Experimental Section

The aqueous acrylic acid polymerizations were carried out in 1-l., three-neck flasks equipped with thermometer, stirrer, and reflux condenser. The mixtures were made up to 300 ml final volume by first mixing acrylic acid solutions and distilled water, bringing this to the reflux temperature and then adding appropriate small volumes of 0.030 *M* potassium persulfate. Since the persulfate decomposes rapidly at elevated temperatures,[4] precautions must be taken to minimize thermal decomposition in the absence of acrylic acid by running the persulfate directly into the vigorously stirred acrylic acid solution. Prior contact of the persulfate with the flask walls or the stirrer shaft must be avoided. In the standard experiments, temperature control was limited to reflux conditions (about 100°). The dead-end yield is relatively insensitive to temperature. The average K (eq 2) for four experiments with 0.0333 N acrylic acid and 0.0005 M persulfate conducted in a thermostated oil bath at 90° was 1.29×10^3 which does not differ significantly from 1.21×10^3 obtained under reflux conditions. Reduced polymer yields were sometimes obtained in a new flask. The yield rose to normal by the second or the third experiment in the same flask. The use of glass wool did not affect the polymer yield after "breaking-in" by one or two experiments. The unpolymerized acrylic acid content of reaction mixtures was determined by three methods which gave concordant results. These were (1) acid permanganate oxidation (8 equiv/mol of acrylic acid), (2) steam distillation of acrylic acid and alkali titration, (3) a bromination procedure. Acrylic acid was purified in two ways, crystallization and distillation; both achieved 99–100% purity. Potassium persulfate (assay 99–100%) was used as purchased.

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The Polymerization of Isoprene with *sec*-Butyllithium in Hexane

J. E. L. Roovers and S. Bywater

Division of Applied Chemistry, National Research Council, Ottawa, Canada.

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ABSTRACT: The polymerization of isoprene in *n*-hexane, initiated by *sec*-butyllithium, has been investigated with particular emphasis on the initiation step. The mechanism of chain initiation appears to be quite different from that previously observed in benzene and involves direct attack of *sec*-butyllithium tetramers on isoprene. The effect of lithium *t*-butoxide has been investigated and found to accelerate the initiation rate but to depress the propagation rate. Some experiments were carried out to determine the rate of intermolecular exchange between *sec*-butyllithium and polyisoprenyllithium.

Lithium alkyl initiated polymerization of olefines in hydrocarbon solvents has received much attention recently. In many cases, the mechanism can be represented schematically as eq 1 and 2 where the ac-

$$(\mathrm{RLi})_n \rightleftharpoons n(\mathrm{RLi}) \tag{1}$$

$$\mathrm{RLi} + \mathrm{M} \xrightarrow{k_i} \mathrm{RM_1Li} \tag{2}$$

tive species is a small fraction of the dissociated alkyl in labile equilibrium with a large excess of associated material. The reaction order in lithium alkyl is, according to this scheme, fractional ($1/n$) and can be correlated with the association number. Two recent reviews[1,2] have examined the evidence for such a mechanism which has been suggested to hold in certain cases, for both initiation and propagation steps, *i.e.*, where R is an initiator fragment or a growing polymer chain, respectively. The validity of this mechanism, generally, has been challenged by Brown.[3]

One case in which this mechanism certainly does not hold is the initiation step in the *n*-butyllithium (*n*-BuLi) initiated polymerization of styrene, butadiene[4] and isoprene[5] in cyclohexane. Similar results have been observed with *sec*-butyllithium.[6] Instead of an initially linear increase in concentration of polymer–lithium species, which falls off as the reagents are depleted, as observed in benzene, the initiation curve is sigmoidal in shape. Some form of autocatalysis (by the alkenyllithium formed) was suggested to occur.[5] The reaction of isoprene with *sec*-butyllithium in hexane, which follows a similar course, has been investigated in an attempt to obtain more detailed information on this type of reaction.

Experimental Section

n-Hexane was stirred with concentrated sulfuric acid until no coloration developed. After washing the solvent to free it from sulfuric acid and drying, it was fractionally distilled from potassium metal. A middle cut was collected and passed twice over activated silica gel. The solvent was stored on the vacuum line over calcium hydride and distilled onto *n*-BuLi prior to use. Isoprene was purified and

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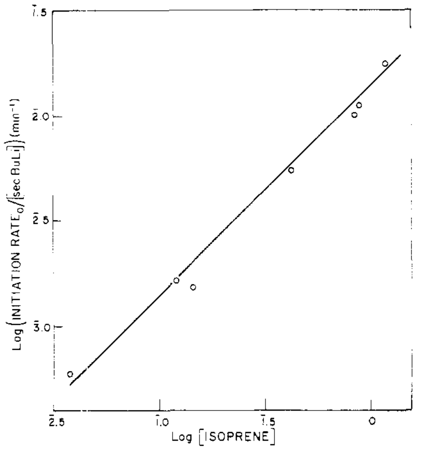

Figure 1. Dependence of the initial rate of the initiation reaction on isoprene concentration; *sec*-BuLi concentration held approximately constant; $T = 30°$.

handled as described earlier.[5] *sec*-BuLi (Foote Mineral Co.) was vacuum distilled before use;[6,7] the pure liquid and its stock solutions in hexane were kept at 0° throughout all manipulations. Lithium *t*-butoxide (*t*-BuOLi) solutions in the presence of *sec*-BuLi were prepared by reacting a fraction of the *sec*-BuLi with *t*-butyl alcohol.[8] These solutions turned pale yellow within 1 month at 0°, presumably due to the enhanced decomposition of *sec*-BuLi in the presence of butoxide.[7,9] Ratios of *t*-BuOLi to *sec*-BuLi higher than 1.8 were not possible because a white precipitate formed slowly in such solutions in hexane.

All experiments were carried out in sealed high vacuum systems having no stopcocks, but utilizing fragile bulbs and break-seals to add reagents. The vessels were washed with butyllithium and rinsed with solvent from its solution before use.[10]

The initiation reaction was started by breaking a fragile bulb containing *sec*-BuLi into the isoprene solution. The formation of polyisoprenyllithium (PILi) was followed spectrophotometrically at 275 mμ using a Bausch and Lomb 505 or Cary 14 recording spectrophotometer. The extinction coefficient of PILi at 270 mμ (maximum) is 6.9×10^3.[5] This value was used throughout all calculations, although it was realized that the maximum of absorption of PILi may be slightly shifted to the ultraviolet spectrum in the presence of a large excess of BuLi. This shift is, however, difficult to observe due to the absorption of BuLi at lower wavelengths. It was observed that the extinction coefficient of PILi at 275 mμ was lowered by less than 10% in the presence of a fourfold excess of *sec*-BuLi. The PILi spectrum in the presence of *t*-BuOLi was not significantly different from the butoxide-free spectrum.

Initial rates of reaction were evaluated as the asymptotic rates at the beginning of the recording, *i.e.*, about 1 min after mixing of the reagents. In most cases, this is the real initial rate of initiation, but in a few reactions, particularly the fastest ones, this method leads to a rate of initiation in the presence of a low concentration of PILi. The latter can be estimated and was always lower than 0.3% of the *sec*-butyllithium.

Propagation rates were measured by following the decrease of the isoprene concentration at 250 or 240 mμ after the initiation reaction was completed.

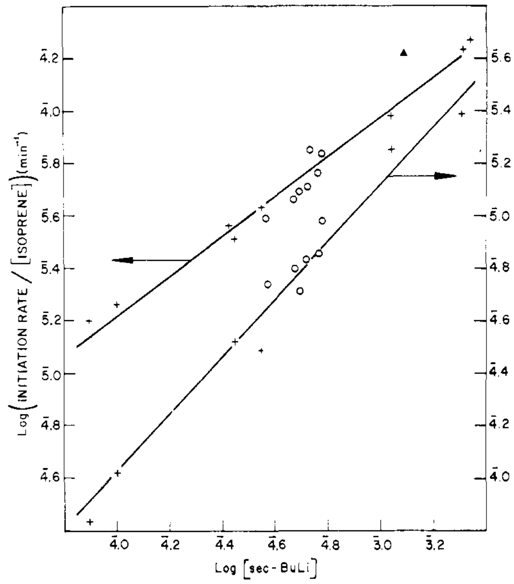

Figure 2. Dependence of initiation rate on *sec*-BuLi concentration: lower line, initial rate; upper line, maximum rate; +, experiments in which [isoprene]$_0$ varied between 3.6 and 6.1×10^{-3} *M*; ○, experiments in which [isoprene]$_0$ varied between 3.7×10^{-2} and 1.2 *M*; ▲, experiment in the presence of 28% PILi; $T = 30°$.

Experiments in which a vacuum viscometer was used are described elsewhere.[8] The measurements made in the vacuum viscometer compared satisfactorily with measurements made in a Ubbelohde viscometer.

Results

A. The Initiation Reaction. In the first series of experiments, the dependence of the initial rate of initiation on the monomer concentration was studied. The isoprene concentration varied between 3.75×10^{-2} and 1.19 *M*, but the *sec*-BuLi concentration was held roughly constant. The results are shown in Figure 1, demonstrating the first-order dependence of the rate on the monomer concentration.

In a second series of experiments, designed to study the dependence of the initiation rate on the *sec*-BuLi concentration, the initial monomer concentration was kept between a narrow range (3.61×10^{-2} to 6.13×10^{-2} *M*). Figure 2 shows that a 1.09 order holds over a 25-fold *sec*-BuLi concentration range. As noted earlier, the rates at high concentrations of *sec*-BuLi may be a little too high because of difficulties in determination of a true initial rate. We may conclude that within experimental error at low conversions the rate is directly proportional to the lithium alkyl concentration.

Figure 2 shows also the results for the maximum rate of initiation, observed between 30 and 60% conversion. The 0.70 order dependence on *sec*-BuLi is identical with that in cyclohexane at 30.0 and 40.0°.[5,6] An activation energy of 17.9 kcal/mol was found for the maximum rate of initiation. The activation energy for the initial rate was not accurately evaluated but estimated to be not much different from this value.

B. The Effect of Added Lithium *t*-Butoxide. Some reports of polymerization initiation in aliphatic solvents

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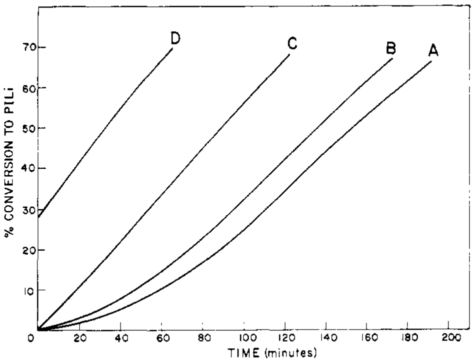

Figure 3. Influence of added t-BuOLi on the rate of initiation: $[\text{isoprene}]_0 = 5 \times 10^{-2}$ M; $[\text{sec-BuLi}]_0$ = (A) 1.11×10^{-3} M, (B) 1.46×10^{-3} M, (C) 1.46×10^{-3} M, (D) 1.23×10^{-3} M; $[t\text{-BuOLi}]/[sec\text{-BuLi}]_0$ = (A) 0.0, (B) 0.63, (C) 1.80; experiment D is described in the text; T = 30°.

do not show sigmoidal rate curves.[11,12] However, at the high concentrations of monomer and lithium alkyl often used, the over-all rate is fast and the slow initial period very short and difficult to detect. The effect of impurities is also important. It was noted previously that introduction of small amounts of air eliminates the slow initial rate for isoprene.[5] One of the two likely impurities present with less rigorous experimental conditions is a lithium alkoxide, the other, the hydroxide, tends to precipitate out. The effect of alkoxide on the initiation step for styrene in benzene is however a marked *decrease* in rate.[8]

On initiating isoprene in hexane with *sec*-BuLi in the presence of *t*-BuOLi it is found that the initial rate of initiation is *increased* but that the maximum rate is only little affected. This leads to an apparent decrease in the induction period and indeed in the case of a 1.8-fold excess of *t*-BuOLi over *sec*-BuLi the induction period is not noticeable. Figure 3, curves A, B, and C, shows reactions with varying amounts of *t*-BuOLi. In the presence of *t*-BuOLi the initial rate of initiation is also near to first order in *sec*-BuLi.

The presence of *t*-BuOLi *decreases* the rate of propagation of PILi in hexane by a factor of 0.65 and 0.25 when the ratio of *t*-BuOLi over PILi is, respectively, 0.63 and 1.80. The one-fourth-order dependence of the rate of propagation of the PILi concentration is maintained in the presence of the amounts of *t*-BuOLi used in this study.

C. The Influence of Intermolecular Exchange of Lithium Alkyls. Intermolecular exchange between different organolithium species at room temperature is an important phenomenon at all times beyond the very initial stages. Morton[13] showed some years ago that butyllithium and polyisoprenyllithium form mixed aggregates by observation of the decrease in viscosity on mixing the two solutions. The exact time scale was not given, but presumably redistribution was complete within a few minutes at most. Brown,[14] however, has studied, by nmr, a system which has some resemblance, namely, intermolecular exchange between *t*-butyllithium and trimethylsilylmethyllithium in cyclopentane. In this case the half-life for redistribution was 5–6 hr.

It was confirmed that on mixing a 0.85% solution of PILi with a fourfold excess of *sec*-BuLi, and measuring the flow time in a vacuum viscometer, that η_{sp}/c of the polymer solution dropped from 0.435 to 0.287 within the 9 min required to measure the flow time. No further change was observed over 6 hr. After hydrolysis with a trace of *t*-butyl alcohol, the value dropped to 0.220. A complete randomization of the species must have occurred in less than 9 min.

A different experiment reduces the time scale further. A normal polymerization was allowed to go to completion and a new threefold excess of *sec*-BuLi plus monomer was added. This models a normal polymerization process at ~30% conversion where the initiation rate is a maximum, except that now at zero time the two lithium species must exist as individual aggregates. If intermolecular exchange between the *sec*-BuLi added and the polyisoprenyllithium already present is slow, a normal initiation reaction between the *sec*-BuLi and monomer would occur. In fact, the initiation step started with no indication of a slow initial rate but at a rate 15% higher than would be observed at ~30% conversion in a normal polymerization (Figure 2 and curve D in Figure 3). The higher rate is explainable because in the latter case some monomer has already been consumed. It must be concluded that intermolecular exchange is rapid and complete within the 1 min required for mixing.

Discussion

The initiation of polymerization by lithium alkyls in aliphatic hydrocarbons has always been recognized to be a complex reaction.[4–6] Only in the very initial stages is it likely that a detailed interpretation of the mechanism will ever be obtained. As soon as appreciable concentrations of polyisoprenyllithium are formed, the solution will contain a series of mixed aggregates (PILi_m–BuLi_n) each of which may react with isoprene or dissociate to different extents and react, all with different rates.

Our results indicate that the initial rate of reaction in hexane is directly proportional to the added concentration of lithium alkyl and monomer, which, taking account of the tetrameric nature of *sec*-BuLi,[6] leads to the conclusion that the reaction involves monomer and associated lithium alkyl directly (eq 3) with a rate constant of 8.5×10^{-4} M^{-1} sec^{-1} at 30°. An alternative process involving a slow rate determining dissociation of the alkyl would lead to first-order kinetics in alkyl concentration but zero order in monomer and can thus be ruled out.

$$(sec\text{-BuLi})_4 + \text{isoprene} \xrightarrow{k_i'} (sec\text{-BuLi})_3(\text{PILi}) \quad (3)$$

The present results can be compared with those obtained in benzene, where the order is one-fourth in lithium alkyl and over 2000 times faster at a concentration

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of 10^{-3} *M*. It is possible that a similar first-order reaction occurs in benzene also but clearly would be swamped by the faster process which we have described previously as dissociative.

The rapidly increasing rate must be connected with the mixed species formed as soon as even minor amounts of polyisoprenyllithium are present. The first product probably will be (*sec*-BuLi)$_3$PILi and the reaction curve can be fitted up to about 3% conversion (where more complex species can be neglected) on the assumption that it reacts about 12 times faster than *sec*-butyllithium tetramers. The increased initial rate with *t*-BuOLi present indicates that incorporation of other polar materials have a similar effect on the rate. An accelerating effect of alkoxide has been observed in the thermal decomposition of *sec*-BuLi[7,9] in aliphatic solvents but in other cases,[8] notably where a fractional external order in alkyl was observed, the effect is to decrease the rate, as was in fact observed at the propagation stage in the present experiments.

Further analysis of the reaction becomes too difficult because of increasing complex products. Thus the meaning of the apparent order of 0.7 at maximum rates is not clear and indeed may be in error because of normalization of the rates to unit *initial* monomer concentration whereas the actual monomer concentration may depart from this value to a varying extent over the range of initiator concentration. Unfortunately it is difficult by spectrophotometric means to analyze for monomer concentration simultaneously, under the conditions used in these experiments.

The change in mechanism and rate of the initiation reactions between benzene and hexane (or cyclohexane) as solvents suggests that the alkyl is much less easily dissociated in aliphatic solvents. It is interesting that this difference parallels Brown's observation[14] of a difference of a factor of 10^3–10^4 in rates of intermolecular exchange in the two types of solvent. The exchange rate between *sec*-BuLi and PILi in hexane is, however, much faster than between *t*-BuLi and trimethylsylylmethyllithium in cyclopentane. It was suggested[14] that the exchange rate is determined by the rate of dissociation of the less easily dissociated species, which in our case would probably be *sec*-BuLi. Rapid dissociation of PILi aggregates is necessary to explain the formation of polymers of narrow molecular weight distribution in anionic polymerization. The fact that the *sec*-BuLi–PILi system exchanges reasonably rapidly is not in disagreement with our postulate of slow dissociation of *sec*-BuLi alone. First, exchange can be promoted by dissociation to the dimer stage only, as pointed out by Brown, whereas our mechanism in benzene is dependent on dissociation to the monomeric form. Second, there exists the possibility that the exchange mechanism is no longer determined by the *sec*-BuLi in presence of the more polar, resonance stabilized carbanion pair of PILi. Some direct attack of dissociated PILi on *sec*-BuLi aggregates may take place.

Macromolecule–Substrate Complexation. A Saturation Phenomenon Exhibited by Poly(4(5)-vinylimidazole) and an Anionic Ester

C. G. Overberger,[1a] R. Corett,[1b] J. C. Salamone,[1a] and S. Yaroslavsky[1c]

Institute of Polymer Research, Department of Chemistry, Polytechnic
Institute of Brooklyn, Brooklyn, New York 11201.

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ABSTRACT: The rates of solvolyses of the neutral ester *p*-nitrophenyl acetate (PNPA) and the negatively charged ester sodium 4-acetoxy-3-nitrobenzenesulfonate (NABS), each catalyzed by poly(4(5)-vinylimidazole), were investigated under conditions in which the substrate concentration was in excess of the catalyst concentration. In contrast to the solvolytic behavior of the neutral ester PNPA, the reaction of the negatively charged ester NABS gave rise to a kinetic scheme similar to that of hydrolytic enzymes in that the initial solvolysis rate reached a limiting value at high substrate concentration. This would appear to indicate the saturation of the polymeric catalyst with anionic substrate. The lack of a saturation effect exhibited by PNPA in the concentration range and pH value investigated can perhaps be accounted for by the inadequacy of hydrophobic forces to sufficiently concentrate the neutral ester in the vicinity of the polymer chain, whereas at intermediate pH the anionic substrate would be strongly attracted to the protonated imidazole sites on the polymer by electrostatic forces. Employing the basic Michaelis–Menten kinetic system, values of K_m and k_2 for the solvolysis of sodium 4-acetoxy-3-nitrobenzenesulfonate were found to be $(3.8 \pm 0.2) \times 10^{-4}$ *M* and 0.63 ± 0.04 min^{-1}, respectively.

The selectivity and efficiency of an enzymic reaction are in part dependent upon a complexation of the substrate to the enzyme, followed by an "intramolecular" catalytic reaction.[2] It has recently been demonstrated that multifunctional catalysis, a unique characteristic of enzymatic reactions, can also be obtained when synthetic, imidazole-containing polymers are employed as catalysts.[3]

The binding sites of enzymes, necessary for a com-

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