Structure of Oligomeric Polybutadienyllithium and Polybutadiene

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ABSTRACT: The ^{1}H nmr spectra of a number of adducts of *tert*-butyllithium and butadiene of different $\overline{\mathrm{DP}}$'s have been examined. Specifically deuterated butadienes were synthesized and used as an aid in the interpretation of spectra. The spectra observed except for that of the 1:1 adduct are rather complex because of penultimate effects. The spectra show that, as in the corresponding study with isoprene, cis and trans forms of the lithium-bearing unit exist. No separate 1,2 structure can be found. The equilibrium cis/trans ratio depends on the solvent. The microstructure of terminated oligomers of butadiene have been examined as a function of reagent concentration. It is found that although abnormally high 1,2 contents are formed in hydrocarbon solvents if high concentrations are used, the oligomers have the same structure as high polymers if formed in dilute solution. The implications of these results to the mechanism of stereospecific polymerization are discussed.

The structure of oligomeric polyisoprenyllithium $R(C_5H_8)_nLi$ has already been studied by nmr techniques, and much information has been derived on the structure of the terminal active unit.[1,2] It would be desirable to examine also similar spectra of the adducts of butyllithium and butadiene. However, attempts to study the equivalent butadienyllithium are generally hampered by the presence of the proton in place of the methyl group of isoprene.[3] The extra hydrogen causes spin coupling between hydrogens in all four positions, with a resultant increase in the complexity of the spectra. By the use of suitably deuterated butadienyllithium this difficulty may be circumvented and well-resolved spectra can be obtained. The chosen deuterated butadiene starting material in this work is 1,1,3,4-tetradeuteriobutadiene, in which the residual two hydrogens are separated by three carbons. Only long-range proton–proton and deuterium–proton coupling occur in the oligomers, and the coupling constants are sufficiently low that no fine structure appears. Some experiments have also been made with a pentadeuteriobutadiene, with the protons unequally shared among the three positions, and also with 2,3-dideuteriobutadiene.

If the results are to be related to the stereospecificity of the lithium-based polymerization of dienes, the microstructure of the oligomers produced must be known. For isoprene these have much the same microstructure as found in high polymers,[4] but many years ago, Ziegler[5] found that the first butadiene unit adds 1,2 in hydrocarbon solvents. Later work[6] has suggested that abnormally high 1,2 contents occur up to surprisingly high molecular weights (>1000), although the high polymer has a predominantly 1,4 structure in this system. As it appeared unlikely that end effects could persist as long as was suggested, this point also has been reexamined.

Experimental Section

The specific deuteriobutadienes were prepared from the corresponding chlorobutadienes by the method of Craig and Fowler,[7] and were purified *via* the sulfone. Perdeuteriobutadiene was prepared from a commercial sample of hexachlorobutadiene. 1,1,3,4-Tetradeuteriobutadiene was prepared from the corresponding tetrachloro compound,[8] which was obtained from hexachlorobutene, the dimer formed from trichloroethylene by radical reaction.[9] The tetrachlorobutadiene could be separated by fractional distillation into two close-boiling isomers, presumably the cis and trans forms. After conversion to the deuterated butadiene both gave equimolar mixtures of both cis and trans isomers. Pentadeuteriobutadiene was prepared from the corresponding chloro compound, which is formed in the aluminum trichloride dimerization of trichloroethylene.[10] The product contained a mixture of the possible isomers, about 60% with the hydrogen in the 2 positions and the remainder shared between the two 1 positions. 2,3-Dideuteriobutadiene was prepared from 1,4-dichlorobutyne.[7] The purity of these compounds was checked by nmr and mass spectrometric analysis. In general, about 98% of the expected deuteration was achieved.

The oligomers were prepared in much the same fashion as were those of isoprene.[2] Most products were made with *tert*-butyllithium-d_9 to avoid masking the α-proton absorption. For the oligomers of higher $\overline{\mathrm{DP}}$, the first part of the chain was normally made with the hexadeuteriobutadiene, and only the end units were of the hydrogen-containing monomer. This decreased as far as possible the contribution to the spectra of the nonliving units which otherwise would be objectionably large.

It was found that the 1:1 addition product of *tert*-butyllithium with butadiene was insoluble in benzene below room temperature, and the reaction mixture set to a thick paste. Warming to 40° caused the paste to become fluid again.

The spectra were all measured at 100 MHz. Solutions were normally about 0.5 *M*.

Results

In the original study[6] showing that the microstructure of the polymer varies with the length of the chain in the early stages of growth, it is noticeable that the monomer concentration was held constant at 4 *M*, and to obtain the lengthening of the chain the initiator concentration was lowered. This leads to doubt if the change in structure was because of the lengthening chain, or because of the change in concentration of growing chains. This latter point was considered by Hsieh, *et al.*,[11] in a later publication, but the range of concentration covered was not sufficient to show the full effect.

In Table I are listed the 1,2 contents, measured by nmr, of three oligomers prepared in cyclohexane at room temperature with similar monomer/initiator ratios, but with greatly

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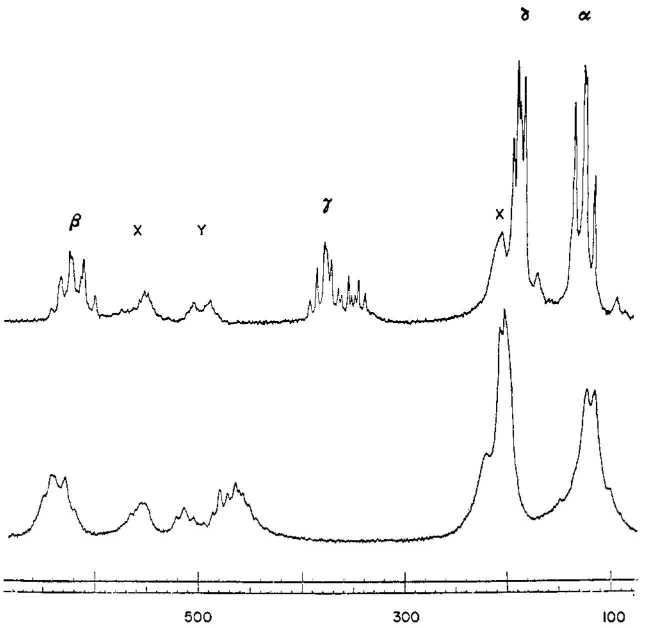


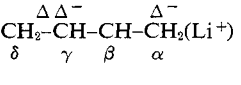
Figure 1. ^{1}H nmr spectra of the adduct of C_4D_9Li and normal butadiene ($\overline{DP} \sim 1.2$) in 50/50 (v/v) methylcyclohexane–tetrahydrofuran (top) and benzene (bottom): (α, β, γ, δ) signals from lithium-bearing unit; (X, Y) signals from second ("dead") unit in oligomer of DP = 2. Scale, hertz downfield from TMS at 100 MHz.

TABLE I
MICROSTRUCTURE OF TERMINATED OLIGOMERS OF $\overline{DP} \sim 9$ PREPARED AT DIFFERENT DILUTIONS AND A ROUGHLY EQUAL MONOMER INITIATOR RATIO IN CYCLOHEXANE

[*tert*-BuLi]	DP	% 1,2
0.005	8.2	7.0
0.05	9.5	10.3
0.5	9.2	47

differing total concentrations. From this table it is evident that the factor governing the 1,2 content of the polymer is the concentration of reagents, particularly that of the lithium compound. At a concentration of the latter comparable to that used in the formation of high polymers, even oligomers have a low 1,2 content. The abnormally high 1,2 contents observed under conditions where oligomers are normally formed decrease rapidly in the concentration range 0.5–0.05 *M*.

The nmr spectrum of an almost 1:1 adduct of *tert*-butyllithium-d_9 and normal butadiene in benzene is shown in Figure 1, together with the spectrum after transferring to a 1:1 mixture of methylcyclohexane-d_{14} and THF-d_8. In the THF-containing solvent, the spectrum is well resolved and it is possible to make a plausible assignment of the shifts and coupling constants, as was also done by Glaze.[12] The relative positions of the peaks are as found by Morton, *et al.*,[13] for higher molecular weight species. The spectrum is interpreted[1,2] as being caused by a mixture of cis and trans structures, basically 1,4 addition products of *tert*-butyllithium and butadiene



$$\underset{\delta}{C_4D_9\text{–}CH_2}\text{–}\overset{\Delta\,\Delta^-}{\underset{\gamma}{CH}\text{–}\underset{\beta}{CH}}\text{–}\overset{\Delta^-}{\underset{\alpha}{CH_2}}(Li^+)$$

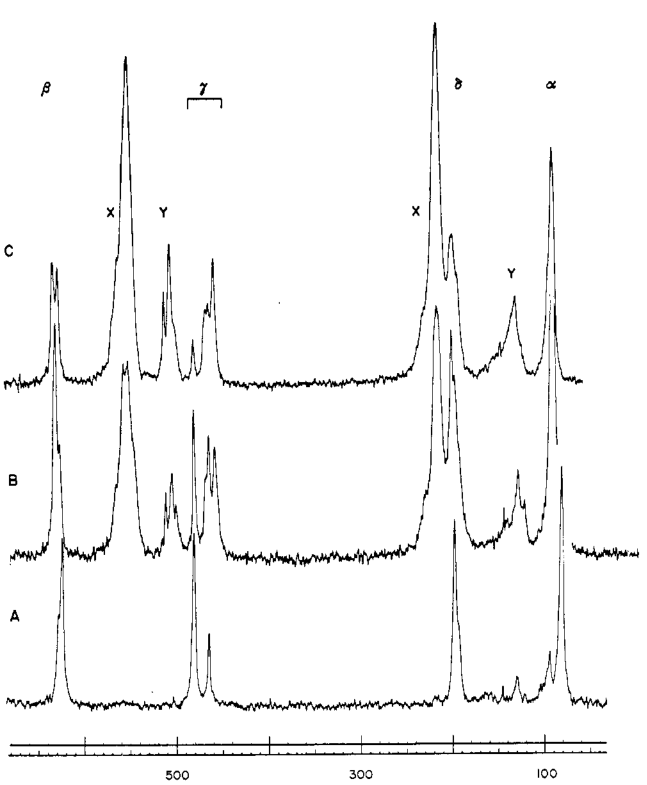


Figure 2. ^{1}H nmr spectra of oligomers $C_4D_9(C_4H_2D_4)_nLi$ formed from 1,1,3,4-tetradeuteriobutadiene in benzene at room temperature; $\overline{DP}$ in ascending order, ~1, ~2.1, ~3.2,: (X, Y) signals from (predominantly) 1,4 and 1,2 units in nonterminal monomer; (α, β, γ, δ) those from terminal (Li) units. Scale as in Figure 1.

TABLE II
CHEMICAL SHIFTS AND COUPLING CONSTANTS; 1:1 ADDUCT OF BUTADIENE AND *tert*-BUTYLLITHIUM

	δ, ppm			J, Hz	
	Cis	Trans		Cis	Trans
α	1.09	1.18	$J_{\alpha\beta}$	10	10
β	6.18	6.06	$J_{\beta\gamma}$	10	14
γ	3.40	3.68	$J_{\gamma\delta}$	7	7
δ	1.82	1.78			

[a] Solvent 1:1 methylcyclohexane–tetrahydrofuran 0°. Shifts downfield from tetramethylsilane.

From the chemical shifts most of the charge resides on the terminal (α) carbon atom (particularly in benzene) although some charge resides at the γ position. Restricted rotation about the β–γ bond leads to cis and trans isomers. The relevant data are shown in Table II. The nmr spectrum of this compound in benzene solution is far less well resolved, although it does resemble the spectrum in THF. The peaks attributed to the γ protons are far further downfield, and those attributed to the α proton are slightly upfield.

The spectrum of the mono adduct of *tert*-butyllithium with 1,1,3,4-tetradeuteriobutadiene in benzene solution is far better resolved; Figure 2. Although the α peak is single, the β, γ, and δ resonances are all double, but only the γ is resolved into two unequal peaks separated by 16 Hz in a ratio 2.6:1. This doubling of the peaks can again be interpreted as due to the cis and trans forms of the butadienyllithium. When the spectra of the higher adducts were measured, however, it was seen that as for isoprenyllithium, the higher oligomer γ resonances are shifted slightly upfield

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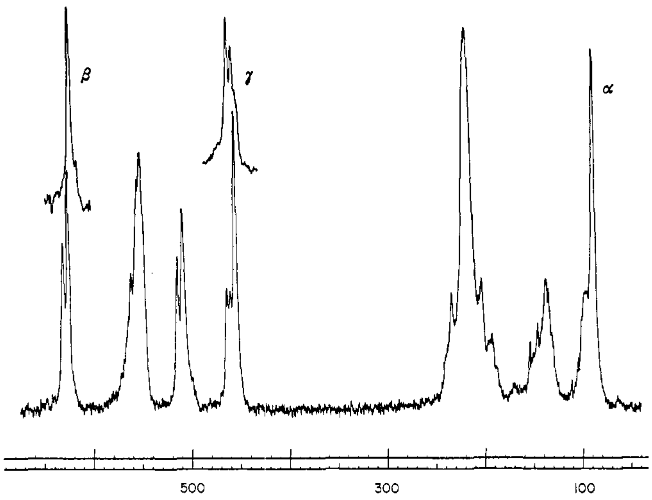

Figure 3. ^{1}H nmr spectra of an oligomer of $\overline{DP} \sim 6$ formed in benzene at ~0.5 M initiator. Inset, the β and γ signals of a similar product formed in dilute solution and then concentrated to about the same final concentration. Scale as in Figure 1.

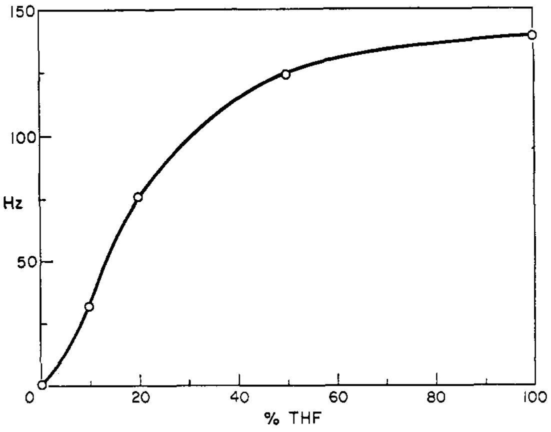

Figure 4. Upfield shift of the higher field γ signal in mixtures of hydrocarbon–tetrahydrofuran as a function of THF concentration.

Table III
Percentage of Low- and High-Field γ Signal in THF Mixtures

% THF	Ratio	Temp, °C
10	63:37	0
20	41:59	0
100	34:66	0
100	17:83	−40

(Figure 2). Unlike the isoprene case, however, the half-width remains small in adducts of DP > 1, and the γ resonance becomes complex in the spectra of oligomers of $\overline{DP} = 2$ and 3. These are necessarily a mixture of oligomers, the one of $\overline{DP} = 2$ being probably a mixture of monomer, dimer, and trimer in a ratio near 1:2:1.

At $\overline{DP} = 6$, such variation of chemical shift could be expected to have disappeared, and in fact the spectrum of an adduct of $\overline{DP} = 6$ is essentially the same as that of the adduct of $\overline{DP} = 10$. Nevertheless, it is seen from Figure 3 that the γ proton still gives a complex peak, not just the two peaks expected from a mixture of only cis and trans forms. The α peak appears single, although the close coincidence of residual hydrogens on the *tert*-butyl group gives the appearance of a shoulder. The β peak is double. The δ-proton absorption is too masked by protons in the "dead" units to be useful diagnostically.

Possible causes of this complex γ peak could be: (a) the presence of a separate and distinct 1,2 chain end, (b) the influence of penultimate units, (c) longer range (allylic) coupling. Cause c could be eliminated because the spectrum is unchanged if the pentadeuteriobutadiene described earlier is used as monomer. The absence of any separate active chain ends having a 1,2 structure in benzene solution was confirmed by adding three units of 2,3-dideuteriobutadiene to a three-unit chain. All the complex γ band was absent in the spectrum of this sample as expected if the structure is basically 1,4. A 1,2 structure would be expected to still show $=CH_2$ signals in this region because the group is γ to the C–Li bond in this configuration. To determine the effect of 1,2 structures in the penultimate units an adduct of $\overline{DP} = 6$ was prepared at a concentration of 10^{-2} molar, where the 1,2 structure content in in-chain units would be low. This solution was then concentrated to the normal range, and portions of the spectrum of this adduct are also shown in Figure 3. Significant differences can be seen between this spectrum and the ones obtained from preparations at 0.5 M initiator, where the in-chain 1,2 content is ~47%. The two low-field peaks in the γ-proton band have grown greatly at the expense of the third peak. This can be explained by attributing the lower field pair of peaks to the cis and trans forms of the ultimate unit preceded by a 1,4 unit and that the third peak is caused by both the cis and trans forms of the ultimate unit when preceded by a 1,2 unit. This third peak is of course large when the polymer is formed at high concentration. Because of the complexity of the absorption, and the small peak separation, a definite measurement of the proportion of cis to trans form in benzene for $\overline{DP} = 6$ is not possible. The lowest field peak appears still to be larger in the inset spectrum in Figure 3, as in the 1:1 adduct. A comparison of the β region for the polymers containing different amounts of in-chain 1,2 units indicates that this signal also is sensitive to penultimate unit structure.

In solutions containing THF, the 1:1 compound from tetradeuteriobutadiene shows double absorption for all four protons, showing clearly the presence of the cis and trans forms. For all oligomers the γ peaks are upfield of their position in benzene, the greater the proportion of the THF the greater the shift. This is shown in Figure 4. In the 1:1 compound the ratio of low-field to high-field absorptions is 60/40 in 50% THF at 0°. In the oligomer of $\overline{DP} = 6$ this ratio changes with the THF content as in Table III. Once more a penultimate effect on the chemical shifts appears. In the hexamer, the lower field γ absorption appears as two peaks separated by 14 Hz, while the higher field absorption shows two peaks with only a 4-Hz separation (Figure 5). Again when the polybutadienyllithium is made in dilute benzene solution to decrease the 1,2 content in the "dead" units, on transferring to THF one of each of these pairs of peaks decreases significantly. This was confirmed by adding to a standard preparation of an oligomer of $\overline{DP} = 6$, to which had been added THF, further $C_4H_2D_4$ to increase the proportion of 1:2 penultimate structure. The proportion of the other peak of the pairs was then increased.

In solutions containing 10% THF the β-proton absorption of the hexamer is split into cis and trans signals, which appear complex because of the effect of penultimate structure. In solvents richer in THF this detail is lost, and only shoulders

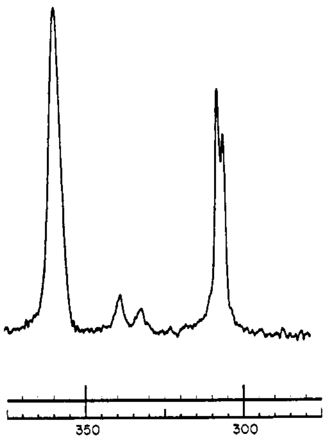

Figure 5. ^{1}H nmr spectrum of the γ region at $-40°$ of an oligomer of $\overline{\text{DP}} \sim 6$ formed in benzene at initiator concentration $\sim$0.5 M and transferred to THF-d_8. Peak at δ 360 Hz caused by residual undeuterated THF. Scale as in Figure 1.

indicate the presence of more than one structure. Similarly, the α peak is little affected by structure.

Discussion

(a) Benzene (or Other Hydrocarbon) Solutions. The nmr results on the lithium compounds are qualitatively similar to those reported earlier for isoprene adducts. Both cis and trans 1,4 forms of the active center can be detected, but no separate 1,2 structure. With both monomers, judging by the signals from the γ protons, one form (the one giving a lower field absorption) predominates. These results apply, of course, to the aggregated form in which the vast majority of the molecules exist in hydrocarbon solvents. Differences appear in the structure of terminated oligomers if the behavior of isoprene is compared with that of butadiene. With the former monomer, the oligomers prepared at high initiator concentration do not differ sensibly in microstructure from high polymers formed at much lower initiator concentrations. Butadiene, however, forms oligomers with abnormally high 1,2 contents (and predominantly trans configuration in the 1,4 units)[6] if the addition is carried out at the high concentrations normally used to form these products. Only if the oligomerization is carried out at dilutions comparable with those used in normal polymerization experiments does the structure of the oligomer become essentially that of high polymer (low 1,2 content; evenly mixed cis/trans ratios in the 1,4 units). These results suggest that in butadiene polymerization, but not with isoprene, the mechanism changes at high initiator concentration (I_0). Under normal polymerization conditions ($I_0 < 10^{-2}$ M), the monomeric dissociation products of the predominantly aggregated lithium compounds appear to carry most of the reaction.[14] Because of the low reaction order ($\sim ^1/_4$) in active centers (total polybutadienyllithium) the propagation rate increases only slightly as the concentration of active centers is increased. A *direct* reaction of monomer with the polybutadienyllithium aggregates would be first order in active centers and could rapidly become important at very high polybutadienyllithium concentrations. This type of reaction could plausibly result in high 1,2 contents in the polymer formed because the γ position will be more exposed. The α position will tend to be buried at the aggregate center and less available for monomer attack. The difference in behavior with isoprene and butadiene could be caused by a much more facile dissociation with the former monomer. We have observed[15] that polyisoprenyllithium aggregates are much more easily dissociated than those of polybutadienyllithium.

The cis/trans ratio in the terminated oligomers and polymers is less easy to rationalize in terms of the structure of the active center. If we assume that the low-field γ signal in benzene corresponds to a trans configuration based on the assignments in THF, the 1:1 adduct has a marked preference (2.6:1, Figure 2) for this structure. Glaze[8] has provided evidence for the validity of this assignment. At $\overline{\text{DP}} = 6$, penultimate effects and the fact that the chemical shift difference between cis and trans structures is small make conclusions less sure. The low-field signal still appears larger in the spectrum in which penultimate effects have been minimized (Figure 3), and it seems reasonable to assume that the active center still prefers a trans configuration. This corresponds to the preference in the completed polymer formed under conditions close to those under which the nmr spectrum was observed. It cannot be assumed that the 1,4 structures even at this concentration were necessarily formed by direct reaction with the aggregates, and it is even less probable in the case of polymerizations carried out at $\sim 10^{-3}$ M initiator. A knowledge of the preferred configuration of the lithium-bearing unit in its nonassociated state would be necessary before a meaningful comparison with polymer microstructure could be made. Unfortunately, this is experimentally unrealizable.

The possibility was raised in the earlier study on isoprene[2] that isomerization might be slow and the configurational preference observed in the aggregates retained in the dissociated state. This hypothesis would be difficult to maintain if the same γ assignments used here are used in the case of isoprene, since it would correspond also to a preference for the trans form of the active center in its aggregated state in benzene. This hardly correlates with the highly cis microstructure of the polymer. In fact, if this assignment is accepted, in polymerizations carried out in dilute hydrocarbon solution at room temperature, the microstructure of polybutadiene or polyisoprene correlates better with the configurational preference of the active center in THF. These results raise the possibility that the monomeric form of the lithium compounds in hydrocarbons resembles more the monomeric (solvated) form known to exist in ether solvents.

(b) THF-Containing Solvents. On addition of THF to hydrocarbon solutions of polybutadienyllithium, the high-field γ signal becomes stronger as more THF is added. The low- and high-field γ signals can be assigned to trans and cis structures on the basis of coupling constants in the 1:1 adduct (Table II) in the THF. Glaze[12] has also suggested this assignment. Isomerization from the benzene-stable form is, however, less complete with polybutadienyllithium than with polyisoprenyllithium. In the latter case only the high-field γ signal appears at equilibrium at all temperatures between -80 and 20°. The differences presumably reflect increased steric preference in isoprene compounds because of the methyl substitution. With increasing amounts of THF, the γ signals move upfield and the α signal moves downfield, but to a lesser extent (1.4 ppm upfield compared to 0.4 ppm downfield in pure THF). The major change in shift occurs in the region in which the aggregated species are known to become dissociated and replaced by THF-solvated species. This must be caused by charge redistribution to the γ position. A preference for the charge on the α position still remains in pure THF, which seems to be a characteristic of increased

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negative charge stability on less substituted carbon atoms. In allyllithium[16] the two positions are equivalent, but in crotyllithium[17,18] substitution makes the γ position less favored for charge. Nevertheless, the increased charge at the γ position leads to high 1,2 contents in the polymer formed.

It is possible to suppose, as have other authors,[13] that a delocalized structure exists only in THF and that the benzene-stable form of the active center is a separate covalent form. The spectral shifts observed in THF mixtures would result as long as equilibration was rapid on the nmr time scale. It seems to us more plausible to regard the changes as caused by variable charge delocalization as the local environment is changed. Even in benzene solution there is evidence for some charge at the γ position, and the appearance in both hydrocarbon and ether solvents of similar ultraviolet absorption bands[19] argues against a covalent form in the former solvents. The evidence in diethyl ether solutions at -70° for a weak γ absorption at about the same position as in benzene, as well as the expected stronger upfield absorption,[13] could have other explanations than slow equilibration between covalent and ionic forms. Apart from the danger inherent in analysis of very weak signals in such systems, the presence of residual amounts of aggregated structures not completely destroyed by ether can be suggested, *i.e.*, slow equilibration between associated and dissociated forms under these conditions. This is evidently not the case with the stronger base THF, for even at -80° no extra γ signals are observed. In addition, the γ absorption still drifts upfield after more THF has been added than is required to dissociate the aggregates.

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Degree of Association of Polystyryl-, Polyisoprenyl-, and Polybutadienyllithium in Hydrocarbon Solvents

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ABSTRACT: The degrees of association of living polymers of styrene, butadiene, and isoprene (Li counterion) have been evaluated principally by means of light-scattering measurements in cyclohexane. Some determinations were made using concentrated solution viscosities. It was confirmed that the association number was two for the styrene compound and four for the butadiene and isoprene polymers. The latter polymer shows partial dissociation to dimers at low concentrations. The difficulties encountered in interpretation of concentrated solution viscosity measurements in these systems are described. It is suggested that these difficulties are responsible for the discordant values of association number found in the literature.

The active chain ends of polymers formed by the action of lithium alkyls on hydrocarbon monomers are associated in hydrocarbon solution.[1–6] There has, however, been disagreement concerning the degree of association. Some reports suggest that it is twofold in all cases,[6] but others state that it varies with the monomer involved.[7–10] Similar disagreements existed in the past about the kinetic order of the propagation reaction in these polymerizations. A half-order with respect to the active chain ends in all cases[11] has been suggested, but other studies found that the order varied with the monomer involved.[2–5,7–9] By the application of improved techniques these differences have been resolved and, it is more generally accepted that the order varies with the monomer.[12]

Unfortunately, whereas in the past there was general agreement that association number and kinetic order were connected, at present there exists, in some reports, a discrepancy.[6,12] Until this is resolved the proposed mechanism of the reaction must be in doubt, as the only detailed mechanism suggested[1] involves the monomeric dissociation product of the aggregates as active species in polymerization. This requires, for a labile equilibrium, that the kinetic order be $1/n$ if the association number is n.

The generally accepted orders for the propagation reaction in the polymerization of styrene, isoprene, and butadiene initiated by lithium alkyls in hydrocarbon solvents are one-half for styrene and one-quarter or less for the dienes. There is general agreement that the degree of association for polystyryllithium is two. A previous report from these laboratories suggested that for polyisoprenyllithium the degree of association was between three and four and that equilibrium might exist between dimer and tetramer leading to a kinetic order close to one-fourth for the reaction.[10] This work has been repeated over a wider range of concentrations and ex-

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