Nuclear Magnetic Resonance Studies of the Propagating Chain End in the Organolithium Polymerization of Dienes. I. Butadiene in Hydrocarbon Media

Maurice Morton,* R. D. Sanderson,† and R. Sakata‡

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

Received September 5, 1972

ABSTRACT: High-resolution nmr studies have been carried out on the organolithium polymerization of butadiene in hydrocarbon solvents. As a measure of any possible complexation between the monomer and the active chain end, the proton resonance spectrum of butadiene was determined in the presence and absence of short-chain poly(perdeuteriobutadienyl)lithum ($x_n \sim 20$) at high concentrations (0.2 *M*) of both, in benzene-d_6 or toluene-d_8. No effect was observed on the proton resonances of the monomer, indicating that, if such complexation does occur, the concentration of the complex must be very low (<1% based on a slow exchange rate). Using ethyllithium-d_5 to initiate short-chain poly(butadienyl)lithium and the technique of "pseudotermination" by butadiene-d_6, it has been found possible to assign the three resonance peaks corresponding with protons on the terminal carbon (α), as well as the penultimate (β) and antepenultimate (γ) carbon atoms in the chain. These peaks indicate that the terminal chain unit has a 1,4 structure (no detectable 1,2), whereas the in-chain units show about 9% 1,2 structure. This has been taken to indicate the existence of an equilibrium between a localized (covalent) and a delocalized (π-allyl) chain-end unit, the latter being in too low a concentration to be detected, but leading to the inclusion of a 1,2 in-chain unit by subsequent monomer addition.

The organolithium-initiated polymerizations of dienes have been the subject of intensive study during the past decade. Such studies have been facilitated by the fact that these reactions can be carried out in homogeneous solution with a variety of hydrocarbon or ether solvents. Yet, despite the apparent simplicity of these systems, little progress has been made in elucidating the detailed mechanism of the reactions. The unresolved phenomena observed in these systems have centered around the following: (1) differences in stereospecificity in the polymerization of different dienes in hydrocarbon media (*e.g.*, high cis-1,4 structure for isoprene but not for butadiene); (2) profound effect of traces of ethers on the chain microstructure (*e.g.*, sharp increase in 1,2 or 3,4 vinyl structures); (3) anomalous behavior in copolymerizations with styrene (*e.g.*, strong preference for butadiene in hydrocarbon media but the reverse in ethers); and (4) very low kinetic orders (*e.g.*, one-fourth to one-sixth) for the propagation rate, with respect to organolithium, in hydrocarbon media.

These peculiarities in behavior of the dienes, especially the first three listed above, have been considered by some as indicating the formation of a complex between the diene monomer and the propagating organolithium species. Such a complex would presumably not form in ether media due to the known propensity of ethers to coordinate with (solvate) organometallic compounds. Hence it has become apparent that the mechanism of these polymerizations could only be elucidated from a detailed knowledge of the structure of the propagating chain end. Fortunately, these polymerizations do not exhibit any chain-termination step, so that the "living" chain end may be studied at will. The use of high-resolution nmr measurements would appear to be especially appropriate for such studies, provided a high concentration of organolithium chain ends were available and provided also that the viscosity of the medium was not too high. Both of these objectives may be attained by preparing oligomers of the dienes, *i.e.*, chains containing from several up to 20 or more monomeric units.

Experimental Procedures

High-Vacuum Apparatus. The high-vacuum system (Figure 1) permits the rapid attainment of very low pressures (<10^{-6} mm) of noncondensable gases. All monomer and solvent purifications were carried out on the vacuum apparatus or in vessels sealed from it. The construction and manipulation of this apparatus has been discussed previously.[1] Modifications have been introduced in the low volume section, A, used for distilling into nmr tubes and in section C, which was used exclusively for handling polar materials.

Sections of the vacuum apparatus used for handling reagents were treated as described previously,[1] after which a further purging technique was employed. In this latter technique, purified *n*-hexane was distilled in at liquid N_2 temperature into the purge bulb Q (Figure 2) and the whole reactor section was sealed from the vacuum system at the inlet constriction. The vessel Q was then warmed and *n*-butyllithium introduced from an attached ampoule (R). The entire reaction section was therefore able to be bathed in *n*-butyllithium-*n*-hexane solution for about 0.75 hr. The solution was then poured back into Q and all the walls of the whole section rinsed several times by refluxing the *n*-hexane and letting it drain back into the purge vessel Q. Thereafter the *n*-butyllithium solution in Q was frozen and sealed off.

Preparation of Materials. Generally materials were purified to a level where there were no spectroscopic impurities, and thereafter further purified so that they contained no contaminant capable of influencing the reaction pattern of the polymerization.

Solvent Purification. *n-Hexane and Cyclohexane.* These solvents were stirred for several days over sulfuric acid. The supernatant liquids were then decanted and distilled on a 3-ft column packed with glass helices at a 10:1 reflux ratio. Only center cuts were taken. The solvents were then degassed on the vacuum apparatus and stirred over a sodium dispersion for 2 days. Thereafter they were distilled onto poly(styryl)lithium–*n*-butyllithium and stored for later use. Measured quantities could then be distilled directly into a reactor.

Toluene-d_8, Benzene-d_6, and Tetramethylsilane. The toluene-d_8 (Diaprep Corp. 99% minimum isotopic purity), the benzene-d_6 (Merck, Sharp and Dohme 99.5% minimum isotopic purity), and the tetramethylsilane (Alfa Inorganics, nmr grade) were degassed, stirred over sodium dispersion, and stored over poly(styryl)lithium-*n*-butyllithium at −10° until used.

Monomer Purification. *Butadiene.* Butadiene (redistilled, practical grade) was degassed at 10^{-6} mm at −78 or −196° and then distilled onto a series of flasks freshly coated with sodium mirrors. It was allowed to remain in each of the flasks for about 1 hr at 0°, and then distilled into a storage flask and kept at −78°. Immediately before use the butadiene was distilled onto *n*-butyl-

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†Department of Chemistry, University of Stellenbosch, Stellenbosch, South Africa.

‡Bridgestone Tire Co., Tokyo, Japan.

(1) L. J. Fetters, *J. Res. Nat. Bur. Stand. Sect. A*, **70**, 421 (1966).

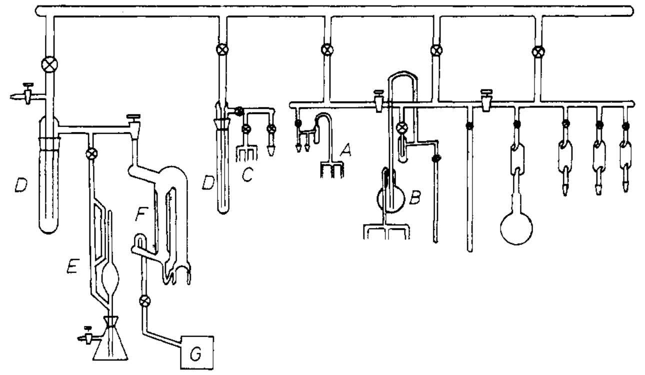

Figure 1. High-vacuum system: (A) low volume drop for attaching nmr subreactor to the vacuum system; (B) drop for attaching various reactors to vacuum system; (C) restricted section for handling polar materials purification and addition to subreactors; (D) −196° traps; (E) McLeod gauge; (F) three-stage Eck and Krebs mercury diffusion pump; (G) mechanical oil pump.

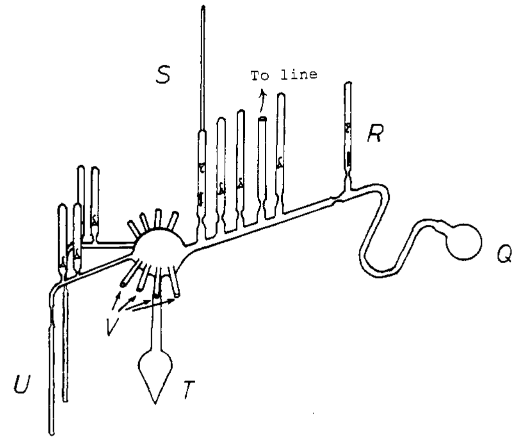

Figure 2. Main reactor and subreactors for nmr studies: (Q) purge section; (R) butyllithium in hexane solution; (S) ethyllithium-d_5 initiator; (T) main reactor bulb; (U) nmr tubes; (V) further nmr subreactors.

lithium and stirred at −10 to 0° until about 5% of the anionic polymer had formed. It was then distilled into a vacuum-measuring buret for direct distillation into a reactor.

Butadiene-d_6. Butadiene-d_6 (Merck, Sharp and Dohme, minimum isotopic purity 98%) was distilled into a flask coated with a sodium film, and allowed to react for 4 hr at 0°. This was sufficient time for a film of polymer to form on the walls of the flask. It was then distilled into a fresh sodium-coated flask and kept at −78° ready for use.

Preparation of Organolithiums. Ethyllithium was chosen as the initiator mainly because it could easily be prepared in the deuterated variety. Preliminary work had shown that the nondeuterated form yielded complex nmr spectra more difficult to interpret.

Ethyllithium and Ethyllithium-d_5. These were prepared from the corresponding bromides and lithium wire in *n*-hexane. For this the method of Talalaeva and Kocheskov[2] was modified for use under vacuum, as described by Morton *et al.*[3] The ethyllithiums were twice recrystallized from *n*-hexane under vacuum and then distributed into smaller iniator ampoules using the apparatus shown in Figure 3. These ampoules were first purged with a *n*-butyllithium solution in a manner similar to that described previously for the reactor apparatus. After the purge section (E) was cut off, the ethyllithium solution was introduced into the apparatus by breaking the breakseal. The solution was then distributed into the initiator ampoules and any excess solution was poured into the storage ampoule (B). The levels in each of the ampoules were marked and then all the surfaces to be cut were prerinsed internally with solvent by cooling the outer surface with cold alcohol from an isopropyl alcohol–Dry Ice bath. After thorough rinsing, the solutions were cooled to −78° and the ampoules were sealed off. The solutions (with their volumes calibrated up to the original mark) could be titrated by the Gilman double-titration method.[4,5] The concentration of noninitiating lithium compounds was negligible. The reproducibility of the organolithium contents in the ampoules was better than 1%. All the organolithium ampoules were stored at −15°.

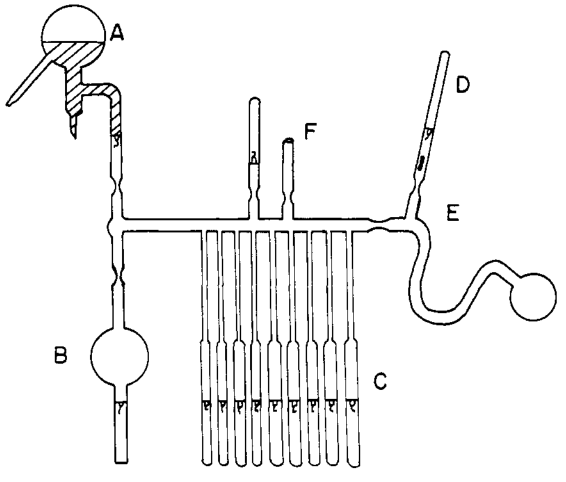

Figure 3. Apparatus for preparing initiator ampoules: (A) large ampoule containing organolithium solution; (B) storage ampoule for excess solution; (C) initiator ampoules; (D) *n*-butyllithium solution; (E) purge section; (F) outlet to vacuum line.

n-Butyllithium. The *n*-butyllithium used to purge glass apparatus was obtained in a hexane solution (1.5 *M*) from Foote Mineral Co. It was syringed under argon into an ampoule fixed to the vacuum apparatus (Figure 4). The arm with the septum cap was then sealed after the solution was cooled (−78°) and degassed. More *n*-hexane was distilled into the ampoule in order to dilute the solution to about 0.1 *M*. The ampoule was then sealed from the vacuum apparatus at constriction A. The ampoule was next attached to an apparatus similar to that shown in Figure 3 except that it had no purge section. The *n*-butyllithium solution was then distributed into smaller ampoules using a method similar to that described previously for preparing initiator ampoules. There were some slight differences from the procedure previously described, in that the apparatus was flamed under vacuum but was not purged as the initiator ampoules were. Also the levels in the ampoules after distribution were not marked nor was an ampoule titrated, since knowledge of the exact amount of *n*-butyllithium used to purge is not needed.

Preparation of Samples for Nuclear Magnetic Resonance Studies. The main reactor apparatus is shown in Figure 2. The nmr tubes (Wilmad Glass Co. 507PP, thin-wall Pyrex) were sealed directly to the arms projecting from the center bulb. The arms were of 4-mm standard wall tubing so that they were able to be sealed off under vacuum at any point. A short length of 2-mm tubing connected these arms to the nmr tubes. This allowed the latter tubes to be sealed off with minimum imbalance along the axis of the tube.

The main reactor was connected to the vacuum system and flamed keeping the nmr tubes cool in moist tissue paper. The purge procedure described earlier was then used to remove any terminating or dislodgeable polar materials from the walls. The ethyllithium-d_5 in *n*-hexane was then introduced from ampoule (S), after which the ampoule was rinsed with hexane by cooling the outer walls. With the solution in (T) frozen (−196°), (S) was removed at its constriction and its volume was determined. The reactor was then reconnected to the vacuum apparatus to remove the *n*-hexane and to quantitatively introduce the desired solvent system and, in certain cases, monomer for preparing the "seed." The latter refers to an oligo(butadienyl-d_6)lithium containing, on the average, 20 molecules of butadiene-d_6 per initiator molecule.

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(2) T. V. Talalaeva and K. A. Kocheskov, *J. Gen. Chem. USSR*, **23**, 399 (1953).

(3) M. Morton, A. A. Rembaum, and J. L. Hall, *J. Poly. Sci., Part A*, 1, 461 (1963).

(4) H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).

(5) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

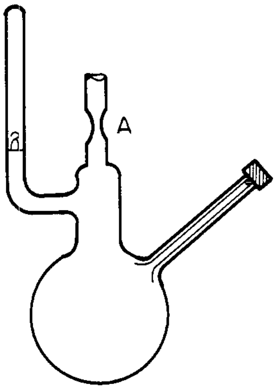

Figure 4. *n*-Butyllithium purge ampoule.

The reactor was sealed from the vacuum system during polymerizations, but could be reconnected *via* a breakseal for a further addition, as when the seed needed to be capped with one or two units of protonic monomer.

The resulting solution was then poured off into the nmr tubes, three at a time. The levels were marked and the arms rinsed with solvent. After readjusting and equilibrating the heights in the nmr tubes, they were simultaneously and gradually frozen, together with the main bulb T, and then sealed off. The nmr tubes were then treated as subreactors, and further additions of monomers and/or additive were then made directly to them, using the low volume section of the vacuum system, A, shown in Figure 1. Additions were estimated reproducibly to 0.0005 cm^3. For the additions, the nmr tubes were kept at −196°, while the material to be transferred was kept at −78°, separated from the nmr tube subreactor by a stopcock. At −78° all materials had negligible vapor pressure. Tetramethylsilane and butadiene were exceptions, but posed no problem since distillation was slow with the stopcock open. The other materials did not distill on opening the stopcock, but distillation could be induced, while maintaining a negligible vapor pressure in the system, by gradually lowering the Dry Ice–isopropyl alcohol cooling bath (−78°) which surrounded the distilling material. The accuracy of the method was shown to be better than 2% by nmr analysis of these added materials, compared to an internal area reference added during the distribution step. All nmr tubes were stored at −78°.

The seed described above, containing 20 units of butadiene-d_6, was used to simplify reaction variables, as follows. First of all, it was found that the ethyllithium was essentially consumed at monomer-to-initiator ratios of 3 or 4 in benzene, thus guaranteeing the absence of any ethyllithium at a 20:1 ratio. Secondly, an oligo(butadienyl)lithium of this chain length can be assumed to be associated in dimers while lower chain lengths have been stated to occur in higher aggregates.[6-8] Finally, the microstructure of polybutadiene has been stated to become constant at chain lengths of 20 units or higher.[6-8]

Hydrolysis and "Pseudotermination." To study the effect of removing the lithium from the active chain end, two methods were tried. These were hydrolysis and "pseudotermination." Hydrolysis was accomplished, as usual, by addition of water to the original reactor, from which a duplicate nmr tube was previously filled with the active material, followed by several rinsings with water, and drying over molecular sieves. By this method the lithium was substituted by a proton, but other complications arose. Thus, the nmr spectra were complicated by several simultaneous factors, *i.e.*, possible loss of volatile components, and changes in the structure of the chain-end unit. Furthermore, as will be seen later, hydrolysis actually enriches the chain end in vinyl content relative to in-chain microstructure.

In contrast, "pseudotermination" afforded a more subtle method of removing the effect of the lithium. This method basically involved the addition of several units of butadiene-d_6 to the active protonic chain end, thus

$$\mathrm{CD_3CD_2[CD_2{-}CD{=}CD{-}CD_2]_{\overline{20}}[CH_2{-}CH{=}CH{-}CH_2]_{2.4}Li} \; + \;
\mathrm{5C_4D_6} \longrightarrow \mathrm{CD_3CD_2[CD_2{-}CD{=}CD{-}CD_2]_{\overline{20}}}\text{-}
\mathrm{[CH_2{-}CH{=}CH{-}CH_2]_{2.4}[CD_2{-}CD{=}CD{-}CD_2]_{\overline{5}}Li}$$

Hence no change was made in the medium other than the addition of five units of "transparent" butadiene-d_6 to the chain, thus separating the protonic units from the presence of the lithium.

A further advantage of this method was the ease with which the in-chain protonic absorptions in the pseudoterminated case could be assigned, based on information available in the literature,[9] or, in certain cases, by resorting to model compound comparisons.

Nuclear Magnetic Resonance Spectra. The nmr proton spectra were recorded on a Varian HA100 spectrometer equipped with a time-averaging computer and spin decoupler as well as on a Varian A60 spectrometer. Care was taken during both the recording and integration of the spectra to avoid saturation. When recording spectra of the samples coniaining ethers, the precaution was taken to record spectra initially at the lowest temperature in the range studied. Thereafter the temperature was incrementally increased and further spectra recorded. In this way the samples were warmed only sufficiently to ensure that initiation or propagation could ensue within a few hours. Thus side reactions could be controlled. Wherever discrete spectral changes occurred with an increase in temperature, a check was made to prove that they were reversible by lowering the temperature again.

Results and Discussion

Complexation with Monomer. A specific complex formed between the monomer and the metal should alter the electron density in the π bands of the monomer. This would have a major effect on the nmr spectrum of the monomer, resulting in changes in both the resonance frequency of the monomer protons and their spin–spin coupling constants. A study of 0.2 *M* butadiene spectra in the presence and absence of poly(perdeuteriobutadienyl)lithium (also 0.2 *M*), in benzene-d_6 showed no difference between the two. Even when toluene-d_8 was used as a solvent and the temperature was reduced to −80°, the monomer spectrum was still insensitive to the added active chains. This means that, if a complex does exist, it must necessarily be in very low concentration, *i.e.*, <1% assuming a slow interchange rate relative to the time scale of the measurement. This is substantiated by the uv spectroscopic measurements by Evans and Worsfold[10] of the rate of reaction between styrene and poly(butadienyl)lithium, both in the presence and absence of butadiene. They found the two rates to be identical.

The idea of orientation of the incoming monomer, however, is not without merit, for even in simple collision theory, the highly polar carbon–lithium bond must play some directive effect on neighboring or colliding molecules which possess a dipole moment.

Assignment of Chain-End Peaks. Figure 5 shows the nmr proton spectra of the active and "pseudoterminated" chain of 22-unit long poly(butadienyl)lithium in benzene-d_6. The microstructure calculated from Figure 5ii or from the in-chain peaks of Figure 5i is 91% 1,4 and 9% 1,2. This compares well with published values for similar systems. There are three additional peaks, in Figure 5i, which have been denoted as α, β, and γ. The following results aid in their assignment. (1) They disappear on "pseudotermination" and reinforce the in-chain peaks. This indicates that they are the peaks belonging to those protons closest to the lithium. (2) The α peak occurs at

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(6) H. S. Makowski and M. Lynn, *J. Macromol. Sci., Chem.*, **1**, 443 (1966).

(7) H. S. Makowski and M. Lynn, *J. Macromol. Sci., Chem.*, **2**, 683 (1968).

(8) H. S. Makowski, M. Lynn, and A. N. Bogard, *J. Macromol. Sci., Chem.*, **2**, 665 (1968).

(9) H. Y. Chen, *Rubber Chem. Technol.*, **41**, 47 (1968).

(10) A. F. Evans and D. J. Worsfold, *Makromol. Chem.*, **85**, 273 (1965).

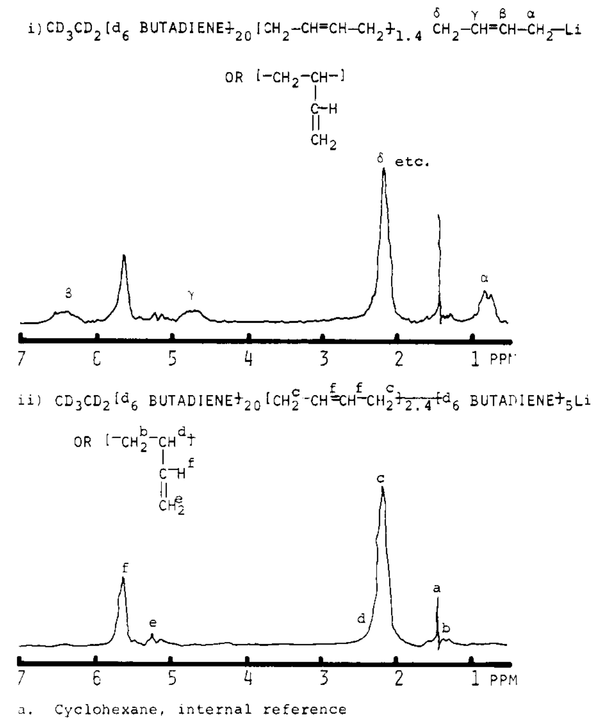


Figure 5. (i) 100-MHz nmr spectra of poly(butadienyl)lithium in benzene-d_6; (ii) after pseudotermination.

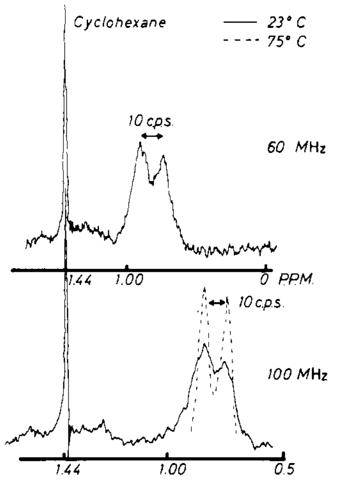


Figure 6. α absorption of poly(butadienyl)lithium (using "seed").

about δ = 0.8 ppm or about 1.2 ppm upfield of the allylic methylene of the in-chain units. Shifts of similar magnitude are experienced by the methylene adjacent to the lithium in alkyllithium compounds, relative to the corresponding alkanes. (3) The α peak is a doublet and not two separate peaks. This is shown in Figure 6 by the effect of spectrometer frequencies. Spin coupling with the β proton would require a doublet in this case. (4) The ratio of the areas of the α:β:γ peaks are 2:1:1 within an error of 4%, suggesting two protons for the α absorption and one each for the β and γ absorptions. (5) The spin decoupling of the β from the α and γ absorptions is shown in Figure 7, demonstrating that the α and β protons are on adjacent carbons and similarly that the β and γ protons are on adjacent carbons. (6) Hydrolysis by water results in the apparent disappearance of the α, β, and γ peaks and the formation of a new peak in the area (1.5–1.7 ppm) where the allylic methyl peak is expected. It consists of two overlapping doublets in the form of an unsymmetrical triplet.

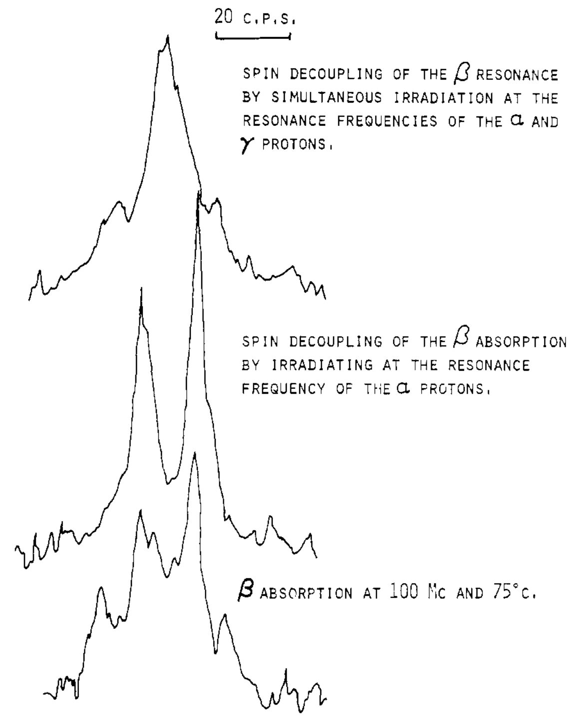


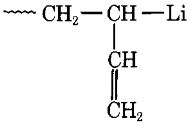
Figure 7. Spin decoupling of β absorption of poly(butadienyl)lithium.

Evidently the cis and trans forms of the hydrolyzed chain-end methyl show a small difference in peak position, just as in the case of the methyl group in the *cis*- and *trans*-2-pentenes (the allylic methyl of *cis*-2-pentene is at 1.53 ppm while that of *trans*-2-pentene occurs at 1.59 ppm). (7) In the initiation of the chain the first peaks to appear are the α, β, γ, and δ peaks.

On the basis of the above evidence, the α, β, and γ absorptions are therefore best assigned to the first, second, and third carbons, respectively, nearest the lithium.

The spectrum of an oligomeric butadienyllithium (Figure 8) ($x_n{}^* = 2.6$, 80% ethyllithium-d_5 consumed) [x_n = number-average number of units per chain, where $x_n = 1$ + number of in-chain units. The number of in-chain units for butadienyllithium = area of in-chain peaks $-\frac{1}{2}$ (area of $\alpha + \beta + \gamma$)] appears to be very similar to the spectrum observed for the polymeric species. Pseudotermination of this oligomeric chain (Figure 8i) again causes the α, β, γ, and δ peaks to disappear and reinforce the in-chain peaks. Evidently the structure of the active chain-end unit is not changed by such factors as the presence of a small excess of ethyllithium-d_5, the low molecular weight, the higher concentration of active centers, or any difference in the association state (expected at these low molecular weights). The poly(butadienyl)lithium prepared with the "seed," is known to be dimeric, while the low molecular weight species is reported to be unusually highly associated.[6-8]

Based on the foregoing results it is seen that the spectra best fit a chain-end structure of the type ~~~~ CH_2—CH=CH—CH_2—Li. If the chain end had some contribution from the 1,2 structure



$$\sim CH_2-\underset{\underset{CH_2}{\overset{\|}{CH}}}{CH}-Li$$

then the secondary α proton could be expected to be found slightly downfield of the observed primary α proton,

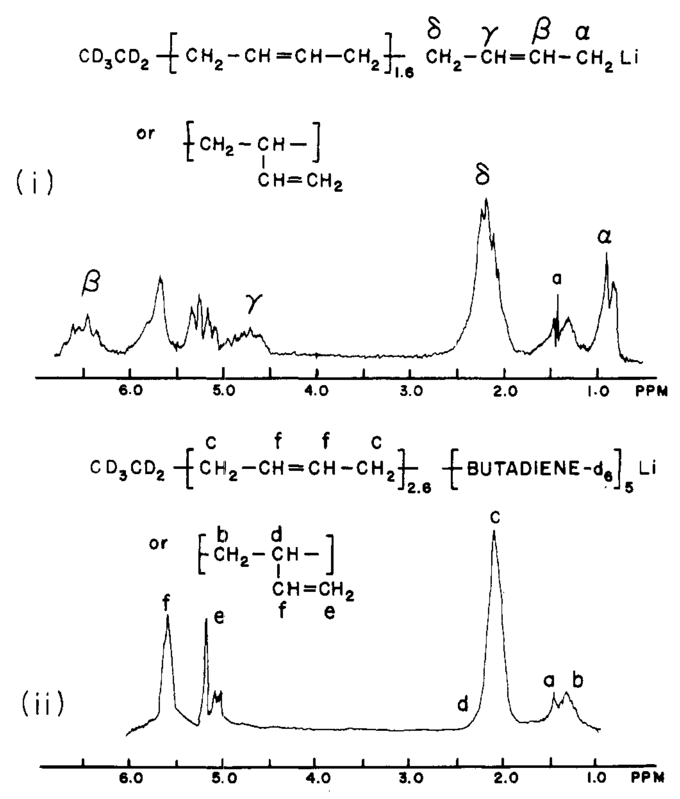


Figure 8. (i) Poly(butadienyl)lithium spectrum (low molecular weight) in benzene-d_6 (100 MHz); (ii) after pseudotermination.

with new γ absorptions close to, but upfield of, the observed γ absorption. The α:γ area ratio would approach 1:2 instead of 2. This indicates that a 1,2-type chain end is improbable. Another structural type which can be ruled out is the π-allyllithium chain end (Figure 9) having a separate existence within the time scale of the experiment. In that case, a higher upfield position would be expected for the γ proton. Furthermore, the double-bond character in the resultant α–β bond would lead to two nonequivalent α protons, while the γ proton resonances would be expected to show large cis,trans differences. Since none of these were observed, it seems evident that there cannot be a substantial concentration of π-allyl chain ends, at least not more than 1 or 2%. The best conclusion therefore is that the chain end is predominantly σ-bonded, with the lithium attached to the α-carbon, and that, within experimental limits (1%), this is the only structure present.

Mechanistic Interpretations. In view of the above results on the structure of the chain-end units, it is necessary to propose a mechanism which reconciles the existence of virtually 100% 1,4 chain ends with the observed 1,2 content of in-chain units. Thus it can be computed from Figure 5 that the in-chain units have a 9% 1,2 structure, and that, after pseudotermination, the in-chain units still have a 9% 1,2 content. This is even more strikingly shown in the low molecular weight butadienyllithium (Figure 8) where the in-chain units are about 45–50% 1,2. Here the addition of perdeuteriobutadiene to the 1,4 σ-bonded chain end still results in 45% 1,2 enchainment of that unit. Hence it appears that, in the process of adding the butadiene-d_6, some of the 1,4 protonic chain ends must have been converted into 1,2 in-chain units. A logical conclusion is that there must be some equilibrium present which modifies the 1,4 chain end either into a 1,2 form or a π-allyl form prior to reaction with the next monomer molecule. Either of these equilibria would associate the lithium with the γ carbon, thus explaining any addition at this γ carbon.

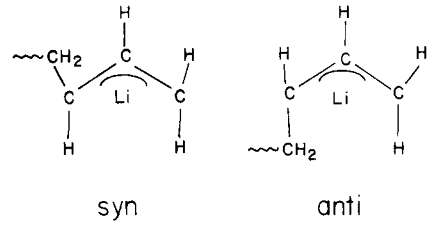


Figure 9. π-Allyl structures of chain ends.

Since no contribution of the 1,2 or π-allyl species was observed in the nmr spectra of the active chain end, it is reasonable to suppose that any such equilibrium must be very rapid relative to the time scale of the measurements. In an effort to freeze out the species involved in such a rapid equilibrium, low-temperature spectra of the chain end in toluene-d_8 were recorded. Unfortunately severe peak broadening resulted and no conclusion could be reached. Raising the temperature from 23 to 75° led to a sharpening of the peaks, but very little chemical shift. This indicated that, if any rapid equilibrium did exist, it had either a very low enthalpy associated with it, or, more plausibly, the species in equilibrium with the essentially localized 1,4 chain end is in very low concentration. It will be possible to discuss this question in more depth in connection with the isoprenyl chain end in the following publication.

A further point to notice is the unusually high 1,2 microstructures noted by Makowski and Lynn.[6-8] Figure 8 corroborates the findings of these authors and shows that their high 1,2 microstructure is not an artifact resulting from hydrolysis of the chain end, but is present in the in-chain units of active as well as pseudoterminated chains (x_n protonic = 1.6–2.6). The above authors suggested that this change in microstructure might correlate with differences in the association state of the butadienyllithium. However, a comparison of Figures 5 and 8 shows no basic difference in the structure of the active chain-end units between the low (x_n = 2.6) and high (x_n = 22.4) molecular weight species. A closer examination of the active chain-end structure during propagation of the first few units does show a downfield shift of about 22 cps in the α doublet. This shift should not change the structural interpretation. It could result, rather, from two possible effects: (1) reduced solvent shielding of the α protons as the chain grows and surrounds the association structure, a minor effect, and (2) a rapid equilibrium between the associated organolithium species, which are changing in concentration as the ethyllithium is reacting. Both of these points will be discussed more fully in the following publications.

Acknowledgments. We acknowledge the financial support, during the course of this research, of two of the authors, by the General Tire & Rubber Co. of Akron, Ohio (R. D. S.), and the Bridgestone Tire and Rubber Co. of Japan (R. S.). We also acknowledge the kind assistance of Mr. E. R. Santee in obtaining the 100-MHz data as well as in their interpretation.