^{1}H n.m.r. spectroscopy of the complexation of polybutadienyllithium by *N,N,N′,N′*-tetramethylethylenediamine[†]

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Partially deuterated oligomeric butadienyllithium was prepared both by capping a d-6 chain with d-4 monomer (1,1,3,4-tetra-deuterobutadiene) and by direct oligomerization of the d-4 monomer. The initiator, sec-butyllithium, was used at low concentration to minimize the level of vinyl addition and the *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was added only after polymerization was complete. The introduction of TMEDA causes the γ proton resonances of the allylic carbanion to move upfield and the β resonances downfield, corresponding to an increase in the extent of charge delocalization. With ratios of TMEDA: Li below 1:1 the carbanions having the *cis* conformation are complexed preferentially.

Keywords Butadiene; polybutadienyllithium; *N,N,N′,N′*-tetramethylethylenediamine; nuclear magnetic resonance; microstructure; anionic polymerization

INTRODUCTION

When butadiene is polymerized by the use of organolithium initiators in hydrocarbon solvents the resulting polymer is predominantly enchained in a 1,4-sense. However, when electron donating substances such as ethers or amines are present, addition in a 1,2-sense becomes important. Details may be found in several reviews[1–3].

Another facet of importance in the anionic polymerization of butadiene is that the incidence of chain transfer with weak acids such as toluene is greatly increased by the presence of chelating bases such as *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)[4]. This constitutes the basis of a commercial process for the telomerization of butadiene although the mechanistic role of the TMEDA is not understood in any detail. It is known that complexation of the chain end of polyisoprenyllithium results in its conformation becoming exclusively *cis*[5] whereas in non-complexing hydrocarbon media the *cis*:*trans* chain end ratio is approximately 2:1[6]. No systematic study of the influence of TMEDA upon polybutadienyllithium seems to have been published.

Study of the n.m.r. spectrum of the anionic chain end of a polymer is inhibited by the dominance of the spectrum by the intense signals arising from the remainder of the chain. One means of obtaining strong signals from the anionic chain end was devised by Morton *et al.*[7]. They first prepared a polymer from d-5 ethyllithium and d-6 butadiene, having a *DP* of *ca.* 20 which they 'capped' with an average of 2.4 units of ordinary protic butadiene. Another possible solution to this problem is to employ polymers of very low *DP*; taken to the extreme of $DP = 1$ the 1:1 adduct of initiator and monomer may be employed. A number of such studies have been made[8–11] and their results are summarized in *Table 1*. It is important to note, however, that the microstructures of very short chains may not be truly representative of those of longer

Table 1 ^{1}H n.m.r. parameters for polybutadienyllithium and model compounds

Compound	Solvent	Conformer	δ_α	δ_β	δ_γ	% *cis*	Ref.
$tC_4D_9CH_2CHCHCH_2Li$	C_6D_{12}	–	0.9	6.2	4.5	25	8
$tC_4D_9CH_2CHCHCH_2Li$	$C_6H_5CH_3$	*trans*	0.77	6.06	4.64		9
		cis	0.80	6.11	4.49	24	
$C_2D_5(C_4D_6)_{20}(C_4H_6)_{2.4}Li$	C_6D_6	–	0.8	6.3	4.7		7
$tC_4D_9CH_2CHCHCH_2Li$	C_6H_6	*trans*	0.8	6.3	4.85		10
		cis	0.8	6.3	4.65	28	
$tC_4D_9CH_2CHCHCH_2Li$	$C_6H_{11}CH_3$/	*trans*	1.18	6.06	3.68	40(0°C)	10
	THF (50:50 v/v)	*cis*	1.09	6.18	3.40		
$tC_4D_9(CH_2CHCHCH_2)_6Li$	d8-THF		0.9	6.2	4.6	66(0°C) 83(–40°C)	10
$C_4H_9CH_2CHCHCH_2Li$	d8-THF	*trans*	1.29	5.98	3.63	42(18°C)	11
		cis	1.19	6.10	3.35		
$C_4H_9CH_2CHCHCH_2Li$	$(C_2D_5)_2O$	*trans*	1.04	5.97	4.06		11
		cis	1.01	6.08	3.89	25	

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chains, particularly with polydienes. Makowski and Lynn[12] were probably the first to draw attention to the dependence of microstructure upon chain length. By way of illustration, the 1:1 adduct of butadiene with tert-butyllithium is reported as 42% *cis* at −18°C by Glaze *et al.* in pure THF and as 40% *cis* by Bywater *et al.*[10] in equimolar THF/methylcyclohexane at 0°C. The latter authors reported, however, that the oligomer ($DP = 6$) is 66% *cis* in pure THF at 0°C and they noted also that the γ resonances shift slightly upfield with increasing *DP* to a limiting position reached by (or before) $DP = 6$. Since the four allylic protons in the anionic chain end of polybutadienyllithium are all inequivalent, the n.m.r. spectrum is very complex. This difficulty can readily be circumvented by the use of 1,1,3,4-tetradeuterobutadiene in which the two residual protons are separated by three carbons, resulting in negligible spin–spin coupling[10].

EXPERIMENTAL

sec-Butyllithium was prepared in n-hexane under high vacuum by the reaction of sec-butylchloride with excess lithium dispersion. The crude product was recovered by filtration of the solution followed by evaporation of the hexane and purification was effected by distillation under high vacuum. The pure product was dissolved in fresh hexane and sealed into ampoules fitted with break-seals. The organolithium concentration was determined by hydrolysing the contents of one ampoule and titrating with standard hydrochloric acid.

TMEDA was refluxed for 2 h over potassium metal and distilled: the fraction, b.p. 121°C/760 mm Hg, was stored over sodium–potassium alloy under high vacuum. Analysis by g.l.c. revealed that the only detectable impurity was *ca.* 0.6% trimethylethylenediamine; this quantity was deemed to be insignificant for the purposes of the present work.

1,1,3,4-d4-butadiene and d6-butadiene were prepared following the procedures described by Craig and Fowler[13]. The crude products were purified by brief contact with solvent-free n-butyllithium. Caution should be exercised in undertaking these syntheses. One batch of crude d6-butadiene exploded violently shortly after isolation. It might have been that an unusually large amount of by-products such as butadiyne, buteneyne or 1,2-butadiene was present.

Solutions for ^1H n.m.r. spectroscopy were prepared using the apparatus shown in *Figure 1*. This was attached to the vacuum line by means of socket A. After pumping for 2 h to remove any adsorbed water, the break-seal on ampoule B was shattered using the magnetic hammer C and the contents, a solution of sec-butyllithium in n-hexane (*ca.* 2.5 cm^3, 0.4 molar), were allowed to drain into the main vessel whereupon the hexane was distilled out. Hexadeuterobenzene (10 cm^3), dried over Na/K alloy, was distilled in and constriction D sealed. Butadiene-d-4 (1 cm^3) was introduced by shattering the break-seal on ampoule E and polymerization was allowed to proceed at ambient temperature for 24 h. After reconnection to the vacuum line by socket F, break-seal G was ruptured and the benzene was removed by distillation. Fresh d6-benzene (1 cm^3) was introduced and the vessel was sealed at H. The required minute quantity of TMEDA was added from ampoule 1 (fabricated from capillary tubing) and after thorough mixing, the polymer solution was poured into the n.m.r. tube J through a porosity 1 sinter and the tube was sealed at K. Simple modification of this procedure enabled the synthesis of poly-d-6-butadienyllithium and its capping with a small quantity of the d-4 monomer.

^1H n.m.r. spectra were recorded on a Perkin Elmer R34 (220 MHz) instrument. Residual protic benzene served as internal reference.

RESULTS AND DISCUSSION

The relative proportions of 1,2- and 1,4-addition occurring when butadiene is polymerized by an organolithium initiator in a hydrocarbon solvent are very sensitive to the initiator concentration. Bywater *et al.* have reported[10] that when cyclohexane is used as solvent, the 1,2-content varies from 7% to 47% as the initiator concentration is changed from 0.005 to 0.5 molar. The results of our similar study in benzene solution are presented in *Table 2*. The values of the *DP* were obtained from g.p.c. measurements and the microstructure was determined from 220 MHz ^1H n.m.r. spectra. An illustrative example of the latter is shown in *Figure 2*. Following Chen[14], the in-chain resonances may be assigned (ppm from TMS): $-CH=$ (1,4-addition) 5.38, $=CHD$(1,2-addition) 4.93, $-CHD-$ 2.0δ. The sec-butyl initiator fragment gives signals at 0.84 (CH_3-), 1.29 (CH_2) and 1.09δ ($-CH$); comparison of the integrated intensities of in-chain and initiator signals permits an estimate to be made of the mean *DP*. It is clear

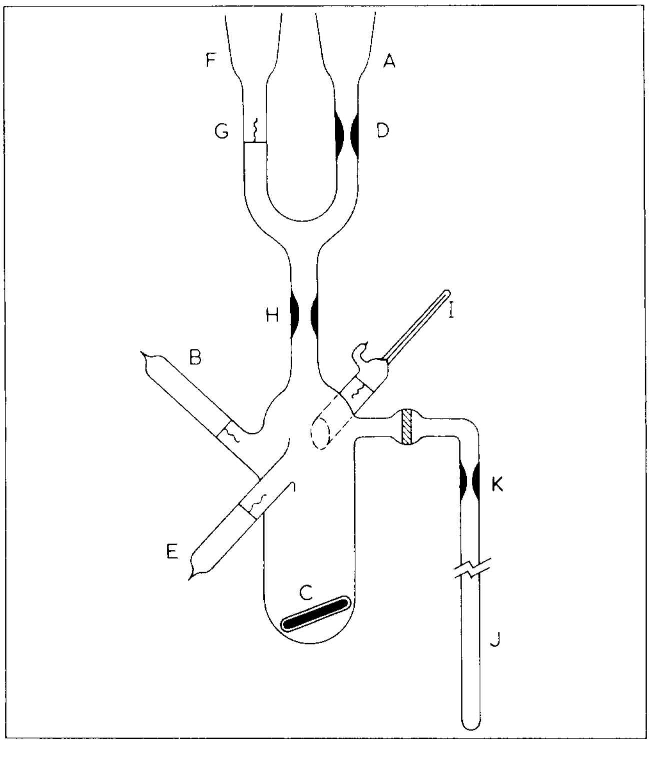


Figure 1 Apparatus used for the preparation of samples for n.m.r.

Table 2 Microstructures of polybutadienes prepared at different initiator concentrations

[sec BuLi] (mol l^{-1})	% 1,2	*DP*
0.005	7	–
0.05	17	19
0.5	38	17

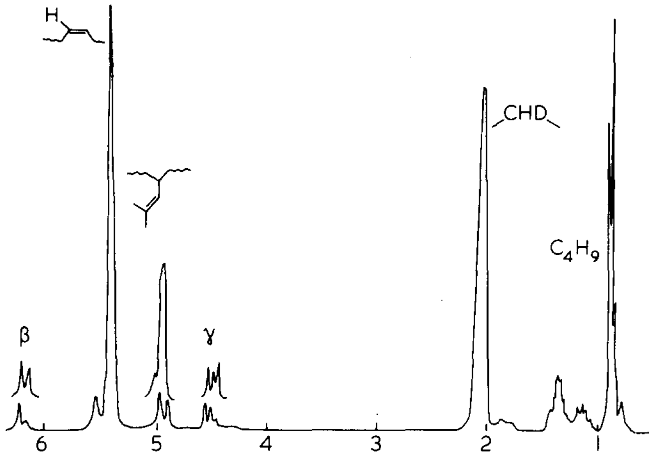
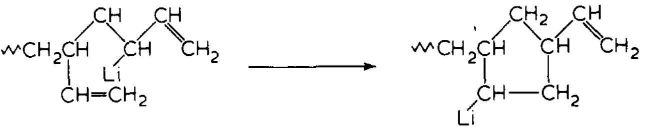


Figure 2 220 MHz ^1H n.m.r. spectrum of oligomeric poly-d_4-butadienyllithium ($DP \simeq 8$)

from *Table 2* that the dependence of microstructure upon initiator concentration is very similar in aromatic and aliphatic solvents.

The percentage of 1,2-content is particularly important when strong bases such as TMEDA are present. Quack and Fetters[15] have shown that when butadiene is polymerized by an organolithium initiator in the presence of TMEDA the resulting polymer contains cyclopentane rings. These are formed (Scheme 1) by attack of the living chain end upon the vinyl residue of a penultimate monomer unit enchained in a 1,2-sense. This reaction is quite rapid and competes with propagation when the monomer concentration is low. In order to minimize this cyclization, which would omplicate the ^1H n.m.r. study, it is clearly necessary to minimize the 1,2-content of the polymer by conducting polymerization in the absence of TMEDA using a low concentration of initiator (*ca.* 0.1 molar) followed by evaporation to a concentration appropriate for n.m.r. spectroscopy (*ca.* 0.6 molar) as described in the Experimental section. In this way the cyclic content generated on the eventual introduction of the TMEDA must amount to not more than about 10% of the chain ends.



The resonances due to the allylic carbanionic protons are located (*Figure 2*) at *ca.* 6.2 and 4.5 δ for the β and γ protons respectively; the α proton resonance is obscured by that due to the methyl groups of the sec-butyl initiator residue at 0.8 δ. The sample was polymerized at an organolithium concentration of 0.1 molar; inset on the figure are the β and γ resonances for a sample prepared at 0.6 molar concentration. Clearly, the γ protons give rise to three signals with that at highest field having an intensity that is greater when the in-chain 1,2-content is greater. Bywater *et al.*[10] observed the same phenomenon, although it was less strongly evident with their 100 MHz spectrometer, and assigned the highest field signal to the *cis* and *trans* conformers of chain ends having a 1,2-enchained penultimate unit. The present results confirm that assignment. Following Bywater *et al.*[10], the remaining two γ resonances are due to chain ends having a 1,4-penultimate unit with the lowest field resonance tentatively assigned to the *trans* conformer and the higher field signal to the *cis*. In a similar manner, the higher and lower field signals due to the β protons may be assigned to those having penultimate units placed in a 1,2- and 1,4-sense respectively.

Initially, it was thought that the most appropriate approach to the study of the ^1H n.m.r. spectrum of polybutadienyllithium would be to prepare samples of 'transparent' d-6 polymer and to cap these by adding one mole equivalent (based on lithium) of the d-4 monomer. Since non-deuterated sec-butyllithium was employed as initiator it was anticipated that the β and γ carbanionic proton resonances would have intensities half that of the proton on the tertiary carbon atom ($-C_2H_5(CH_3)CH-$) of the initiator fragment on the other end of the chain. In practice, it was found that the allylic signals were somewhat lower than expected on this basis. The most obvious explanation is that some chains acquired more than one d-4 monomer molecule and some none; this would not be unexpected since the 'crossover' from a d-6 to a d-4 chain end would have virtually an identical rate constant to that of subsequent d-4 propagation. The observation of resonances at 2.0 and 5.4 δ, corresponding respectively to in-chain $-CHD-$ and $-CH=$, is in accord with this analysis. In order to ensure rapid consumption of the d-4 monomer, capping was performed with about 0.5 molar chain-end concentration at the expense of generating quite large amounts of 1,2-enchainment. TMEDA was added to a number of such solutions and illustrative examples are shown in *Figure 3*.

One experiment was performed in which oligomeric d-8 polystyryllithium in benzene was reacted with d-4 butadiene (Li:d-4 BD = 1:1). Crossover was extremely rapid, but regrettably, the slow tumbling of the rather stiff polystyrene chain segment resulted in the production of spectra having unacceptably broad lines at ambient temperature; raising the temperature could not be countenanced since this would have inevitably led to the decomposition of the anionic chain ends.

Investigation showed that oligomeric d-4 polybutadienyllithium having a $DP \simeq 8$ does give rise to a ^1H n.m.r. spectrum in which the anionic chain end resonances can be adequately observed and characterized. In view of

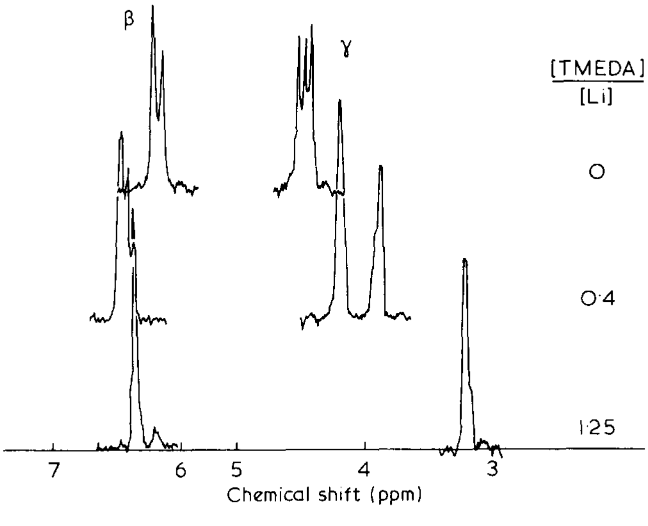


Figure 3 Influence of the addition of TMEDA upon the spectra of the β and γ protons of poly-d6-butadienyllithium capped with one unit of d-4 butadiene

Table 3 ^1H n.m.r. data for polybutadienyllithium in the presence of TMEDA

[TMEDA]/ [Li]	Intensity ratio β/γ	Chemical Shifts		
		β		γ
0	0.70	6.21	6.15	4.55, 4.49, 4.4
0.06	0.65	6.28	6.18	4.59, 4.56, 4.52, 4.43
0.11	0.73	6.34	6.25	4.51, 4.48, 4.46, 4.3
0.20	0.65	6.43	6.36	4.48, 4.24
0.40	0.64	6.47	6.43	4.28, 3.96
0.63	0.61	6.52		3.89, 3.69
0.91	0.78	6.53		3.53, 3.49
1.95	0.92	6.46	6.41	3.21, 3.18
4.7	0.67	6.26	6.21	3.0, 2.94

the relative simplicity of preparation and the close correspondence of these spectra to those of the d-4 capped d-6 polybutadienyllithium solutions, all subsequent work was conducted using d-4 oligobutadienyllithium.

Provided that the propagating centres attach each terminal carbon atom of the d4-monomer with equal facility, the probability of finding a deuterium atom in the carbanionic β and γ positions is 1/2. However, as shown in *Table 3* in the form of the integrated intensity ratio, the odds are better at the β carbon and worse at the γ. (Of course the addition of TMEDA to a completely polymerized solution will not affect the distribution of the isotopes). Evidently there is a kinetic isotope effect favouring the reaction $\sim CD_2CHCDCHCLi + CD_2CHCDCHD \rightarrow \sim(CD_2CHCDCHD)_2Li$.

The addition of a small amount of TMEDA to polybutadienyllithium ($r = [TMEDA]/[Li] \simeq 0.05$) results in the formation of an additional γ resonance at higher field. The original three γ signals remain substantially in the same positions but that due to the *cis* conformer preceded by a 1,4-enchained penultimate unit is reduced in intensity suggesting that this species, complexed with TMEDA, is responsible for the new resonance. The β resonances are moved downfield by the presence of TMEDA ($r \simeq 0.05$), the change being greater for chain ends preceded by 1,4-units than for those preceded by 1,2-units. Raising r to 0.4 causes the γ proton signals to move markedly upfield. Only two peaks are evident; that at higher field can be attributed to *cis* chain ends, preceded by a 1,4-unit, that at lower field to the *trans*. It may be presumed that the high field signal also represents the γ protons of the chain ends preceded by a 1,2-unit. However, the possibility that some of these may have cyclized cannot be totally ruled out. At $r = 0.4$, the β resonances have moved downfield and three peaks are evident. The weakest of these is at highest field and may be assigned to chain ends with a penultimate 1,2-unit; moving downfield the remaining two peaks of greater (and near equal intensity) are due to the *trans*, then the *cis*, chain end with a penultimate 1,4-unit. The three β peaks are also seen in *Figure 3* for $r = 0.4$. Increasing the value of r to 0.6 causes the β proton signals to collapse into a broad single peak and causes the γ protons to move further upfield, the change for the *trans* γ proton being greater than that for the *cis*. This trend continues with increasing r until at $r = 1$ the *cis* and *trans* γ signals have almost merged into a single peak at 3.2 δ. Analogous changes are shown by the β proton signals which merge into a single peak when $r = 0.6$, but continue to move downfield with further increase in r. At still higher values of r (*Table 3* and *Figure 5*) there is further upfield movement of the γ protons and downfield movement of the β protons which might suggest that either (i) complexation of the lithium to form the 1:1 complex is incomplete at $r = 1$ because of a dissociative equilibrium or (ii) a second complex, perhaps of the stoichiometry RLi·2TMEDA, is formed at high values of r. Studies of the viscosities of much more dilute solutions (*ca.* 10^{-3} molar in organolithium) suggest that (i) is very unlikely[16]. Suggestion (ii) is quite plausible but since the composition of the solvent is changing markedly (at $r = 5$ TMEDA accounts for more than 40% of it) it would be unwise to draw a firm conclusion.

The observation that the γ-proton resonances move upfield and those of the β protons move downfield with increasing r shows that when complexed by TMEDA, the charge on the terminal carbon atom of the chain becomes more delocalized. The lithium atom is no longer substantially σ-bonded to the α carbon atom as it is in the absence of a base. The greater charge density at the γ carbon atom is consistent with the observation by Antkowiak *et al.*[17] that when TMEDA is present, the anionic polymerization of butadiene by organolithium initiators results in large proportions of 1,2-concatenation.

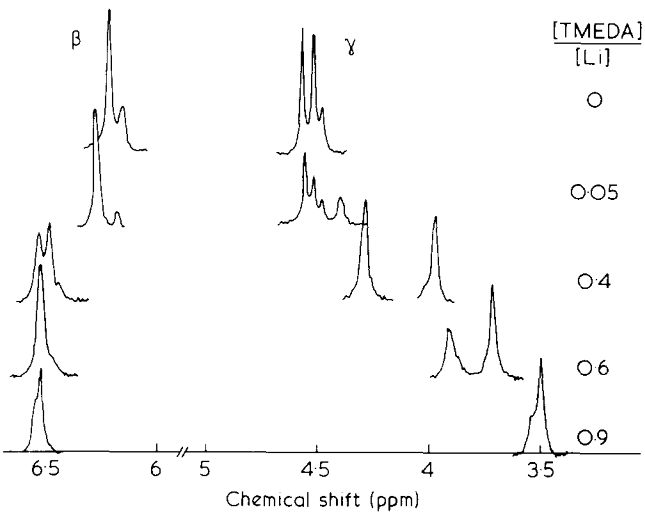


Figure 4 Influence of the addition of TMEDA upon the spectra of the β and γ protons of poly-d4-butadienyllithium

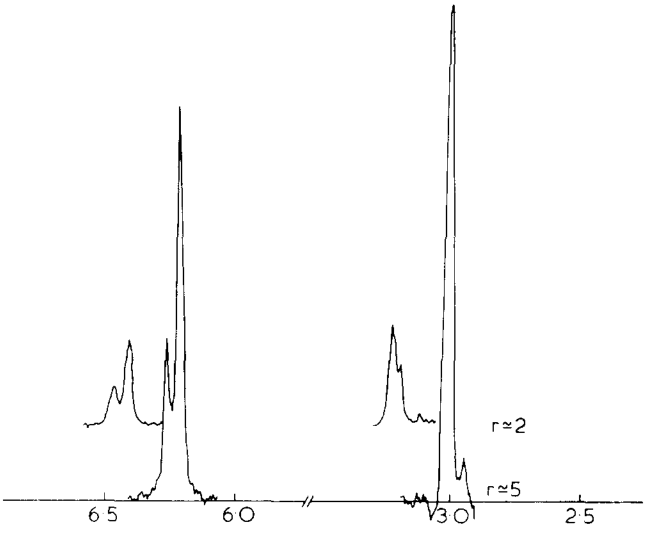


Figure 5 Influence of large additions of TMEDA upon the spectrum of the β and γ protons of poly-d4-butadienyllithium

The only comprehensive study by ^{1}H n.m.r. spectroscopy of the influence of added base upon polybutadienyllithium available for comparison with the present work is that of Bywater *et al.*[10] They found that the addition of THF also causes an upfield shift of the γ proton signals and a downfield shift of that due to the β protons. There are, however, a number of differences in detail. Whereas dramatic changes in the spectrum were caused by the addition of very small amounts of TMEDA, corresponding changes required the addition of massive proportions of THF. By way of illustration, to achieve the spectral shifts created by TMEDA at values of r equal to 0.5 and 1.0 it was necessary to add *ca.* 20 and 35% by volume of THF. Even in bulk THF the highest-field γ resonance (3.15 δ) was downfield of that with TMEDA at $r = 5$ (2.94 δ). These results underscore the remarkable complexing ability of TMEDA. It is interesting to note that a similar comparison may be made of the results obtained[11] (*Table 1*) for the adduct of butyllithium with one molecule of butadiene: the resonances of the γ protons in the feeble solvating medium diethylether are markedly downfield of the same solute in THF. Bywater *et al.*[10] presented detailed data only for the high-field γ proton resonance and make no comment concerning preferential solvation of the *cis* conformer in their system. However, two features are noteworthy in the spectrum they show of their polymer in bulk THF at −40° (a) the resonance of the *cis* γ proton is some 0.3 ppm upfield of the *trans* and (b) both *cis* and *trans* signals consist of two peaks reflecting penultimate 1,2 and 1,4 units. Feature (a) is reminiscent of solutions containing TMEDA at a value of r somewhere between 0.6 and 0.9, i.e. where complexation is less complete, particularly for the *trans* conformer. Feature (b) is unlike the TMEDA system in which the carbanionic ends having penultimate 1,2-units cyclise.

Of the solutions examined in the present study, those having r values in the range 0.2 to 0.6 have only two γ proton resonances in their n.m.r. spectra. These correspond to the two conformational forms and each signal is the weighted average for the complexed and non complexed species, i.e. the processes

$$cis\ \text{PLi} + \text{TMEDA} \rightleftarrows [cis\ \text{PLi.TMEDA}] \qquad (1)$$

$$trans\ \text{PLi} + \text{TMEDA} \rightleftarrows [trans\ \text{PLi.TMEDA}] \qquad (2)$$

are fast on the ^{1}H n.m.r. timescale, but the interconversion

$$cis\ \text{PLi} \rightleftarrows trans\ \text{PLi} \qquad (3)$$

is slow. The observed chemical shift δ is related to that of the uncomplexed species δ_u and that of the complexed species δ_c by the equation

$$\delta = \delta_u(1-f) + \delta_c f \qquad (4)$$

where f is the weight fraction of complexed species. The uncomplexed chain ends are known to be aggregated, a phenomenon which will complicate the equilibria, but which will not invalidate Equation 4. The estimated fractions of the *cis* and *trans* conformers complexed by TMEDA at several values of r are listed in *Table 4*. It is difficult to estimate the likely errors, which largely are a reflection of errors in δ_u and δ_c.

Table 4 Estimated fractions of polybutadienyllithium conformers complexed by TMEDA

r	*Trans* fraction	*Cis* fraction
0.20	0.05	0.2
0.40	0.2	0.4
0.63	0.5	0.6
0.91	0.8	0.8

Unless the enthalpy change is zero, equilibrium (3) must exhibit temperature-dependence. As a preliminary step to a more systematic investigation, a sample in which $r = 0.2$ was examined at 30°C (the highest temperature at which thermal decomposition could be confidently discounted) and at 5° (the freezing point of benzene, the solvent). At the higher temperature the high field γ signal increases in intensity at the expense of the low field γ signal, showing that the *cis* conformation is more favoured. Applying the van't Hoff equation to the ratios of the integrated intensities gave a rough estimate of the enthalpy change as 2.4 kJ mol^{-1}. Similar calculation based on two data points (at 0° and −40°) for the bulk THF system reported by Bywater *et al.*[10] estimates the enthalpy change for that system as 12.5 kJ mol^{-1}. It is clear that, as might be anticipated, the energy difference between *cis* and *trans* allylic ions is quite small.

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