A Rapid-Injection Nuclear Magnetic Resonance Study of the Butyllithium-Initiated Polymerization of Styrene

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ABSTRACT: The polymerization of styrene in THF initiated by the various isomers of butyllithium was studied at low temperature utilizing the rapid-injection NMR technique. The order of reactivity was found to be *sec*-BuLi > *tert*-BuLi > *n*-BuLi. The reactivity order is different than that observed in hydrocarbon solvents: *sec*-BuLi > *n*-BuLi > *tert*-BuLi. These reactivity differences are explained by noting the different aggregation states of the butyllithium reagents. A complexation mechanism is proposed where the styrene coordinates with the lithium of the BuLi and then undergoes subsequent reaction. MNDO calculations support this behavior and predict the relative reactivities found in the RINMR experiments.

Introduction

Organolithium reagents are extremely versatile compounds, finding a variety of uses in organic chemistry. They are the reagents of choice for many metalation reactions and nucleophilic additions and as anionic polymer initiators. Organolithium reagents are valued for their high reactivity, being more reactive than Grignard reagents and more stable than organosodium and potassium reagents. The utility of organolithiums lies in their ease of preparation, their solubility in hydrocarbons, and their commercial availibility. However, there is not a clear understanding of the mechanism by which organolithium compounds react.

The study of organolithium reagents is complicated by their propensity toward self-association. These reagents form bridged structures in solid, solution, and even in the gas phase, causing sometimes dramatic reactivity differences between isomers. The tendency for self-aggregation is so great that virtually all organolithiums are known to be in a dynamic self-aggregated equilibrium state in both polar or nonpolar solvents with a few exceptions.[1] Several factors influence the degree to which these compounds self-aggregate, namely, the alkyl group, solvent, temperature, and concentration.

n-Butyllithium (*n*-BuLi), for example, exists primarily as a hexameric aggregate in hydrocarbon solvents, while the more bulky *sec*- and *tert*-butyl isomers are primarily tetrameric species in the same solvents.[2,3] In tetrahydrofuran, *n*-BuLi has been determined by NMR experiments to exist in a tetramer–dimer equilibrium.[4] Below −90 °C, *sec*-butyllithium has been reported to exist in a dimer–monomer equilibrium and *tert*-butyllithium was found to be monomeric.[1a] Resonance-stabilized organolithiums, such as styryllithium, exist as dimers in hydrocarbon solvents.[5]

The reactivity of organolithium reagents is intimately linked to their degree of aggregation. Generally, lowering the aggregation state of these reagents will cause an apparent increase in their reactivity.[6] It has been shown that various isomers of butyllithium have different reactivities toward vinyl monomers in hydrocarbon solvents.[7] The order of reactivity for styrene was determined to be *sec*-BuLi > *n*-BuLi > *tert*-BuLi. The order differed for the polymerization of isoprene and butadiene: *sec*-BuLi > *tert*-BuLi > *n*-BuLi.[7] The apparent difference in reactivity order for the isomers of butyllithium, in seemingly similar systems, may stem, in part, from comparing organolithium reagents of different aggregation states.

The aggregation of organolithium reagents is important in understanding their reactivity. Since they can react in aggregates and yield lithium products, formation of mixed/product aggregates is possible. The formation of cross-associated species is another complication in the study of organolithium reagents. The polymerization of styrene by *n*-butyllithium in hydrocarbon solvents begins with a hexameric butyllithium initiator and proceeds to a dimeric poly(styryllithium) (PSLi). During the course of initiation there exist various aggregates of *n*-BuLi with PSLi.[8] It has been reported in other systems that the formation of cross-associated aggregates can alter the course of an ongoing reaction by influencing the selectivity of the reagents and the stereochemistry of the products.[9] It would be reasonable to expect cross-associated aggregates can, likewise, influence anionic polymerization.

In an attempt to understand the influence aggregation plays in anionic polymerization, we report our findings on the polymerization of styrene and 3-methylstyrene with *n*-, *sec*-, and *tert*-BuLi in THF by ^{1}H and ^{7}Li rapid-injection NMR spectroscopy (RINMR). These experiments provides a method to simultaneously observe all reagents during the reaction, including the initiator and its aggregated state. RINMR is essentially a stop-flow NMR experiment, although inherently slower and less sensitive than stop-flow IR and UV–visible techniques, it offers the advantage of more structural information and quantification of all reagents.[10]

We have selected reaction conditions that promote monomeric species in THF and could directly compare *sec*- and *tert*-BuLi in monomeric forms. We were unable, however, to force or observe monomeric *n*-BuLi and have used semiempirical calculations to calculate the activation energy for the monomeric forms of the butyllithium isomers with styrene. In this way, we were

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able to make comparisons of the reactivity of these isomers without the influence of aggregation and also gain insight as to the importance of higher aggregation states in anionic polymerizations.

Experimental Section

Equipment and Instrumentation. All NMR spectra were obtained with a 7.1-T QE 300 NMR instrument operating at 300.2 MHz for proton and 116.7 MHz for ^{7}Li analysis. Proton chemical shifts were reported relative to the residual α protons of THF-d_8 (δ 3.58). Molecular weights and polydispersities were determined using a Waters 150C GPC/ALC instrument with a refractive index detector. The mobile phase was HPLC-grade tetrahydrofuran, with a flow rate of 0.7 mL/min. Five columns, Phenomenex 10^5, 10^4, 10^3, and 500 Å columns and a Waters 100 Å column, were connected in series. The calibration curve was calculated using narrow polystyrene standards ranging from 10^6 to 10^3 molecular weights, obtained from Supelco. Column, pump, and injector compartment temperatures were kept at 35 °C. All data manipulation was calculated using Waters Maxima 820 software on a NEC computer.

MNDO calculations were carried out on a Cray Y-MP 8/464 or a Silicon Graphics 4D workstation. The MNDO Hamiltonian was used from either AMPAC 4.5 or MOPAC 6.0. The keywords SADDLE and TS were used in finding the transition states. The IRC keyword was used to verify that the transition states found were indeed transition states for the reaction of interest. All structures and energies are reported with the PRECISE convergence criteria.

Reagent Purification. Benzene-d_6 (99% d; Aldrich) and tetrahydrofuran-d_8 (99.5% d; Cambridge) were dried and distilled from a sodium/potassium alloy in a glovebox with a N_2 atmosphere. Tetrahydrofuran was distilled under nitrogen from a blue potassium/benzoylbiphenyl ketyl. Styrene (Aldrich) for the RINMR experiments was vacuum distilled from lithium aluminum hydride and stored at −60 °C until needed. The 3-methylstyrene was passed through an alumina column and degassed just prior to use. Methylcyclohexane-d_{14} (99% d; Cambridge) was used as received. The living polymers were terminated with degassed ethanol. All organolithiums were obtained from the Lithium Division of FMC, sometimes the solvent was removed and replaced with methylcyclohexane-d_{14} or benzene-d_6.

Rapid-Injection NMR Experiment. The manipulation of air-sensitive materials was carried out under nitrogen using a glovebox and a combination of septa, syringe, and Schlenk techniques. In a typical experiment, 20 μL of a 25% solution of styrene in perdeuterated methylcyclohexane was injected into a solution of the initiator in THF-d_8 (330 μL, 0.04 M BuLi) at −80 °C. When *n*-butyllithium was used, the initiator was added to the THF-d_8 in the glovebox. For the experiments with *sec*- BuLi or *tert*-BuLi the initiator was added to the NMR tube after it was cooled to −80 °C outside of the glovebox. 2,2-Dimethoxypropane (1 μL) or ferrocene (10 μL, 0.25 M in benzene-d_6) was added as an internal standard for determining concentrations.

Table 1. Summary of the Molecular Weight Data and Molecular Weight Distributions of the Organolithium-Initiated Polymerization of Styrene Conducted by RINMR

run no.	initiator	M_0/I_0[b]	I_∞/I_0[b]	M_n[d]	M_n(calc)[e]	MWD
1A	*n*-BuLi	3.6	0.79	9500	430	1.89
1B	*n*-BuLi	3.4	0.90	9000	400	1.65
1C	*n*-BuLi	5.4	0.58	8600	620	1.47
1D	*n*-BuLi	3.7	0.80	7800	440	1.39
1E	*n*-BuLi	5.3	0.81	8000	620	1.17
1F[a]	*n*-BuLi	18.5	0.79	6700	1980	1.62
1G[a]	*n*-BuLi	18	0.73	6900	1930	1.59
2A	*sec*-BuLi	5.3	0.0	700	600	1.12
2B	*sec*-BuLi	7.1	0.10	800	800	1.40
2C	*sec*-BuLi	7.0	0.30	1100	800	1.19
2D	*sec*-BuLi	6.2	0.19	1200	700	1.18
2E[a]	*sec*-BuLi	20	0.0	3400	2100	1.16
2F[a]	*sec*-BuLi	29.4	0.0	3400	3100	1.22
3A	*tert*-BuLi	5.1	-	900	600[f]	1.45
3B	*tert*-BuLi	6.8	-	900	760[f]	1.62
3C	*tert*-BuLi	5.9	-	900	670[f]	1.62
3D[a]	*tert*-BuLi	19.7	-	4000	2100[f]	1.16
3E[a]	*tert*-BuLi	17.6	-	6500	1900[f]	1.18

[a] The monomer was 3-methylstyrene. [b] Monomer/initiator ratio. [c] Ratio of the remaining initiator to the initial amount of initiator after the monomer was completely consumed. [d] Number-average molecular weight based on GPC data. [e] $M_n(\text{calc}) = M_w(\text{styrene})\, M_0/I_0 + M_w(\text{Bu})$. [f] The *tert*-BuLi concentration before injection could not accurately be determined because there are no hydrogens adjacent to the lithium to integrate by NMR.

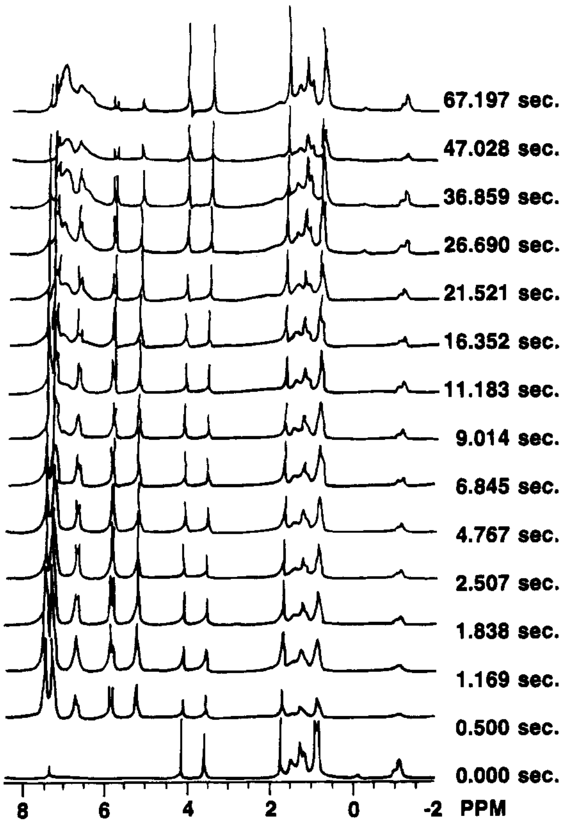


Figure 1. Plot of ^{1}H NMR spectra vs time for the polymerization of styrene initiated by *n*-BuLi.

Results and Discussion

The polymerization of styrene in THF at −80 °C was studied using *n*-BuLi, *sec*-BuLi, or *tert*-BuLi as the initiator at a degree of polymerization of ~5. For polymerization reactions with higher degrees of polymerization, 3-methylstyrene was used as the monomer, since neat 3-methylstyrene would not freeze at −80 °C.[11] These results are summarized in Table 1. For experiment 1A, the initiator used was *n*-BuLi and the calculated degree of polymerization was 4. Approximately 20% of the *n*-BuLi is consumed during the polymerization, causing a higher than calculated molecular weight of ~9500. A stacked plot of this rapid-injection experiment, in THF, showing the NMR spectra at various times for the reaction of *n*-BuLi with styrene is shown in Figure 1. The initial spectrum at time zero shows the residual protons of THF-d_8 at δ 3.58 and 1.73. The protons due to the internal standard (ferrocene) appear at δ 4.15. The peaks due to the methylene protons adjacent to lithium in *n*-BuLi appear at δ −1.1. The resonances seen at δ 7.2 are due to residual protons from the benzene-d_6 solvent. After injection of styrene, the first spectrum at 0.5 s shows the appearance of the styrene vinyl protons at δ 5.1, 5.87, and 6.3 and the

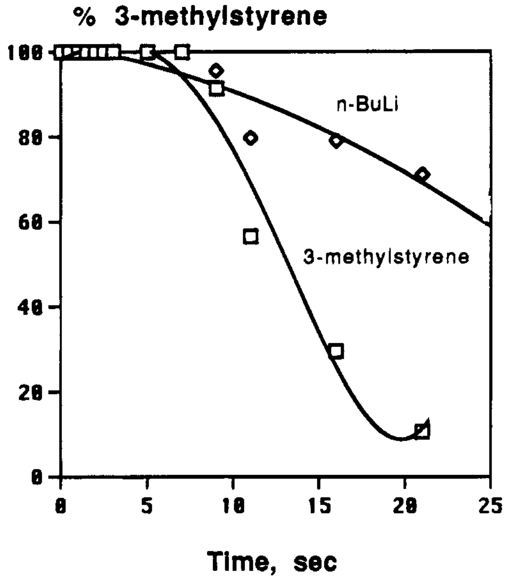


Figure 2. Plot of 3-methylstyrene and n-BuLi consumption vs time.

aromatic protons at δ 7.1. The polymerization was judged complete when the vinyl resonances of styrene disappeared. From each spectrum the vinyl hydrogens of styrene are integrated against the internal standard to calculate the amount of styrene remaining in the reaction. The concentration of styrene could not accurately be determined by the injection volume. The concentration was determined by comparing the integration of the aromatic protons to the integral from the internal standard protons.

Examination of the integration in Figure 1 reveals that there is very little change in the spectra initially after injection, neither the styrene nor n-BuLi is consumed. The vinyl signals from styrene then proceed to decrease with time. The region from δ −0.9 to −1.3 clearly shows the dimer (δ −1.2) and the tetramer (δ −1.1) of n-BuLi. The reaction of n-BuLi with styrene consumes only a small amount of n-BuLi (15–20%) during the polymerization. During the course of the polymerization, the ratio of tetramer to dimer increases and then decreases, equilibrating to something very close to the initial value at the end of the reaction. This experiment was repeated, and similar results were observed with higher degrees of polymerization using 3-methylstyrene as the monomer. A plot of both monomer and initiator consumption vs time reveals the presence of an induction period where the concentration of both species changes little followed by a rapid decrease in both and a leveling off of both the n-BuLi and styrene concentrations (Figure 2). This induction period was observed for all polymerizations initiated by n-BuLi.

The polymerization was also followed by ^{7}Li RINMR (Figure 3). In the initial spectra only peaks due to n-BuLi dimer (δ 0.0), tetramer (δ −0.4), and a small impurity n-Bu$_3$Li$_4$O-n-Bu (δ −1.1) were observed.[12] The n-BuLi dimer peak was arbitrarily assigned to δ 0.0. We were unable to prepare a sample without this alkoxide impurity. The ^{7}Li RINMR data show behavior similar to that of ^{1}H RINMR experiments. Upon injection, the dimer and tetramer peaks appear to broaden due to turbulence of mixing. The peaks narrow after the turbulence subsides and return to a ratio similar to the initial ratio of dimer to tetramer. After an induction period, the signal due to the lithium of the poly(styryllithium) can be observed in the spectrum at δ −2.2. During the induction period we also note the appearance of a new peak centered at δ −1.0. This new peak overlaps with one of the peaks from the impurity peak (n-Bu$_3$Li$_4$O-n-Bu) in the initial butyllithium solution. This new peak arises from the formation of a cross-associated product between the n-BuLi and the poly(styryllithium). This mixed aggregate may be the mixed dimer, n-BuLi$_2$PS. Attempts to prepare this mixed aggregate independently by mixing n-BuLi with a freshly prepared poly(styryllithium) solution showed no formation of the mixed aggregate by ^{7}Li spectra (Figure 4). This suggests that the mixed dimer is formed only from the reaction of styrene with the n-BuLi aggregate.

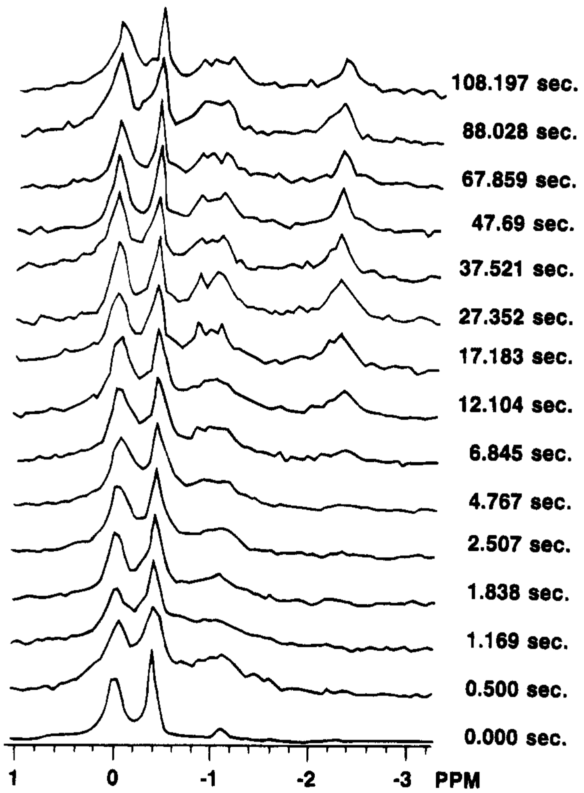


Figure 3. Plot of ^{7}Li NMR spectra vs time for the polymerization of styrene initiated by n-BuLi.

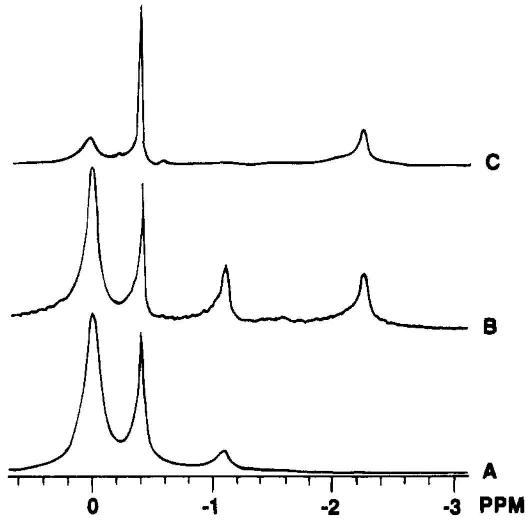


Figure 4. ^{7}Li NMR spectra of n-BuLi with poly(styryllithium). (A) n-BuLi (0.017 M) before the injection of styrene. (B) n-BuLi after the injection of styrene. (C) Intimate mixture of poly(styryllithium) and n-BuLi (0.09 M).

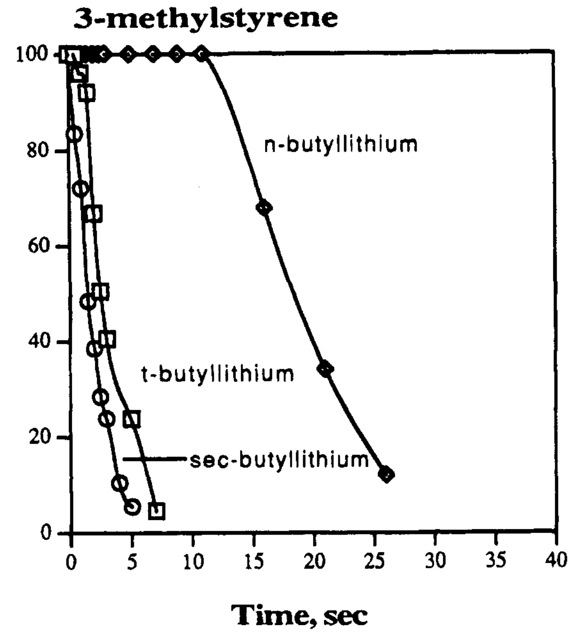


Figure 5. 3-Methylstyrene consumption as initiated by isomeric butyllithiums.

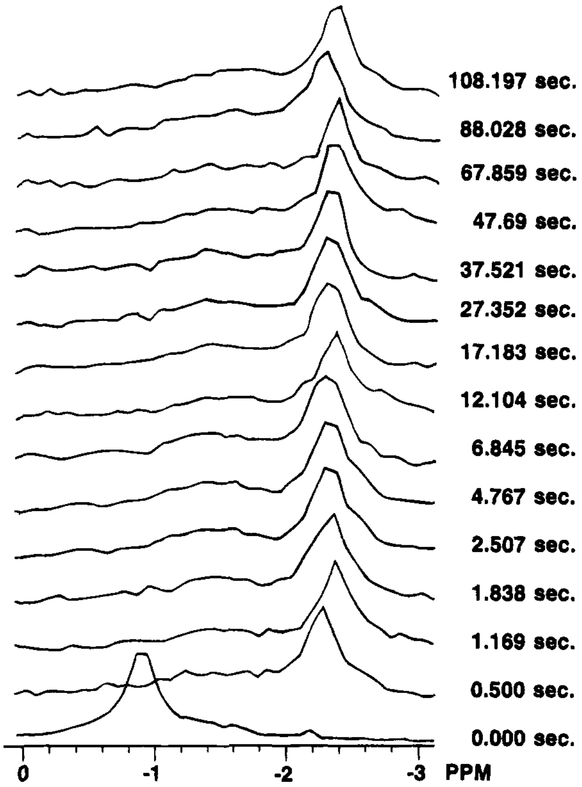


Figure 6. ^{7}Li NMR of *sec*-BuLi before and after injection of styrene.

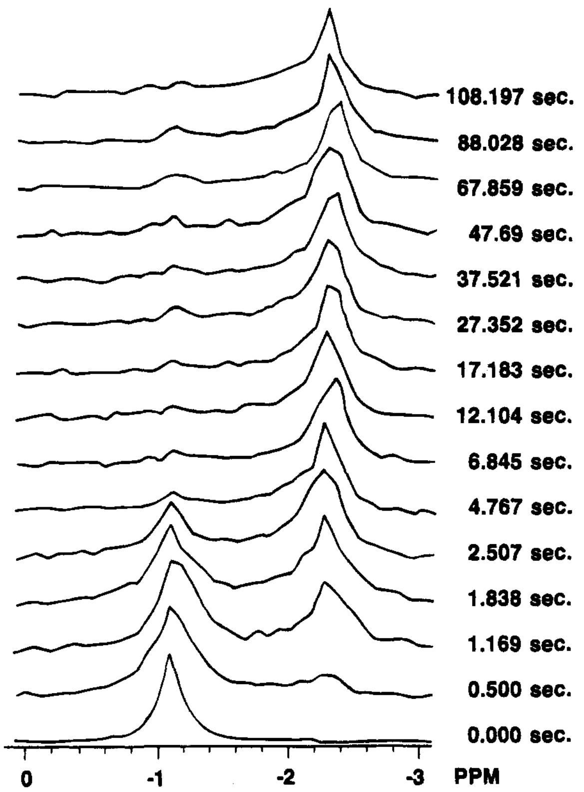


Figure 7. Plot of ^{7}Li NMR spectra vs time for the polymerization of styrene initiated by *tert*-BuLi.

In the rapid-injection experiments initiated with *sec*-BuLi, the polymerization was much faster than that with *n*-BuLi and had no observable induction period (Figure 5). With a degree of polymerization of approximately 5, approximately 90% of the initiator was consumed. All of the *sec*-BuLi that was consumed had reacted within the first half second. At higher degrees of polymerization virtually all of the *sec*-BuLi was consumed within 0.5 s of injection. In the ^{7}Li RINMR experiments (Figure 6) only two species are observed. The *sec*-BuLi in the initial spectra before injection shows a single peak since it is probably monomeric in THF at the low concentrations used in this study. In the first spectrum after injection, the *sec*-BuLi peak is gone and the PSLi peak appears. It seems that the initiation is complete within the first half second. All subsequent spectra showed only one peak due to the PSLi. There was no evidence for cross-association between *sec*-BuLi and PSLi during the polymerization, which seems understandable since both are monomeric under these conditions. After the polymerization an aliquot of *sec*-BuLi was added to PSLi. Using ^{7}Li NMR we were unable to detect any mixing between the two organolithiums.

The polymerization initiated by *tert*-BuLi had a rate of polymerization between that of *n*-BuLi and *sec*-BuLi, and there was little or no induction period (Figure 5). This polymerization is problematical for analysis, since there are no protons adjacent to lithium and the methyl protons of the *tert*-butyl group are difficult to distinguish between reacted and unreacted species. The presence of *tert*-BuLi cannot be followed by the ^{1}H RINMR technique. Therefore, the presence of *tert*-BuLi at the end of the polymerization was determined by using ^{7}Li RINMR experiments. This result was supported by performing a polymerization on the bench. The polymerization was terminated with chlorotrimethylsilane, and the presence of *tert*-butyltrimethylsilane, resulting from reaction of the chlorosilane with residual *tert*-BuLi, was identified using GC-MS. At low monomer/*tert*-BuLi ratios (DP ~ 5) only approximately 50% of the initiator was consumed. With higher ratios (DP ~ 30) nearly all of the *tert*-BuLi was consumed (~95%). The ^{7}Li RINMR (Figure 7) showed initially one peak for the *tert*-BuLi, and with time this signal diminished as PSLi grew. There is no evidence for cross-association between *tert*-BuLi and PSLi since no other peaks were observed in the ^{7}Li RINMR during the course of the polymerization. Both species are monomeric in THF, and there appears to be no mixing between the two different organolithiums.

The molecular weights and molecular weight distributions of the resultant polymers formed were determined by GPC on several of the RINMR runs and are summarized in Table 1.

The *n*-BuLi-initiated experiments (1A–1E) gave much higher molecular weights ($M_n \sim 8000$) than predicted from the calculated molecular weight ($M_n \sim 500$). The resultant polymers have rather broad molecular weight distributions (see Table 1), indicating the presence of lower molecular weight oligomers. Only approximately 20% of the *n*-BuLi is consumed during the polymerization experiments. Initiator remaining at the end of the polymerization indicates that propagation is faster than initiation under the conditions used for *n*-BuLi. A more rapid propagation step and/or incomplete initiation would lead to broad molecular weight distributions, which were observed. These trends are consistent when the degree of polymerization is increased (1F–1G).

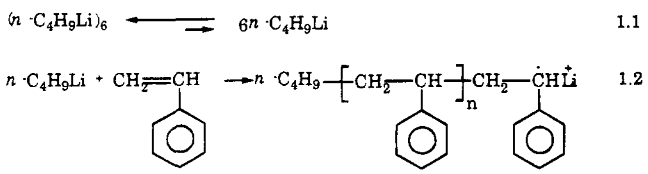
The GPC data reveal that, with *sec*-BuLi as the initiator, the calculated molecular weights were close to the experimentally determined value and that good enough mixing occurs in the NMR tube to synthesize polystyrene oligomers with reasonable molecular weight values. For the experiments 2A–2C between 70–90% of the *sec*-BuLi was consumed during the polymerizations which was more than that for the *n*-BuLi experiments. The molecular weight distributions for these polymers were narrower than those for *n*-BuLi-initiated polymerizations. Indeed, for the experiments 2E and 2F (Table 1) all of the *sec*-BuLi was consumed, leading to polymers with narrow molecular weight distributions. These data indicate that the initiation rate for *sec*-BuLi is greater than that for *n*-BuLi.

For the experiments initiated by *tert*-BuLi, the molecular weights were slightly higher than the calculated value. For the experiments 3A–3C (Table1) the amount of *tert*-BuLi remaining at the end of the polymerization was approximately 50%, determined using ^{7}Li NMR. This is indicative of a slower initiation step, which would account for the broader molecular weight distributions seen for these polymerizations. An increase in the monomer concentration (3D and 3E) increases the amount of *tert*-BuLi consumed (~95%). From ^{7}Li NMR it is seen that initiation occurs within the first half second and continues for several seconds for experiments 3D and 3E.

From Figure 5, it is clear that the rate of polymerization of either styrene or 3-methylstyrene is dependent upon the type of organolithium used as the initiator. The relative order of reactivity was independent of the degree of polymerization, whether the degree of polymerization was approximately 5 or 30. The plot reveals that the rate of polymerization follows the order *sec*-BuLi > *tert*-BuLi > *n*-BuLi. This is in contrast to the relative rate of polymerization in hydrocarbon solvents, where the order is *sec*-BuLi > *n*-BuLi > *tert*-BuLi for the polymerization of styrene.[6]

The structure of the organolithium reagent has been shown to affect polymerization kinetics.[6] Using arguments based on electron donation of alkyl groups, one would predict the order of reactivity of the butyllithium reagents to be *tert*-BuLi > *sec*-BuLi > *n*-BuLi. However, *tert*-BuLi is less reactive than *n*-BuLi toward styrene in hydrocarbons. The order of reactivity of the isomeric butyllithiums is different for the polymerization of dienes.[6] This is indicative that the reactivity is dependent upon the organolithium, the type of monomer used, and the solvent. Our results suggest that the reactivity of organolithium reagents must be more dependent upon its state of aggregation and steric bulk than its inherent basicity.

Scheme 1



There have been numerous kinetic studies on the polymerization of styrene initiated by organolithium reagents.[13] The reactivity of the organolithium reagents is complicated because of their aggregation. This aggregation effect leads to fractional order kinetics in organolithium.

One of the first studies which differentiated initiation and propagation reactions was conducted by Worsfold and Bywater. In the reaction of *n*-BuLi with styrene in benzene, they found a $^1/_6$-order dependence on the *n*-BuLi concentration.[13] They argue that the fractional order of the initiator was due to the hexameric structure of the initiator. They propose that an equilibrium existed between the aggregated structure and a monomeric form of *n*-BuLi. It was assumed that only the monomer was the reactive species. This species was presumed to initiate the polymerization (Scheme 1).

Other kinetic studies were done that supported this theory, where the reaction order was equal to the reciprocal of the aggregation state. This theory fits for the reaction of *n*-BuLi with either styrene or 1,1-diphenylethylene. The reaction order is $^1/_6$ in *n*-BuLi concentration for both reactions.[14] When *tert*-BuLi was used as the initiator the reaction order was $^1/_4$ in *tert*-BuLi concentration for the reaction with styrene or 1,1-diphenylethylene.[15] Although this is an attractive argument, there are several pitfalls in this mechanism.[16] For these systems the data may be interpreted in terms of the dissociative mechanism; however, there has never been any evidence confirming the existence of organolithium monomers under the conditions studied.[1a] There are also several systems where the dissociative mechanism clearly does not hold, for example, the coupling reaction between ethyllithium and benzyl chloride in benzene and the alkylation of naphthalene with *tert*-BuLi.[17,18] Hsieh has also found that the system involving *n*-BuLi-initiating butadiene in toluene exhibits a change in reaction order from first order to $^1/_3$ order in *n*-BuLi concentration over the concentration range studied.[19]

Compared to aliphatic hydrocarbon solvents, polymerizations conducted in aromatic hydrocarbons have a rapid initiation, with the rate of polymerization slowing down as the polymerization proceeds and the monomer supply is depleted. However, the use of aliphatic solvents causes dramatic changes in the reaction kinetics. It has been observed that the reaction orders are not directly related to the association state of the organolithium. There is a pronounced induction period which is followed by a slow initiation that increases to a maximum rate and then slows down as the monomer is consumed.[20] This would seem to suggest that at least in aliphatic hydrocarbons initiation involves reaction between the aggregated organolithium and the monomer.[21]

The dissociative mechanism has been challenged by Brown on energetic grounds.[22] The enthalpy change to dissociate the hexamer to monomer is approximately 100 kcal/mol for an appreciable reaction to occur. There is also an unfavorable entropy effect; therefore, the free energy of the system would be very large and positive. Also the mechanism does not take into account the formation of cross-associated species between the living polymer-lithium and the *n*-BuLi.[8] The *n*-BuLi hexamer can react with the formation of a new aggregate, which either can react at a new site and propagate or can react at a BuLi site and initiate. These new aggregates can effect the reaction orders.[7]

Another argument against reaction through monomers is the reaction of *n*-BuLi with benzaldehyde at low temperatures in THF, where the solvent and temperature favor lower aggregates. In this case both the dimer and tetramer of *n*-BuLi were found to react and no monomer could be found. The dimer was found to be approximately 10 times more reactive than the tetramer toward benzaldehyde.[4]

The addition of Lewis bases (such as amines and ethers) to a polymerization causes a dramatic increase in the rate of polymerization. This effect is usually attributed to the peptizing of the organolithium aggregates. Schleyer has forcefully argued that solvation is more important to the transition state, lowering the energy of the transition state relative to the starting materials.[23] The *tert*-BuLi and *sec*-BuLi are both monomeric in THF at these concentrations and low temperatures, making for meaningful comparisons between them. The *n*-BuLi is a dimer/tetramer under the same conditions, so when comparing *n*-BuLi to *tert*-BuLi and *sec*-BuLi, the comparison would be between different aggregation states. Since *tert*-BuLi is a less active initiator than *sec*-BuLi, the logical conclusion would be that the reactivity is a result of the steric bulk of the *tert*-butyl group. If this were the case, then monomeric *n*-BuLi monomer in THF would react faster still. Since a direct comparison between these three butyllithium isomers as unaggregated structures is not experimentally possible, we looked to semiempirical calculations as a mechanism for comparison.

The computations were carried out on the butyllithium isomers with three solvent molecules present. Water was chosen as the solvent rather than THF to simplify the calculations, realizing, of course, that any steric effects would be magnified with THF as the solvent. The energy diagram for the reaction paths is shown on Figure 8 and tabulated in Table 2. The starting monomeric butyllithiums, **1**, were calculated to be solvated by three solvent molecules. In all cases the first step is the displacement of one solvent molecule to get styrene coordinated η^2 through the vinyl carbons, **2**. This η^2 coordination is very sterically demanding, more demanding than the coordination of a carbonyl group η^1 through the oxygen. The transition state, **3**, is calculated to be a four-centered transition state with a pentavalent carbon and is considerably reorganized from the coordinated intermediate, **2**. The interatomic distances and bond orders for the transition state structures suggest that on going from *n*-BuLi to *sec*-BuLi to *tert*-BuLi the transition state proceeds later and later along the reaction path. The product is calculated to be a benzyllithium with three coordinated water molecules and the lithium is situated over the phenyl ring coordinated η^7, **4**. The calculated activation energies for these reactions give a relative reactivity for the monomeric butyllithiums *n*-BuLi > *sec*-BuLi > *tert*-BuLi (Table 2). The transition state is pictured for the reaction of *n*-BuLi with styrene (Figure 9). Proceeding from *n*-BuLi to *sec*-BuLi to *tert*-BuLi, the distance between the anionic butyl carbon and lithium increases steadily, indicating more bond breaking. While in each of the three transition state structures the new bond formation is comparable. We believe this is an effect of steric crowding of the transition state as the bulk of the butyl group increases. In order to arrive at the transition state, the C−Li bond breaking must be further and further along the reaction path as the bulk of the alkyllithium increases.

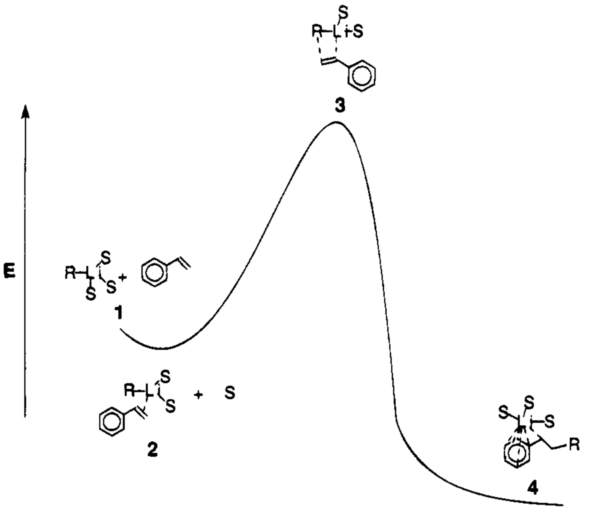


Figure 8. Reaction coordinate diagram for the reaction of the butyllithium monomer with styrene.

Table 2. Calculated MNDO Energies for the Butyllithium Styrene Reactions

RLi	H_f 1	2	3	4	E_a
tert-BuLi	−203.88	−204.24	−176.98	−215.74	27.26
sec-BuLi	−201.92	−203.37	−180.23	−222.65	23.14
n-BuLi	−199.96	−202.42	−182.28	−228.64	20.14
$(n\text{-BuLi})_2{\cdot}4H_2O$ *n*-BuLi dimer	−332.92	−332.59	−301.70	−345.68	31.22

Calculations on the reaction of dimeric *n*-BuLi, $(n\text{-BuLi})_2{\cdot}4H_2O$, with styrene result in the initial displacement of water with the coordination of styrene being slightly endothermic. The transition state (Figure 10), is 5-centered where the vinylic carbons are inserting into the carbon−lithium bond. This process has an activation energy higher than that for a monomeric *tert*-BuLi initiator. The product formed in this reaction is a mixed dimer between *n*-BuLi and the benzyllithium (Figure 11). This may correspond to the unidentified peak observed in the ^{7}Li RINMR for the reaction of *n*-BuLi with styrene (Figure 4). This gives a predicted relative reactivity that looks like the following: $(n\text{-BuLi})_1 > (sec\text{-BuLi})_1 > (tert\text{-BuLi})_1 > (n\text{-BuLi})_2$.

Our computational results are in good agreement with the *ab initio* results for the reaction of ethylene with unsolvated methyllithium monomer.[24] The transition states are very similar for these reactions.

The experimental results agree with the computational results. *tert*-BuLi and *sec*-BuLi react much faster than *n*-BuLi since the *n*-butyl isomer is aggregated. The aggregation would lower the rate of initiation in two ways. In addition to aggregated *n*-BuLi being less reactive in a monomeric form, the effective concentration of *n*-BuLi is lower by at least a factor of 2−4

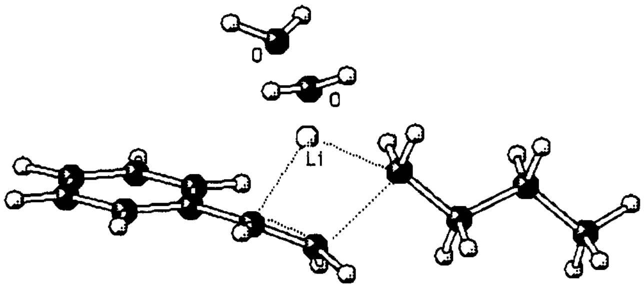


Figure 9. MNDO transition state for the reaction of *n*-BuLi with styrene.

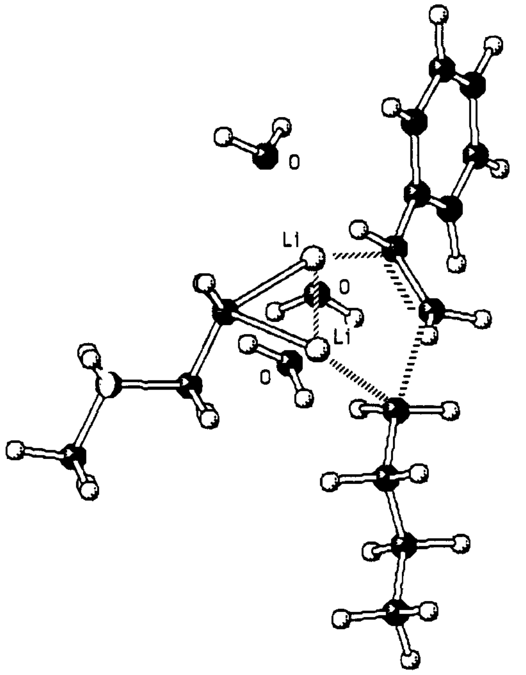


Figure 10. Transition state structure for the reaction of *n*-BuLi solvated dimer with styrene.

because of the aggregation, probably much more since the tetrameric *n*-BuLi is even less reactive than the dimeric *n*-BuLi. The calculated first step, complexation of substrate, has been observed for organolithiums in hydrocarbon solvent,[25] and coordination of benzene to methyllithium has also been noted.[26]

The presence of the induction period for the reaction of *n*-BuLi with styrene is more difficult to rationalize. We note that an induction period is only observed for the aggregated *n*-BuLi and not for *sec*- and *tert*-BuLi. There are reports of induction periods in polymerization in hydrocarbon solvents where the alkyllithium initiator is aggregated. We conclude that the aggregation is somehow related to the induction period. We can only speculate on this phenomenon.[27] Perhaps it is due to the unfavorability of the coordination step to an aggregate. The coordination of styrene requires the carbon–carbon double bond to complex in an η^2 fashion. This is considerably more sterically demanding than the complexing of the THF solvent. The steric demands are very high on the face of the aggregate, but would be much less with monomeric organolithiums. We would expect that there would be little or no induction period with *sec*-BuLi and *tert*-BuLi since these are monomeric.

There is cross-association between PSLi and BuLi in hydrocarbon solvents.[8] The situation is different in THF since PSLi, *sec*-BuLi, and *tert*-BuLi are all monomeric. It seems logical to expect there to be little or no cross-association between the monomeric organolithium species. However, the interaction between *n*-BuLi and PSLi might allow for cross-association since *n*-BuLi is aggregated even in THF at low temperature. The data from the ^{7}Li NMR spectra suggest that the styrene reacts with the *n*-BuLi aggregate and the resultant PSLi is formed in the aggregate and stays there, equilibrating only slowly at this temperature.[28] Having a monomeric organolithium associated with an aggregated structure is not unprecedented. Burley and Young have demonstrated that a mixed aggregate of *n*-butyllithium and 1,3-diphenyl-1-butenyllithium in ethereal solvents is formed. The 1,3-diphenyl-1-butenyllithium exists as a monomeric moiety in ethereal solvents by itself.[29] The PSLi cross-associated structure may have a different reactivity than the initiator alone, thereby affecting the propagation rate.

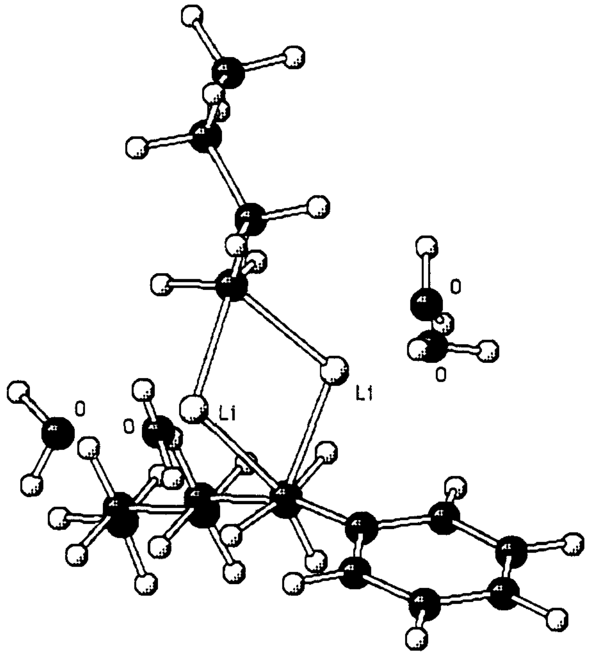


Figure 11. MNDO calculated mixed dimer from the reaction of *n*-BuLi dimer with styrene.

Conclusions

The polymerization of styrene initiated by various isomers of BuLi was studied in THF at −80 °C. As in hydrocarbon solvents the polymerization rate is dependent upon the type of butyllithium used as the initiator. The rate of polymerization of styrene in THF follows the order *sec*-BuLi > *tert*-BuLi > *n*-BuLi. Computationally it was found that the order for initiation of styrene by the solvated isomeric butyllithium would be $(n\text{-BuLi})_1 > (sec\text{-BuLi})_1 > (tert\text{-BuLi})_1 > (n\text{-BuLi})_2$, where the subscripts 1 and 2 refer to monomeric and dimeric forms. *sec*- and *tert*-BuLi react with styrene without an induction period, whereas *n*-BuLi exhibits a substantial induction period (5 s). These results show that organolithium compounds can react through their aggregated structures as in the case with *n*-BuLi. The steric bulk seems to have the greatest effect on the reactivity of the butyllithium reagents.

Further evidence for reaction of the organolithium through the aggregate is obtained by the presence of the mixed aggregate between PSLi and *n*-BuLi. *n*-BuLi appears to react with styrene and form a mixed aggregate. This mixed aggregate is not formed from an intimate mixture of the two, suggesting that the aggregated *n*-BuLi reacts in its aggregated state.

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(11) The 3-methylstyrene has a freezing point of −82.5 °C. This allowed a neat solution of monomer to be injected for a higher monomer/initiator experiment.

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