Conformational Structure of Polyethylene Chains from the Infrared Spectrum of the Partially Deuterated Polymer

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ABSTRACT: Quantitative conformational information can be obtained from the infrared spectrum of a disordered polymethylene chain into which has been randomly incorporated a low concentration of deuterated methylene groups. The method is based on the observation that the rocking mode vibration of an isolated CD_2 group is localized and has a frequency which is dependent on the conformation of the C–C bonds adjacent to it. Frequencies associated with trans,trans, trans,gauche, and gauche,gauche bond pairs are well separated and fall into a region of the spectrum of polyethylene which is relatively free of interfering absorption bands. The ratio of bond pairs gt:tt was found to be smallest for a polycrystalline film, larger for a pressed film, and by far the largest for the molten polymer.

Most of the properties which distinguish polymers from other substances are associated with their amorphous rather than their crystalline state. It is the crystalline state, however, which is much easier to describe and which is much more amenable to diffraction and spectroscopic techniques, and this no doubt is one reason why crystalline rather than amorphous polymers may tend to be preferred subjects for study. This is not to say that such studies have not been unrewarding or even necessary first steps. In many cases, the details of chain conformation, and packing have been firmly established by X-ray methods. In addition, the vibrational dynamics of many crystalline polymers have been worked out to about the same level as those of molecules of a complexity comparable with the repeat unit of the polymer.

Much less is known about the conformational structure of chains in the noncrystalline phase for the reason that diffraction methods are not suited to the investigation of aperiodic systems.

Vibrational spectroscopy has often been successfully used to determine the conformational structure of relatively simple molecules. Unfortunately, there have not been comparable successes in attempting to use this technique to unravel the conformational structure of disordered polymer chains. It is not difficult to understand why this is the case. A vibrational spectrum, infrared or Raman, does not contain information which relates directly to structure, but rather contains information about transitions between vibrational energy levels. These energy levels depend in varying degrees upon conformational structure and if this relationship is understood the vibrational spectrum can be used to identify or eliminate a proposed structure. This works well if the number of possible rotamers is relatively small and if each rotamer has a spectrum which in some region can be clearly distinguished. For example, the trans and gauche isomers of *n*-butane are easily identified in the liquid state since their spectra are simple and quite different. Three rotamers of *n*-pentane (tt, tg, and gg) can be identified in vibrational spectra of the liquid. Higher members in this series of *n*-alkanes cannot be completely analyzed. In the case of *n*-hexane each of the seven rotamers have a complex vibrational spectrum and normal coordinate calculations are needed to sort them out. Only a few of the rotamers of *n*-heptane can be identified with certainty and beyond *n*-heptane the situation becomes nearly hopelessly complex.[1] Thus the problem represented by an infinitely long conformationally disordered polymer chain, is so much more complex than that of a relatively small molecule, so as to be a problem of another kind. There is, of course, no possibility of establishing the precise conformation of a disordered polymer molecule. Any description of the chain must be statistical and defined in terms of relatively short conformational sequences.[2] Before discussing the relationship between the disordered chain and its observed vibrational spectrum, we should first consider briefly the case of the regular chain having translational symmetry.

The vibrations of a regular chain are conveniently described using dispersion curves, which relate phase differences between neighboring displacement coordinates (which can sometimes be associated with chemical groups) and the frequency of vibration. The manner in which neighboring coordinates are vibrationally coupled determines the shape of the dispersion curve. An important point is that all vibrations of an infinitely long chain having translational symmetry also have translational symmetry and thus each vibration involves the complete chain, *i.e.*, the vibrations are never localized. The situation for the disordered chain is different. If two coordinates are separated by a bond about which internal rotation can occur, the coupling between them will depend to some extent on the rotational state associated with the bond. Thus in a disordered chain, coupling between coordinates is not regular and this promotes localization of vibrations to some degree.

The degree of localization depends in part on the degree of coupling and in part how much it changes in going from one conformation to another. The random polymethylene chain itself offers several situations illustrating this point. The discussion is based on results to be found in ref 1.

In the case of C–H stretching modes, adjacent methylene groups are only weakly coupled so that these vibrations appear as relatively sharp bands having shapes which are rather insensitive to conformation. On the other hand, C–C stretching coordinates are quite strongly coupled. Here, however, the coupling is not much affected by conformational change. What is observed then in the infrared is a very broad band in the frequency region spanned by the dispersion curve of the fully extended chain. However, the actual shape of the absorption band does not correspond to the density of states curve derived from the dispersion curve for at least two reasons. (1) An examination of the normal coordinates of these modes

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(1) R. G. Snyder, *J. Chem. Phys.*, 47, 1316 (1967).

(2) P. J. Flory, "Statistics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969.

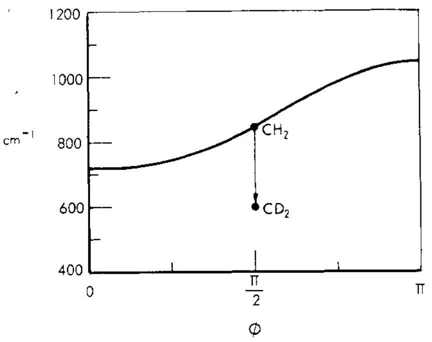

Figure 1. Isolated CD_2 rocking mode frequency shown relative to the $(CH_2)_\infty$ rocking-twisting mode dispersion curve.

shows that other kinds of coordinates, not present in the case of the extended chain, now are mixed with the C-C stretches and that these contribute to the intensity of each mode in a way which varies with the frequency of the mode; (2) the effect of conformation on transition moments will result in intensity variations, between different modes, particularly for infrared transitions. In consequence this broad C-C stretching band representing nonlocalized vibrations leads us to little new conformational information.

On the other hand, the methylene wagging modes represent a particularly favorable case. The coupling between methylene groups is strong if the bond between them is trans and weak if it is gauche. The infrared spectrum of the disordered chain shows in the region 1370-1250 cm^{-1} a number of absorption bands not present in the spectrum of the extended chain. Some of these can be associated with specific localized conformations. Even then because the bands tend to overlap and because their transition moments show a large dependence on conformation and in addition because the vibrations they represent are not entirely localized, these modes do not lead us to new conformational enlightenment.

The purpose of the present work is to demonstrate how some of these difficulties can be alleviated through deuterium substitution.

The dispersion curve for the methylene rocking-twisting branch of an infinite regular polymethylene chain is shown in Figure 1. The approximate frequency of the rocking vibration of an isolated CH_2 is found near $\varphi = \pi/2$. This hypothetical vibration occurs at about 850 cm^{-1} and if the group were replaced by CD_2 this vibration would be moved to about 600 cm^{-1} $(850/(2)^{1/2})$. Since this vibration is well outside the dispersion curve it could be expected to occur without greatly coupling with CH_2 rocking modes. In Figure 2 the approximate form of this vibration is shown for the extended chain. The significant involvement of the adjoining CH_2 groups suggests that the CD_2 rocking frequency may be affected by the conformation of the adjoining CH_2 groups. This turns out to be the case and fortunately all frequencies of interest fall in a region of the spectrum relatively free of interferring absorption bands. Two systems were studied.

In the first and simpler system, isolated CD_2 groups were introduced by polymerization of a mixture of $CH_2{=}CD_2$ and $CH_2{=}CH_2$ in the ratio 1:20. If we assume a random distribution of CD_2 groups in the resulting polymer, 97.5% of these have CH_2 nearest neighbors on both sides. If the two C-C bonds adjoining the isolated CD_2 group are trans, the rocking mode frequency associated with this bond pair, TT, has a calculated value of 616 cm^{-1}; if one bond is trans and the other gauche, the calculated frequency is 649 cm^{-1} for the equivalent bond pairs, TG, TG′, GT, and G′T; the double gauche bond pairs, GG and G′G′ have a calculated frequency near 680 cm^{-1}.

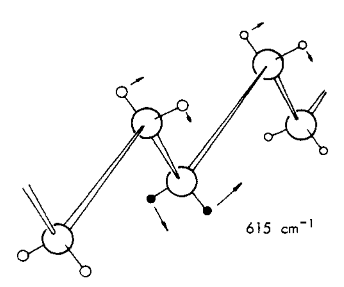

Figure 2. Form of the CD_2 rocking mode in a *trans*-polymethylene chain.

In a second system, CD_2CD_2 groups were isolated by polymerization of a mixture of $CD_2{=}CD_2$ and $CH_2{=}CH_2$ in the ratio 1:20. In this system, localized rocking vibrations occur in the region 730-500 cm^{-1}. The frequencies depend on the conformation of the bond connecting the CD_2 groups as well as the conformation of the two outer adjoining bonds. The greater number of conformational possibilities leads in principle to more information, but this is largely offset by the increased difficulty in interpreting this more complex spectrum. The results will be described in more detail after outlining the experimental procedures.

Experimental Section

Polymerization of Samples. The polymerization was carried out using a Ziegler catalyst (α-$TiCl_3$ + $AlEt_2Cl$) in dried, redistilled *n*-heptane. A total of 20 l. of ethylene was used in a 0.7-l. pressure reactor. The reactants were initially at room temperature and under a pressure of 350 psi. One liter of either 1,1-ethylene-d_2 or ethylene-d_4 was used with 19 l. of ethylene. The deuterated ethylene was obtained from Merck of Canada and the ethylene was Phillips Pure Grade.

The first samples we prepared showed a very broad infrared band centered near 700 cm^{-1} which was attributed to an aluminum oxide impurity. A film of this polymer thick enough (approximately 0.5 mm) to display the bands of interest was nearly opaque in the critical region below 700 cm^{-1}. Initially it was thought that the impurity was present in a particulate form unassociated with the polymer. Various attempts were made to remove it by extraction, chemical means, and filtration. Even the strongest measures such as filtration of xylene solutions at high temperatures under nitrogen pressure through a 0.5 μ Millipore filter failed to provide a polymer sufficiently free of the impurity.

Abandoning efforts to purify the polymer, we repeated the polymerization under different conditions. The impurity concentration correlated inversely with molecular weight. It was found that the $TiCl_3$ concentration was a more important factor than that of $AlCl_2Et$. A polymer was finally obtained, which was highly linear and highly crystalline and had a molecular weight of about 200,000.

Preparation of Polycrystalline Mattes. Polyethylene crystals were grown from dilute (0.1%) solutions of xylene and tetrachloroethylene. After crystallization, the sample was redissolved and the solution was brought back slowly to room temperature over a period of 10 hr. In the first experiments, the mattes were dried under vacuum at 60°. It was found that this treatment somewhat altered the crystallinity and that the solvent could not be entirely removed. Therefore, during the filtration of the crystals from the solvent, small quantities of acetone or methanol were added, and then the matte was washed several times. Even with repeated washing, the crystals formed in xylene and other aromatic solvents tended to retain some of the solvent. Complete absence of aromatic solvents is especially important since these molecules have bands in the region of interest. However, the polymer crystallized from C_2Cl_4 in the same manner showed no detectable solvent impurity. After the mattes had been completely dried a room temperature *in vacuo*, they were pressed at room temperature at 10,000 psi for 2 min. Several thin test samples wer pressed at 35,000 psi for 5 min and compared with the unpresse

Table I
Crystallinity of Polyethylene Samples

Sample	d (g/cm^3)	% Crystallinity From ρ	 From Ir
(CH$_2$)			
Matte	0.976	86	85
Pressed Film	0.940	63	60
5% CD$_2$			
Matte	0.980	89	88
Pressed Film			>50
5% CD$_2$CD$_2$			
Matte	0.978	87	88
Pressed Film			>45

Table II
Calculated Frequencies (cm^{-1}) of the CD$_2$ Rocking Modes of 4,4-n-Heptane-d_2 and 5,5-n-Nonane-d_2

$CH_3CH_2CH_2CD_2$-$CH_2CH_2CH_3$		$CH_3CH_2CH_2CH_2$-$CD_2CH_2CH_2CH_2CH_3$	
(t)tt(t)	616	(tt)tt(tt)	615
(g)tt(t)	615		
(g)tt(g)	615		
(g)tt(g′)	615		
(t)tg(t)	649		
(g)tg(g)	649		
(g)tg(t)	654		
(g′)tg(t)	649		
(t)gg(t)	678	(tt)gg(tt)	689
(t)gg(g)	677		
(g)gg(g)	676		

mattes. Although the spectra obtained from the unpressed mattes were poor, there was no apparent change in crystallinity as shown by the bands at 1894, 1368, and 1350 cm^{-1} and by the 731–720-cm^{-1} doublet. In order to obtain satisfactory semitransparent films, higher pressing pressures are needed for mattes from which the solvent has been completely removed than for those from which it has not been.

One sample of each polymer was isothermally crystallized at 70° for 36 hr in an oil bath. Mattes made of these materials were less uniform and less crystalline than mattes prepared as described earlier. Films of comparable thickness were made from the melt by pressing the samples at 190° and 5000 psi for 3 min and then quickly cooling them to room temperature by immersion in water. The per cent crystallinity of both the pressed films and the crystalline mattes is tabulated in Table I. The density measurements were carried out in a gradient column; the infrared measurements were made on the pressed crystalline mattes.

Infrared Spectra. For low-temperature spectra the samples were sandwiched between two CsBr plates in a cold cell and cooled to liquid nitrogen temperatures. Spectra in the region 1500–500 cm^{-1} were measured using a Cary-White (Model 90) spectrometer with a constant resolution of 5 cm^{-1} and were rerun in the region 700–500 cm^{-1} using a Beckman IR-11 spectrometer with a resolution of 2.5 cm^{-1}.

Vibrational Calculations. It is not possible to write in closed form the vibrational equations for an infinite polymer chain which is not periodic. Because our interest is in those modes which tend to be localized, a molecule representing a finite segment of the polymer serves as a satisfactory model provided all the atoms which are significantly involved in the localized mode in the infinite chain are represented in the segment.

In these calculations we have used a valence force field previously derived from the frequencies of the rotational isomers of a series of n-paraffins.[1]

We find that the calculated frequencies of both the CD$_2$ and (CD$_2$)$_2$ polymers are consistently lower (by 5 ± 5 cm^{-1}) than the observed ones. Such a trend is to be expected since we have used a force field derived from the observed frequencies of nondeuterated n-paraffins rather than from harmonic frequencies, *i.e.*, frequencies corrected for the effects of anharmonicity. Usually, observed frequencies are lower than harmonic frequencies; but the difference between the two is less for deuterated than for undeuterated systems. The result is calculated frequencies for deuterium compounds which tend to be lower than the observed.

Table III
Normal Coordinates of the CD$_2$ Rocking Modes of 4,4-n-Heptane-d_2

Conformation	ν_{calcd} (cm^{-1})	L_{ik} CH$_2$	 CH$_2$	 CD$_2$	 CH$_2$	 CH$_2$
tttt	615	0.015	0.202	0.489	0.202	0.015
tgtt	650	−0.033	−0.065	0.435	0.298	0.060
tggt	678	−0.094	−0.201	0.420	−0.201	−0.094

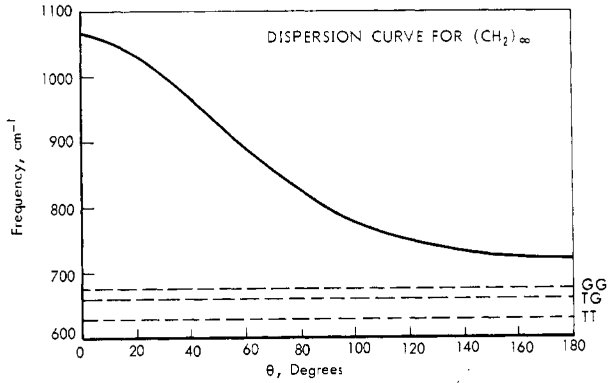

Figure 3. Relationship between the methylene rocking-twisting dispersion curve and the "characteristic" frequencies for an isolated CD$_2$ group.

The -(CH$_2$)$_m$CD$_2$(CH$_2$)$_n$-System

Calculated Frequencies. For an isolated CD$_2$ group, we have used as a model the molecule 4,4-n-heptane-d_2. Most of the possible conformations of this n-paraffin were considered except those having the energetically unfavorable bond pair GG′. It is apparent from the results shown in Table II that there is a characteristic frequency associated with the conformation of the bonds adjoining the CD$_2$ group.

A rough sketch indicating the nature of this vibration for the trans molecule is shown in Figure 2. In Table III normal coordinates for the tttt, tgtt, and tggt conformations of 4,4-n-heptane-d_2 are listed. In each case, localization is apparent. Although the CD$_2$ group has the largest amplitude and therefore is responsible for the lowered frequency, there remains, however, considerable participation by adjacent CH$_2$ groups by virtue of large kinetic energy coupling between neighboring methylene groups. The strength of this coupling is conformationally dependent and leads to different frequencies for different conformations. Groups beyond the nearest neighbors of the deuterated methylene are much less involved so that the frequencies are nearly independent of them.

There are at least two complicating factors which make it necessary to qualify and expand this simple picture.

In discussing the first factor, it is appropriate to refer to the dispersion curve calculated[3] for the lower branch of the methylene rocking-twisting modes of polyethylene shown in Figure 3. The calculated frequencies of the CD$_2$ modes have also been included. We note that all three of these latter frequencies fall outside the frequency range of the dispersion curve. In the present case where there is strong coupling, this is a necessary condition for localization to occur at all. The modes represented by the disper-

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(3) R. G. Snyder, *J. Mol. Spectrosc.*, **23**, 224 (1967).

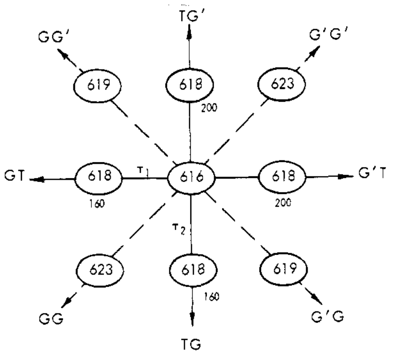

Figure 4. Frequency (cm^{-1}) of the CD_2 rocking mode as a function of the adjoining dihedral angles (τ_1 and τ_2) around the tt conformation ($\tau_1 = \tau_2 = 180°$).

sion curve in the region near 720 cm^{-1} will nevertheless interact to some extent with the CD_2 modes and most intensely with the gg bond pair vibration, whose frequency most closely approaches the 720-cm^{-1} limit.

Just how serious this effect may be is indicated in Table II where we compared the frequencies of the CD_2 rocking modes of 4,4-*n*-heptane-d_2 with those of 5,5-*n*-nonane-d_2 in which case the two additional CH_2 groups bring the molecule a little closer to the real polymer. For the ttttt form of this latter molecule the calculated frequency is 615 cm^{-1}, to be compared to nearly the same value of 616 cm^{-1} for tttt *n*-heptane-d_2; on the other hand, for the ttggtt form, the frequency is 689 cm^{-1}, 11 cm^{-1} higher than the 678 cm^{-1} of tggt *n*-heptane.

A second factor whose perturbation is again felt more strongly by the gg mode concerns the frequency dependence of the rocking vibrations on the dihedral angles defining conformations. These angles have been assigned equilibrium values of 180° for the trans conformation and ±67° for the gauche. These are values which the angles would assume if the molecule were unperturbed by its environment. However, the presence of surrounding molecules can be expected to result in a distribution of equilibrium values for the dihedral angles though the average value will probably remain close to 180 or ±67°. We note it takes very little energy to effect such deviations. For an ethane-like threefold barrier having a height of 3000 cal/mol, only 100 cal/mol are needed for a ±6.7° displacement from equilibrium and 200 cal/mol for a 9.9° displacement. Even smaller energies may be needed to effect the same displacement in polyethylene since the potential energy surfaces calculated for longer *n*-paraffins indicate not only minima which are shallower than expected but even unexpected minima.[4]

An estimate of the dependence of the frequency of the CD_2 rocking mode on dihedral angles is shown in Figures 4 and 5 for the regions around the tt and gg conformations. These summarize calculations on 4,4-*n*-heptane-d_2; in all cases, the two bonds adjacent to the central pair of bonds are trans. Planes of symmetry considerably reduce the number of independent points. (For each point, all the vibrations of the molecule must be computed.) The tg bond pair, which has no symmetry, can be assumed to lie between the tt and gg cases. For the tt bond pair, there is only a small dependence on the dihedral angles (τ_1 and τ_2) associated with the adjoining bonds. In the direction of maximum change (toward gg or g′g), it is about 0.25 cm^{-1}/deg; and in the direction of minimum change (toward tg or tg′, or gt or g′t), about 0.1 cm^{-1}/deg. On

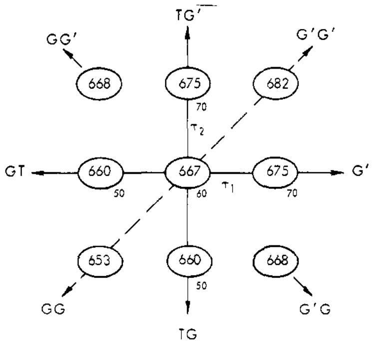

Figure 5. Frequency (cm^{-1}) of the CD_2 rocking mode as a function of the adjoining dihedral angles (τ_1 and τ_2) around the gg conformation ($\tau_1 = \tau_2 = 60°$).

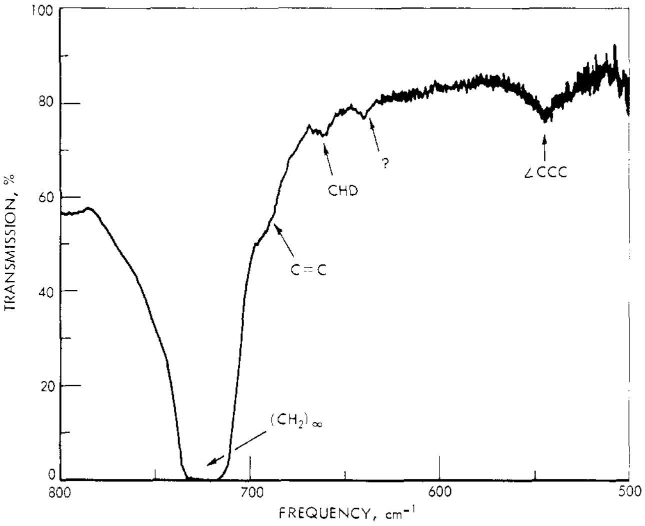

Figure 6. Infrared spectrum of a pressed film (0.53 mm) of polyethylene at 77°K.

the other hand, for the gg bond pair the maximum and minimum are 1.1 and 0.1 cm^{-1} per deg, respectively. Thus, for the same degree of disorder, the band of a gg vibration will be broadened much more than a band of a tt vibration.

This factor probably does not significantly affect the tt band itself. The calculated frequency shift is always upward when the dihedral angles are displaced from their 180° positions. Yet, as we will see (Figures 7 and 9), the observed tt band remains symmetrical, and its position appears unchanged in going all the way from the solid at −196° to liquid at 150°.

Complications also arise from the presence of isotopic entities other than isolated CD_2.

About 2.5% of the CD_2 groups will have CD_2 neighbors. In an extended chain, an isolated CD_2CD_2 has a rocking mode whose frequency is calculated to be 556 cm^{-1}, fortunately well removed from the region of interest. If two CD_2 groups are separated by a single CH_2 group, they are vibrationally speaking nearly isolated from each other. For example, the calculated CD_2 frequencies of trans 4,4,6,6-*n*-nonane-d_4 are 622 and 609 cm^{-1}, only slightly displaced from the 616 cm^{-1} calculated for a completely isolated CD_2 so that the effect of such pairs then will be to slightly broaden the band of the isolated CD_2 group.

The 1,1-ethylene-d_2 used to prepare the polymer contained about one percent ethylene-d_1. The calculated frequency (*trans*-5-*n*-nonane-d_1) of the deuterium mode is 658 cm^{-1}, and this is uncomfortably near to the tg frequency of CD_2.

Frequency Assignment. The spectrum of a thick film

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(4) R. L. McCullough and P. E. McMahon, *J. Phys. Chem.*, **69**, 1747 (1965).

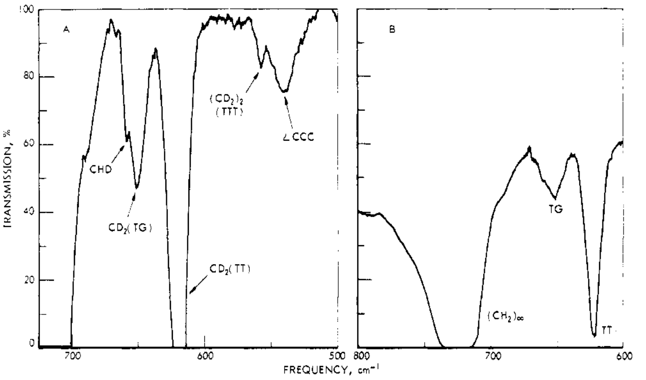

Figure 7. Infrared spectra of a pressed film of polyethylene (77°K) containing 5% CD_2 groups.

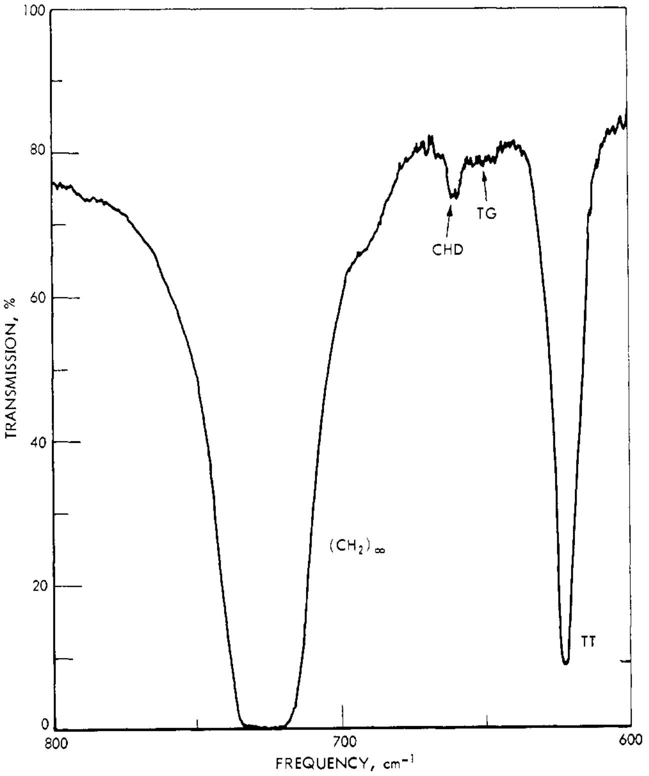

Figure 8. Infrared spectrum of a polycrystalline matte of polyethylene (77°K) containing ~5% CD_2 groups.

of polyethylene synthesized in exactly the same manner as the isotopically substituted polymer is shown in Figure 6. In the region of interest (700-500 cm^{-1}) four very weak bands appear. One of these, at 640 cm^{-1}, does not appear in the spectrum of Marlex polyethylene and, therefore, is probably not associated with the polymer chain itself. Another, broad and centered near 540 cm^{-1}, is probably associated with the cutoff frequency of the ν_5 branch whose calculated frequency[5] is about 560 cm^{-1}. Of the two remaining bands, observed at 690 and 661 cm^{-1}, the former probably is caused by the presence of a small amount of cis double bond and the latter to CHD groups. Finally, it should be mentioned that ν_3 of CO_2 absorbs strongly at 667 cm^{-1}, and we were not always able to prevent it from distorting our spectra.

Table IV
Frequencies (cm^{-1}) and Assignments of Bands Observed in the Infrared Spectrum of 5% CD_2 Polyethylene in the Region 730-500 cm^{-1}

Frequencies (cm^{-1})	Assignments
725 (vvs)	$(CH_2)_\infty$, $(t)_\infty$, CH_2 rocking (ν_8)
690 (vvw, sh)	$(CH_2)_\infty$, cis C=C
661 (vvw, sh)	CHD, tt (calcd 658)
652 (vw)	CD_2, tg (calcd 650)
622 (w)	CD_2, tt (calcd 615)
562 (vvw)	CD_2CD_2, ttt (calcd 556)
540 (vw)	$(CH_2)_\infty$, ∠CCC bend cutoff (ν_5)

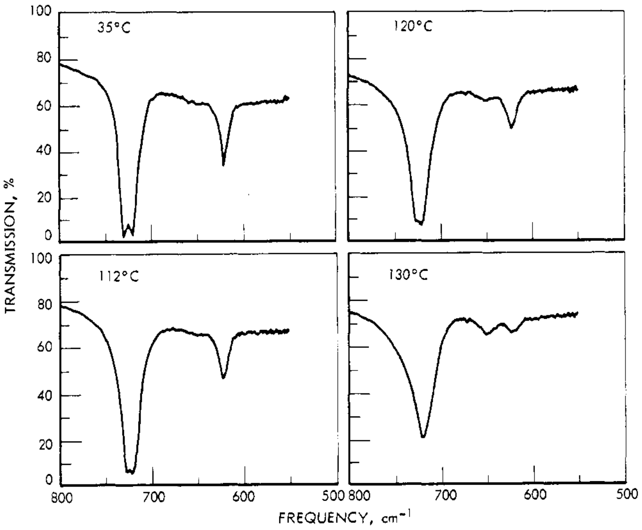

Figure 9. Temperature dependence of a pressed film of polyethylene containing 5% CD_2 groups.

The infrared spectrum in the region 700-600 cm^{-1}, of a pressed film of 5% CD_2 polyethylene at 77°K, is shown in Figure 7. The spectrum of a polycrystaline matte is shown in Figure 8. The dominant feature in these spectra is the 622-cm^{-1} band which can be confidently identified with the tt bond pair whose rocking mode had been predicted to occur at 616 cm^{-1}. This band is, of course, not split by chain interaction as is the CH_2 rocking fundamental of polyethylene, whose components appear at 735 and 722 cm^{-1}.

A much weaker band observed at 562 cm^{-1} indicates the presence of $(CD_2)_2$ in trans conformation (calculated frequency 556 cm^{-1}).

There are two other new absorption bands in this region. The stronger is at 651 cm^{-1}. As its temperature behavior will confirm, it belongs to the vibration characteristic of the tg bond pair (calculated frequency 650 cm^{-1}). The second, at 660 cm^{-1}, appears as a shoulder on the 651-cm^{-1} band and is attributed to the presence of isolated CHD groups. We have noted earlier that such groups have a mode whose frequency is calculated to be 658 cm^{-1}. These assignments are summarized in Table IV.

Melting the polymer will, of course, greatly increase the tg concentration at the expense of tt. In Figure 9 are shown a series of spectra of the polymer from room temperature to above the melting point. Except for some band broadening, there is little change in the spectrum up to about 100°. At 120° there is a significant increase in the intensity of the 651-cm^{-1} band, though the persistence of the 730-722-cm^{-1} doublet shows most of the sample is still unmelted. At 130° this doublet disappears and a large increase in the intensity of the 651-cm^{-1} band is accompanied by a comparable decrease in the intensity of the 616-cm^{-1} band. Further heating, to 150°, has little effect.

Determination of the Bond Pair Ratio. From the in-

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[5] M. Tasumi, T. Shimanouchi, and T. Miyazawa, *J. Mol. Spectrosc.*, 9, 261 (1962).

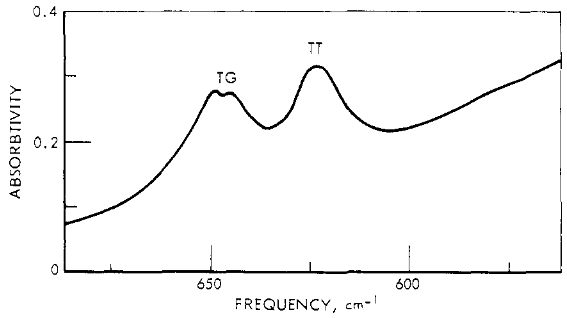

Figure 10. Infrared spectrum of 4,4-*n*-heptane-d_2 at 25° in the CD_2 rocking mode region.

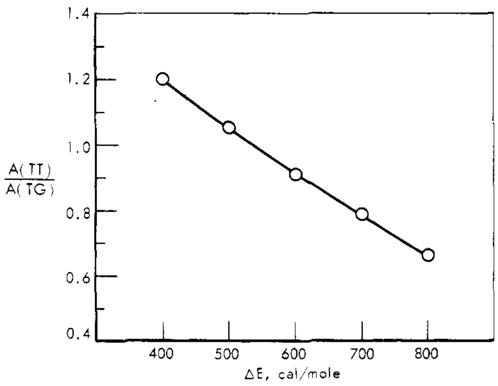

Figure 11. Ratio at the absorbtivities of the tt and tg bonds as a function of ΔE for 4,4-*n*-heptane-d_2.

frared spectrum of the polymer at 140° (very similar to the 130° spectrum shown in Figure 9) we can measure the ratio of the integrated intensities of the two bands associated respectively with tt and tg bond pairs. From this ratio I(tt):I(tg) we can compute the ratio of the numbers of bond pairs N(tt):N(tg) at 140° provided we know the ratio of the intensity of a tt mode relative to a tg mode. Because these modes are similar in form their intensity ratio A(tt):A(tg) may be expected to have a value near unity.

We have estimated this latter ratio from measurements on the model compound 4,4-*n*-heptane-d_2. The infrared spectrum of this compound at 25° in the region of interest is shown in Figure 10. The tt band occurs at 621 cm^{-1} while the tg band is a doublet with maxima at 643 and 648 cm^{-1}. The presence of two tg bands of nearly equal intensity is unexpected and indicates two vibrationally distinguishable forms of the molecule having a central tg bond pair. Cooling the sample reduced the intensity of the 643 cm^{-1} relative to that of the 648-cm^{-1} band and demonstrates that the latter band is due primarily to the tgtt form of the molecule. At 27° the observed ratio of the integrated intensities I(tt):I(tg) was measured to be 0.79 ± 0.1.

The ratio N(tt):N(tg) for *n*-heptane can be calculated given ΔE, the energy difference between the gauche and trans conformations of a C-C bond in a polymethylene chain. Although there is still some uncertainty about the correct value of ΔE, it can be safely assumed to fall within the range 400-800 cal/mol. The rotamer distribution of *n*-heptane as a function of ΔE has been used to calculate the absolute intensity ratio A(tt):A(tg) as shown in Figure 11. Finally, if we assume that ΔE is the same for polyethylene as for *n*-heptane, the observed value of 1.05 for I(tt):I(tg) for polyethylene at 140° leads to the calculated values for N(tt):N(tg) which are shown in Figure 12. The theoretical curve in this figure was calculated using formulas derived for the rotational isomeric state model of a polymethylene chain (ref 2, chapter III).

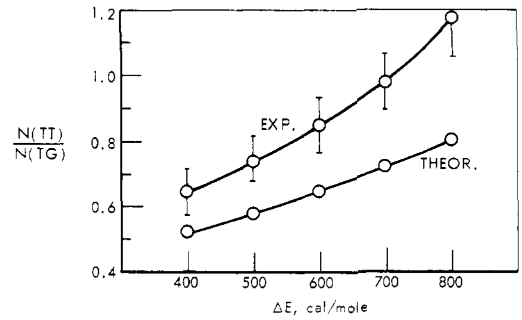

Figure 12. Ratio of tt to tg bond pairs for polyethylene at 140°.

Table V
Percentages of Bond Pairs in a Polyethylene Chain at 140° for Various Values of ΔE

ΔE (cal/mol)	Bond Pair			
	tt	tg	gg	gg′
400	29.4	56.2	13.3	1.2
500	32.1	55.1	11.8	1.0
600	35.0	53.6	10.4	0.9
700	37.9	52.4	9.1	0.8
800	40.8	50.6	7.9	0.7

Table VI
Calculated Frequencies (cm^{-1}) of the CD_2CD_2 Rocking Modes of 4,4,5,5-*n*-Octane-d_4[a]

$CH_3CH_2CH_2CD_2CD_2CH_2CH_2CH_3$	
Conformation	Calcd Frequencies (cm^{-1})
(t)ttt(t)	(664), 556
(t)gtt(t)	688, 569
(t)gtg′(t)	(724), 581
(t)gtg(t)	719, 595, 503
(t)tgt(t)	662, 640
(t)ggt(t)	692, 636
(t)ggg(t)	726, 640

[a] The frequencies in parentheses are infrared inactive.

The observed values of N(tt):N(tg) in Figure 12 have an indicated error whose value follows from an estimated error of 10% in the observed ratio I(tt):I(tg) for polyethylene. If this estimated error were increased to 20% the theoretical value of N(tt):N(tg) would fall just inside the error limits of the experimental value. Thus the evidence for a serious discrepancy between our experimental results and the theoretical predictions is not totally conclusive. If the discrepancy were real, it could be said that the rotational isomeric model underestimates the number of adjoining trans pairs relative to the number of trans, gauche pairs. At this point it can only be said that in view of the importance of testing the applicability of the model to the system at hand, the experiment merits repeating under conditions conducive to increased accuracy. This will be undertaken in the near future.

There is no indication of the presence of the band from gg bond pairs in the observed spectrum of the melt. This is perhaps not surprising since the concentration of such pairs is only about 10% of the total (Table V). Also, such a band may well be broadened through the mechanisms discussed earlier.

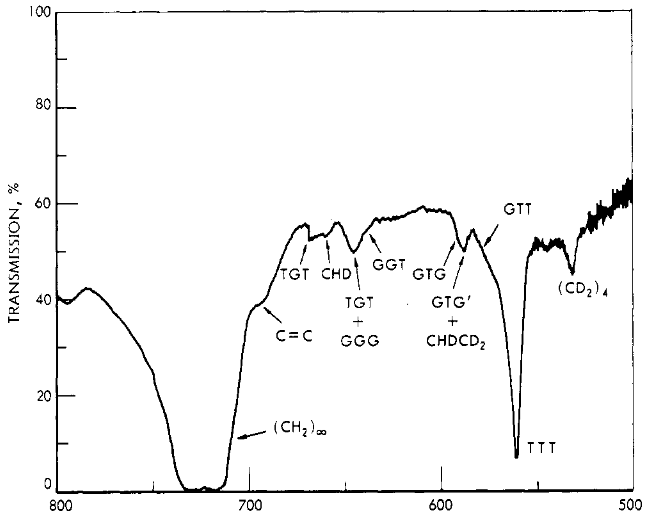

Figure 13. Infrared spectrum of a pressed film of polyethylene (77°K) containing ~5% (CD_2CD_2) groups.

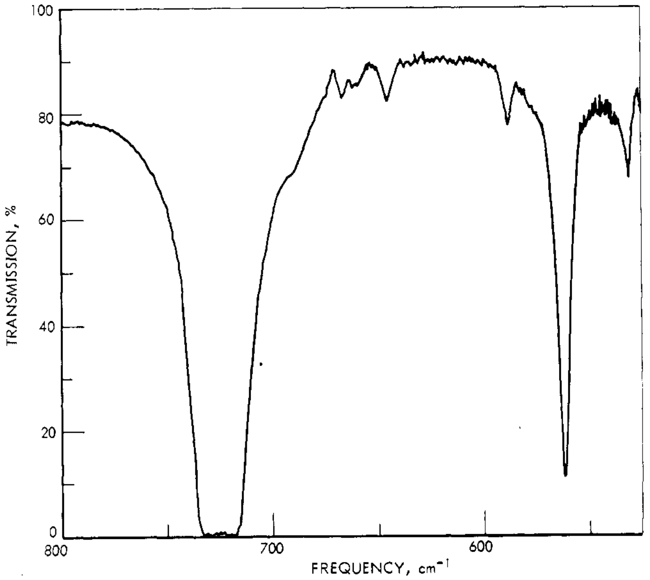

Figure 14. Infrared spectrum of a polycrystalline matte of polyethylene (77°K) containing ~5% (CD_2CD_2) groups.

In the solid state, the *N*(tt):*N*(tg) ratio is, of course, much larger than for the melt. In the case of the pressed films, its value was about 4. For the polycrystalline matte, it was larger yet, about 20, a value which is in keeping with the higher order expected in the crystalline state.

The -$(CH_2)_mCD_2CD_2(CH_2)_n$-System

Calculated Frequencies. There are seven conformationally distinct bond triads which are energetically reasonable, as compared to three bond pairs for the CD_2 case. Their vibrational frequencies were calculated using 4,4,5,5-*n*-octane-d_4 as a model. In each case, the outermost bonds were fixed in the trans position. These results are summarized in Table VI.

In the first approximation we expect two rocking modes since there are two CD_2 groups. From the normal coordinates, we find this to be only a fair description of this more complex system. There is some tendency for mixing of CD_2 rocking coordinates with carbon skeletal coordinates. Also as we found for the CD_2 system, we may expect perturbations to these modes to become increasingly serious the closer their frequencies are to the 722-cm^{-1} fundamental.

Table VII
Frequencies (cm^{-1}) and Assignments of Bands Observed in the Infrared Spectrum of 5% $(CD_2)_2$ Polyethylene in the Region 730–500 cm^{-1}

Freq, Rel Intensity	Assignment	Rel Integrated Intensity	
		Film	Cryst
725 (vvs)	$(CH_2)_\infty$, CH_2 rocking (ν_8)		
690 (vvw, sh)	$(CH_2)_\infty$, cis C═C	0.05_5	0.06_9
666 (vvw, sh)	$(CD_2)_2$, tgt (calcd 662)	0.02_0	0.00_7
662 (vvw)	CHD, ttt (calcd 658)	0.02_9	0.03_4
645 (vw)	$(CD_2)_2\left\{\begin{array}{l}\text{tgt (calcd 640)}\\ \text{ggg (calcd 640)}\end{array}\right.$	0.05_5	0.03_4
640 (vvw, sh)	$(CD_2)_2$, ggt (calcd 636)	0.02_9	0.00
625 (vvw)	?		
600 (vvvw)	$(CD_2)_2$, gtg (calcd 595)		
589 (vw)	$(CD_2)_2$, gtg′ (calcd 581) $CHDCD_2$, ttt (calcd 583)	0.07_9	0.07_2
575 (vvw, sh)	$(CD_2)_2$, gtt (calcd 569)	0.06_7	0.00
562 (vw)	$(CD_2)_2$, ttt (calcd 556)	1.00	1.00
~542 (vvw, b)	$(CH_2)_\infty$, ∠CCC bend cutoff (ν_5)		
531 (vvw)	$(CD_2)_4$, t_5 (calcd 527)		

It is natural to classify the triads according to the conformation of the central bond. If this bond is trans, one rocking mode falls in the region 664–724 cm^{-1} and the other in the region 556–595 cm^{-1}. The higher frequency vibration is symmetric with respect to the local inversion center between the CD_2 groups, which symmetry in the case of the ttt and gtg′ triads extends to the nearest CH_2 groups as well. The lower frequency vibration is antisymmetric to this center and is, consequently, infrared active. This is fortunate since a mode having a lower frequency is less subject to complicating interactions as we have previously noted.

If the central bond is gauche, the two modes fall in the less well separated regions, 726–662 and 640–636 cm^{-1}, and their intensities may be more nearly equal. In the lower region, all three triads have nearly the same frequency, and it will prove impossible to separate them. Although there is a greater frequency separation in the upper region, these bands are subject to the broadening factors previously discussed; and, in fact, only the tgt mode is not totally obscured by the 722-cm^{-1} fundamental.

Interpretation of the Spectrum. The infrared spectrum of the $(CD_2)_2$ polymer at 77°K is rich in bands in the region 700–500 cm^{-1} (Figures 13 and 14). The strongest is at 562 cm^{-1} and belongs, of course, to the ttt mode (calculated 556 cm^{-1}). Another much less intense band at 531 cm^{-1} which is also readily assignable belongs to the trans sequence $(CD_2)_4$ (calculated frequency 527 cm^{-1} for *trans*-3,3,4,4,5,5,6,6-*n*-nonane-d_8).

The principal isotopic impurity is $CHDCD_2$, which may be present in concentrations as high as 5% of that of CD_2CD_2. Vibrations of this group in a trans chain have frequencies calculated to be 681 and 583 cm^{-1}. At least part of the intensity of the band observed at 589 cm^{-1} probably is due to this impurity.

Most of the remaining bands can be assigned to one or more of the triads. This assignment is summarized in Table VII, where we note that the calculated frequencies are lower than the observed by 2–9 cm^{-1}. This is the expected effect of anharmonicity, and the consistency of the shift tends to support the assignments.

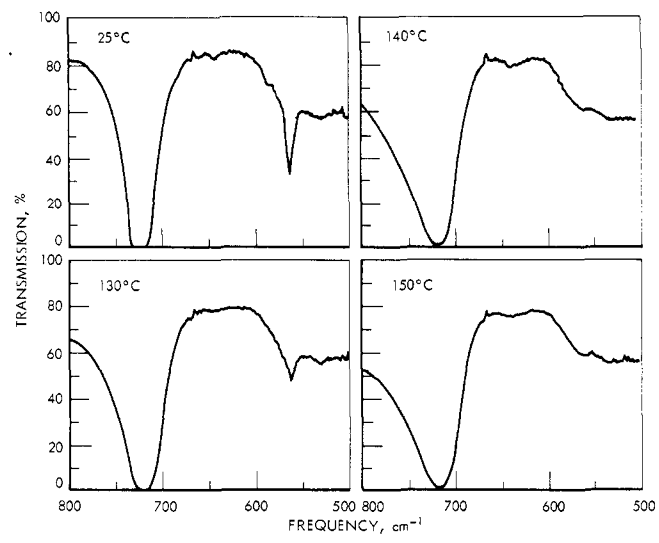

Figure 15. Temperature dependence of a pressed film of polyethylene containing 5% CD_2CD_2 groups.

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).