown in Fig. 16, against the ratio [BuOLi]/[PILi]. The dotted curve is the curve shown in Fig. 8, illustrating the depressive effect of the butoxide, in case I. When the initiation goes to completion,

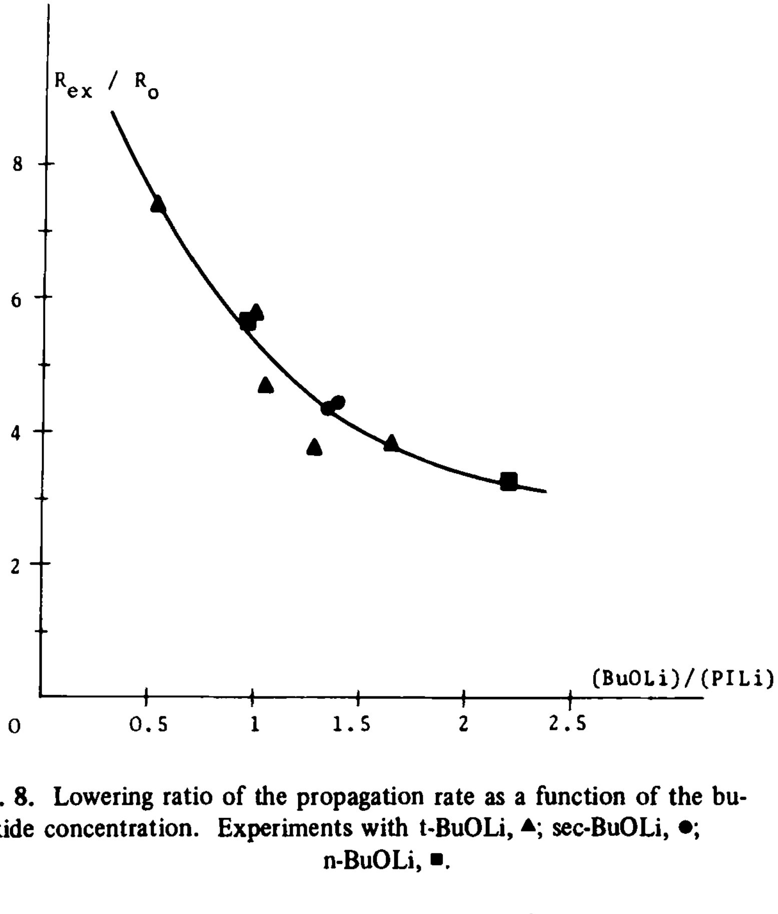

Fig. 8. Lowering ratio of the propagation rate as a function of the butoxide concentration. Experiments with t-BuOLi, ▲; sec-BuOLi, ●; n-BuOLi, ■.

the experimental curves join the dotted one. This feature is observed when the initiation is carried out using either sec-BuLi or t-BuLi. In all cases, independent of the nature of the initiator or the butoxide, one observes at the end of the initiation process a synergistic effect of the initiator, since the calculated depressive effect may be higher than that of the butoxide only. The situation is the reverse during the first part of the initiation process, and in fact, for an experiment where the initiator was sec-BuLi, the propagation rate observed was initially greater than the calculated value assuming no butoxide. The decrease in the proper depressive effect of the butoxide is higher when its concentration is lower (compare Fig. 16 and the last column of Table 1).

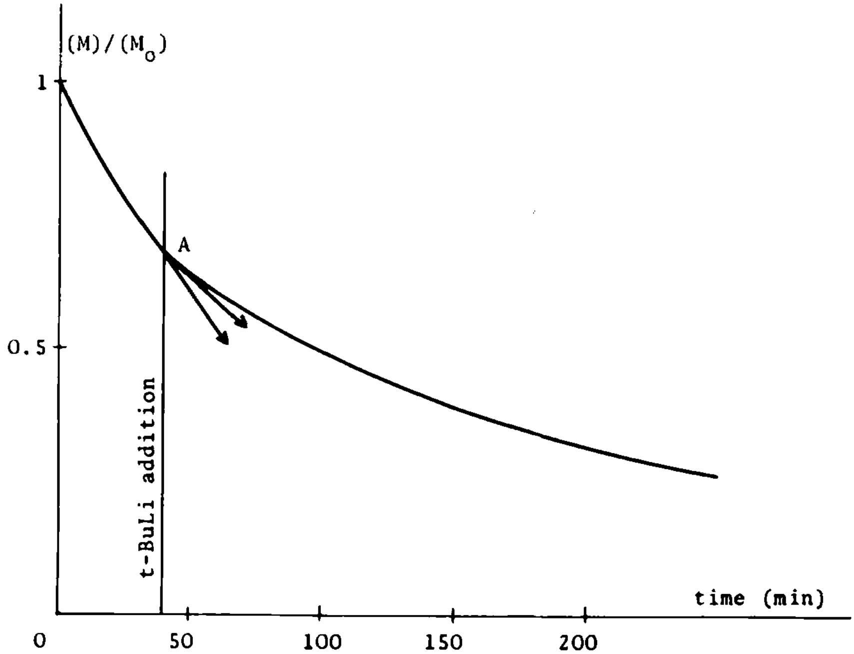

Fig. 9. Influence of addition of t-BuLi on the propagation reaction. $[M_0] = 0.067$ mole/liter, $[M_A] = 0.0427$ mole/liter, [t-BuLi] = 14.7×10^{-3} mole/liter.

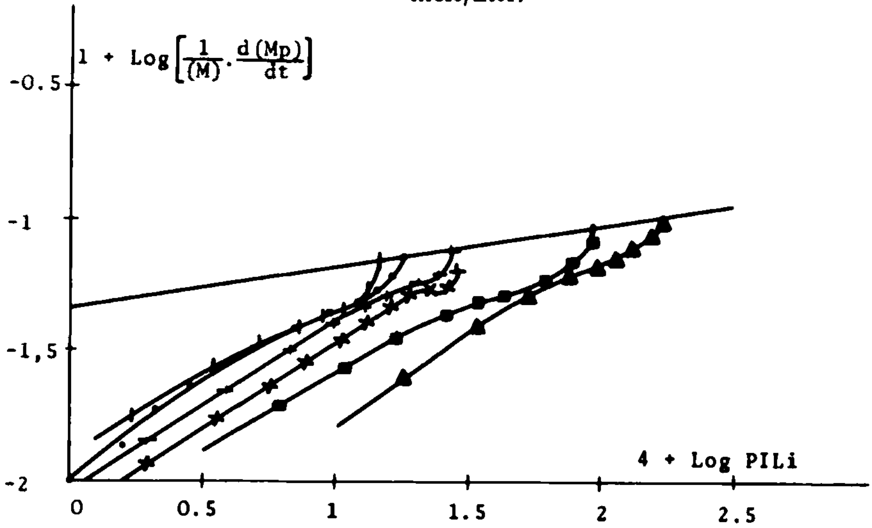

Fig. 10. Dependence of the propagation rate on PILi concentration in the presence of t-BuLi.

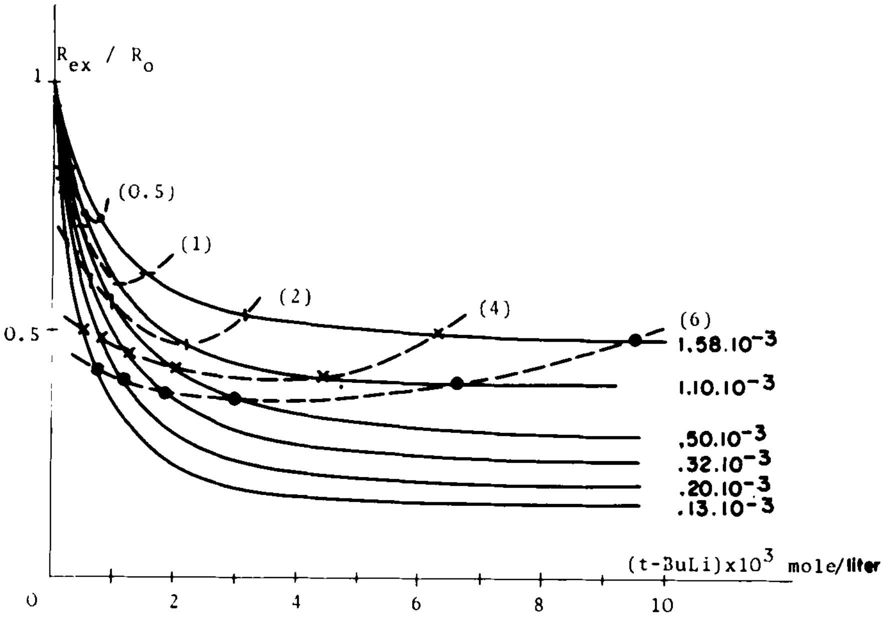

Fig. 11. Influence of t-BuLi on the propagation rate, in the absence of butoxide. The continuous lines correspond to the indicated PILi concentrations; the dotted lines correspond to the indicated values of [BuLi]/[PILi].

DISCUSSION

Our results in Fig. 5 on the apparent order of the propagation reaction versus the PILi concentration are not very conclusive for the experiments carried out at 25°C, and, on this ground, the distinction is not very clear between the one-sixth order and the more generally accepted one-fourth order [3-5]. However, we think that at 50°C a one-fourth order is ruled out. The one-fourth order reflects the fact that the PILi is associated in particles containing four molecules; these particles are dissociated only to a very limited extent into individual molecules which are the sole active species in the propagation reaction. It is not possible that the degree of association would be higher at higher temperature. So

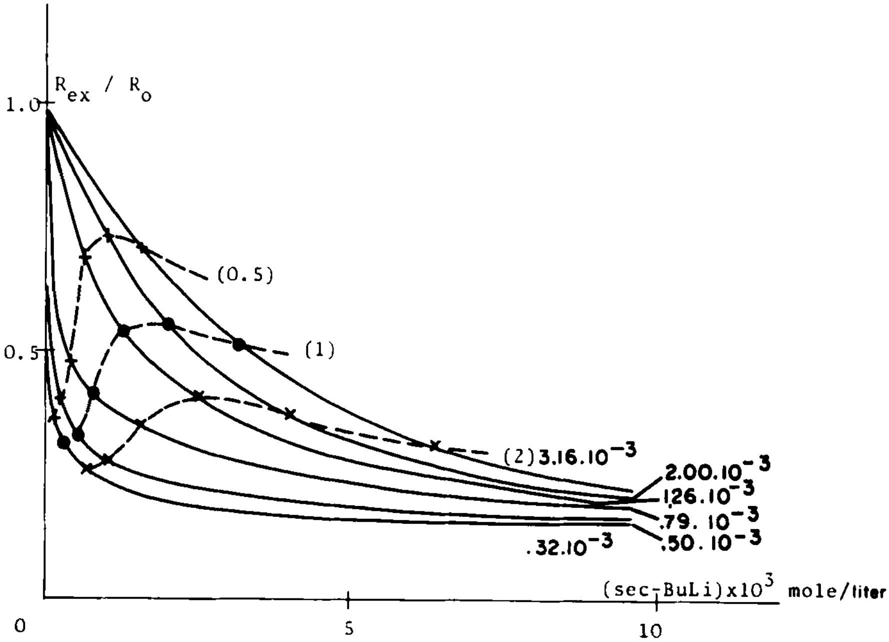

Fig. 12. Influence of sec-BuLi on the propagation rate, in the absence of butoxide. The continuous lines correspond to the indicated PILi concentrations; the dotted lines correspond to the indicated [BuLi/[PILi] values.

we prefer an alternative explanation. The activity involves essentially ion pairs with localized anionic charge: obviously the charge is localized in the unassociated PILi molecules, but it may also be localized in some associated particles which may then be active in the propagation reaction; the effect of the higher temperature would then be to enhance the delocalization of the charge in the associated particles, so that the proportion of active PILi molecules would be lower.

When lithium butoxide is present, mixed associated particles are formed. They cannot be very active because, as pointed out by Szwarc [10] and Makowski and Lynn [11], when they form ion pairs with charge localization, the anion is more probably an oxanion than a carbanion:

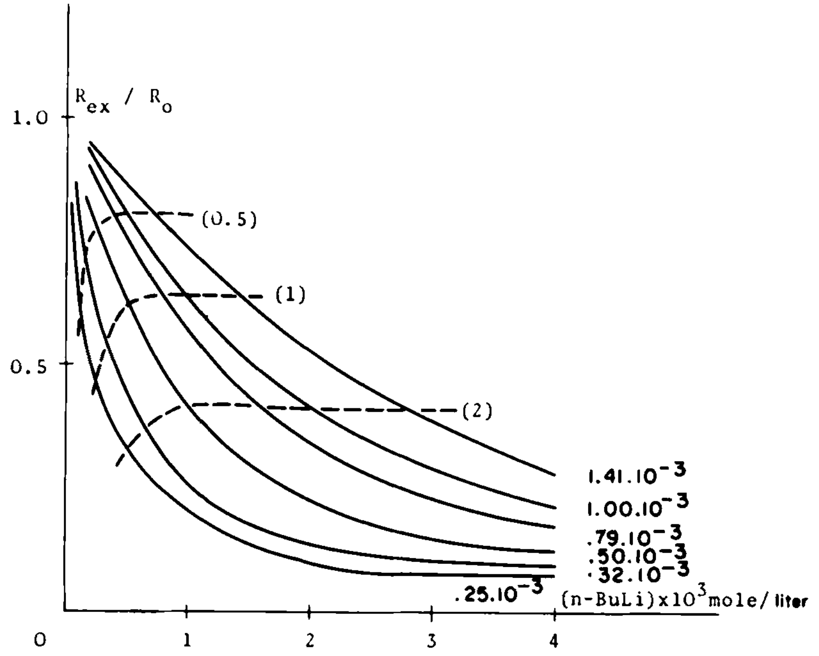

Fig. 13. Influence of n-BuLi on the propagation rate in the absence of butoxide. The continuous lines correspond to the indicated PILi concentrations; the dotted lines correspond to the indicated [BuLi]/[PILi] values.

$$(Li_x, PI_y, OR_z - \rightleftharpoons (Li_x, PI_y, OR_{z-1})^+, {}^-OR$$

In this case the activity would be due essentially to unassociated PILi ion pairs. In this connection the nature of the lithium butoxide may influence the propagation rate only via the dissociation constant of the mixed particles. This influence is not very important, as shown by the results illustrated in Fig. 8. Recently Makowski and Lynn [11] showed that in the case of polybutadienyllithium the addition of BuOLi changes markedly the microstructure of the polymer, increasing the amount of 1,2 units. This fact proves the activity of associated mixed particles in the propagation reaction. However, in the case of isoprene polymerization, the effect is less important, as shown by the results reported by Worsfold and Bywater [3], and our experiments show that indeed it is very limited.

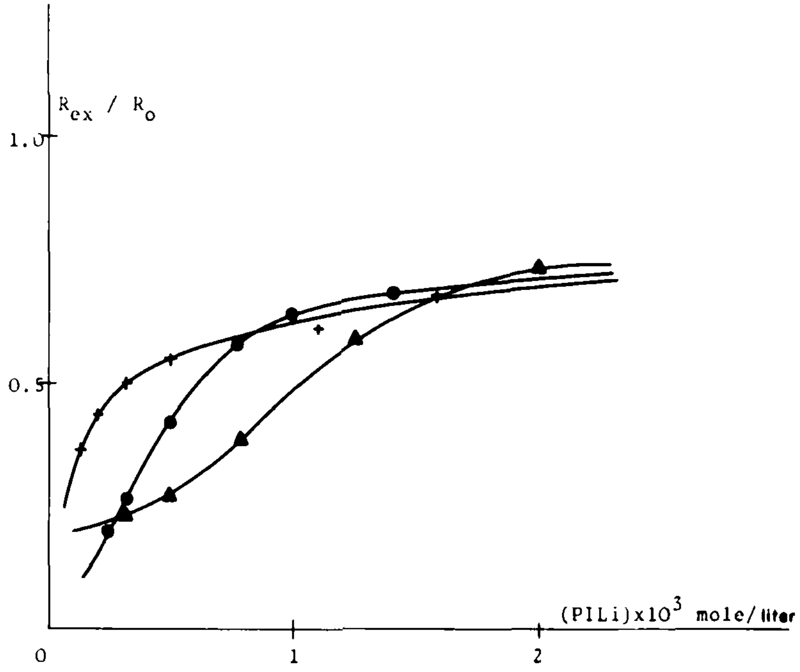

Fig. 14. Influence of the different BuLi, for [BuLi] = 1 X 10^{-3} mole/liter, on the propagation rate. ●, n-BuLi; ▲, sec-BuLi; +, t-BuLi.

Further, it has been shown in our laboratory [12] that the NMR spectra of the polyisoprenes are not dependent on the molecular weight in the range 400-40,000 (except for the contribution of the terminal butyl groups), while Makowski and Lynn [13] reported that the first butadiene units incorporated in a growing polymer chain are 80% 1,2. We may conclude that the participation of the associated particles in the propagation reaction is much more limited in isoprene polymerization than in butadiene polymerization.

The depressive effect of the initiator upon the propagation rate clearly indicates that mixed particles are more firmly associated than the pure polyisoprenyl particles. When the ratio PILi/BuLi is high enough, the depressive effect is independent of the nature of the BuLi (Fig. 14) and pure PILi particles are probably present; the propagation is due chiefly to the PILi ion pairs in equilibrium with these particles. When the ratio

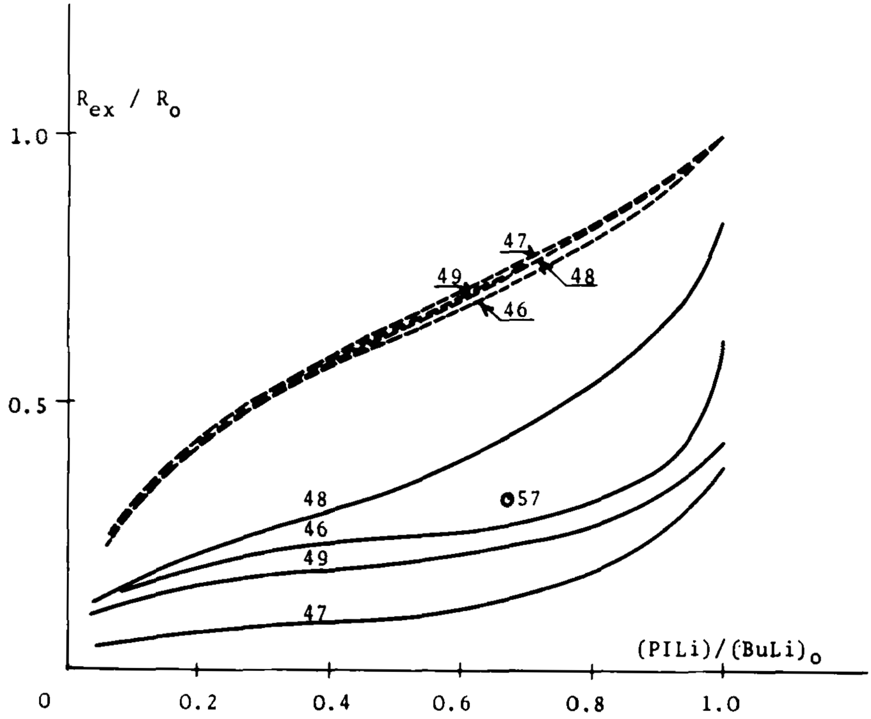

Fig. 15. Propagation rate in the presence of lithium butoxides compared with the rate in the absence of butoxide (dotted line) during initiation. Numbers refer to experiments listed in Table 1.

is low, the individuality of the concerned BuLi has a strong influence upon the behavior of the system. Thus, the effect of sec-BuLi is limited, because sec-BuLi tetramers, which are the most efficient in the initiation reaction, may be dissociated more easily. It may be noted also that the acceleration of the initiation reaction is most pronounced in this case [1]. On the other hand, n-BuLi, which is more associated and less efficient in the initiation reaction, is probably more active in decreasing the propagation rate at very low PILi/BuLi ratios. At moderate PILi/BuLi ratios, the behavior is more complex and, in our opinion, reflects the distribution of the associative agglomerates between pure BuLi or PILi particles and the different kinds of mixed particles. So, the proportion of pure BuLi particles may be, for the same concentration values, in the order (see Fig. 14) sec-BuLi < n-BuLi < t-BuLi. It may be noted also that the depressive effect

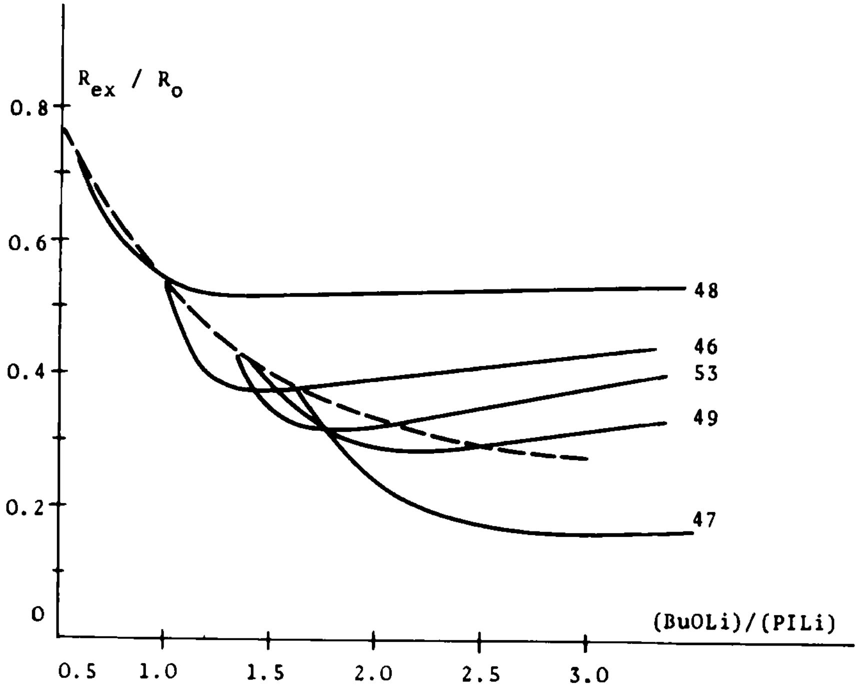

Fig. 16. Propagation rate in the presence of BuOLi + BuLi (continuous line) compared with the rate when there is only propagation in the presence of butoxide (dotted line). Numbers refer to runs listed in Table 1.

is relatively more important at low concentrations of the reactants; it is known that at low concentrations the degree of ionic dissociation is greater. Thus, the effect observed may indicate that the degree of ionic dissociation (more precisely here, the degree of charge localization) of the mixed particles is lower than that of the pure PILi particles.

The same considerations may be used to discuss the results about the combined effects of BuOLi and BuLi; but the situation is much more complex and the depressive effect probably reflects the distribution of the components in the different kinds of particles, which may be unary, binary, or ternary with different degrees of association and stability.

Obviously, as in the case of the initiation reaction, a better knowledge of these different particles, their relative composition, their exchange rates, and their degree of ionic charge localization is necessary for a good understanding of the propagation reaction. Such knowledge would involve a number of physicochemical studies such as molecular weight, conductance, NMR, and other measurements, and it is hoped that such data will soon be available.

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