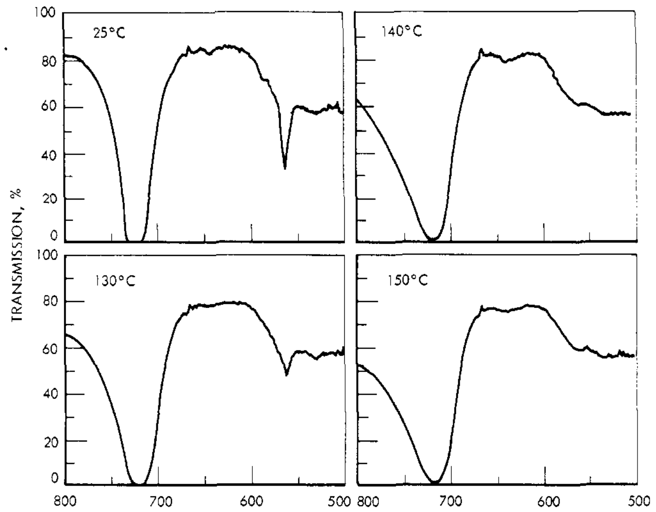

Figure 15. Temperature dependence of a pressed film of polyethylene containing 5% CD_2CD_2 groups.

The spectrum of a polycrystalline matte (Figure 14) differs from the spectrum of the pressed film (Figure 13) in that for the latter, the bands associated with gauche conformations are more intense. In Table VII we compare the relative integrated intensities for some bands of the two spectra. Since to a first approximation the ttt triad concentration should be constant, we have assumed the 562-cm^{-1} band to have the same intensity in both spectra. We note that the intensities of those bands attributed to isotopic impurities tend to remain constant. Although the intensities of all triads involving gauche bonds are less in the matte, but whether or not all the triads diminish to the same extent is uncertain. The intensities of the ggt, gtg, and gtt triads appear to have diminished to a greater extent than the tgt and gtg′ triads. However, until better spectra can be obtained from samples prepared from higher purity C_2D_4, we prefer not to speculate on the structural implications of these spectra.

A series of infrared spectra of this polymer below and above its melting point are shown in Figure 15. Above the melting point the ttt band persists; but it is much diminished, while increased absorption occurs in two broad bands centered near 575 and 642 cm^{-1}. The former represents overlapping bands from the gtt, gtg, and gtg′ triads (average calculated frequency 582 cm^{-1}), and the latter the bands of the tgt, ggt, and ggg triads (average calculated frequency 639 cm^{-1}). Unfortunately, overlapping and uncertainties in the background absorption preclude quantitative estimates of triad concentration.

Conclusions

The vibrational spectrum of a conformationally disordered polymer is enormously complex. However, the introduction of a low concentration of an isotopic impurity may result in localized vibrations whose frequencies are dependent in a relatively simple way on conformation. This approach to conformation analysis was applied to polyethylene in which case two partially deuterated samples were synthesized, one containing about 5% CD_2 groups and a second containing about 5% $(CD_2)_2$ groups.

Calculations on model *n*-paraffin molecules show that an isolated CD_2 group in a polymethylene chain vibrates in a (rocking) mode which is localized and whose frequency depends on the conformation of the two C-C bonds adjoining the CD_2 group. Frequencies associated with tt, tg, and gg dyads are well separated and fall in a region of the infrared spectrum of polyethylene which is relatively free of interferring absorption bands. Both the tt and gt dyads were observed in the infrared spectrum of the CD_2 polymer. The intensity ratio gt:tt was smallest for a polycrystalline sample, larger for a pressed film and much the largest for the melted polymer.

In the infrared spectrum of the $(CD_2)_2$ polymer, we identified ttt, gtt, tgt, ggt, and gtg′ conformational triads. Detailed interpretation was made difficult by the presence of bands from isotopic impurities and by the low intensities of the bands.

Assignment of Cis and Trans Structures to 2,5,5-Trimethylhexen-2-yllithium

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ABSTRACT: The structure of the active chain end in the anionic polymerization of isoprene in hydrocarbon solvents has been studied *via* the model compound 2,5,5-trimethylhexen-2-yllithium. The studies have been made with both ^1H and ^{13}C nuclear magnetic resonance measurements on the model, the parent hydrocarbon and on the high polymer. The evidence suggests strongly that the chain end has a predominantly trans structure about its double bond, despite the fact that the high polymer formed has a largely cis structure.

The product of the addition of *tert*-butyllithium to isoprene has been shown by means of nmr analysis to be 2,5,5-trimethylhexen-2-yllithium (I).[1,2] When formed in hydrocarbon solution it appears to exist in two forms, assumed to be the cis and trans isomers in amounts in the ratio of one to two. Higher oligomers with two or three isoprene units have also these isomeric forms of the terminal lithium bearing unit, in similar relative amounts to I at room temperature. It also has been shown that in these higher oligomers, the structure of the unit derived from isoprene, and situated next to the *tert*-butyl group (*i.e.*, the unit fixed by further addition of isoprene to I) has a

(1) F. Schué, D. J. Worsfold, and S. Bywater, *J. Polym. Sci., Part B*, 7, 821 (1969).

(2) F. Schué, D. J. Worsfold, and S. Bywater, *Macromolecules*, 3, 509 (1970).

high cis content similar to that of the polymer obtained when isoprene is polymerized by lithium based catalysts in hydrocarbon media.[3]

On this basis it seems reasonable to assume that I is a satisfactory model for the growing end in the anionic polymerization of isoprene under these conditions. In the previous publications[1,2] the isomer found in larger amounts was tentatively assigned the cis structure, on the grounds that the product on further addition of isoprene also had a predominantly cis structure. It was stressed that not all evidence was in accord with this. Further doubt was cast on this assignment when the corresponding oligomer in the polymerization of butadiene, 5,5-dimethylhexen-2-yllithium (II) was studied,[4,5] where cis–trans configurations are more easily assigned from coupling constants.

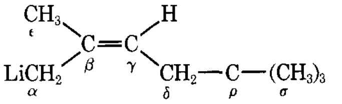
It was thus necessary to acquire more evidence to clarify the isomer assignments of I, as this is relevant to the mechanism of the reaction. Here the existing evidence is reviewed and also evidence from the Overhauser effect on the proton spectrum, and from ^{13}C spectra added.

Experimental Section

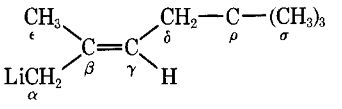
Sample preparation was the same as in the previous study.[1,2] Proton resonance spectra and Overhauser enhancement measurements were made at 100 MHz on a Varian Associates HA-100D spectrometer. ^{13}Carbon resonance spectra were made at 25.2 and 22.6 MHz on Varian Associates XL-100 and Bruker Instruments HFX-90 spectrometers respectively, with the hydrogens noise decoupled.

Results and Discussion

The two structures of I are



A



B

These structures have been drawn as covalent structures only for convenience. In fact charge separation and charge delocalization occurs,[1,2] but it is not relevant to this discussion.

The structure A is said to be the cis structure to conform with the usual 1,4-poly(isoprene) nomenclature. The labeling of the carbon atoms is in accord with those in earlier papers on this subject, but is not the same as that used by Duch and Grant[6] in their ^{13}C nmr studies on poly(isoprene) and poly(butadiene) quoted later.

Several lines of evidence may be used to assign these structures. (1) The proton resonance spectra of I formed from *tert*-butyllithium-d_9 and isoprene, and the peak assignments[1,7] are shown in Figure 1. The presence of the two forms is shown by the doubling of the α and ϵ singlets and the γ triplet. The δ doublet seems unaffected by structure. The minor peaks *x* are caused by the presence of some product formed by the addition of two isoprene molecules.

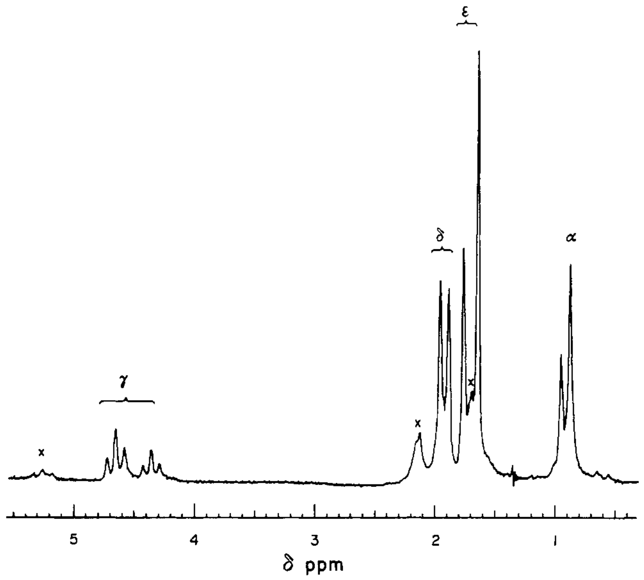


Figure 1. Proton resonance spectrum of 2,5,5-trimethylhexen-2-yllithium in benzene at 60°. *tert*-Butyl group fully deuterated.

In the spectrum of the corresponding II formed from butadiene, the low-field γ multiplet has been assigned from coupling constants to be the trans form, comparable to B.[4] Hence by inference the larger low-field γ triplet in I should also be given by the trans form.

(2) In poly(isoprene) spectra the δ values of the methyl (ϵ) peak in the cis and trans forms at 25° are 1.75 and 1.63 ppm, respectively. The minor and major ϵ-methyl peaks in the spectrum of I are at 1.72 and 1.60 ppm, respectively. This suggests that the major peak is due to the trans form.

(3) When water is added to I, the 2,5,5-trimethylhexene-2 (III) formed no longer exhibits cis–trans isomerism, but shows two separate peaks in its nmr spectrum for the protons of the two methyl groups next to the double bond. The peak which is diminished most when deuterium oxide is used in place of water, is the lower field methyl peak. If the termination occurs without isomerization, and the methyl peaks are in the same relative position in the polymer and in III, this would indicate that in I the original peak was the trans form.

(4) Some measurements were made of the Overhauser effect[8] in this compound's spectrum. From the areas of the γ proton resonance peaks in the olefinic region, and from the intensities of the ϵ-methyl peaks, the concentration of the two forms B and A are in the ratio 1.85 ± 0.05. If the methyl group of the more abundant species is irradiated, the ratio of the intensities of the two olefinic protons is 1.75 ± 0.03, as it also is if the irradiating frequency is in an empty region of the spectrum. If the less abundant methyl group line is irradiated, however, the ratio of the two olefinic proton peaks becomes 1.47 ± 0.15. This corresponds to a positive Overhauser effect of 16%, and indicates that the smaller peak is associated with the cis form A.

A similar comparison using peak areas rather than peak heights gives Overhauser enhancements of −4.7% for the more abundant species, and 8.9% for the less abundant. Values in the literature vary from 9 to 20% for the cis species, and from −4 to 1% for trans species of similar stereochemistry.[8]

(5) The values for the chemical shifts of the ^{13}C nuclei in *cis*- and *trans*-1,4-poly(isoprene) have been reported and are listed in Table I.[6] The assignments of the β, γ, and ϵ

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(3) F. Schué and S. Bywater, *Bull. Soc. Chim. Fr.*, 271 (1970).

(4) W. H. Glaze, J. E. Hanicak, M. L. Moore, and J. Chaudhuri, *J. Organometal Chem.*, **44**, 39 (1972).

(5) S. Bywater, D. J. Worsfold, and G. Hollingsworth, *Macromolecules*, **5**, 389 (1972).

(6) M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).

(7) M. Morton, R. D. Sanderson, and R. Sakata, *J. Polym. Sci., Part B*, **9**, 61 (1971).

(8) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect; Chemical Applications," Academic Press, New York, N. Y., 1971.

Table I
^{13}C Nmr Shifts in ppm from Solvent C_6D_6, of Poly(isoprene) and Compounds I and III

Carbon		Poly(isoprene) This Work	Poly(isoprene) D & G[6]	I	III
α	cis	101.0	(101.9)[a]		96.2[b]
	trans	101.0	(101.7)[a]		
	3:4	16.3			
β	cis	−7.3	−6.9	−19.8	−4.4
	trans	−7.3	−6.5	−22.3	
	3:4	−19.5			
γ	cis	3.2	2.4	27.8	5.7
	trans	4.2	2.4	27.8	
	3:4	85.9			
δ	cis	95.2	(96.2)[a]	84.0	85.4
	trans	87.4	(88.7)[a]	84.6	
	3:4	87.7			
ε	cis	104.1	105.3	104.0	110[b]
	trans	111.7	112.8	106.6	
	3:4	110			
ρ				100.3	101.7
σ				98.0	98.4

[a] The α and δ values have been reversed from the original paper.[6]
[b] α and ε are not strictly assignable in this compound, and are interchangeable.

carbons (using the nomenclature in this paper) were established by selective proton decoupling. In the original paper[6] the assignments of the α and δ carbons could not be assigned in this manner, but were suggested by theoretical arguments. It has been found necessary to reverse these assignments to conform with the results on the oligomers, and they appear reversed in Table I, together with the values found here. More evidence is required, perhaps from specifically substituted enriched ^{13}C poly(isoprene), before the α and δ peaks can be definitely assigned. There is good agreement in peak positions; any differences can be ascribed to different conditions of solvent and temperature.

Spectra were taken of a very high cis 1:4 synthetic poly(isoprene) (a, Figure 2) to give the cis peaks, and of a butyllithium initiated poly(isoprene) containing about 70% cis 1:4, 24% trans 1:4, and 6% 3:4 units (b). In b the positions of the peaks of both the cis and the trans 1:4 units are identical with those found in a wholly cis or trans polymer, which is rather unexpected in a polymer of such mixed structure. Similar behavior was observed for poly(butadiene) of mixed cis and trans 1:4 structure, and was attributed by Mochel[9] to the two structures appearing as blocks of all-cis or all-trans structure.

Also measured was the spectrum of a polymer containing approximately 55% 3:4, 30% 1:2, and 15% trans 1:4 structures (c, Figure 2), formed by butyllithium initiation in H_4furan. If it is assumed that the five largest peaks are given by the 3:4 units, they can be assigned the positions given in the table. The apparent reversal of the methylene and methine peaks follows Mochel's[9] analysis of 1:2-poly(butadiene) which he established by continuous wave decoupling techniques. The peaks appear complex, but as was also pointed out by Mochel, the possibility of different tacticities occurs as well as effects due to neighboring groups. It is noticeable that the side-chain carbon peaks in the 3:4 structure appear unchanged as minor peaks in the spectrum of polymer b, but the γ and δ peaks are shifted from the region of 86 ppm to 96 ppm presumably because of neighboring group effects.

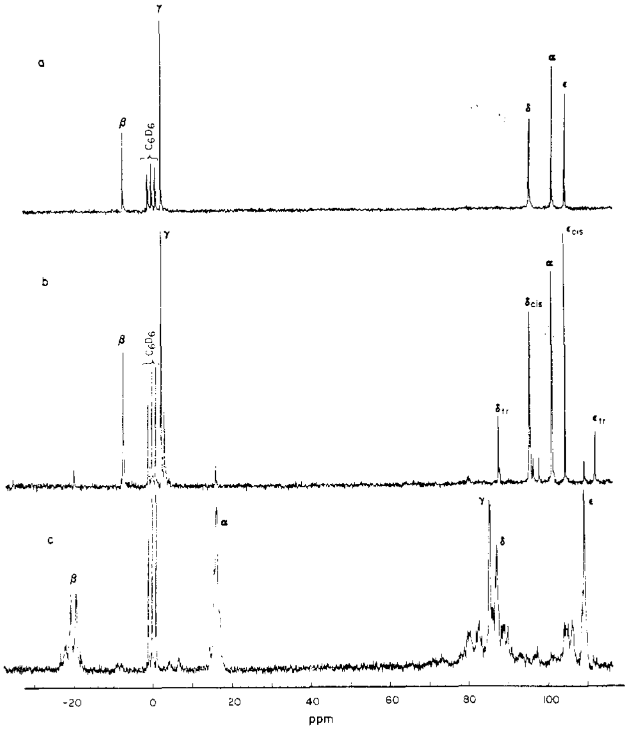

Figure 2. ^{13}C nmr spectra of synthetic poly(isoprenes) of structure: (a) pure cis 1:4, (b) 70% cis 1:4; 24% trans 1:4, 6% 3:4, (c) 55% 3:4, 30% 1:2 and 15% trans 1:4. All spectra with C_6D_6 solvent with protons noise decoupled.

The ^{13}C spectrum of *tert*-butyllithium was also measured. This was found to consist of a very sharp single peak at 94.8 ppm upfield from benzene, attributed to the three equivalent methyl carbons. There was no evidence for any peak due to the tertiary carbon, which should have been readily detected if coupling occurred only with a single lithium-7 nucleus. Evidently as the *tert*-butyllithium exists as a tetramer, coupling must occur with more than one lithium in the aggregate, and the complex signal becomes lost in the noise. The presence of this coupling was also noted in the ^{7}Li spectrum of this compound.[10]

A spectrum of the adduct of isoprene and *tert*-butyllithium in deuteriobenzene is shown in Figure 3a. Four different preparations were measured, and although the minor peaks varied in intensity from sample to sample, the major peaks were more constant. Present in the mixture is the major component I, but also some product with two isoprene units and also some unreacted *tert*-butyllithium. Normally about 80–85% of the product is I, and the major peaks may be ascribed to this. Nevertheless because of the three equivalent methyl carbons in the unreacted *tert*-butyllithium, this signal should also be significant.

The easiest line to assign is that of the three equivalent methyl carbons, σ in the diagram, which is the largest peak present. The peak of the quaternary carbon ρ, from the work of Schneider *et al.*,[11] should be a little upfield, and is taken to be the peak at 100.3 ppm upfield of benzene. The excess butyllithium absorbs at 94.6 ppm. The two olefinic carbons in I will be the two low-field groups at about −20 and 28 ppm, assigned to β and γ, respectively. Their positions are shifted down and upfield respectively from the polymer spectra presumably because of the induced charge at these positions. The group at 85 ppm coincides with a peak in the high polymer of trans structure and both are assigned to the δ carbon. The two

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(9) V. D. Mochel, *J. Polym. Sci., Part A-1*, **10**, 1009 (1972).
(10) L. D. McKeever and R. Waak, *Chem. Commun.*, 750 (1969).
(11) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

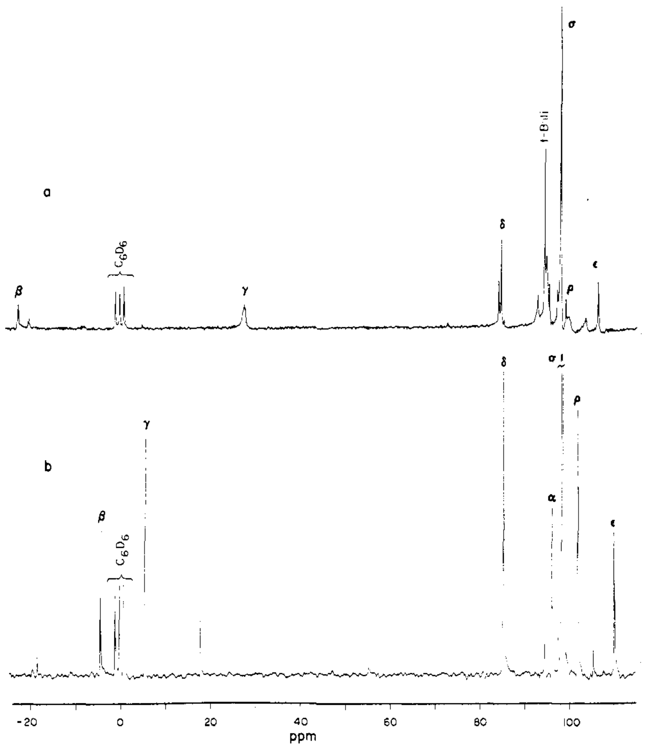

Figure 3. ^{13}C nmr spectra of: (a) 2,5,5-trimethylhexen-2-yllithium; (b) 2,5,5-trimethylhexene-2. Both in C_6D_6 solvent with protons noise decoupled.

upfield peaks (at 104 and 106.6 ppm) are taken to be those due to the ε carbon. There is now no peak remaining which obviously belongs to the main species present, but the α carbon has no peak assigned. There are certainly several unassigned peaks, mostly of a minor character, but it is possible that the Li atom is sufficiently interacting with the α carbon to cause splitting of this peak. A detailed confirmation of the correctness of the assignment of these peaks was provided by an off-resonance proton decoupling experiment.

Each of the β, δ, and ε resonances appears to be a double peak, roughly in the ratio of 2:1, caused by the presence of the cis and trans isomers. In the polymer the cis and trans β peaks coincide, so no assignment of those in I is possible. The δ resonances in the polymer are quite different, but in I much of the structural difference is lost because of the adjacent *tert*-butyl group in place of another isoprene unit. The ε-methyl carbon, however, probably is significant in the assignment of stereo structure. One of the peaks, the smaller assigned to the ε atom in 1, is coincident with that of the ε carbon in the cis polymer. The other, larger, peak is only a little downfield of that of the ε carbon in the trans polymer. These two peaks are hence assigned to these two structures, and again it appears that the major species is the trans form.

It is interesting to compare the spectrum of III formed from I by replacement of Li with H (Figure 3b). The two olefinic carbons are moved close to their positions in the high polymer. The δ, ρ, and σ peaks are almost coincident with those of I and one of the methyl carbons attached to the double bond absorbs close to the trans ε of the high polymer. The other methyl group absorbs near the δ position in the trans polymer rather than at higher field and the whole spectrum strongly resembles that of the trans polymer itself. The spectrum of III contains signals due to 10% of the 3,4 isomer which was not separated by preparative gas chromatography.

There remains the possibility that in the living oligomer the *cis*-methyl would also absorb at lower field than in the high polymer in a region where there are certainly unassigned peaks. The assignment given is preferred since the partial decoupling experiments suggested that the two highest field peaks correspond to methyl groups.

Conclusions

None of the reasoning presented above could be termed definite proof of the structure of the isomers of I, although the Overhauser effect experiments are fairly strong evidence. Nevertheless, the sum of the evidence amounts of a convincing argument that the major structure of A is the trans form.

This leaves the anomaly, that although the primary structure of the chain end in the polymerization of isoprene by lithium based catalysts is trans 1:4, the polymer produced is cis 1:4 in structure. The structure measured is, of course, that of a fourfold associated species, and the actual reactive species is a monomeric dissociation product of this. Only if the attack were on the aggregate would the structure of the growing chain be locked in at this stage. In the case of butadiene, at high concentrations when direct reaction with the aggregate may occur,[5] the attack seems to be at the γ carbon.

The structure of monomeric poly(isoprenyllithium) is not known in benzene and it seems unlikely that it will ever be possible to determine it, as its concentration must be very small. It was pointed out in an earlier paper[5] that the structure of the high polymers of dienes formed in benzene relates better to the structure of the monomeric (solvated) form of the active center in H_4furan at room temperature and that the monomeric form of the latter in benzene (or other hydrocarbon solvent) may resemble in structure the H_4furan form. The difficulty in this interpretation is that in H_4furan the rate of isomerization of the monomeric species can be measured. The half-life is a few minutes at −40° and must be a second or less at room temperature. The rate of isomerization of the monomeric form in benzene would presumably be less as the charge is more localized on the α carbon producing increased double-bond character in the β-γ bond. Although the rate of monomer addition to the active center is not known, the isomerization rate does not seem sufficient to allow isomerization to the cis form before reaction. The monomeric form is however the end product of dissociation *via* the dimer and it is possible that the whole dissociation process would allow for isomerization. Otherwise one must suppose that the preference for cis placements is a result of a faster reaction of the cis form of the active species to re-form the cis isomer. Similarly the trans isomer would reform on monomer addition. This would tend to give blocks of cis and trans isomers in accord with the suggestion of Mochel for the structure of lithium-catalyzed poly(butadiene).

Acknowledgments. We thank Drs. R. Lapper and C. Tanzer for carbon resonance spectra.