efficient stirring into the organolithium solution (THF + C_6H_6) kept at the selected temperature. In most cases, concentrations are within the following ranges: [PMMA] = 0.2–0.4 mol L^{-1}, THF–C_6H_6–HMPA = 4:3:1 (v/v). The initial ratios $[HetCH_2Li]_0/[PMMA]_0$ and the reaction times and temperatures are given in Tables VII and VIII. At the end of the reaction, the medium is quenched by stoichiometric amounts of CH_3CO_2H ($[CH_3CO_2H]/[HetCH_2Li] = 1$); after removal of CH_3CO_2Li by filtration or centrifugation, the clear solution is concentrated on a rotary evaporator and precipitated into a large excess of a CH_3OH–Et_2O mixture (1:3 v/v). The isolated copolymer is thoroughly washed overnight under efficient stirring in H_2O–CH_3OH mixtures, filtered, and vacuum dried. The final purification step is carried out by precipitation of the copolymer solution in acetone (DMF for the higher $\overline{DS}_m$) into a large excess of CH_3OH–Et_2O (1:3 v/v).

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Effects of Dibutylmagnesium on Alkyllithium-Initiated Polymerizations

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ABSTRACT: Dialkylmagnesium, by itself, is not an active initiator for diene and styrene polymerization, but it participates in polymerization when complexed either with the alkyllithium initiator or with the propagating polymer–lithium molecules. In the latter case a bimodal distribution is formed. For butadiene the participating factor, which is defined as the ratio of the effective amount of dibutylmagnesium participating in the initiation to the total amount of dibutylmagnesium initially charged, is in the range 1.1–1.4 in cyclohexane and 1.5–1.8 in cyclohexane/THF. For styrene, the participating factor is around 0.7 in cyclohexane and 1.4–1.9 in cyclohexane/THF. A 1:1 complex and an equilibrium between a 1:1 and a 2:1 complex are proposed to explain the observed results. The presence of R_2Mg retards the rate of polymerization, but it does not affect the stereochemistry of the diene polymerization.

Introduction

Alkyllithium can form complexes with other metal alkyls such as those of Mg, Zn, and Cd; e.g.

$$\tfrac{1}{2}(LiR)_4 + MR'_2 \rightarrow Li_2MR_2R'_2$$

Thus, methyllithium was reported to form a 2:1 complex with $(CH_3)_2Mg$ in tetrahydrofuran solution, whereas the proton and lithium-7 NMR spectra of the zinc system are consistent with an approximately equal molar mixture of 2:1 and 1:1 complexes.[1] Only the 1:1 complex predominates in the cadmium system. Lithium and methyl group exchange between the excess methyllithium and the complex in each system occurs at a comparably rapid rate. In diethyl ether solution, however, 2:1 and 3:1 complexes were found for all three metal alkyls, although there has been no evidence obtained for or against the formation of a 1:1 complex with methyllithium.

Smets and his co-workers[2] reported that a 1:1 complex between ethyllithium and diethylzinc was formed in pure benzene. Another example of 1:1 complex formation is

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Table I
Polymerization of Butadiene with Butyllithium and Dibutylmagnesium

mmol[a] of DBM init charged	init *sec*-BuLi/DBM mol ratio	% conv[b]	GPC analysis				% unsaturation		calcd eff DBM,[c] mmol[a]	PF[d]
			$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	$M_n \times 10^{-3}$ adj to 100% conv	vinyl	trans		
0	1/0	100	77	73	1.06	73	7.4	50	0	0
0.2	1/0.15	100	64	61	1.06	61	7.2	51	0.27	1.4
0.4	1/0.29	100	56	53	1.06	53	7.3	52	0.52	1.3
0.6	1/0.44	98	52	49	1.06	50	7.5	52	0.63	1.1
0.8	1/0.58	97	45	43	1.05	44	7.7	51	0.87	1.1
1.0	1/0.73	86	38	36	1.05	42	7.3	51	1.02	1.0

[a] Based on 100 g of monomer in 1 L of cyclohexane and 1.37 mmol effective *sec*-BuLi which was added to the monomer solution with DBM following immediately. [b] Polymerization at 50 °C for 4 h. [c] Calculated as 100 g/$M_n \times 10^{-3}$ (g/mmol) − 1.37 mmol (effective *sec*-BuLi), after M_n adjusted to 100% conversion. [d] PF = (effective DBM)/(total DBM initially charged).

LiMg(n-Bu)$_3$, formed by mixing equal molar amounts of n-BuLi and (n-Bu)$_2$Mg in a cyclohexane/benzene medium.[3] The rapid exchange among the butyl groups was proved through proton NMR studies. Only one uniquely positioned chemical shift (442 Hz upfield from benzene) was observed for the methylene protons on the carbon α to the metal. This indicated the complex is a unique organometallic species rather than a mixture. The same analogy was also found for the *tert*-butyl analogue in its 2:1 form of the Li$_2$Mg(t-Bu)$_4$ complex, as well as for all alkyl groups in a mixed magnesium alkyl species, such as (n-Bu)(*sec*-Bu)Mg. Such mixed species combine a stoichiometric amount of a highly soluble, dimeric, α-carbon-branched di-*sec*-butyl- or di-*tert*-butylmagnesium with insoluble polymeric n-butylmagnesium to produce a hydrocarbon-soluble complex.[3,6]

It was clear then that addition of a metal alkyl from group IIA (2) or IIB (12)[14] would notably change the nature of alkyllithium-initiated polymerization. Hsieh has been interested in the zinc system and reported that the (Et)$_2$Zn "ate" complex with t-BuLi would effectively increase the initiation rates.[4] He also disclosed that butadiene and styrene can be polymerized with reduced molecular weight by the introduction of n-Am$_2$Mg in n-BuLi in the presence of THF.[5] Liquid polybutadiene samples with a narrow molecular weight distribution were prepared by Kamienski and Eastham by using a mixture of *sec*-Bu$_2$Mg and *sec*-BuLi.[6] More recently, Halasa et al.[7] disclosed the polymerization of butadiene with (n-Bu)(*sec*-Bu)Mg plus BuSLi or Bu$_2$NLi. It is apparent to us that although R$_2$Mg by itself is not an active initiator for diene and vinyl polymerization, it does participate in the initiation reaction when complexed with an alkyllithium. We were particularly interested in this phenomenon and undertook a further systematic study.

Experimental Section

Materials. Polymerization-grade cyclohexane was dried by countercurrent scrubbing with nitrogen, followed by two consecutive passages through Alcoa F-1 activated alumina. Phillips special-purity butadiene was flashed at 46 °C from dimer and inhibitor and then condensed through activated alumina into a container at −15 °C under nitrogen pressure. Styrene monomer was doubly distilled from CaH$_2$ under reduced pressure before use. *sec*-Butyllithium (*sec*-BuLi) in hexane was purchased from Alfa Products and further diluted into dry cyclohexane. The concentration was determined by titration as total alkalinity against standardized aqueous HCl solution. Dibutylmagnesium (DBM) which had an approximate 1:1 molar ratio of n-butyl to *sec*-butyl in heptane was used as received from Lithium Corp. of America.

Polymerization and Polymer Characterization. Bottle polymerization and rate measurement techniques have been described previously.[8] Gel permeation chromatography (GPC) in tetrahydrofuran was used to determine M_n and M_w for the polymers, using universal calibration.[9] The hydrodynamic volume V at each point i on a chromatogram or portion of a chromatogram representing an individual component

$$V_i = KM_i^{a+1}$$

was converted to molecular weight by using the Mark–Houwink–Sakarada parameters K and a previously determined for each structure.[9] The resulting molecular weight distribution was then used to calculate M_w and M_n. The diene unit microstructure was determined by IR analysis, and the styrene content was determined by UV as reported in an earlier publication.[10]

Results and Discussion

Homopolymerization. Although dibutylmagnesium, (n-Bu)(s-Bu)Mg (DBM), was not suitable as the sole initiator to polymerize butadiene and styrene, its "ate" complex with *sec*-butyllithium (*sec*-BuLi) in a hydrocarbon medium could initiate the polymerization of both. To polymerize butadiene, various amounts of DBM were added following immediately a constant quantity of *sec*-BuLi so that the ratio of lithium alkyl to magnesium alkyl was varied from 1.4 to 6.7 (Table I). The polymerizations were carried out at 50 °C for 4 h. The decreased molecular weight as a function of increasing amounts of DBM implies that a portion of DBM in association with *sec*-BuLi in the complex becomes involved in the polymerization. On the basis of the known concentrations of both organometals charged and the calibrated M_n (adjusted to 100% conversion), we suggest that at least one of the alkyl–magnesium bonds was involved in the initiation step. The participating factor (PF), which is defined as the effective DBM divided by the total DBM initially charged, was calculated to be in the range 1.1–1.4. Noteworthy also is the narrow molecular weight distribution (MWD) (~1.06) obtained in all cases, which reflects the rapid initiation as in the "living" anionic polymerization.

Apparently, the lithium and magnesium alkyls can form the complex instantly upon mixing, and the rapid exchange of all alkyls coordinated in the complex provides one unique organometallic species, not a mixture. The organoalkalis exerted a synergistic effect on the magnesium alkyls, causing the carbon–magnesium bonds to participate in the anionic polymerization.[3] These features were further demonstrated by the incremental addition of a fixed amount of DBM during the course of those polymerizations originally initiated by *sec*-BuLi. Table II lists the polymerization conditions, and Figure 1 compares the resultant GPC traces. The bimodal GPC curves in Figure 1, characteristic of experiments 2–4 in Table II, clearly illustrate that DBM, added during the process of polymerization, can also form complexes with dissociated polymer–lithium molecules. As a result, the carbon–magne-

Table II
Incremental Addition of Dibutylmagnesium to Butyllithium-Initiated Polymerization of Butadiene

	first addition		second addition		% unsaturation		GPC analysis			
expt	mmol[a] of *sec*-BuLi	polymn time, h	mmol[a] of DBM	polymn time, h	vinyl	trns	no. of peaks	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
1	1.4	6.0	0	0	7.1	51	1	74	70	1.05
2	1.4	1.5	0.6	4.5	7.3	51	2	6.7 72	6.6 68	1.02 1.05
3	1.4	1.0	0.6	5.0	7.0	51	2	13.3 71	13.0 68	1.03 1.05
4	1.4	0.5	0.6	5.5	6.8	51	2	24.7 66	24.3 63	1.02 1.03
5	1.4	0	06	6.0	7.1	52	1	52	48	1.07

[a] Based on 100 g of monomer in 1 L of cyclohexane; polymerization at 50 °C for a total of 6 h with 100% conversion.

Table III
Incremental Addition of DBM or *sec*-BuLi to Butyllithium-Initiated Polymerization of Butadiene

	first addition			second addition, mmol[a]	GPC analysis: peak 1				GPC analysis: peak 2				% unsaturation	
expt	mmol[a] of *sec*-BuLi	THF part[a]	polymn time, min		%	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	%	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	vinyl	trans
1	0.95	0	20	0.5 (*sec*-BuLi)	81	86	82	1.04	19	46	45	1.02	7.2	50
2	0.95	0	20	0.5 (DBM)	79	89	85	1.05	21	43	41	1.06	7.6	50
3	0.95	1.0	10	0.5 (*sec*-BuLi)	78	88	84	1.04	22	50	48	1.03	35	38
4	0.98	1.0	10	0.5 (DBM)	61	79	76	1.04	39	43	42	1.03	36	39

[a] Based on 100 g of monomer in 1 L of cyclohexane; polymerizations run at 50 °C for a total of 5.0 h with 100% conversion. Effective *sec*-BuLi of first addition = 1.25 mmol (total charged) − 0.3 mmol = 0.95 mmol/100 g of monomer.

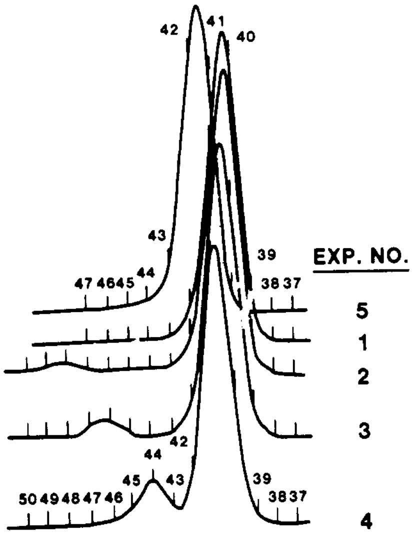


Figure 1. GPC comparison of Table II.

sium bonds as new propagation sites are generated, which leads to the GPC peak of lower molecular weight shown in Figure 1.

The induced ionic feature of DBM was also compared with the control run, where the same amount of *sec*-BuLi was incrementally added instead (see experiments 1 and 3 in Table III). The GPC curves in Figure 2 imply no significant difference by incremental addition between DBM and *sec*-BuLi, provided no polar solvent, such as THF, is present. The GPC results meant that the carbanionic character of DBM so induced is similar to that of *sec*-BuLi. Such similarity and the previously calculated PF value of 1.1–1.4 for DBM recommend a possible 1:1 Li/Mg alkyl complex for DBM with dissociated alkyllithum or polymer–lithium, which is presumed as depicted in eq 1.

$$^{1}/_{4}(R'Li)_4 + RR'MG \xrightarrow{\text{no THF}} (RR'_2MgLi) \quad \text{1:1 complex} \tag{1}$$

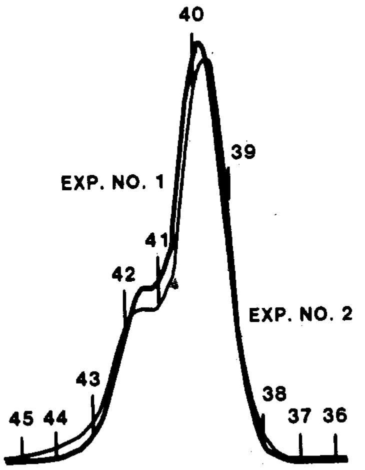
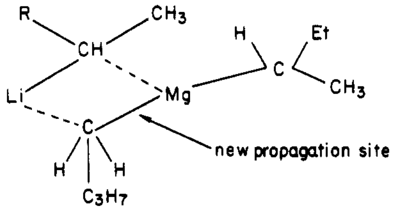


Figure 2. GPC traces of experiments 1 and 2 in Table III.

The simplified structure of the 1:1 complex might be speculated as



and all alkyl groups involved in the complex exchange rapidly according to Kamienski's findings[3,6] and others.[1]

When trace amounts of THF are present and other conditions kept as constant as in Table I (where no THF is involved) the characterization data and the PF values in Table IV are obtained. Here, the PF value increases to the range 1.56–1.8. Expectedly, the presence of a polar solvent, such as THF, exerts an influential solvating effect. This can increasingly break up the self-associated alkyllithium or polymer–lithium aggregates and allow some

Table IV
Polymerization of Butadiene with Butyllithium and Dibutylmagnesium in the Presence of 1 Part[a] THF

mmol[a] of DBM init charged	init sec-BuLi/ DBM mol ratio	% conv[b]	GPC analysis $M_w \times 10^{-3}$	GPC analysis $M_n \times 10^{-3}$	GPC analysis M_w/M_n	% unsaturation vinyl	% unsaturation trans	calcd eff DBM,[c] mmol[a]	PF[d]
0	1/0	100	79	74	1.06	34	36	0	0
0.2	1/0.15	100	64	61	1.05	35	37	0.29	1.5
0.4	1/0.30	100	51	49	1.04	34	37	0.69	1.7
0.4	1/0.44	100	45	43	1.04	36	37	0.98	1.6
0.8	1/0.59	100	38	36	1.04	35	38	1.41	1.8
1.0	1/0.74	95	34	32	1.04	35	38	1.61	1.6

[a] Based on 100 g of monomer in 1 L of cyclohexane and 1.35 mmol effective *sec*-BuLi, which was added to the monomer solution with DBM following immediately. [b] Same as footnotes *b* in Table I. [c] Calculated as 100 g/$M_n \times 10^{-3}$ (g/mmol) − 1.35 mmol (effective *sec*-BuLi), after M_n adjusted to 100% conversion. [d] Same as footnote *d* in Table I.

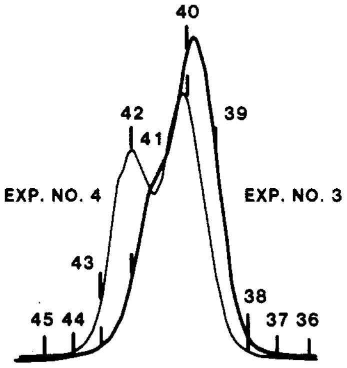


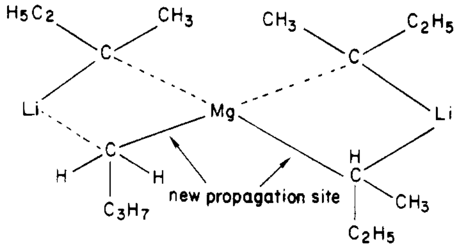
Figure 3. GPC traces of experiments 3 and 4 in Table III.

formation of the 2:1 complex in equilibrium with the 1:1 complex as proposed in eq 2 and 3.

$$\frac{1}{4}(R'Li)_4 + RR'MG \xrightarrow{\substack{\text{1 part}\\ \text{THF}}} (RR'_2MgLi) \quad \text{1:1 complex} \quad (2)$$

$$RR'_2MgLi + \frac{1}{4}(R'Li)_4 \rightarrow (RR'_3MgLi_2) \quad \text{2:1 complex} \quad (3)$$

The 2:1 complex in its simplified structure could be postulated as



Statistically, more than one but less than two carbon–magnesium bonds are ionized to some extent, which can account for the observed increase in PF value. The actual structure of the complex is quite complicated and has not been fully elucidated despite the reported stoichiometry of the 2:1 and 1:1 complex cited in the $CH_3Li/(CH_3)_2Zn$ system.[1] Nevertheless, such highly induced ionic features of carbon–magnesium bonds were further displayed by the medium content of vinyl addition, about 35%, observed in all cases where 1.0 g of THF was present per 100 g of monomer. This is further reminiscent of the solely alkyllithium-initiated polymerization of diene monomers under the same conditions. The higher PF values o 1.5–1.8 of DBM due to THF can be easily differentiated in Figure 3 through the incremental addition of DBM compared to

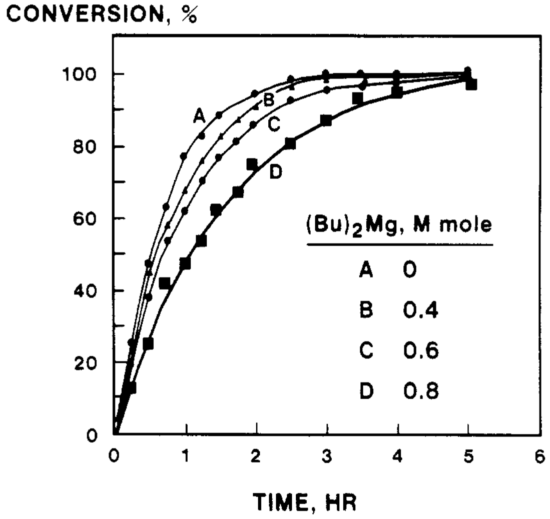


Figure 4. Rate of polymerization of butadiene: butadiene, 100 g; cyclohexane, 1 L; *sec*-BuLi, 1.6 mmol; 50 °C.

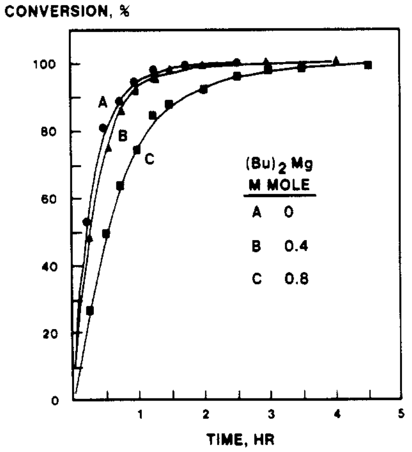


Figure 5. Rate of polymerization of butadiene: butadiene, 100 g; cyclohexane, 1 L; *sec*-BuLi, 1.6 mmol; THF 1 g; 50 °C.

that of *sec*-BuLi (experiments 3 and 4 of Table III) in the *sec*-BuLi-initiated polymerization of butadiene.

A participating factor of DBM was also measured in the polymerization of styrene. In the presence of THF (Table V) the value of 0.7 is comparably less than that in butadiene polymerization. It is assumably acceptable to take into account the steric hindrance imposed by the phenyl group on the α-carbon of the polystyryl anion. The close proximity of the phenyl groups around the lithium counterions tends to allow fewer carbon–magnesium bonds to be associated in forming active complexes. The smaller PF value and the inherent nature of the polystyryl anion

Table V
Polymerization of Styrene with Butyllithium and Dibutylmagnesium

mmol[a] of DBM init charged	init *sec*-BuLi/DBM mol ratio	GPC analysis			calcd eff DBM,[c] mmol[a]	PF[d]
		$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n		
0	1/0	72	69	1.04	0	0
0.2	1/0.14	66	63	1.05	0.14	0.7
0.4	1/0.28	62	58	1.07	0.27	0.7
0.6	1/0.41	57	53	1.08	0.44	0.7
0.8	1/0.55	56	52	1.08	0.47	0.6
1.0	1/0.69	52	48	1.08	0.63	0.6

[a] Based on 100 g of monomer in 1 L of cyclohexane and 1.45 mmol effective *sec*-BuLi, which was added to the monomer solution with Bu_2Mg following immediately. [b] Polymerization at 50 °C for 4 h all with 100% conversion. [c] Calculated as 100 g/$M_n \times 10^{-3}$ (g/mmol) − 1.45 mmol (effective *sec*-BuLi). [d] PF = effective DBM/total DBM.

Table VI
Polymerization of Styrene with Butyllithium and Dibutyllithium in the Presence of 1 Part[a] THF

mmol[a] of DBM init charged	init *sec*-BuLi/DBM mol ratio	GPC analysis			calcd eff DBM,[c] mmol[a]	PF[d]
		$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n		
0	1/0	83	78	1.05	0	0
0.2	1/0.16	64	60	1.06	0.39	1.9
0.4	1/0.32	56	52	1.08	0.64	1.6
0.6	1/0.47	47	43	1.07	1.05	1.7
0.8	1/0.63	45	41	1.09	1.16	1.4
1.0	1/0.79	40	37	1.08	1.42	1.4

[a] Based on 100 g of monomer in 1 L of cyclohexane and 1.28 mmol effective *sec*-BuLi, which was added to the monomer solution with Bu_2Mg following immediately. [b] Polymerization at 50 °C for 4 h all with 100% conversion. [c] Calculated as 100 g/$M_n \times 10^{-3}$ (g/mmol) − 1.28 mmol (effective *sec*-BuLi). [d] PF = effective DBM/total DBM.

causes styrene to polymerize much faster than butadiene in this *sec*-BuLi/DBM system. The solvating effect in the presence of THF in the styrene polymerization (Table VI) is again revealed by DBM's higher PF value of 1.4–1.9 which is analogous to that in the butadiene system as reported in Table IV.

Rate Study. Although positive PF values suggest additional propagation sites are available, the utilization of DBM decreases the overall polymerization rate (Figures 4–6), which is opposite to what was observed in the $(Et)_2Zn$/BuLi system.[4] The rate-depressing effect was shown to be slightly greater for butadiene than for styrene polymerization, especially when there is no THF involved in dissociating the self-associated carbon–lithium aggregates. Apparently, as more DBM participates in complexing with polymer–lithium, more adverse effect was observed on the overall polymerization rate.

The GPC's of all polymers so prepared, however, indicated a narrow MWD (<1.09) n all cases using *sec*-BuLi/DBM molar ratio ranges 1.3–7.0. Such near monodispersity is, of course, typical for most "living" anionic polymerization.[11-13] The observed narrow MWD may be because the rate of initiation is still unaffectedly faster or at least equal to that of propagation as in the unmodified alkyllithium-initiated polymerization.

Copolymerization. Addition of DBM to *sec*-BuLi-initiated copolymerization of styrene (25 wt %) and butadiene (75%) exhibited a similar "inversion" phenomenon compared to using *sec*-BuLi alone.[11-13] DBM retarded the rate of copolymerization analogous to those of homopolymerizations of both monomers. Figure 7 illustrates the comparison in terms of conversion, reaction time, and percent bound styrene. The inflection point in the conversion curves for the mixtures can be easily identified by the appearance of a brownish-yellow color, which is characteristic of the styryl anion. Percent bound styrene analysis of the polymer samples at corresponding conversion vs. reaction times is also depicted in the bottom part of the figure. Styrene contents, which are found to be initially much lower than 25% in the monomer charge, gradually increase until the inflection point of the conversion curve is attained. Thereafter, they increase rapidly to about 24%. As compared to the control rate, which contains only 1.6 mmol of *sec*-BuLi as initiator, the inflection point is delayed when 0.4 mmol of DBM was cocharged, and even more so as the amount of DBM was doubled. Essentially tapered block copolymers were obtained in such systems where no polar medium is present, showing similar behavior to the unmodified copolymerization.

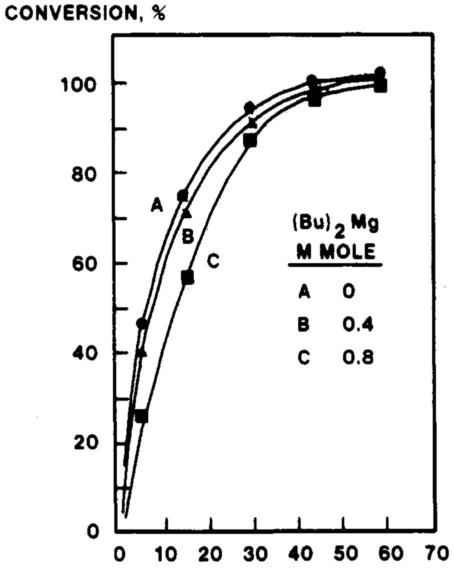


Figure 6. Rate of polymerization of styrene: styrene, 100 g; cyclohexane, 1 L; *sec*-BuLi, 1.6 mmol; 50 °C.

On the other hand, the presence of trace amounts of

Table VII
Diblock Copolymerization of Styrene and Butadiene with Butyllithium and Dibutylmagnesium

mmol[a] of DBM	mmol[a] of *sec*-BuLi	wt %[b] B-S	% block styrene found	GPC analysis		
				$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
0.2	1.6	50-50	48	93	83	1.12
0.4	1.6	50-50	49	66	60	1.10
0.6	1.6	50-50	49	61	55	1.10

[a] Based on 100 g of monomer in 1 L of cyclohexane at 50 °C. [b] Equal amount of butadiene and styrene was sequentially charged.

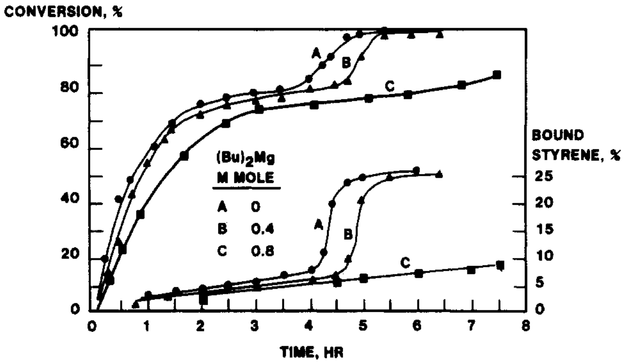


Figure 7. Copolymerization of butadiene and styrene: butadiene, 75 g; styrene, 25 g; cyclohexane, 1 L; *sec*-BuLi, 1.6 mmol; 50 °C.

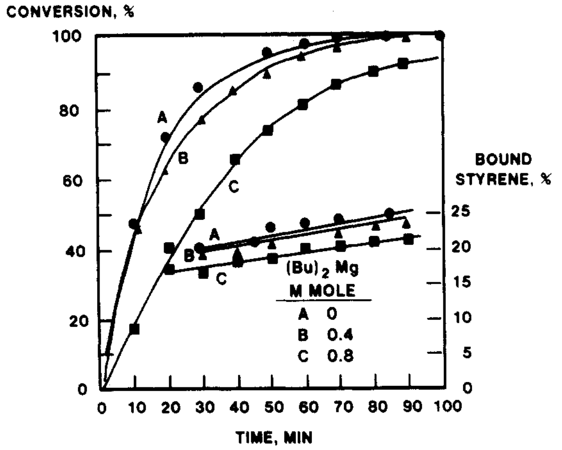


Figure 8. Copolymerization of butadiene and styrene: butadiene, 75 g; styrene 25 g; cyclohexane, 1 L; THF, 1 g; *sec*-BuLi, 1.6 mmol; 50 °C.

THF randomizes the incoming monomers, which is evidently shown in Figure 8 where no inflection points occur in the conversion curves. The styrene contents are nearly evenly incorporated in the polymer samples from low to high conversion. The addition of DBM as coinitiator with *sec*-BuLi in the form of a complex virtually behaves similarly to *sec*-BuLi. Only the rates of copolymerizations are depressed. Furthermore, the diblock copolymers using the DBM/sec-BuLi complex system were also prepared successfully through sequential monomer addition, and the resulting characterization data are listed in Table VII.

Conclusion

Dialkylmagnesium by itself is not an active initiator for diene and styrene polymerization, but it participates in polymerization when either complexed with the alkyllithium initiator or complexed with the propagating polymer-lithium molecules. The "participating factor" depends on the polarity of the solvent used, the types of monomer and the Li/Mg ratio. The presence of R_2Mg retards the rate of polymerization, but it does not affect the stereochemistry of the diene polymerization.

Registry No. (*n*-Bu)(*sec*-Bu)Mg, 39881-32-8; (*sec*-BuLi), 598-30-1; polybutadiene (homopolymer), 9003-17-2; polystyrene (homopolymer), 9003-53-6; (styrene)·(butadiene) (copolymer), 9003-55-8; butadiene, 106-99-0; styrene, 100-42-5.

References and Notes

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(14) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.