ing simple single excitations from the ground configuration, since considerable mixing of several excited configurations of the same symmetry is found to occur.

Acknowledgments. The authors wish to thank M. Hackmeyer for helpful discussions concerning the CI calculations. Support of this research by National Science Foundation Grant No. GP-7875 is gratefully acknowledged. Services and computer time made available by the State University of New York Computing Center have been invaluable in this study.

Discrimination of Stereochemical Configurations of 2,4-Dichloropentane, 2,3-Dichlorobutane, and Poly(vinyl chloride) by Carbon-13 Nuclear Magnetic Resonance

C. J. Carman,*[1a] A. R. Tarpley, Jr.,[1b] and J. H. Goldstein[1b]

Contribution from the B.F. Goodrich Company, Research Center, Brecksville, Ohio 44141, and the Department of Chemistry, Emory University, Atlanta, Georgia 30322. *Received September 10, 1970*

Abstract: Natural-abundance carbon-13 nuclear magnetic resonance spectra, with proton noise decoupling, have been obtained for pure *meso*- and *rac*-2,4-dichloropentane, pure *meso*- and *rac*-2,3-dichlorobutane, and two samples of poly(vinyl chloride) of different stereochemical configuration. The ^{13}C chemical shifts of the chlorinated hydrocarbon models are interpreted in terms of their rotational isomers. The sensitivity of ^{13}C shifts to stereoisomers was found to be an order of magnitude greater than that of proton shifts. Triad sequences were easily distinguished for poly(vinyl chloride), but the diad, tetrad, or pentad structures may be more difficult to extract from ^{13}C spectra than from proton spectra taken at high frequency.

Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C nmr) has provided microstructural information on a number of polymer systems.[2-4] The determination of stereochemical configurations by ^{13}C nmr has been demonstrated by Schaefer[2b] on homopolymers of poly(propylene oxide) and by Bovey[4] on homopolymers of poly(vinyl methyl ether), polystyrene, poly(methyl methacrylate) and polypropylene. Differences observed in ^{13}C chemical shifts of carbons differing only in stereochemical configuration were greater than the corresponding differences reflected by proton chemical shifts.

Stereochemical configuration in poly(vinyl chloride), PVC, has been the subject of many proton nmr investigations.[5-22] Proton nmr spectra of PVC provide diad[9]–tetrad[12,21] information from the methylene resonances and triad[9]–pentad[20-22] information from the methyne resonances. However, complexity due to proton coupling and the overlapping of the many proton chemical shifts leads to ambiguities in tacticity analyses except perhaps at 220 MHz.[21] Even here accurate quantitative analyses of pentad structures are questionable.[21-22]

In this article results are described for the investigation of PVC by ^{13}C nmr. Since *meso*- and *rac*-2,4-dichloropentane have been used as model compounds for the interpretation of proton nmr spectra of PVC,[7,10,11,23-25] these same compounds are used as models for ^{13}C studies. In addition, ^{13}C spectra have been obtained of pure *meso*- and *rac*-2,3-dichlorobutane. The stereochemical environments of these model compounds have been interpreted and related to the ^{13}C spectra of PVC samples having different amounts of syndiotacticity as indicated by ir and X-ray diffraction studies.

Experimental Section

2,3-Dichlorobutane was obtained from Aldrich Chemical Co. and 2,4-dichloropentane was prepared by the method of Pritchard.[26]

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(1) (a) B. F. Goodrich Co.; (b) Emory University.

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The stereoisomers were separated using a Varian Aerograph Autoprep gas chromatograph, Model 700. *meso*- and *rac*-2,4-dichloropentane were separated using the following conditions: injection port temperature, 190°; detector temperature, 170°; collector temperature, 140°; column temperature, 140°; helium flow, 38 ml/min; back pressure, 50 psi; 250-μl sample; 0.25 in. × 20 ft column of 30% 1,2,3-tris(2-cyanoethoxy)propane on 30/60 mesh Chrom R. *meso*- and *rac*-2,3-dichlorobutane were separated using the same conditions except that the column temperature was 110° and the injection port temperature was 160°.

One PVC sample was a commercial polymer made at +50° while the other was a fraction of a polymer made at +40° with *n*-butyraldehyde as a chain-transfer agent. This polymer fraction was low molecular weight ($\sim$2100) and gave a low-viscosity solution in *o*-dichlorobenzene. The polymer fraction was approximately 20% crystalline by X-ray diffraction studies and the ratio of the 635- to 690-cm^{-1} infrared bands was 2.0; slightly higher than for a commercial polymer.[27]

All ^{13}C nmr spectra were obtained in the frequency-sweep mode with a Bruker Scientific HFX-90 spectrometer operating at 22.62 MHz. Proton noise decoupling was employed in all cases and the spectra were time averaged using a Fabri-Tek 1074. Both 10- and 13-mm sample tubes were used and ^{19}F external lock was obtained on hexafluorobenzene contained in a 5-mm capillary inserted into the larger sample tubes.

All chemical shifts are expressed in parts per million relative to 10% internal CS$_2$ and were measured using a sweep width of 2 Hz/cm and a sweep rate of 3 Hz/sec. The model compounds were run as neat liquids and accumulated for about 16 scans to obtain good definition. Polymer samples were run as 10% (w/v) solutions in *o*-dichlorobenzene, and resonance positions were determined after accumulating for 1000–2000 scans at 4 Hz/cm and 6 Hz/sec. Under these conditions it is estimated that the absolute chemical shifts are good to approximately 2.0 Hz or 0.1 ppm, but the uniform conditions employed make the relative chemical shifts internally very consistent, to at least 0.5 Hz or 0.025 ppm.

Results

Table I gives the ^{13}C chemical shifts for *meso*- and *rac*-2,4-dichloropentane. The value for the chemical shift is an average to ±0.1 ppm measured from spectra of the pure isomer and from spectra of the mixture of meso and racemic isomers. Also included in this table are the differences in ^{13}C chemical shifts between the meso and racemic isomers and, for comparison, the differences in ^{1}H chemical shifts between these isomers. The same data are given for *meso*- and *rac*-2,3-dichlorobutane in Table II. The ^{13}C chemical shifts for PVC are given in Table III. The ^{13}C chemical shifts for the methyne carbon in a syndiotactic, hetereotactic, and isotactic triad are given as well as the ^{13}C chemical shift differences among the three kinds of triad sequences. For comparison, corresponding proton shift differences for the triad sequences are reported. The two ^{13}C chemical shifts reported for PVC methylene carbons are for two broad methylene resonances apparent in the spectra. No assignment as to sequence configuration was made. Corresponding differences in proton chemical shifts are given for comparison.

Table I. ^{13}C Chemical Shifts[a] for *meso*- and *rac*-2,4-Dichloropentane

Carbon	Meso	Racemic	Δ^{13}C (m − r)[b]	Δ^{1}H (m − r)[c]
>CHCl	138.3	137.2	1.13	0.19
>CH$_2$	142.3	142.1	0.20	−0.04; −0.30
-CH$_3$	168.1	167.3	1.00	−0.02

[a] ^{13}C chemical shifts are in parts per million upfield from internal CS$_2$. [b] The difference (ppm) in the ^{13}C chemical shifts between the meso and racemic isomers. [c] The difference (ppm) in the ^{1}H chemical shifts between the pure meso and racemic isomers; from ref 10.

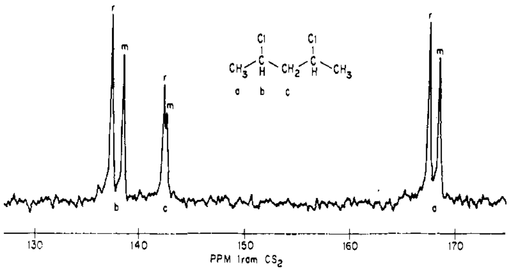

Figure 1. Proton noise-decoupled, natural-abundance 22.62-MHz ^{13}C nmr spectrum of a mixture of *meso*- and *rac*-2,4-dichloropentane. The sweep width was 20 Hz/cm, the sweep rate 30 Hz/sec. The spectrum is time averaged for 16 scans. The chemical shifts are in parts per million upfield from CS$_2$.

Table II. ^{13}C Chemical Shifts[a] for *meso*- and *rac*-2,3-Dichlorobutane

Carbon	Meso	Racemic	Δ^{13}C (m − r)[b]	Δ^{1}H (m − r)[c]
>CHCl	131.2	132.3	−1.09	0.136
-CH$_3$	170.7	172.8	−1.99	−0.038

[a] ^{13}C chemical shifts are in parts per million upfield from internal CS$_2$. [b] The difference (ppm) in the ^{13}C chemical shifts between the meso and racemic isomers. [c] The difference (ppm) in the ^{1}H chemical shifts between the pure meso and racemic isomers; from A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **84,** 743 (1962).

Table III. ^{13}C Chemical Shifts[a] for Poly(vinyl chloride)

Carbon	^{13}C chemical shift	Δ^{13}C (s − h); (h − i)[b]	Δ^{1}H (s − h); (h − i)[c]
-CHCl			
Syndiotactic	135.7	−1.1	−0.10
Heterotactic	136.8		
Isotactic	137.8	−1.0	−0.12
-CH$_2$	145.9		
	146.9		

[a] ^{13}C chemical shifts are in parts per million upfield from internal CS$_2$. [b] The difference (ppm) in the ^{13}C chemical shifts between syndiotactic and heterotactic carbons and heterotactic and isotactic carbons, respectively. [c] The difference (ppm) in the ^{1}H chemical shifts between syndiotactic and heterotactic protons and heterotactic and isotactic protons, respectively; from ref 9.

Discussion

Figure 1 shows a proton noise-decoupled ^{13}C spectrum of a mixture of *meso* and *rac*-2,4-dichloropentane. The two resonances near 168 ppm are due to the methyl carbons, one resonance arising from the meso structure and the other from the racemic structure. The area of the peaks near 142 ppm is half the peak area of the peaks near 138 ppm. Since there is one methylene carbon to two methyne carbons in 2,4-dichloropentane, the resonances at 142 ppm are assigned to the meso and racemic methylene carbons and the resonances at 138 ppm to the methyne carbons. Meso and racemic assignments were made by measuring the ^{13}C chemical

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(27) Private communication from Dr. C. E. Wilkes, B. F. Goodrich Co., Research Center, Brecksville, Ohio.

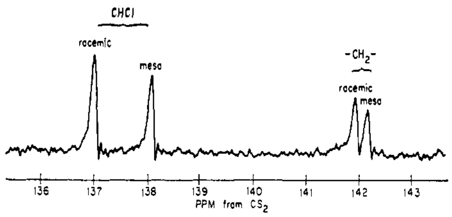


Figure 2. Proton noise-decoupled, natural-abundance 22.62-MHz ^{13}C nmr spectrum of methyne and methylene carbons of *meso*- and *rac*-2,4-dichloropentane. The sweep width was 4.0 Hz/cm, the sweep rate 6 Hz/sec. The spectrum is time averaged for 16 scans. The chemical shifts are in parts per million upfield from CS_2.

shifts of the pure meso and pure racemic compounds and comparing these shifts to those found for the mixture. Confirmation of these assignments was obtained by increasing the concentration of either the racemic or meso compound in the mixture. Figure 2 shows the methylene and methyne carbon resonances at higher resolution.

Although 2,3-dichlorobutane is not actually a model compound for PVC, the ^{13}C spectra of its stereoisomers aided the interpretation of the spectra of the *meso*- and *rac*-2,4-dichloropentanes. The methyl and methyne ^{13}C chemical shifts were assigned for the pure isomers and for a mixture of isomers in the same manner as for the isomers of 2,4-dichloropentane. The ^{13}C shifts are given in Table II.

Proton nmr and infrared studies[23–25] have shown that the principal rotational isomer of *rac*-2,4-dichloropentane, present at room temperature, is the TT conformation shown in Figure 3a. However, two rotational conformers of *meso*-2,4-dichloropentane are possible at room temperature. These are the energetically equivalent GT and TG forms shown in Figure 3b. Flory[28] has suggested that the principal conformer comprises 86% of the structure of either the *meso*- or *rac*-2,4-dichloropentane. A distribution of the other possible conformations contributes to the rest of the structure. Molecular models of *rac*-2,4-dichloropentane, in the TT conformation, clearly show that both methyl carbons are always trans to the methyne carbon and conversely the methyne carbon is always trans to the methyl carbon. For the principal conformation of the meso isomer, half the methyl carbons are trans and half are gauche to a methyne carbon. Consequently, the average environment for both the methyl and methyne carbons of the meso isomer has gauche conformations that the corresponding carbons in the racemic isomer never experience. These different rotational conformations that the carbons are experiencing seem to be a reasonable explanation for the 1.00- and 1.13-ppm differences in ^{13}C chemical shift between the meso and racemic methyl and methyne carbons. The much smaller ^{13}C chemical shift difference (0.20 ppm) found for the methylene carbons is attributed to the fact that there is no carbon present with which the methylene can form a trans or gauche conformation. The fact that there is a chemical shift difference, however, does show that the meso and racemic methylenes are not chemically equivalent. Our data for *meso*- and *rac*-2,4-dichloropentane and the

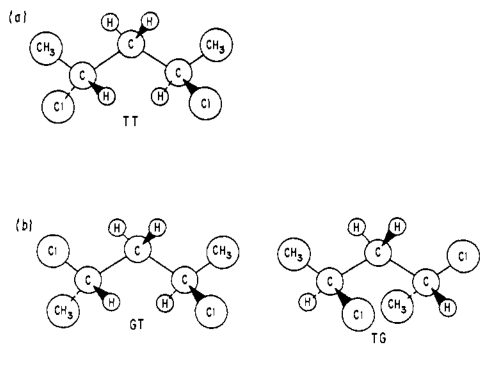
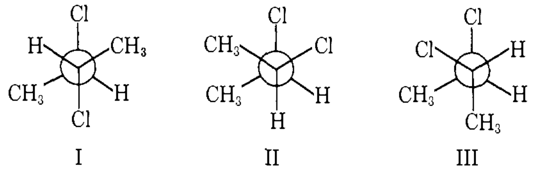


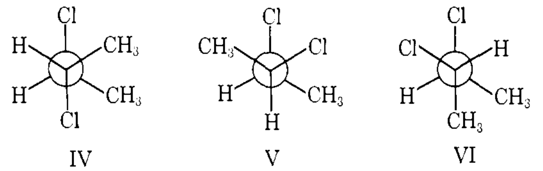
Figure 3. Most stable room-temperature rotational conformation for (a) *rac*- and (b) *meso*-2,4-dichloropentane (ref 23–25).

interpretation based upon rotational isomers are in agreement with previously reported data[29] that carbons in the gauche conformation are more shielded and shifted further upfield than are carbons in corresponding trans conformations.



I II III

meso rotamers



IV V VI

racemic rotamers

Such an interpretation is strengthened by the data for *meso*- and *rac*-2,3-dichlorobutane. Table II shows that both the methyne and methyl carbons of the meso isomer are further downfield than for the racemic isomer, just the opposite to our findings for the 2,4-dichloropentanes. Proton nmr[30] has shown that the most stable rotamer for *meso*-2,3-dichlorobutane is the rotamer with the chlorine atoms trans (I). This rotamer has trans methyl carbons which are predicted to be downfield relative to methyls in gauche environments. Proton nmr has also suggested[31] that the most stable rotamer for *rac*-2,3-dibromobutane would be IV, which has trans halogen atoms and gauche methyl groups. One might infer that rotamer IV would also be the most stable for the *rac*-2,3-dichlorobutane. However, based on the magnitude of proton coupling constants, Bothner-By[30] has proposed that all three rotamers are equally populated for *rac*-2,3-dichlorobutane. Thus, rotamers IV and VI, which gave gauche methyls, account very nicely for the fact that the ^{13}C methyl shifts of *rac*-2,3-dichlorobutane are upfield from those for the meso isomer. The difference between the methyl ^{13}C chemical shifts of the meso and racemic isomers of 2,3-dichlorobutane is larger than

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[28] P. J. Flory and A. D. Williams, *J. Amer. Chem. Soc.*, **91**, 3118 (1969).

[29] E. F. Mooney and P. H. Winson, *Annu. Rev. NMR Spectrosc.*, **2**, 157 (1969).

[30] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **84**, 743 (1962).

[31] F. A. L. Anet, *ibid.*, **84**, 748 (1962).

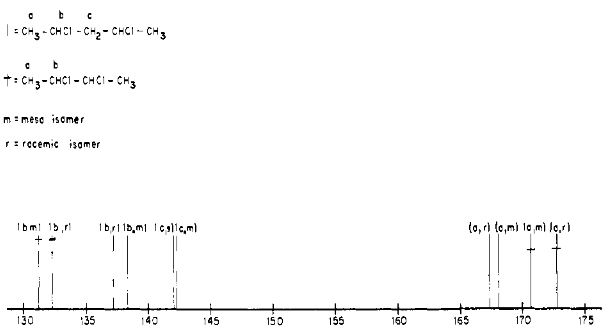


Figure 4. ^{13}C chemical shifts in parts per million upfield from CS_2 for the stereoisomers of 2,3-dichlorobutane and 2,4-dichloropentane.

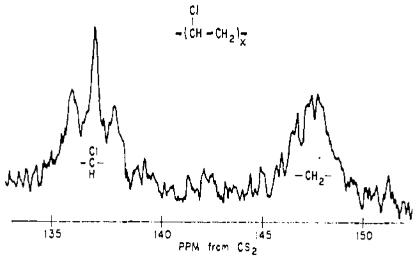


Figure 5. Proton noise-decoupled natural-abundance 22.62-MHz ^{13}C nmr spectrum of commercial poly(vinyl chloride) made at +50°. The spectrum, obtained from a 10% (w/v) solution in *o*-dichlorobenzene, was time averaged for 720 scans at ~40° using a sweep width of 10 Hz/cm and a sweep rate of 15 Hz/sec. Resonance positions are given in parts per million upfield from CS_2.

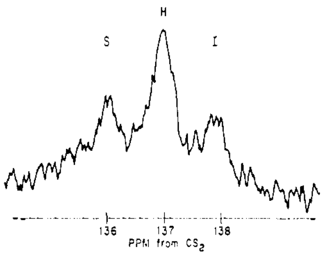


Figure 6. Proton noise-decoupled natural-abundance 22.62-MHz ^{13}C nmr spectrum of methyne carbons in commercial PVC made at +50°. The spectrum, obtained from a 10% (w/v) solution in *o*-dichlorobenzene, was time averaged for 2100 scans at ~40° using a sweep width of 4.0 Hz/cm and a sweep rate of 6 Hz/sec. Resonance positions are given in parts per million upfield from CS_2.

that for the methyl shifts of *meso*- and *rac*-2,4-dichloropentane (1.99 *vs.* 1.00 ppm). We are postulating that this is because the average environment of the methyl carbon in *rac*-2,3-dichlorobutane has relatively more gauche methyls than in *meso*-2,4-dichloropentane. From Figure 3b, half the methyls of the most stable conformations of *meso*-2,4-dichloropentane are gauche, whereas two out of three methyls for *rac*-2,3-dichlorobutane are gauche.

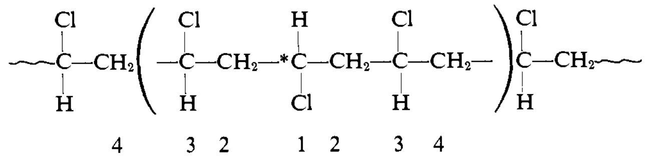
Also, as shown in Table II, the methyne ^{13}C chemical shift of *rac*-2,3-dichlorobutane is 1.09 ppm upfield from that of the meso isomer. Since the methyne carbon cannot form trans or gauche structures, this ^{13}C chemical shift difference between the methyne carbons in the meso and racemic isomers must be related to differences in the steric orientations of the two chlorine atoms. In rotamer I of the meso isomer the methyne carbon is situated between trans chlorine atoms, whereas in rotamers V and VI of the racemic isomer the methyne carbons lie between gauche chlorine atoms. This ^{13}C chemical shift difference is additional evidence[30] that all possible rotamers contribute to the structure of *rac*-2,3-dichlorobutane, for if rotamer IV with trans chlorines were the most stable rotamer then the methyne would have the same environment as rotamer I and no chemical shift difference would be observed.

Figure 4 shows the ^{13}C chemical shifts for the stereoisomers of both 2,4-dichloropentane and 2,3-dichlorobutane. In all cases ^{13}C chemical shifts are at least an order of magnitude more sensitive for differentiating stereoisomers than are the corresponding proton chemical shifts (Table II). One should also notice that a methyne in a 2,3-dichloro structure is 6 ppm downfield from a methyne in a 2,4-dichloro structure. The proton chemical shift difference is only 0.12 ppm.[25,30] Consequently, the carbon nucleus is much more sensitive than the proton nucleus to chlorine substitution in a hydrocarbon.

Preliminary results on measurements of peak areas in the model compounds indicate that within experimental error the nuclear Overhauser effects are the same for each carbon.[32-34] Consequently, we conclude that dipole–dipole coupling dominates the relaxation mechanism[34] and is the same regardless of stereochemical configuration.

Proton noise-decoupled ^{13}C spectra for commercial PVC are shown in Figures 5 and 6. The ^{13}C shifts of PVC carbons are in the same general regions as are the methyne and methylene carbons of the model compound, 2,4-dichloropentane. The methylene carbons occur at about 146 ppm while the methyne carbons are assigned to the group of resonances around 137 ppm. As shown in Figure 6, the methyne region consists of essentially three resonances resulting from syndiotactic, heterotactic, and isotactic triads. The assignment of the lowest field resonance at 135.7 ppm to the syndiotactic triads comes from analogy with the shift in *rac*-2,4-dichloropentane, while the highest field resonance at 137.8 ppm is assigned to the isotactic triads by analogy with the meso isomer of the model compound. The remaining resonance at 136.8 ppm is then assigned to the heterotactic triads.

There appears to be less pentad information available from the methyne carbon region than can be obtained from proton nmr[20-22] data. It was shown earlier that the chemical shifts of the dichloropentanes and dichlorobutanes can be accounted for in terms of rotational conformations formed by four-carbon chains. Assuming that similar conformations are the major structural features determining the ^{13}C shifts in PVC, consider a segment of PVC five monomers long. The example chosen is a syndiotactic triad with a vinyl chloride monomer placed meso on each end.



$$\sim\!\sim\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}\!-\!\mathrm{CH_2}\left(-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}\!-\!\mathrm{CH_2}\!-\!{}^{*}\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}\!-\!\mathrm{CH_2}\!-\!\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}\!-\!\mathrm{CH_2}\!-\right)\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}\!-\!\mathrm{CH_2}\!\sim\!\sim$$

4 3 2 1 2 3 4

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(32) K. F. Kuhlmann and D. M. Grant, *J. Amer. Chem. Soc.*, **90**, 7355 (1968).

(33) K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).

(34) A. J. Jones, D. M. Grant, and K. F. Kuhlmann, *J. Amer. Chem. Soc.*, **91**, 5013 (1969).

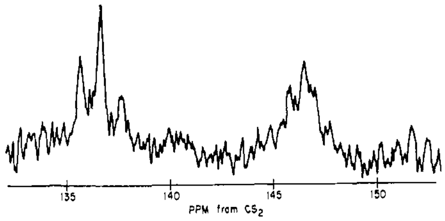

Figure 7. Proton noise-decoupled natural-abundance 22.62-MHz ^{13}C nmr spectrum of the low molecular weight fraction of butyraldehyde-modified +50° PVC. The spectrum was accumulated at ~40° for ~2000 scans from a 10% (w/v) solution in *o*-dichlorobenzene at a sweep width of 10 Hz/cm and a sweep rate of 15 Hz/sec. Resonance positions are in parts per million upfield from CS_2.

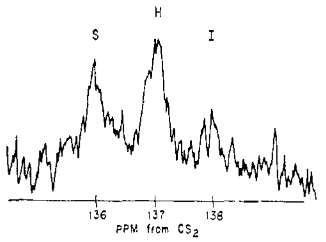

Figure 8. Proton noise-decoupled natural-abundance 22.6-MHz ^{13}C nmr spectrum of the low molecular weight fraction of butyraldehyde-modified +50° PVC. The spectrum was accumulated from a 10% (w/v) solution in *o*-dichlorobenzene at ~40° for ~2000 scans at a sweep width of 4 Hz/cm and a sweep rate of 6 Hz/sec. Resonance positions are in parts per million upfield from CS_2.

If the designated carbon has a chemical shift determined by a four-carbon chain, then only three monomers plus the methylene of one adjacent monomer are involved. Thus, it appears reasonable that the methyne carbons in PVC may be relatively insensitive to pentad structure.

However, if the methyne resonances are not complicated by pentad overlap effects, then the peak areas for syndiotactic, heterotactic, and isotactic sequences may be measured and related directly to tacticity in PVC. Thus, the spectrum of a low molecular weight PVC which should be higher in syndiotacticity[27] is shown in Figures 7 and 8. Comparison of Figures 8 and 6 shows that for the low molecular weight PVC the syndiotacticity increased relative to the heterotacticity, whereas the isotacticity decreased. The line widths observed for the low molecular weight polymer are somewhat smaller than those in commercial PVC, perhaps due to the lower viscosity of the low molecular weight polymer solution. We hope to clarify this point with spectra obtained at elevated temperatures. Also it is hoped that subsequent ^{13}C spectra for commercial PVC at elevated temperatures may lead to better definition of the triad resonances in the methyne region and enable us to make accurate area measurements.

As shown in Figure 5, the methylene region of commercial PVC appears as a broad resonance having some discernible fine structure. According to the above interpretation, based on the conformation of four-carbon chains, this broad resonance must be the result of all possible tetrad structures, each tetrad having a slightly different ^{13}C chemical shift. For the low molecular weight PVC, as shown in Figure 7, the methylene region changed relative to the commercial PVC and appears to contain two major resonances at about 145.9 and 146.9 ppm upfield from CS_2, possibly reflecting some diad information.

The ^{13}C chemical shift for the methyne carbons in 2,3-dichlorobutane is ~6 ppm downfield from the "PVC-like" methyne in 2,4-dichloropentane. Thus, the existence of any tail-to-tail structures in PVC could probably be easily identified. The limitation would be the long time that would be necessary for time averaging. Also, the generally large ^{13}C chemical shift differences observed for 2,3-dichloro structures compared with 2,4-dichloro structures suggest that the structure of chlorinated PVC could be more easily determined using ^{13}C rather than proton nmr studies.[35,36]

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