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## **Anionic Polymerization Characteristics of the 1:1 Complex of n-Butylsodium and n-,s- Dibutylmagnesium (Sodium Tributylmagnesiato)**

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### ABSTRACT

The behavior of isoprene and styrene polymerizations initiated by the complex of n-butylsodium and n-,s-dibutylmagnesium (sodium tributylmagnesiato) has been examined. The styrene-benzene sys-

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tem was found to yield stable active centers and polymers of predictable molecular weight and narrow molecular weight distributions. Isoprene, however, did not follow this behavior and yielded polydisperse material having molecular weights lower than those predicted on the basis that only *n*-butylsodium is capable of initiating chain growth. The polyisoprene microstructure was found to consist of ~60% 3,4 and ~40% 1,4 units.

## INTRODUCTION

Alkylorganometallic compounds involving alkali metals other than lithium are generally insoluble in hydrocarbon solvents and lack long-term stability at room temperature. Thus, these compounds have received only infrequent attention insofar as their capacity as anionic polymerization initiators is concerned. It has been recognized for some time that alkyl- and aryllithium compounds will form "ate" complexes [1, 2] with metal alkyls such as those containing magnesium [3, 4], zinc [5], or cadmium [5]. The polymerization behavior of organolithiums complexed with organomagnesium or organozinc compounds has been reported [6, 7]. The complexes formed involving organolithiums are generally 1:1 when equimolar amounts of the two organometallics are combined.

To date, the corresponding complexes involving sodium have not been examined. The 1:1 complex formed from *n*-butylsodium and *n*-, *s*-dibutylmagnesium (sodium tributylmagnesiate) is soluble in hydrocarbon solvents. This characteristic thus facilitates the evaluation of this complex in hydrocarbon-solvent-based anionic polymerizations in a fashion parallel to organolithiums. This has been done with isoprene and styrene.

## EXPERIMENTAL

The sodium tributylmagnesiate (Lithium Corporation of America) was prepared in a cyclohexane-methylcyclohexane mixture. Dibutylmagnesium (1:1 *n*-butyl-*sec*-butylmagnesium containing ~5 mol% di-*n*-octylmagnesium) (Lithium Corporation of America) in cyclohexane (2 M) was treated with sodium dispersion in methylcyclohexane at 40°C for 30 min, and the mixture was filtered after cooling and settling. The resultant amber-colored solution had a total alkalinity of 1.47 N and a magnesium concentration of 0.50 M (Na/Mg = 0.95). Concentration of this solution to about one-sixth its original volume produced a clear, oily phase, which could be readily dissolved in benzene (2 M).

NMR analysis of the benzene solution showed the center of the alpha-protons to be 480 cps from benzene. (The sodium tributylmagnesiate in solution was found to be stable for no less than 3 months at room tem-

perature.) This compares with an NMR band of 446 cps from benzene for the center of the alpha-protons in a solution of dibutylmagnesium alone. Malpass [8] showed a similar large change (+48 cps) in chemical shift on forming  $\text{NaMg}(\underline{3}\text{Bn})_3$  from  $(\underline{c}\text{Bn})_2$  Niq. Moreover, Kamienski [9] has shown that, for such single-alkyl-containing lithium trialkylmagnesiates, only one type of alpha-proton is found, indicating a single environment for all alkyl groups present. The techniques used for solvent and monomer purifications were those described elsewhere [10]. Polymerizations, at 20°C, were done in benzene in purged and sealed glass reactors using vacuum line procedures.

The molecular weights and polydispersities of the resultant polymers were evaluated by size exclusion chromatography (Waters 150C), low-angle laser light scattering (Chromatix KMX-6 photometer), and membrane osmometry (Hewlett-Packard 503). The Waters 150C and Chromatix KMX-6 instruments were combined for on-line measurements of molecular weights and the resultant molecular weight distributions.

The stability of the polystyryl active centers was examined by UV-visible spectroscopy (Perkin-Elmer 559) in either benzene or tetrahydrofuran. Quartz cells (0.1 cm path length) attached to the glass reactors were used. Polydiene microstructure was determined by the use of a Varian 300 MHz <sup>1</sup>H-NMR spectrometer.

The extinction coefficient for the styrylsodium dibutylmagnesiante entity was found to be  $9.5 \times 10^3$  L/mol·cm compared with that of styrylsodium, which is  $1.2 \times 10^4$ .

## RESULTS AND DISCUSSION

### Active Center Stability

The stability of the polystyryl active center formed by the use of sodium tributylmagnesiante was examined by measuring the visible spectrum of this species. Figure 1 shows various spectra of the styryl active center in benzene at 20°C as a function of time. The following points can be made.

The adsorption maximum ( $\lambda_{\text{max}}$ ) is 315 nm, a value significantly lower than that of 335 nm for polystyryl lithium [11] and 332 nm for polystyryl sodium [12] in benzene. This implies that the carbon-sodium bond in the polystyryl sodium:dibutylmagnesiante complex possesses more covalent character than the styryllithium and sodium and sodium entities under equivalent conditions. Also, the visible absorption spectrum (Fig. 1) is relatively sharp compared to that of polystyryl sodium [11] (in tetrahydrofuran); the shoulder seen in the polystyryl lithium spectrum (400-500 nm) [11] is absent.

These spectral results also showed that the initiation event is relatively slow (Curves 1 and 2 of Fig. 1) compared to what would

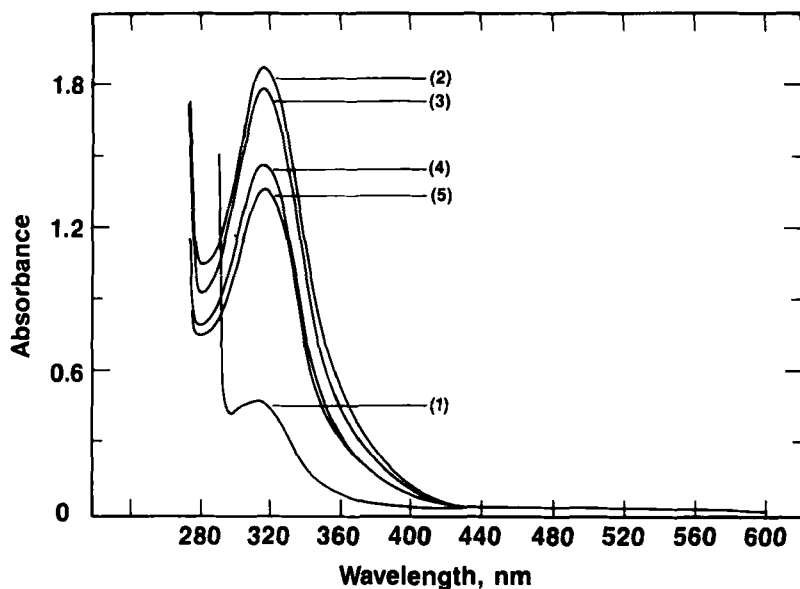


FIG. 1. Spectra of the styrylsodium-dibutylmagnesiato complex in benzene at 20°C as a function of time: (1) 11 min, (2) 3.8 h, (3) 72.4 h, (4) 455.5 h, (5) 792.3 h. Monomer concentration, 80 mmol/L; active center concentration (based on sodium), 2 mmol/L.

be observed for *s*-butyllithium and styrene [13]. Although, kinetic and detailed rate analyses were not done, it is clear that the reaction rate of styrene with sodium tributylmagnesiato is markedly slower in benzene than with organolithium initiators [14].

The long-term evaluation of the stability of the polystyryl sodium dibutylmagnesiato (Fig. 1) showed negligible decay even after 3 days at 20°C. Unlike the reported [15-17] decay mechanism for polystyryl sodium in tetrahydrofuran (where the rate of decomposition is approximately the same as that observed in this work), the attenuation of the primary peak is not accompanied by the concurrent formation of peaks at higher wavelength. This finding demonstrates that the proposed mechanism [15-17] for polystyryl sodium does not hold for the magnesiato complex. This generally accepted scheme involves the elimination of sodium hydride and the subsequent formation of the 1,3-diphenylallylic negative ion via a metallation of the  $\gamma$ -carbon of the terminal unit having the newly formed carbon-carbon double bond. This latter ion is taken to be the source of a peak at 535 nm. The failure to observe such a band even after more than 1 month indicates that the slow decay of the polystyryl sodium:dibutylmagnesiato complex is limited to a single process, e.g., the elimination of sodium hydride. (A UV analysis of "aged" and methanol-terminated oligomeric polystyrene

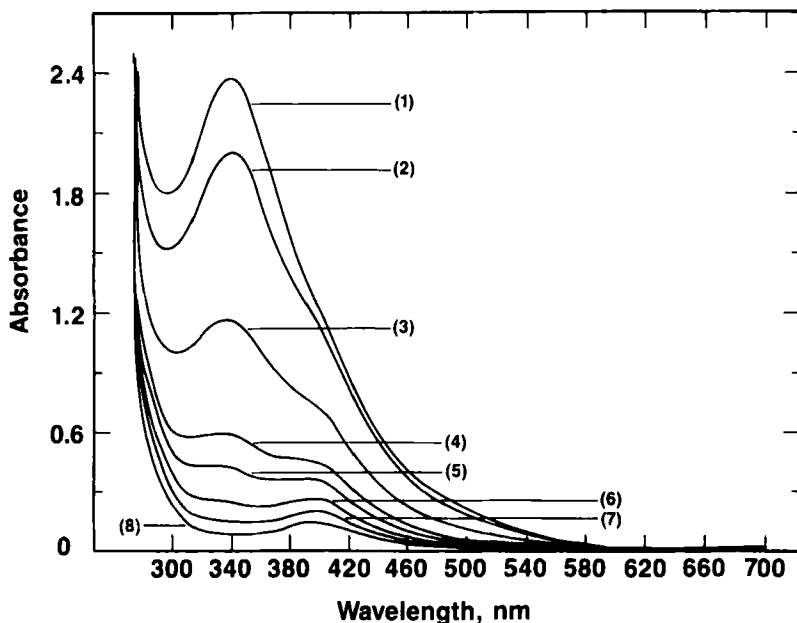


FIG. 2. Spectra of the styrylsodium-dibutylmagnesiato complex in tetrahydrofuran at 20°C as a function of time: (1) 12 min, (2) 1.3 h, (3) 5.2 h, (4) 15.7 h, (5) 22.9 h, (6) 40 h, (7) 74.1 h, (8) 213.4 h. Monomer concentration, 82 mmol/L; active center concentration (based on sodium), 4 mmol/L.

prepared by the styryl sodium-dibutylmagnesium complex showed the

presence of some  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}=\text{C}-\phi \end{array}$  chain ends. This indicates that the elimination of NaH does occur. However, at the juncture, the presence of other concurrent termination events should not be ruled out.) If such a step is the cause of the attenuation of the peak at 315 nm, it must be concluded that the subsequent metallation event does not occur, probably as the result of the lack of reactivity of the complexed active center.

In tetrahydrofuran this active center exhibits decreased stability relative to that seen in benzene (Fig. 2). In parallel with the benzene system, the 535 nm absorption band is absent although a minor peak at 398 nm is observed (see Fig. 3). (A recent compilation of the results on the aging of polystyryl anions [18] does not list the 398-nm band as being previously observed.) The species responsible for this band is unknown and speculation regarding the structure responsible for this absorption is inappropriate at this time.

Several other features of this spectra deserve brief comment. In

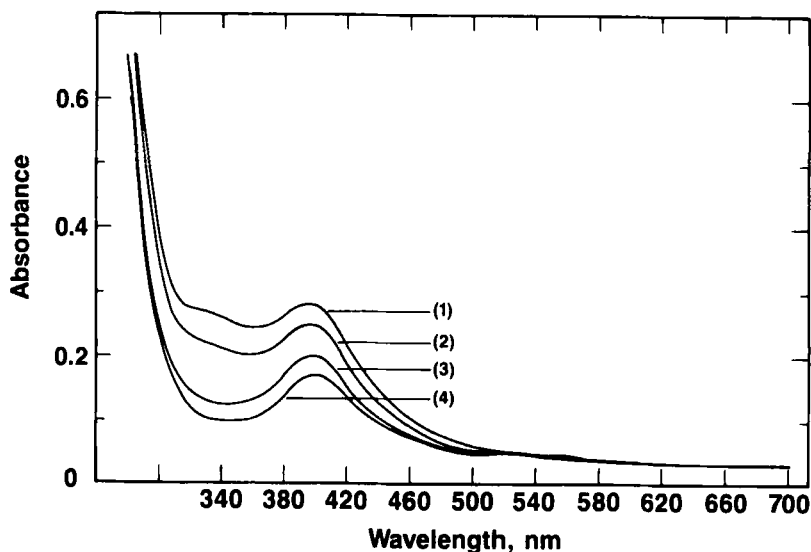


FIG. 3. Spectra of the styrylsodium-dibutylmagnesiato complex in tetrahydrofuran at 20°C as a function of time: (1) 40.5 h, (2) 52.6 h, (3) 126.0 h, (4) 226.7 h. The spectra are presented to emphasize the band at 398 nm. Reaction conditions are identical to those given in Fig. 2.

tetrahydrofuran,  $\lambda_{\max}$  is found to be at 338 nm, which is very close to that for polystyryl sodium (340 nm) [15, 16]. However, unlike that active center, the magnesiato complex does not exhibit an isosbestic point accompanying the formation of the higher wavelength (398 vs 535 nm) band. Clearly, constant stoichiometry for the process observed in this work does not hold. A close examination (Fig. 3) of the spectra involving the secondary peak at 398 nm reveals the trace presence of peaks at  $\sim 530$  and 560 nm. The former may be an indication of the minute formation of the 1,3-diphenyl allyl negative ion. However, the attenuated nature of these peaks precludes any meaningful interpretation. Thus, in consonance with the findings in benzene, the elimination of sodium hydride as the primary decay process seems a logical assumption.

Although  $\lambda_{\max}$  in tetrahydrofuran is found at 338 nm, we believe that it would be premature to assume that this solvent has caused the complete breakdown of the magnesiato complex. For example, a 1:1 complex is apparently formed [5] between ethyllithium and diethylcadmium in tetrahydrofuran. In the absence of the needed information involving the presence or absence of solvated complexes involving the

active center(s), speculation regarding the structure of such species is unwarranted.

### Polydispersity and Molecular Weights

The role of the complexed dibutylmagnesium in propagation involves its role in initiation, i.e., how many propagating active sites does the tributyl sodium magnesiate form? This question can, of course, be answered by the determination of the stoichiometry of the polymerization process. This evaluation was thus carried out for the styrene-benzene system, as was the parallel examination of the polydispersity indices of the resultant polystyrenes (see Table 1).

The findings presented in Table 1 show that, at virtually complete conversions, the polystyrene number-average molecular weights are very close to the stoichiometric values ( $\bar{M}_s$ ) when the latter is calculated on the sole assumption that initiation and propagation involve only the complexed carbon-sodium center, i.e., the carbon-magnesium sites do not participate directly in the polymerization. Germane to this conclusion is our observation that dibutylmagnesium is ineffectual in polymerizing styrene and dienes in either hydrocarbon or ether solvents. These combined results lend credence to the assumption that the dibutylmagnesium influences the stability and reactivity of the polystyryl sodium active center through complexation and not by direct participation in chain propagation.

In addition to the styrene system, some preliminary evaluations

TABLE 1. Molecular Characteristics of Polystyrenes

Sample M	$\bar{M}_s \times 10^{-4}$ <sup>a</sup>	$\bar{M}_n \times 10^{-4}$ <sup>b</sup>	$\bar{M}_w \times 10^{-4}$ <sup>c</sup>	$M_w/M_n$ <sup>d</sup>
PS-1	2.6	2.7	2.8	1.05
PS-2	3.9	3.4	3.6	1.05
PS-3	4.2	4.4	4.6	1.05
PS-4	4.6	4.2	4.4	1.06
PS-5	20.3	19.3	20.5	1.06

<sup>a</sup> $\bar{M}_s = \text{g monomer}/[n\text{-C}_4\text{H}_9\text{Na}]$ .

<sup>b</sup>Osmometry.

<sup>c</sup>Light scattering.

<sup>d</sup>Size-exclusion chromatography.



TABLE 2. Molecular Characteristics of Polyisoprenes

Sample	Percent conversion	Polymerization <sup>b</sup> temperature, °C	$\bar{M}_s \times 10^{-4}$ C	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$M_w/M_n^d$
PI-1	41.4	20	7.0	1.15	1.72	1.49
PI-2	90.5	50	21.3	4.54	8.1	1.79
PI-3	93.2	50	1.5	0.83	1.04	1.26
PI-4	26.6	20	14.5	2.8	3.8	1.34

<sup>a</sup>PI = polyisoprene.

<sup>b</sup>polymerization time 72 h.

<sup>c</sup>Calculated on the basis of n-butylnsodium content (5.2 mmol/L) of the complexed magnesiate and the observed extent of conversion. Monomer concentration was 0.48 mmol/L.

<sup>d</sup>Size-exclusion chromatography.

of the sodium tributylmagnesiato in diene polymerizations were done. This took the form of molecular weight, polydispersity, and microstructure studies (see Table 2). The polyisoprene microstructure were assayed to be ~40% 1,4 and ~60% 3,4 units.

Table 2 shows that the near correspondence between predicted and measured number-average molecular weights observed for styrene is absent in the isoprene case, with the measured values being uniformly lower than anticipated from the stoichiometry of the reaction. This could be ascribed to the presence of a chain-transfer step, an event which has been proposed to occur for the n-butyllithium/diethylzinc-cyclohexane/butadiene system in the presence of tetrahydrofuran [7]. An alternative explanation would involve the participation of the sites in the dibutylmagnesium directly in the propagation step, i.e., where more than one growing chain is generated per sodium tributyl magnesiato complex. Since the limited molecular weight results (Table 2) show (in three out of four cases) that  $M_n < \frac{1}{3}M_s$ , the tentative conclusion can be drawn that both chain transfer and alkyl exchange processes are present.

It is apparent from the findings in Table 2 that the isoprene system shows more complex behavior than does styrene, behavior which is perhaps emphasized as a consequence of the slow rate of polymerization. The relatively broad molecular weight distributions point to a propagation process not devoid of complications, e.g., chain branching, different reactive sites, and/or chain transfer. These side reactions are missing, under the proper conditions, in polymerizations involving the lithium counterion.

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