Butyllithium Polymerization of Butadiene. III. Effect of Inactive Lithium Compounds

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SUMMARY

    The effect of some lithium salts on the microstructures of low-DP polybutadienes was determined. Lithium alkoxides markedly increased extent of 1, 2 addition, and the increase was a function of the alkoxide/butyllithium ratio. Other salts, such as lithium hydride and lithium hydroxide, had little, if any, effect on polybutadiene microstructure. The product from the reaction of 1-hexyne and butyllithium increased 1, 2 addition and also resulted in polybutadienyl lithium solutions that were very high in viscosity or gelled.

    The effect of lithium salts was taken as good evidence that the active species in monomer insertion is the organolithium complex which proceeds through the ionic species, $\text{Li}_n\text{R}_{(n-1)}^{\oplus}\text{R}^{\ominus}$.

    The viscosity effects obtained with hexynyl lithium were explained on the basis of the known facile formation of dilithio acetylides,

$$\text{R--CH--C}\equiv\text{C--Li}$$
$$\text{|}$$
$$\text{Li}$$
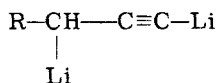
with the assumption that the propargylic lithium was an active initiator.

INTRODUCTION

Based on the results obtained at low $\overline{\text{DP}}$ in the butadiene polymerization with butyllithium, it was concluded that organolithium

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compounds with different degrees of association incorporate mono-
mer differently [1, 2]. It would be desirable to study in more detail
the effects of various degrees of association (DA) of organolithium
compounds on mode of monomer incorporation. However, DA is
high only at very low $\overline{DP}$ and decreases rapidly to a limiting value
of 2 at higher $\overline{DP}$. Ideally, to study the effect of higher DA the agglo-
merate should not change with $\overline{DP}$ under normal polymerization con-
ditions. In theory this is possible by coassociating the active or-
ganolithium species with polymerization inactive and associated
lithium compounds. Indeed, even at higher molecular weights, lithium
salts have been demonstrated to affect the microstructures of poly-
isoprenes and polybutadienes [3-5].

This paper describes the effects of various polymerization
inactive lithium compounds on the microstructres of polybutadienes
prepared with butyllithium, and the relationship of the observed ef-
fects to associative phenomena in organolithium polymerization.

EXPERIMENTAL

Starting Materials

Butadiene (The Matheson Co., C.P. grade) was passed through a
5-ft column packed with calcium sulfate and condensed into a drop-
ping funnel for liquid addition to the catalyst solution.

n-Butyllithium was obtained in hexane and heptane solvents from
the Foote Mineral Company.

n-Heptane (Phillips Petroleum Co., pure grade) and toluene
(Fischer Scientific Co.) were treated with sodium ribbon and stored
under nitrogen prior to use.

Lithium t-butoxide was obtained from the Foote Mineral Co.
n-Butyl alcohol, s-butyl alcohol, i-butyl alcohol, and t-butyl alcohol
(Matheson, Coleman & Bell) were purified by refluxing over and dis-
tilling from calcium hydride.

1-Hexyne, phenyl acetylene, and 1, 6-heptadiyne (Farchan Acety-
lenic Chemicals) were dried over anhydrous $MgSO_4$ and distilled
prior to use.

Phenol (Baker Chemical Co., analyzed reagent grade) was dried
by azeotroping with toluene and then vacuum-distilled.

Lithium hydride (Matheson, Coleman & Bell, 90% technical grade)
and sodium methoxide (Matheson, Coleman & Bell) were used as
received.

Natural Attapulgus clay (200/up mesh RVM) was obtained from
the Minerals and Chemicals Philipp Corp.

Analytical Methods

The procedures used for the determination of kinematic viscosities, number-average molecular weights, and microstructures of liquid polybutadienes have been described previously [1, 2].

Lithium Salts

Lithium salts were normally prepared from the starting butyllithium initiator. Lithium t-butoxide was both used preformed and prepared in situ. Lithium hydride and sodium methoxide were used directly. Lithium hydroxide was generated by the addition of water.

For the $\overline{DP}$ studies at 4 t-BuOLi/BuLi 4 moles of t-butyl alcohol was added to 5 moles of butyllithium, and the solution was cautiously stripped under reduced pressure to a suitable concentration. The total concentration of lithium compounds in the concentrate was determined by titrating an aliquot directly with standard HCl solution.

Polymerizations

Polymerizations were conducted in round-bottomed flasks at atmospheric pressure as described previously [1, 2]. Preformed lithium salt or the reagent required to produce the desired lithium salt was introduced to the catalyst solution, and the resultant solution or slurry was stirred for at least 30 min.

Dry butadiene was condensed into an addition funnel, and the liquid butadiene was added to the butyllithium solution over a period of 1 hr. The polymerization solutions were then stirred from 16 to 66 hr. Polymer solutions were worked up as described previously [1, 2].

In every case with the lithium butoxides homogeneous catalyst solutions resulted, and the solution remained homogeneous throughout butadiene addition and polymerization. Lithium ethoxide, although per se of limited solubility in hydrocarbons, gave a homogeneous solution, even at a ratio of 2 EtOLi/BuLi. The addition of phenyl acetylene, 1, 6-heptadiyne, phenol, and water resulted in precipitates which never dissolved. Added LiH similarly did not dissolve.

With 1-hexyne homogeneous catalyst solutions were obtained up to a 1-hexyne/BuLi ratio of 0.5. Above this ratio some precipitate remained. In all cases of homogeneous catalyst solutions the addition of butadiene resulted in an initially cloudy solution. Nevertheless, in, every case, i.e., whether precipitate was present initially or not, the precipitated solids dissolved during the course of polymerization.

At a 1-hexyne/BuLi ratio of 0.5 the resultant polymer solution was much more viscous than usual. Upon the addition of Attapulgus clay the usual, fluid solution was obtained.

At a 1-hexyne/BuLi ratio of 0.67 the precipitate present initially gradually dissolved until a clear, gelled solution resulted. However, when Attapulgus clay was added the gel gradually but totally decomposed, resulting again in a fluid solution.

Details on the preparation and properties of polybutadienes are given in Tables 1-5.

RESULTS

The effect of a lithium salt on the course of butyllithium polymerization of butadiene was measured primarily by the resultant polybutadiene microstructure. With the catalyst system resulting from 1-hexyne and butyllithium, in addition to microstructure changes, extraordinarily high viscosities were obtained.

The effect of lithium t-butoxide/butyllithium ratio (t-BuOLi/n-BuLi) on polybutadiene microstructure is detailed in Tables 1 and 2 and illustrated in Fig. 1. Both preformed t-BuOLi and t-BuOLi generated from butyllithium and t-butyl alcohol were very effective in increasing extent of 1,2 addition. Preformed t-BuOLi was perhaps more effective than in situ t-BuOLi, although the reason for this is not known. In any event, 1,2 addition increases markedly up to a t-BuOLi/BuLi ratio of 4, after which there is at best a slight increase in 1,2 addition. With preformed t-BuOLi a polybutadiene of $\overline{Mn} = 600$ was obtained which contained almost 70% 1,2 addition and yet had a bulk viscosity of only 1.27 stokes. Such a combination of high 1,2 addition and low viscosity has, to the best of our knowledge, never been achieved before.

The changes in microstructure with $\overline{DP}$ for the system 4 t-BuOLi/BuLi are detailed in Table 3 and illustrated in Fig. 2. At very low $\overline{DP}$, where 1,2 addition and, presumably, degree of association are high, alkoxide has no measurable effect on microstructure. However, at about $\overline{DP} = 10$ the alkoxide effect is readily detected resulting in increased 1,2 addition. With increasing $\overline{DP}$ there is a reduction in overall 1,2 addition, but the extent of 1,2 addition remains considerably higher than with butyllithium alone. In these runs it was noted in many instances that not all the butadiene had reacted even after 20 or more hours reaction time. In the absence of alkoxide butadiene conversion is quantitative within this period of time. This observation is a qualitative demonstration of the rate-reducing effect of alkoxide in alkyl lithium polymerization.

The effects of a number of lithium compounds on polybutadiene microstructure were examined. These are given in Table 5. All lithium butoxides and lithium ethoxide were effective in increasing 1,2 addition. One particular run dramatically illustrates the effect of alkoxide on polybutadiene microstructure. With 10 t-BuOLi/BuLi in toluene at 60°C, a polybutadiene of $\overline{Mn} = 2500$ was obtained which

Table 1. Polymerization of Butadiene with t-BuOLi/n-BuLi in Heptane (Preformed t-BuOLi)
(Kinetic $\overline{DP} = 10$)

n-Butyllithium, moles	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Lithium t-butoxide, moles	0.0	0.05	0.10	0.15	0.20	0.40	0.80
t-BuOLi/n-BuLi	0.0	0.25	0.50	0.75	1.00	2.00	4.00
Butadiene, moles	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Total solvent, ml	972	432	432	432	432	432	432
Yield, g	82.3	100.7	99.3	103.3	103.2	105.7	103.8
Polybutadiene properties							
Number-average mol. wt.	830	645	600	630	600	610	600
Kinematic viscosity, stokes	1.25	0.81	0.60	0.57	0.55	0.92	1.27
Microstructure							
1,2, %	28.3	35.2	34.9	32.4	36.7	60.3	68.6
1,4-cis, %	29.6	25.5	28.7	29.5	26.2	18.8	15.3
1,4-trans, %	42.1	39.3	36.4	38.1	37.2	20.9	16.1

Table 2. Polymerization of Butadiene with t-BuOLi/n-BuLi in Heptane (In Situ t-BuOLi)
(Kinetic $\overline{DP}$ = 10)

n-Butyllithium, moles	0.20	0.30	0.45	0.50	0.55	0.70	0.80	0.90	1.00	1.40	1.80	2.20
t-Butyl Alcohol, moles	0.0	0.10	0.25	0.30	0.35	0.50	0.60	0.70	0.80	1.20	1.60	2.00
t-BuOLi/n-BuLi	0.0	0.50	1.25	1.50	1.75	2.50	3.00	3.50	4.00	6.00	8.00	10.00
Butadiene, moles	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Total solvent, ml	972	972	972	972	972	972	972	972	972	972	972	972
Yield, g	82.3	89.0	88.8	86.8	89.5	73.4	89.5	93.6	71.3	91.1	84.7	63.9
Polybutadiene properties												
Number-average mol. wt.	830	770	690	590	610	530	620	610	510	570	660	870
Kinematic viscosity, stokes	1.25	1.21	0.97	0.65	0.72	0.54	0.83	0.81	0.47	0.73	1.29	3.00
Microstructure												
1,2, %	28.3	37.0	51.1	49.5	53.0	55.0	58.2	59.2	58.9	61.3	64.0	63.2
1,4-cis, %	29.6	25.4	20.2	19.7	19.7	18.7	18.0	17.7	18.1	17.4	16.5	16.7
1,4-trans, %	42.1	37.5	28.6	30.8	27.3	26.3	23.7	23.1	23.0	21.3	19.5	20.0

Table 3. Preparation and Properties of Polybutadienes Derived from n-BuLi and 4 t-BuOLi/n-BuLi in Heptane at 25°C

Theoretical $\overline{DP}$	3	5	7.5	10	12	14	16	18	20	25	30	40	50	60	70	80	100
n-Butyllithium, moles	0.667	0.400	0.253	0.200	0.167	0.150	0.125	0.111	0.100	0.080	0.067	0.050	0.040	0.0335	0.0285	0.025	0.02
Butadiene, moles	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Total solvent, ml	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Kinetic mol. wt.	220	328	463	598	706	814	922	1030	1138	1408	1678	2218	2758	3298	3838	4378	5458
Control (No t-BuOLi)																	
Yield, g	107.1	98.8	97.8	103.0	93.1	93.6	92.6	80.5	94.2	91.9	97.0	89.6	89.2	84.5	81.8	—	71.7
Number-average mol. wt.	390	480	645	760	780	850	980	990	1200	1320	1460	1830	2190	2210	2770	—	3570
Kinematic viscosity, stokes	0.178	0.323	0.713	0.997	1.12	1.26	1.67	1.65	1.90	3.00	3.73	6.06	9.13	10.8	14.7	—	79.5
Density, g/cc	0.8358	0.8463	0.8562	0.8627	0.8653	0.8659	0.8703	0.8701	0.8707	0.8772	0.8795	0.8815	0.8841	0.8854	0.8871	—	0.8871
Microstructure																	
1,2, %	44.1	40.7	36.5	33.8	32.2	31.3	29.4	27.9	27.4	23.5	21.7	18.1	14.2	12.4	11.8	—	9.2
1,2-cis, %	22.7	23.8	25.9	26.7	27.5	28.0	28.7	29.5	29.7	31.2	32.4	34.5	36.5	37.3	37.7	—	39.2
1,4-trans, %	33.2	35.5	37.6	39.5	40.3	40.7	41.9	42.6	42.9	45.3	45.9	47.4	49.3	50.3	50.5	—	51.5
4 t-BuOLi/n-BuLi																	
Yield, g	73.5	113.4	90.3	97.6	106.8	111.4	103.3	93.4	98.2	88.6	79.1	59.7a	49.8a	42.0a	79.7	60.1	—
Number-average mol. wt.	280	320	420	510	580	645	745	760	895	1060	1090	1170	1220	1330	2540	2530	—
Kinematic viscosity, stokes	0.179	—	0.255	0.508	0.791	1.22	1.72	1.79	2.76	3.96	4.14	4.03	4.05	4.61	27.6	31.2	—
Microstructure																	
1,2, %	51.8	56.2	63.2	63.8	63.4	63.1	62.3	60.6	61.0	57.4	53.6	49.0	46.7	43.2	37.6	36.0	—
1,4-cis, %	23.2	20.3	16.9	16.5	16.6	16.6	16.5	17.3	16.9	18.3	19.0	20.8	21.8	23.2	25.6	26.1	—
1,4-trans, %	25.0	23.5	19.8	19.6	20.0	20.3	21.2	22.1	22.1	24.3	27.4	30.2	31.5	33.6	36.8	37.9	—

a Butadiene still present after stirring time.

Table 4. Polymerization of Butadiene with 1-Hexynyl Lithium/n-BuLi Catalyst in Heptane

Kinetic $\overline{DP}$	10	10	10	10	10	10	20	20	20	15
n-Butyllithium, moles	0.20	0.25	0.30	0.35	0.40	0.60	0.20	0.40	0.60	0.2
1-Hexyne, moles	0.0	0.05	0.10	0.15	0.20	0.40	0.0	0.20	0.40	0.2
Hexynyl-Li/n-BuLi	0.0	0.25	0.50	0.75	1.00	2.0	0.0	1.00	2.00	∞
Butadiene, moles	2.0	2.0	2.0	2.0	2.0	2.0	4.0	4.0a	4.0a	3.0
Total solvent, ml	972	432	432	432	432	432	1000	432	432	800
Yield, g	82.3	84.6	90.6	73.0	81.0	95.5	94.2	80.0	62.0	Trace
Polybutadiene properties										
Number-average mol. wt.	830	740	610	530	480	440	1200	930	720	—
Kinematic viscosity, stokes	1.25	0.80	0.526	0.476	0.457	0.405	1.90	2.55	2.10	—
Microstructure										
1,2, %	28.3	24.3	27.2	41.7	47.5	55.1	27.4	42.7	55.2	—
1,4-cis, %	29.6	33.6	32.4	23.3	22.5	22.4	29.7	21.2	17.1	—
1,4-trans, %	42.1	42.1	40.4	35.0	30.0	22.5	42.9	36.1	27.7	—

a Butadiene added in two equal portions. First portion added and stirred 24 hr. Then second portion added and stirred again 24 hr.

Table 5. Effect of Lithium Salts on Microstructures of Polybutadienes Prepared with n-BuLi

Kinetic D̄P̄	10	10	10	10	10	10	20	50	10
n-Butyllithium, moles	0.20	0.40	0.40	0.40	0.20	0.40	0.15	0.10
Coagent	—	n-BuOH	i-BuOH	s-BuOH	t-BuOLi	EtOH	EtOH	t-BuOLi
Moles	0.0	0.20	0.20	0.20	0.20	0.20	0.10	1.0
Ratio Li salt/n-BuLi	0.0	1.0	1.0	1.0	1.0	1.0	2.0	10.0
Butadiene, moles	2.0	2.0	2.0	2.0	2.0	4.0	2.5	5.0
Solvent	Heptane	Heptane	Heptane	Heptane	Heptane	Toluene	Toluene	Heptane
volume, ml	972	972	972	972	432	1300	600	900
Reaction temp., °C	23-25	23-27	23-25	23-25	21-26	30-40	30-60	60
Yield, g	82.3	92.3	76.0	87.0	103.2	157	127	194
Polybutadiene properties								
Number-average mol. wt.	830	770	760	800	600	1000	2310	2450
Kinematic viscosity, stokes	1.25	1.04	1.13	1.40	0.55	1.14	9.5	28.6
Microstructure								
1,2, %	28.3	47.5	48.5	51.6	36.7	37.5	22.5	52.5
1,2-cis, %	29.6	21.1	20.9	19.5	26.2	19.8	32.7	20.5
1,4-trans, %	42.1	31.4	30.6	28.8	37.2	42.7	44.8	27.0

Kinetic D̄P̄	10	10	10	10	10	20	20
n-Butyllithium, moles	0.40	0.40	0.40	0.40	0.20	0.40	0.20
Coagent	1-Hexyne	Phenyl acetylene	1,6-Heptadiyne	Phenol	LiH	H_2O	NaOMe
Moles	0.20	0.20	0.10	0.20	0.20	0.2	0.20
Ratio Li salt/n-BuLi	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Butadiene, moles	2.0	2.0	2.0	2.0	2.0	4.0	4.0
Solvent	Heptane	Heptane	Heptane	Heptane	Heptane	Toluene	Toluene
volume, ml	432	972	972	972	972	1000	1000
Reaction temp., °C	23-27	23-27	23-27	23-26	23-27	30	30-80
Yield, g	81.0	77.5	80.0	76.7	86.9	192	187
Polybutadiene properties							
Number-average mol. wt.	480	610	950	740	430	750	1200
Kinematic viscosity, stokes	0.457	0.52	1.83	0.99	1.07	0.66	1.93
Microstructure							
1,2, %	47.5	29.5	34.0	29.7	30.1	19.9	23.9
1,2-cis, %	22.5	28.9	27.8	28.8	28.6	35.0	31.8
1,4-trans, %	30.0	41.6	38.2	41.5	41.3	45.1	44.3

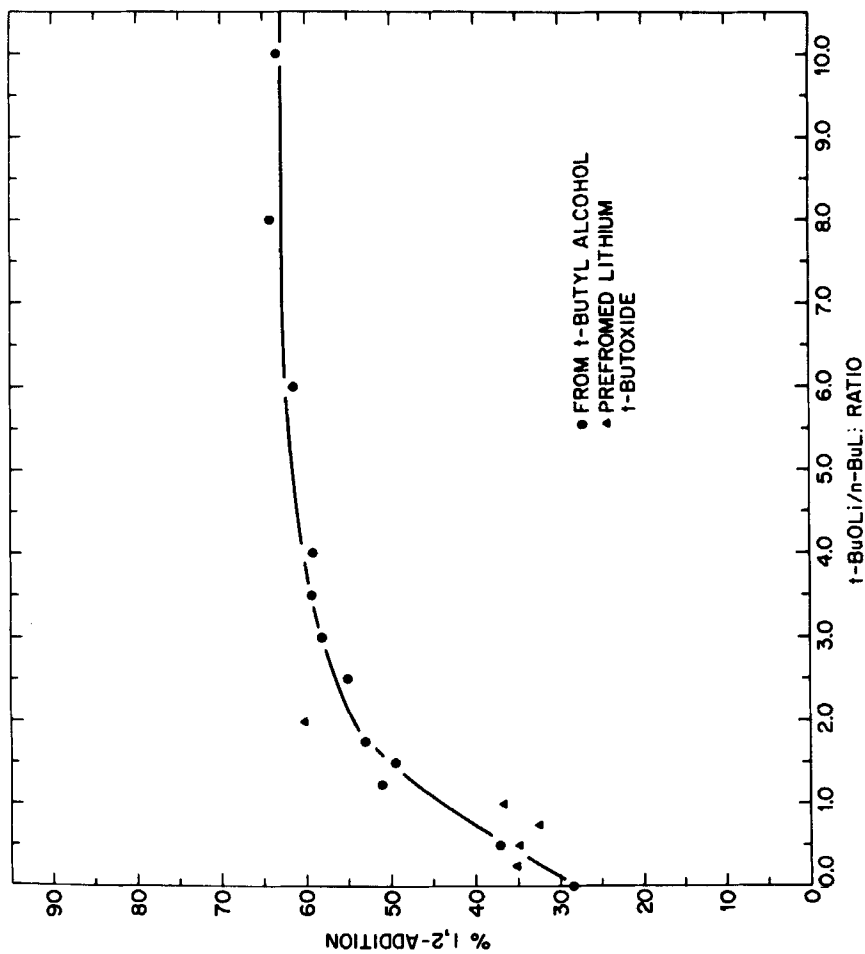*Henry S. Makowski and Merrill Lynn*

Fig. 1. Effect of t-BuOLi/n-BuLi ratio on polybutadiene micro-structure. Kinetic $\overline{DP} = 10$.
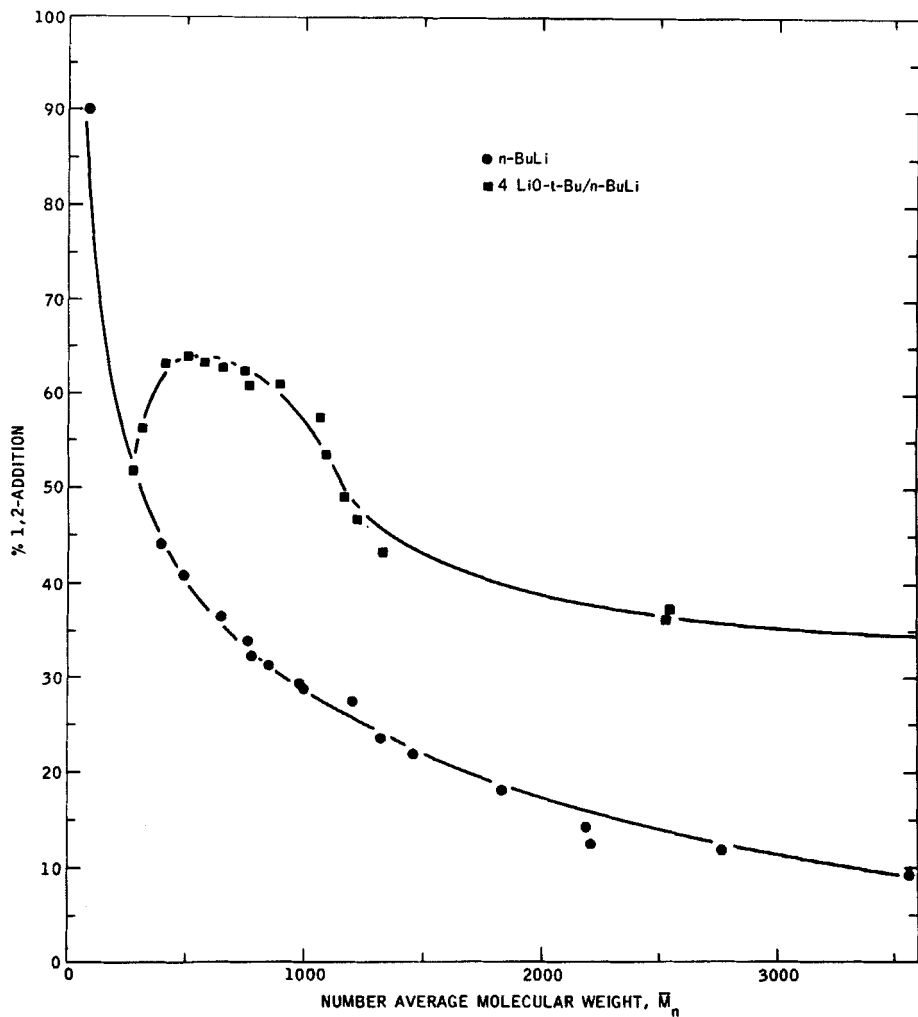
Fig. 2. Polybutadiene microstructure as a function of $\overline{DP}$.

contained over 50% 1, 2 addition. Under these conditions in the absence of alkoxide only 10% 1, 2 addition is obtained [2].

Lithium phenoxide, lithium hydride, lithium hydroxide, and the products derived from the reaction of butyllithium with phenyl acetylene and 1, 6-heptadiyne had little effect on polybutadiene microstructure. Sodium methoxide increased the amount of 1, 2 addition but it is not certain just how significant the change is.

Interesting results were obtained with the products derived from the reaction of butyllithium with 1-hexyne. It is now recognized that alkynes react under the conditions utilized in these polymerizations to form not only hexynyl lithium but also at least some dilithio compounds, $LiC\equiv C-CHLi-R$ [6-8]. For the sake of simplicity the reaction products obtained from 1-hexyne will be referred to as hexynyl lithium. The results obtained with hexynyl lithium are detailed in Table 4 and illustrated in Fig. 3. Hexynyl lithium does result in in-
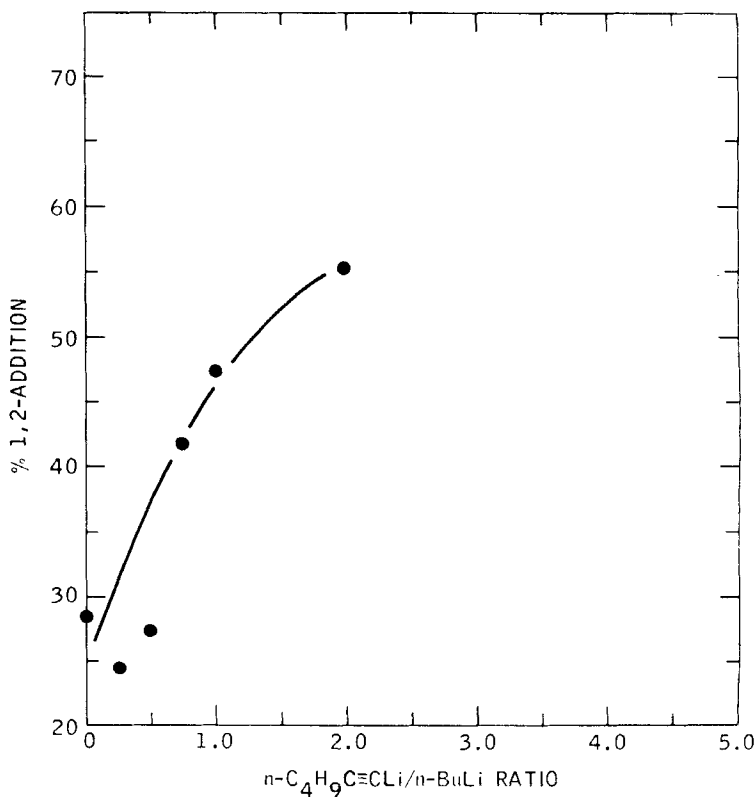

Fig. 3.   Effect of hexynyl lithium on polybutadiene microstructure.

creased 1, 2 addition, although in fact the increases are not as large when molecular weights are taken into account. Unfortunately, it is difficult to study hexynyllithium/BuLi ratios higher than 2 because of solubility limitations. However, it was noted that as the amount of hexynyl lithium was increased relative to butyllithium the molecular weight of the resultant polybutadiene decreased. In fact, at a 2 : 1 ratio of hexynyl lithium/BuLi the molecular weight was about one half that obtained in the absence of hexynyl lithium. The most interesting findings with hexynyl lithium were the observations regarding solubilization of initially precipitated hexynyl lithium during the course of polymerization and the resultant highly viscous polymerization solutions. Hexynyl lithium/BuLi at 1 : 1 gave a clear solution in heptane, and the resultant solution after butadiene polymerization was a very viscous, clear solution. With 2 : 1 hexynyl lithium/BuLi a large amount of precipitate was present initially, but this precipitate dissolved during the course of butadiene polymerization. The final "solution" actually was a gel. Upon reaction with water (supplied by Attapulgus clay) the thick or gelled solutions decomposed to fluid clear solutions, and the polymers isolated therefrom were low molecular weight, low viscosity fluids.

DISCUSSION

In recent years more detailed information has been gathered on the effects of lithium salts on organolithium polymerizations. Lithium salts have been demonstrated to affect reactivity [9, 10], stereoregularity [3-5, 11, 12], and initiation and propagation rates [13]. In virtually all cases the changes from the normal have been attributed to some form of coassociation of the growing organolithium compound with the polymerization inactive lithium salt. The results reported herein again demonstrate, perhaps in a more quantitative fashion, the effects of lithium salts on the course of organolithium polymerization.

A large amount of useful information has been obtained with low molecular weight polybutadienes. These materials are quite simple to make and are readily characterized with regard to microstructure, number-average molecular weight, and, in a relative way, molecular weight distribution.

The effect of t-BuOLi/BuLi ratio on polybutadiene microstructure at $\overline{DP} = 10$ is illustrated in Fig. 1. Lithium t-butoxide was chosen for these studies because of its high solubility in hydrocarbons. It should be noted that even in the absence of alkoxide a $\overline{DP} = 10$ polybutadiene already is high in 1, 2 addition, about 30%. Starting from this relatively high level, 1, 2 addition increases steadily up to a t-BuOLi/BuLi ratio of 3-4. Further increases in this ratio up to 10 did not further increase the 1,2 addition, which

remained at about 62%. These polybutadienes closely resemble in
microstructure those obtained with sodium and alkyl sodium. It
should be pointed out that the same correlation would not be ex-
pected for all levels of $\overline{DP}$, or more fundamentally degree of associa-
tion (DA), of polybutadienyl lithium. The tendency of alkoxide to
coassociate and thereby affect mode of monomer insertion must be
a function of the compositions and DA's of both alkoxide and organo-
lithium.

The studies with $\overline{DP}$ = 10 polybutadiene show a leveling off in
1,2 addition at a t-BuOLi/RLi ratio of 4. The system 4 t-BuOLi/BuLi
in heptane at 25°C produces a polybutadiene of $\overline{Mn} \sim 2500$ with about
35% 1,2 addition whereas the system 10 t-BuOLi/BuLi in toluene at
60°C (cf. Table 5) produces a polybutadiene with greater than 50%
1,2 addition at the same $\overline{Mn}$. The latter result is all the more extra-
ordinary when it is considered that both toluene solvent and increased
polymerization temperature markedly reduce 1,2 addition [2].

Lochmann et al. have shown that even simple alkyllithiums and
lithium alkoxides give cocomplexes varying in composition depending
on the structures and concentrations of the individual components
[14]. Of course, lithium alkoxides are associated in hydrocarbon solu-
tions. t-BuOLi has a DA of about 6 in cyclohexane solution [15].
Kamienski and Lewis conclude that straight-chain alkoxides, such as
n-butoxide, should have considerably higher DA's than the branched-
chain alkoxides [16]. Brown et al. have concluded that with ethyl-
lithium-lithium ethoxide coassociation occurs but not with disrup-
tion of the ethyllithium hexamer [17]. Of course, the nature of alko-
xide coassociation with polybutadienyl lithiums with DA considerably
less than 6 is not known. Nevertheless, if DA itself is important in
stereoregularity of butadiene polymerization, the effectiveness of
structurally different alkoxides would be expected to be different.
The effectiveness of normal, secondary, iso, and tertiary alkoxides
in increasing 1,2 butadiene addition was examined at an alkoxide/
BuLi ratio of 1 (cf. Table 5). t-Butoxide was less effective than the
other three, which were about equivalent in this respect. Similarly,
ethoxide appears to be more effective than t-butoxide when the de-
pressing effect of toluene is taken into account.

Ultimately the whole significance of these considerations is that
alkoxide can exert, perhaps a variable, but indeed strikingly large
effect on polybutadiene microstructure. Further, the manner of
change is significant. Alkoxides increase 1,2 butadiene addition,
and this result is more consistent with the active organolithium com-
pound being ionic in nature [18]. In the absence of lithium salts, the
extent of 1,2 addition decreases with decreasing DA [1]. Thus, based
on the results reported herein and the coassociative tendencies of
lithium salts and alkyllithiums, it is reasonable to conclude that the
increased 1,2 addition due to alkoxides is related to the retention of
a high DA of the growing organolithium compound. It follows that the

associated organolithium compound is itself active in monomer insertion. Indeed the lithium salt effects are taken as good evidence that the associated complex is the active species in organolithium polymerizations.

The change of polybutadiene microstructure with $\overline{DP}$ with the system 4 t-BuOLi/BuLi is illustrated in Fig. 2. Little effect is noted at very low $\overline{DP}$, where 1, 2 addition is already very high in the normal butyllithium polymerization. At about $\overline{DP} = 10$ alkoxide substantially increases 1, 2 addition over the normal. With increasing $\overline{DP}$ overall 1, 2 addition decreases but remains considerably higher than the normal. The minimum and maximum in this curve are considered to be real. At very low $\overline{DP}$ in the absence of alkoxide DA is very high [1], and so alkoxide would not be expected to exert an influence. With increasing $\overline{DP}$, as DA normally decreases, the alkoxide serves to maintain a high DA and, therefore, high 1, 2 addition.

In these $\overline{DP}$ studies with the system 4 t-BuOLi/BuLi (cf. Table 3 and Fig. 2), it was noted that in some instances butadiene was still present after polymerization times normally sufficient for complete monomer conversion. This is another qualitative observation of the rate depressing effect of alkoxide, the effects of lithium salts having been previously noted [9, 10, 13]. Seitz and Brown have concluded that lithium salts at low relative concentration should decrease the reactivity of alkyllithium compounds which behave as electrophiles in noncomplexing solvents [17]. If ionic dissociation is considered to occur, then the species $Li_nR_{(n-1)}X$ should dissociate into

$$Li_nR_{(n-1)}^{\oplus} + X^{\ominus}$$
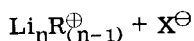
when $X^{\ominus}$ is a more stable anion than $R^{\ominus}$, thereby at least partially inactivating the R groups.

One of the problems we have been concerned with has been the synthesis of high 1, 2 polybutadienes with narrow molecular weight distribution. We have found not been able to accomplish this through the use of organic donor molecules [19]. The use of alkoxides has most closely approached the solution to this problem. As reported herein, relatively high 1, 2 polybutadienes have been synthesized with low bulk viscosities. However, acceptably high 1, 2 addition still occurs only at very low molecular weights.

Perhaps the most fascinating effects of lithium salts on the course of organolithium polymerization were obtained with products derived from the reaction of 1-hexyne with butyllithium. It was assumed initially that the highly insoluble and presumably highly associated alkynyllithium, $R-C\equiv CLi$, which itself does not initiate polymerization, was the only reaction product formed. It followed that the acetylide would maintain a high degree of association when complexed with a polymerization active alkyllithium. Subsequently reports is-
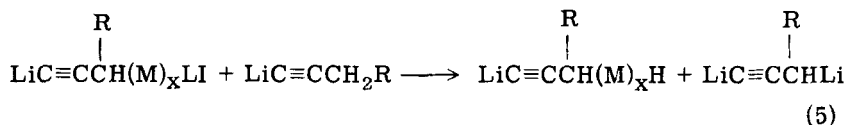
sued demonstrating the rather facile formation of dilithio compounds [6-8]:

$$R-\underset{\underset{Li}{|}}{CH}-C\equiv C-Li$$
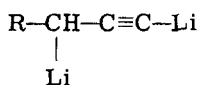
These reports are helpful in explaining the observed phenomena with acetylides in the butyllithium polymerization of butadiene.

At 1-hexyne/butyllithium ratios of 0.5 and 0.67 increased 1,2 butadiene addition resulted. In addition, extraordinary increases in polybutadienyl lithium solution viscosities were obtained. At a ratio of 0.5 the initiating solution was clear and contained no precipitate. After butadiene polymerization the resultant solution was still clear but very viscous. At a ratio of 0.67 the initiating solution contained a substantial amount of precipitate which dissolved during the course of butadiene polymerization, resulting in a gelled polybutadienyl lithium solution. Yet in both cases decomposition of the organolithium compounds with water gave highly fluid polybutadiene solutions and polybutadienes with low $\overline{Mn}$ and low bulk viscosities. Finally, it was noted that the $\overline{Mn}$ of the resultant polybutadienes decreased progressively with increasing 1-hexyne.

All these results can be best explained with just one assumption, i.e., that the propargylic lithium in dilithio-1-hexyne is polymerization-active. Presumably, all the 1-hexyne is converted immediately and first to hexynyl lithium, $C_4H_9C\equiv CLi$, and this acetylenic lithium compound is polymerization-inactive. Subsequently, some of the dilithio compound is formed and competes with butyllithium according to the following series of reactions:

$$BuLi + RCH_2C\equiv CLi \longrightarrow \quad R-\underset{\underset{Li}{|}}{CH}C\equiv CLi + BuH \qquad (1)$$

$$BuLi + xM \longrightarrow \quad Bu(M)_xLi \qquad (2)$$

$$LiC\equiv C\underset{\underset{|}{}}{C}HLi + xM \longrightarrow \quad LiC\equiv CCH(M)_xLi \qquad (3)$$

(with R above each CHLi/CH group)

$$Bu(M)_xLi + LiC\equiv CCH_2R \longrightarrow \quad Bu(M)_xH + LiC\equiv C\overset{R}{\underset{|}{C}}HLi \qquad (4)$$

$$LiC\equiv C\overset{R}{\underset{|}{C}}H(M)_xLI + LiC\equiv CCH_2R \longrightarrow LiC\equiv C\overset{R}{\underset{|}{C}}H(M)_xH + LiC\equiv C\overset{R}{\underset{|}{C}}HLi$$

$$(5)$$

To account for lowering of $\overline{M}n$ it is at least necessary for dilithio-1-hexyne to be polymerization-active [Eq. (3)]. Equation (4) may be sufficient to explain the chain transfer observed, but there is no reason why further transfer according to Eq. (5) should not also occur.

The high solution viscosity or gel formation that was observed is readily explicable on the basis of the polymeric dilithio compound

$$\overset{\displaystyle R}{\underset{\displaystyle |}{\vphantom{x}}}$$
$$LiC\equiv C-CH(M)_xLi$$
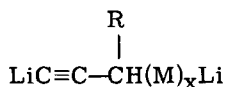
Both ends of this molecule are associated in the usual way to a DA of at least 2. In the absence of PBD-Li this must give a highly cross-linked network where the DA of at least one chain end is higher than 2 or a linear polymer of very high molecular weight where the DA of each chain end is exactly 2. For every PBD-Li present with a normal DA of 2, one "cross-link" or "polymer chain" is effective broken.

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