Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

NMR Studies of Polyaldehydes

Edward G. Brame JR.[a][b]; O. Vogl[c]
[a] ELASTOMER CHEMICALS DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE [b] The 60-MHz NMR studies were performed in the Plastics Department, [c] CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE

To cite this Article Brame JR., Edward G. and Vogl, O.(1967) 'NMR Studies of Polyaldehydes', Journal of Macromolecular Science, Part A, 1: 2, 277 — 289
To link to this Article: DOI: 10.1080/10601326708053971
URL: http://dx.doi.org/10.1080/10601326708053971

J. MACROMOL. SCI. (CHEM.), A1(2), 277–289 (1967)

NMR Studies of Polyaldehydes

EDWARD G. BRAME, JR.*
ELASTOMER CHEMICALS DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE

AND

O. VOGL
CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE

Synopsis

The large differences in chemical shifts that result from oxygen's being incorporated into the polymer backbone yield more accurate qualitative and quantitative analysis through NMR than those polymers that do not have oxygen in the backbone. Configuration effects are observed without interference from methylene groups that frequently interfere in the analysis of polymers. However, the results obtained on polyacetaldehyde with the new 200-MHz Varian Instrument at ambient temperature show a much more complete definition of the configuration than can be obtained with lower-frequency instruments. They show that there are more isotactic triads than syndiotactic triads for the methyl group in "atactic" polyacetaldehyde and that this polyacetaldehyde is nearly a random polymer. By means of the new 220-MHz Varian Instrument and heating of the samples to elevated temperatures for better-resolved lines complete configurational analysis of polyacetaldehyde should become possible.

High-resolution NMR spectroscopy has been increasingly used in the structure determination of polymers. It has been used successfully in determining compositions and configurations of various kinds of polymers. Among those copolymers whose compositions have been determined by NMR and reported in the literature are butadiene–isoprene (*1*), oxyethylene–oxypropylene

---

[*] The 60-MHz NMR studies were performed in the Plastics Department.

(2), styrene–methyl methacrylate, and styrene–methyl styrene. The mole ratio of the monomers was obtained in all cases.

Polymers whose configuration has been determined by NMR and reported in the literature included polymethyl methacrylate (3), polypropylene (4), polytrifluorochloro ethylene (5), and polyvinyl chloride (6). In each of these different cases NMR proved to be a very powerful tool in tacticity analysis, and the results obtained were shown to be independent of, and complementary to, other methods.

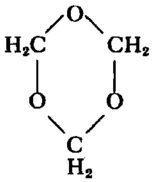
In the application of NMR to the compositional and configurational analysis of polymers that contain oxygen in the backbone several advantages are found. One of these is the elimination of methylene groups in the backbone and the other is the large inductive effect of oxygen on adjacent proton groups, causing a large shift of the lines attributed to these groups from other lines in the spectra. The net result is that a large separation occurs among the several possible lines. Quantitative measurement of each individual line is consequently enhanced, with the result that the composition of these polymers is determined more accurately. The results reported in this article represent the latest developments in a continuing study of polyaldehydes (7).

RESULTS AND DISCUSSION

The polymer that results from aldehyde polymerization contains alternating oxygen and carbon in the backbone. These alternating oxygen atoms have a greater effect on the intermediate carbon groups in shifting the proton lines than on the carbon groups adjacent to just one oxygen, as in the case of polyethylene oxide, for example. The results of shift measurements made on monomers and polymers of various oxymethylene and oxyethylene combinations at 80°C in *p*-chlorophenol solutions (8) are shown in Table 1. All measurements were made at the same concentration of 12% w/v. The shift values are given in delta units, which express the numbers in parts per million downfield from the reference line of tetramethylsilane. The proton assignments for each of the shift values shown are given in the second column. Beginning at the top a methyl group adjacent to an oxygen appears at $\delta = 3.36$. Normally, a methyl group attached to a long aliphatic chain has a value of $\delta = 0.90$; thus, the shift from $\delta = 0.90$ to $\delta = 3.36$ repre-

TABLE 1

Polymers of Oxymethylene and Oxyethylene (*8*)

Chemical shift δ	Proton assignments
3.36	$CH_3—O—C$
3.72	$—O—(CH_2—CH_2—O—)_n—C—$
4.72	$—C—O—CH_2—O—C—$
4.94	$—O—(CH_2—O—)C_n—$
5.04	

sents the effect of the proximity of oxygen on the methyl resonance. In the case of methylene groups surrounded by oxygen the shift value is seen to be either δ = 4.72 or δ = 4.94. These values are in contrast with δ = 1.25 for a methylene group in a chain of methylene groups. Again the effect of oxygen is seen. The difference of 0.22 ppm between δ = 4.72 and δ = 4.94 is attributed to the difference in the kind of carbon groups attached to the surrounding oxygens. Thus, the replacement of only one of the methylene groups with a methyl is seen to shift the resonance 0.22 ppm.

In the case of the polymer of oxyethylene two methylenes are surrounded by oxygen instead of one. This reduction in the inductive effect of oxygen is seen to shift the resonance line to higher fields, yielding the value of δ = 3.72. Therefore, it is not surprising to detect low levels of oxyethylene in copolymers of oxyethylene and oxymethylene. The literature reports that as low as 1 mole-% of oxyethylene in polyoxymethylene can be detected. The last chemical shift value shown is that for the cyclic trimer trioxane. A single sharp peak is seen at δ = 5.04 for the methylene protons of trioxane. This shift value is only slightly, but still distinctively, different from the value shown for the methylene protons of polyoxymethylene. In each of the examples only sharp single lines were seen. No fine structure was observed. Hence, there are no apparent spin–spin couplings occurring among the proton groups, including those in the oxyethylene polymer.

In contrast to the polymers of oxyethylene and oxymethylene, polyacetaldehyde has a methyl substituent on each carbon atom and therefore is capable of existing in different stereoregular configurations. The various tacticity forms, if present, might be observed if the tools to be used in detecting them were sensitive enough. Because of the direct approach of high-resolution NMR in measuring tacticity, samples of polyacetaldehyde were examined at 60MHz with the Varian A-60 Spectrometer. Figure 1 shows the spectrum of a 10% solution of polyacetaldehyde in perchloroethylene. Two sets of lines are observed. The stronger set at the right is attributed to the methyl group; the weaker set at the left is attributed to the tertiary proton group. The latter is broader than that at the right because of the spin coupling interaction occurring between the two proton groups.

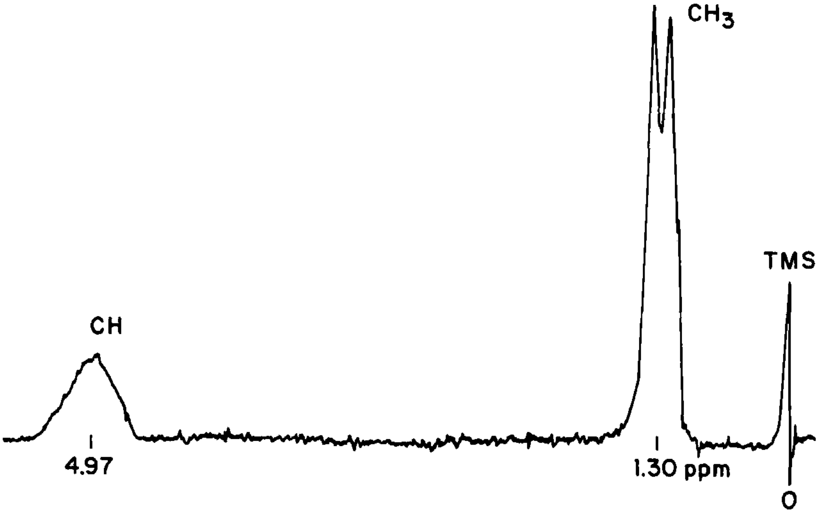


FIG. 1. 60-MHz NMR spectrum of a 10% solution of polyacetaldehyde in perchloroethylene at 32°C (7).

Upon heating the sample of polyacetaldehyde in perchloroethylene to 93°C the line widths of the two sets narrowed sufficiently to produce reasonably well resolved lines. Figure 2 shows this pattern. The lines on the right show two sets of doublets, while the lines on the left show at least one quartet pattern. Because of the distortion seen in the intensity pattern of the quartet there appears to be a second set of quartet lines overlapping on the right. This conclusion can be supported by the fact that two sets of doublets are readily observed for the methyl resonance, the weaker set being to the right of the stronger set. Thus, the weaker lines in both sets are the result of their respective proton groups' interacting with each other. The stronger lines in both sets are the result of the interaction of those respective proton groups. The methyl lines were decoupled from the tertiary proton lines, yielding a decoupled spectrum, which showed the weaker lines more clearly resolved than is observed in Fig. 2. To assign the two sets of lines observed in either the methyl or the tertiary proton group region, several model compounds were selected for examination. One of these was the all-*cis* cyclic trimer of acetaldehyde, paraldehyde. The spectrum of paraldehyde appears the same as that of acetaldehyde except for the position of the two sets of lines. The shift values for the lines in this spectrum, besides those for acetaldehyde, metaldehyde, and polyacetaldehyde, are shown in Table 2. The

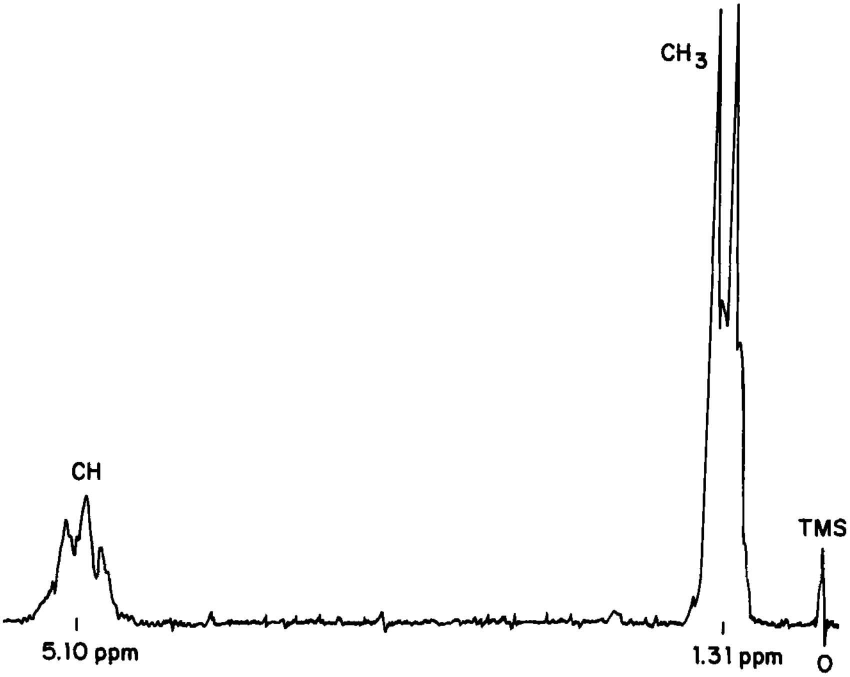


FIG. 2. 60-MHz spectrum of a 10% solution of polyacetaldehyde in perchloroethylene at 93°C (*7*).

TABLE 2
NMR Data of Acetaldehyde and Its Polymers

Sample	Temp., °C	Solvent	Chemical shift δ	
			CH	CH_3
Acetaldehyde	32	$CDCl_3$	9.80	2.20
Paraldehyde	105	—	5.02	1.28
Metaldehyde	100	CCl_2CCl_2	4.99	1.31
Polyacetaldehyde	93	CCl_2CCl_2	5.10	1.32, 1.30

shift values were obtained at elevated temperatures for each of these samples except for acetaldehyde, which was obtained at 32°C, the ambient temperature for the Varian A-60 Instrument. Immediately it is seen that the shift values of the two groups for acetaldehyde are greatly different from those of the two groups in the other compounds, with the result that little interference occurs if some acetaldehye is present in these other samples.

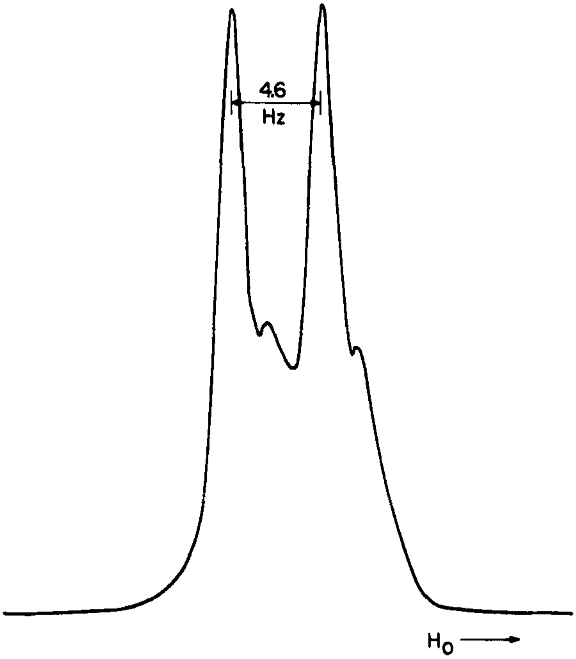


FIG. 3. 60-MHz methyl spectrum of a 10% solution of polyacetaldehyde in perchloroethylene at 93°C (7).

Paraldehyde shows its shifts at slightly higher fields than does polyacetaldehyde. The same thing is seen for metaldehyde, which is the all-*cis* cyclic tetramer of acetaldehyde. Its shifts are about the same as those observed for paraldehyde. However, because of the small variation in the measurement of the shift values and because of shift dependence on solvent and concentration in the solvent the method that was used in assigning the chemically shifted lines in the spectrum of polyacetaldehyde was to spike the polymer solution with appropriate model compounds. This spiking technique is important in view of the findings of Jungnickel and Reilly (9). They observed a slight difference in the chemical shifts of the equatorial methyls between the *cis-trans* cyclic trimer ($\delta = 1.24$) and the all-*cis* cyclic trimer ($\delta = 1.26$). Even though these shifts are only slightly different, they are sufficiently different to cause a possible error in the line assignments of polyacetaldehyde without the spiking experiment. Furthermore, cyclic compounds and, specifically, the *cis-trans* isomer should be used only as a first approximation. Linear model compounds are to be preferred; work on the synthesis and structure of these model compounds is under way in Goodman's* laboratory.

Figure 3 shows the methyl spectrum of polyacetaldehyde that was obtained from a 10% solution in perchloroethylene at 93°C. The spin coupling constant measured for the lines is seen to be 4.6 Hz. The weak pair of lines seen to the right of the strong pair are well enough resolved to show the effect of spiking the sample with paraldehyde. Figure 4 shows the result of the spiking experiment.

It is seen that the lines attributed to the methyl protons of paraldehyde coincide exactly with the weak lines in the methyl spectrum of polyacetaldehyde. These weak lines in the polymer spectrum may therefore be attributed to isotactic methyls, which are equivalent to the all-*cis* methyls in paraldehyde. Then it follows that the stronger lines must be assigned either to syndiotactic methyls or to heterotactic methyls. If they are assigned to syndiotactic methyls, elastomeric polyacetaldehyde would be a block copolymer of isotactic and syndiotactic sequences. Since this is unlikely, the lines must be assigned to heterotactic methyls. Some syndiotactic structure could still be present, but because of its

---

* M. Goodman, private communication, 1965.

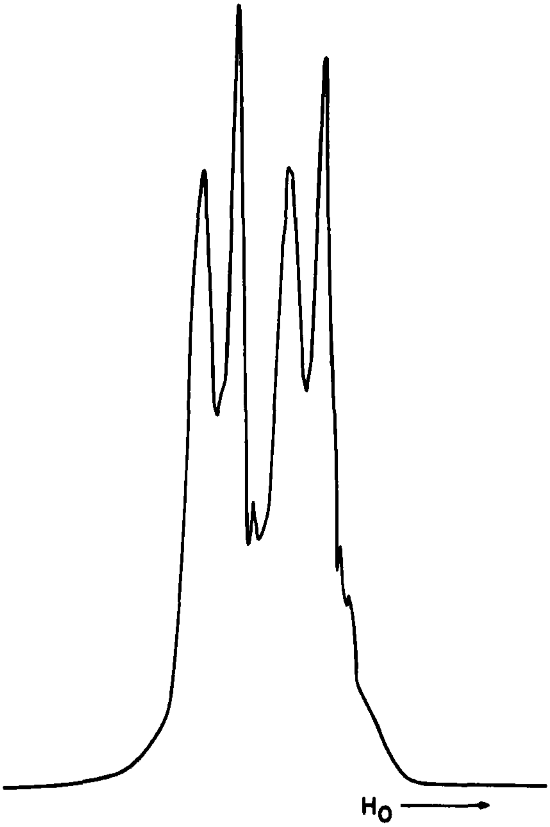


FIG. 4. 60-MHz methyl spectrum of a 10% solution of polyacetaldehyde in perchloroethylene at 93°C, to which some paraldehyde has been added (7).

relatively low amount lines attributed to its methyls could easily be masked by the strong heterotactic methyl lines.

Chemical shift data were taken from the literature to be compared with results obtained from polyacetaldehyde. In Table 3 the chemical shift values of methyl groups in isotactic-heterotactic-syndiotactic sequences are given for poly-α-methyl styrene and polymethyl methacrylate. In both of these cases the isotactic methyls appear at low field of the heterotactic methyls, and the syndiotactic methyls appear at high field of the heterotactic methyls. This relationship is just the opposite to that observed for polyacetaldehyde, because the isotactic methyls are observed to appear at high field of the heterotactic methyls in the spectrum of poly-

TABLE 3

Chemical Shifts (δ) of CH_3 Groups in Stereoregular Polymers

Sample	Isotactic	Heterotactic	Syndiotactic
Poly-α-methylstyrene[a]	0.82	0.35	0.14
Poly(methyl methacrylate)[b]	1.22	1.05	0.91

[a] Data of Brownstein (*10*).
[b] Bovey and Tiers (*3*).

acetaldehyde. Therefore, there appears to be no consistent relationship in the relative positions of the different tactic methyls among the stereoregular polymers that have been examined by NMR; consequently, this method of assigning tactic groups in NMR spectra should not be used. From the NMR studies of other polymers Ramey and Field (*11*) also arrived at this conclusion.

In a final confirmation of the assignment of the weak lines in the spectrum of polyacetaldehyde to isotactic groups and the strong lines to heterotactic groups Fig. 5 shows the spectra obtained on the model compounds of α- and β-parachloral. α-Parachloral is the *trans-cis-trans* isomer of the trimer of trichloroaldehyde. β-Parachloral is the all-*cis* isomer of the trimer of trichloroaldehyde.

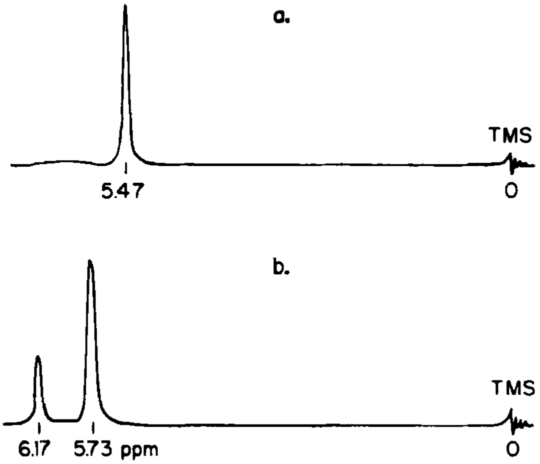


FIG. 5. 60-MHz spectra of 50% solution of parachloral: (a) all-*cis* isomer, (b) *trans-cis-trans* isomer (*7*).

It is immediately seen that there is only one line for the all-*cis* isomer and that there are two lines of 1:2 intensity for the *trans-cis-trans* isomer. It is further seen that the line assigned to the protons of the all-*cis* isomer appears at higher fields than the lines assigned to the protons of the *trans-cis-trans* isomer and that the weaker line of the two lines in the spectrum of the *trans-cis-trans* isomer appears at the lowest field. The analogy between the results shown in this figure for α- and β-parachloral and the results shown in Figs. 3 and 4 for polyacetaldehyde support the assignments made in the spectrum of polyacetaldehyde, since the all-*cis* structure is essentially equivalent to an isotactic structure in polymers.

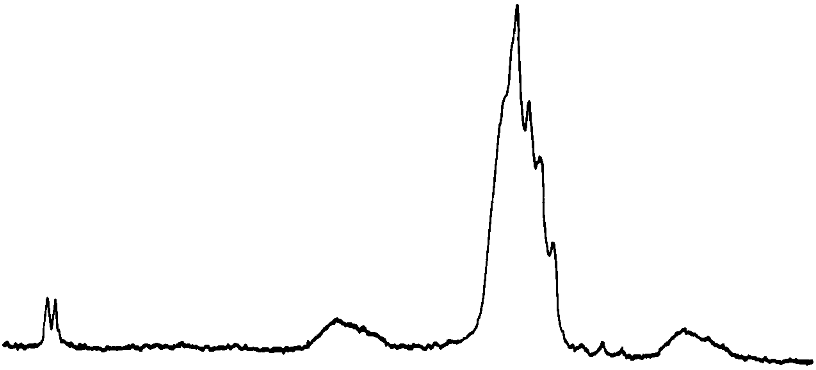


FIG. 6. 200-MHz methyl spectrum of a 25% solution of polyacetaldehyde in perchloroethylene at 26°C.

The data shown and discussed previously were obtained on an instrument operating at 60 MHz. In going to higher-frequency field instruments the possibility exists of observing lines due to syndiotactic groups. Goodman and Brandrup (*12*), who also have been active in this area, reported the NMR results obtained with polyacetaldehyde at 100 MHz. They found a pattern similar to that obtained at 60 MHz for the methyl resonance, except for a shoulder on the low-field side. They indicated that it could be attributed to syndiotactic structure and that is represented only a small concentration in the structure of the polymer. Because of our interest in defining the tacticity composition of polyacetaldehyde more carefully an examination was made with a new Varian Spectrometer that operates at 200 MHz and utilizes a superconducting magnet system. Figure 6 shows the spectrum obtained with this instrument.

Only the methyl lines are shown. Since the instrument was not equipped with a variable temperature probe, the sample was at 26°C for the scan. The resolution of the 200-MHz spectrometer can be seen from the methyl resonance of acetaldehyde, which was present as an impurity. Its weak doublet is seen at the left of the spectrum. The two broad lines on each side of the methyl resonance of polyacetaldehyde are attributed to spinning side bands. It is apparent from this 200-MHz spectrum that more than only two pair of lines are present. The question arises whether there are only three pair of lines due to the three different tacticity forms or whether there are more than three pair of lines present. Figure 7 shows a high-resolution pattern obtained for the methyl line in polyacetaldehyde at 200 MHz. Besides the three partly resolved lines appearing at high field of the strongest line in the pattern there are two shoulders that appear at low field of this strongest line. By means of the du Pont Model 310 Curve Resolver an analysis of the pattern was performed. The result is shown in Fig. 8. The analysis shows that there are five pair of lines that contribute to the pattern. Two pair are assigned to isotactic methyls, two to heterotactic methyls, and one to syndiotactic methyls. The two pair due to isotactic methyls are at the high-field part of the pattern, and one pair due to syndiotactic methyls is at the low-field part. The two remaining pair due to the heterotactic methyls are intermediate in position. Area measurements

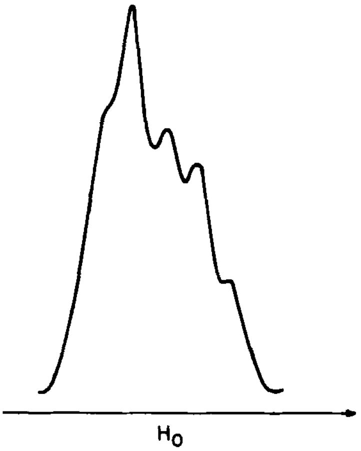


FIG. 7. 200-MHz methyl spectrum of polyacetaldehyde.

show that 14% of the area of the complex pattern is attributed to syndiotactic methyls, 62% to heterotactic methyls and, finally, 24% to isotactic methyls. If only the effect of adjacent carbon groups on a given carbon group is considered, so that we are dealing with triads, then one can say that these area measurements are attributed to three different kinds of triad in the polymer, but because of the appearance of two sets of pairs for the isotactic and heterotactic methyls some secondary effects appear to be occurring as well. The indication is that carbon groups further removed than only adjacent groups are affecting the carbon groups under examination (pentads). The examination of normal polyacetaldehyde and polyacetaldehyde deuterated on the tertiary hydrogen position with the new 220-MHz Varian Instrument at elevated temperatures should confirm these results and yield a more accurate quantitative determination of the polymer configuration. On the basis of the results obtained thus far it can be said that polyacetaldehyde is nearly random but that the polymerization favors the formation of more isotactic sequences over that of syndiotactic sequences.

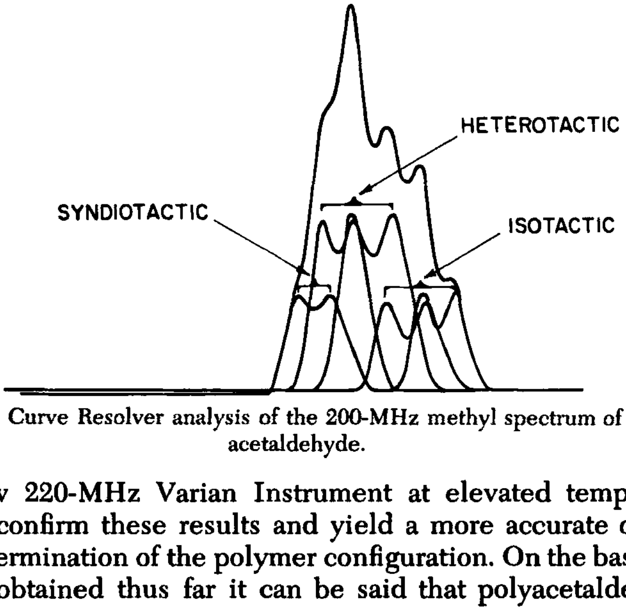


FIG. 8. Curve Resolver analysis of the 200-MHz methyl spectrum of polyacetaldehyde.

Goodman, with whom we are actively in contact, suggests that the polymer is built up from the following sequences . . . LLDDLLLLDDLLDDDD . . . (*12*). Since the heterotactic sequences are made up of switchovers between L and D units, both isotactic and syndiotactic sequences must be on the order of about 3 units in length to give the high concentration of heterotactic units seen in NMR analysis.

Acknowledgment

We wish to thank R. C. Ferguson of Central Research Department for obtaining the 200-MHz spectrum for use in this study.

REFERENCES

1. Y. Y. Chen, *Anal. Chem.*, **34**, 1134 (1962).
2. A. Mathias and N. Mellor, *Anal. Chem.*, **38**, 472 (1966).
3. F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).
4. J. C. Woodbrey, *J. Polymer Sci.*, **B2**, 315 (1964).
5. G. V. D. Tiers and F. A. Bovey, *J. Polymer Sci.*, **A1**, 833 (1963).
6. F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).
7. E. G. Brame, Jr., R. S. Sudol, and O. Vogl, *J. Polymer Sci.*, **A2**, 5337 (1964).
8. G. Allen and R. Warren, *Chem. Ind. (London)*, **15**, 623 (1964).
9. J. L. Jungnickel and C. A. Reilly, *J. Mol. Spectr.*, **16**, 135 (1965).
10. S. S. Brownstein, *Makromol. Chem.*, **48**, 127 (1961).
11. K. C. Ramey and N. D. Field, *J. Polymer Sci.*, **B3**, 69 (1965).
12. M. Goodman and J. Brandrup, *J. Polymer Sci.*, **A3**, 327 (1965); J. Brandrup and M. Goodman, *J. Polymer Sci.*, **B2**, 123 (1964).

Received by editor September 9, 1966
Submitted for publication September 9, 1966