The Observation and Identification of Tetrad Sequences in Deuterated Poly(vinyl methyl ether)

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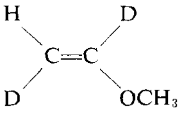
ABSTRACT: Stereospecifically deuterated *cis*- and *trans*-vinyl methyl ether monomers have been polymerized to isotactic and atactic polymers at low temperature. The polymers were analyzed by 100-MHz high-resolution nmr spectroscopy and the methylene region was interpreted in terms of tetrad sequences of monomer units. The moderately overlapping triad and tetrad peaks were resolved and component areas integrated by computer analysis. Specific tetrad assignments have been made and tested.

The proton nmr spectrum of poly(vinyl methyl ether) has been used in many investigations of the various possible configurations of this polymer.[1-6] Initial 60-MHz observations by Kern[1] showed only a singlet for the methoxyl group and complex multiplets for the methinyl and methylene protons. Brownstein and Wiles[3] later showed that the methoxyl group was indeed sensitive to configuration. Similarly, working at 100 MHz, Ramey[4] observed three absorptions for the methoxyl group and reported that the three methoxyl absorptions (with increasing field strength) correspond to syndiotactic, heterotactic, and isotactic sequences in the polymer. Using proton–proton spin decoupling at 60 MHz, Bovey[2] clearly observed dyads in the methylene region. The meso and racemic dyad assignments made by Bovey were later confirmed by Ramey[4] from the 100-MHz spin decoupled spectra of atactic and isotactic poly(vinyl methyl ether). Recently Johnson, Heatley, and Bovey[7] obtained the decoupled ^{13}C spectrum of poly(vinyl methyl ether) and observed the absorptions corresponding to racemic and meso carbons as well as possible pentad fine structure for the methoxyl carbon.

Recent improvements in chemical techniques and instrumentation such as stereospecific deuteration and spin–spin decoupling have allowed additional fine structure to be observed in the methylene proton region for a number of different polymers.[8-12] Fine structure in the methylene region occurs because the methylene proton resonance is sensitive not only to the configuration of the adjacent α carbons (dyad structure) but also to that of the next nearest α carbons (tetrad structure). Thus, the influence of a sequence of four monomer units on the central methylene resonance can be detected. Up to the present time, however, there has been no report of the observation of tetrad sequences for poly(vinyl methyl ether).

In this paper we wish to report the high-resolution nmr spectra of poly(vinyl-α,*cis*-β-d_2 methyl ether), prepared from monomer I, and poly(vinyl-α,*trans*-β-d_2 methyl ether), prepared from monomer II. Analysis of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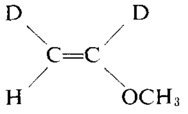
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these polymer spectra with a computer curve fitting program allowed the various overlapping triad and tetrad intensities to be estimated. With this information at hand, we were able to test and confirm our tetrad assignments, as well as demonstrate consistency between tetrad and triad frequencies.

The stereospecific introduction of deuterium atoms in vinyl monomers represents a convenient technique for polymer spectra simplification. By replacing the methylene CH_2 with a CHD and the α H with α D, the complications of geminal and vicinal proton couplings are eliminated and individual resonances for tetrad sequences can be seen and assigned. Deuterium exhibits only weak coupling with protons. A proton–deuterium coupling constant is approximately one-seventh of the corresponding proton–proton constant.[13] Also, the absorptions of protons coupled with deuterium are not appreciably broadened because deuterium has a small electrical quadrupole moment.[14]

Results and Discussion

Figure 1 shows the contrasting 100-MHz proton nmr spectra of (a) isotactic poly(vinyl methyl ether) and (b) the deuterated analog poly(vinyl-α,*trans*-β-d_2 methyl

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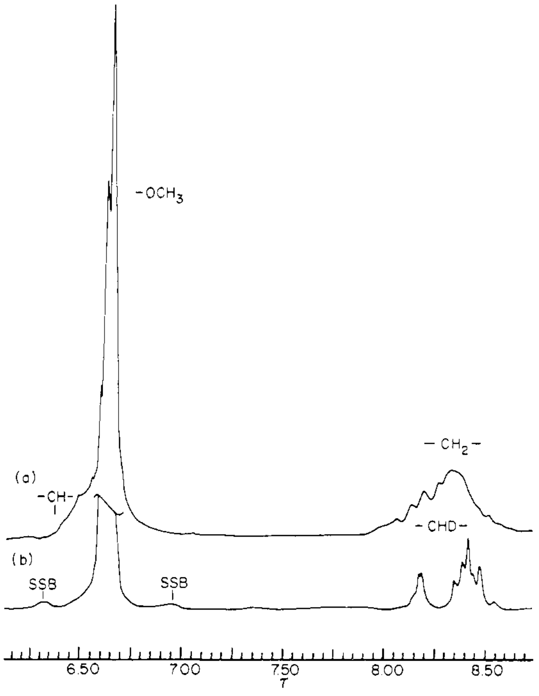

Figure 1. 100-MHz proton nmr spectrum (10% w/v in $CDCl_3$ at 35°) of (a) isotactic poly(vinyl methyl ether), (b) poly(vinyl-α,*trans*-β-d_2 methyl ether.)

ether). Both polymers were prepared with $BF_3 \cdot OEt_2$ (1.0 mol %) in toluene solvent at −60°. An obvious feature of Figure 1b is the absence of the α-H multiplet which, in the case of the nondeuterated polymer, appears as a shoulder at about τ 6.5 on the downfield side of the methoxyl absorption. Elimination of the α-H resonance from the deuterated polymer spectrum is especially advantageous, since it allows the methoxyl triads to be observed and measured without interference from the overlapping methinyl proton multiplet. Previous attempts to assess quantitatively the methoxyl triad resonances relied on measurement of relative peak heights[3,4] rather than peak areas. Figure 2a shows the 100-MHz slow sweep expansion of the methoxyl resonance for poly(vinyl-α,*trans*-β-d_2 methyl ether) (polymer **3b**). The corresponding calculated triad curve (Figure 2b) was generated from appropriate estimates of peak height, position, and line width, for each peak, by curve fitting with a curve resolution computer program.[15] A sufficient number of data points was taken to define adequately the shape of the experimental nmr curve. For the triad curves presented in Figures 2a and 2b, the difference between the experimental and calculated curves was 5.26%, calculated as shown in the Experimental Section. Integration of each resolved triad peak was subsequently performed with the same program and the values are presented in Table I.

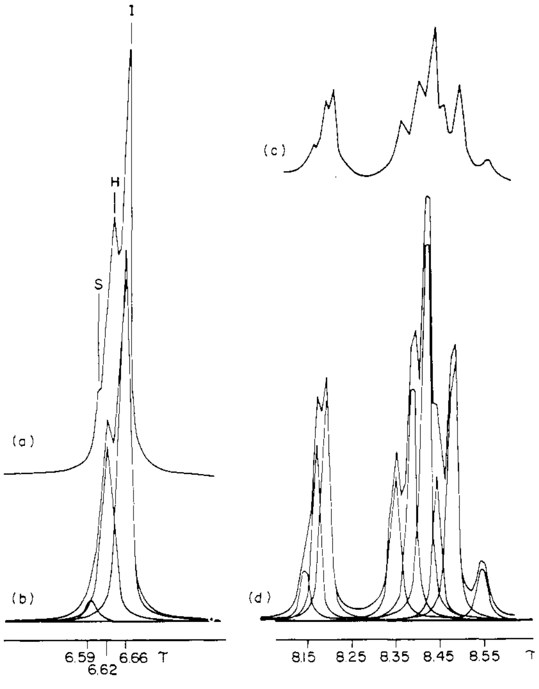

Figure 2. (a) 100-MHz slow sweep expansion of methoxyl triads, (b) computer calculated triad curve, (c) 100-MHz slow sweep expansion of β-CHD tetrads, (d) computer calculated tetrad curve.

TABLE I
COMPARISON OF OBSERVED METHOXYL TRIADS IN DEUTERATED POLY(VINYL METHYL ETHER) WITH THOSE CALCULATED FROM METHYLENE TETRADS

POLYMER	OBSERVED TRIADS			CALCULATED TRIADS		
	(S)	(H)	(I)	(S)	(H)	(I)
3 a	0.10	0.35	0.55	0.11	0.35	0.56
3 b	0.09	0.36	0.54	0.09	0.35	0.53
3 c	0.11	0.52	0.37	0.13	0.50	0.38

Comparison of Figure 1a and 1b also shows that the complex methylene multiplet between τ 8.0 and 8.5 of poly(vinyl methyl ether) collapses in the deuterated species to nine observable peaks. Since all proton–proton spin couplings have been effectively removed by deuteration, the resonances for the single methylene proton now appear as singlets corresponding to tetrad configurational sequences for the β-CHD group. As indicated by Bovey,[16] the meso resonance may be resolved into three tetrad resonances (mmm, mmr, and rmr),[16] all heterosteric,[17] giving six different chemical shifts. The six meso resonances are due to the three erythro-meso and three threo-meso sequences. The terms erythro and threo (or syn and anti)[18,19] refer to the methylene protons on the same side and opposite side of the backbone plane, respectively, as the methoxyl groups, when an isotactic sequence is depicted in a planar zigzag conformation. Similarly, the racemic resonance should be split into two homosteric[17] resonance (rrr and mrm) and one heterosteric resonance (rrm) giving a total of ten possible observable β-CHD tetrad chemical shifts

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(15) A. Sarko, unpublished Fortran program.

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TABLE II
TETRAD FRACTIONS OBTAINED FROM COMPUTER INTEGRATION OF 100-MHZ SPECTRA OF DEUTERATED POLY(VINYL METHYL ETHER)

POLYMER	DOWNFIELD MESO TETRADS			RACEMIC TETRADS			UPFIELD MESO TETRADS		
	mmm (8.19T)	mmr (8.16T)	rmr (8.14T)	rrr (8.44T)	rrm (8.35T)	mrm (8.38T)	mmm (8.41T)	mmr (8.47T)	rmr (8.55T)
3a	0.274	0.136	0.043	0.065	0.083	0.134	0.173	0.086	0.005
3b	0.165	0.071	0.035	0.088	0.075	0.138	0.253	0.154	0.019
3c	0.088	0.143	0.068	0.066	0.140	0.179	0.167	0.121	0.027

for a polymer which is not too highly stereoregular. In the present case, nine tetrad peaks are clearly discernible.

The moderately overlapping tetrad resonances were similarly resolved by computer analysis. Figures 2c and 2d show the 100-MHz slow sweep expansion of tetrad peaks for poly(vinyl-α,*trans*-β-d_2 methyl ether) (polymer **3b**) and the corresponding computer calculated tetrad curve. The difference between the experimental and calculated sum curves was found to be 6.28% for polymer sample **3b**. For the other polymer samples analyzed (**3a** and **3c**), the average difference between the experimental and calculated tetrad curves was 5.01%. The integrated tetrad fractions are presented in Table II.

Figures 3a and 3b show the expanded β-CHD region (between τ 8.05 and 8.65) for the polymers prepared from the corresponding *trans*- and *cis*-α,β-dideuterated monomers I and II. The polymerization of *cis*- and *trans*-α,β-dideuterated monomers represents a convenient and independent method for distinguishing erythro- and threo-meso tetrads from racemic tetrads. Since polymers 3a and 3b have fairly high isotactic triad contents (55.4 and 54.9%, respectively), and the number average sequence length of meso placements, $\mu_{(m)}$,[20] was calculated to be between 4 and 5, meso mmm tetrads were expected to be most prominent. Furthermore, interchange between the erythro-meso and threo-meso mmm tetrad intensities was expected for the polymers prepared from the cis and trans monomers. Comparison of Figures 3a and 3b indicates that the tetrad peaks at τ 8.19 and 8.41 represent the most prominent tetrad fractions as well as the most significant exchange of peak intensities. On this basis, the peaks at τ 8.19 and 8.41 were assumed to be the downfield and upfield meso mmm tetrads, respectively.

The mmr tetrad resonance was expected to be the next most frequent meso resonance on the basis of the calculated sequence length of meso placements for polymers **3a** and **3b**. The peaks at τ 8.16 and 8.47 are presumably the downfield and upfield mmr tetrads, respectively, and again exhibit the expected interchange of peak intensities between **3a** and **3b**. The remaining meso tetrad resonances located at τ 8.14 and 8.55 are presumably the downfield and upfield rmr tetrads, respectively. The assignment of upfield meso tetrads corresponds to the expected inverted order of shielding from the downfield meso tetrads. A similar relationship was also observed for the meso tetrads of poly(vinyl-α-d_1 chloride)[10] and poly(propylene-*cis*- and -*trans*-d_3).[11] At the present time, however, it is not known whether the erythro-meso proton is less shielded or more shielded than the threo-meso β proton in poly(vinyl methyl ether).

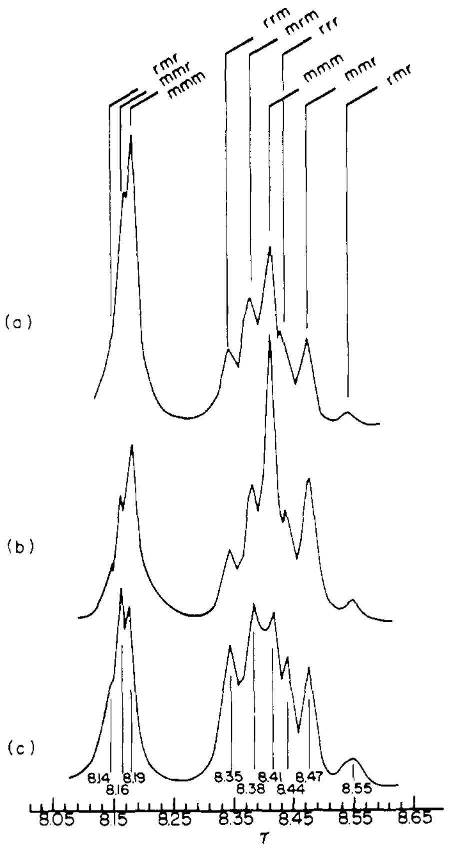

Figure 3. 100-MHz proton nmr expansion of β-CHD region of (a) poly(vinyl-α,*cis*-β-d_2 methyl ether) and (b) poly(vinyl-α,*trans*-β-d_2 methyl ether): (a) and (b) both prepared with $BF_3 \cdot OEt_2$ in toluene at −60°; (c) poly(vinyl-α,*cis*-β-d_2 methyl ether) prepared with PF_5 catalyst in hexane at −60°.

The assignment of meso tetrads in the present study agrees rather closely with the reported decoupled spectra of poly(vinyl methyl ether).[2,4] The centers of the upfield and downfield meso mmm tetrads in Figure 3 are coincident with the centers of the decoupled meso methylene dyad protons reported for poly(vinyl methyl ether). The mean difference in the chemical shifts observed for the upfield and downfield mmm protons in Figure 3 is 0.22 ppm in $CDCl_3$ at 35°. For poly(vinyl methyl ether), the difference in the chemical shifts of the meso methylene protons for the decoupled meso dyads is also 0.22 ppm in chlorobenzene–methylene chloride at 37°, as reported by Ramey.[4] Nmr measurements recently made by Matsuzaki and others[21] for the dimer model compound, *meso*-2,4-dimethoxypentane, demonstrate that the two methylene protons of the dimer model are magnetically nonequivalent and observable. However, the difference in the chemical shifts of the meso methylene protons is reported to be more substantial than for either poly(vinyl methyl ether) or the deuterated analog. This result is not unusual since the meso methylene protons in polystyrene and its corresponding meso dimer model show similar behavior.[22]

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In contrast with the meso tetrads, the racemic tetrads remained relatively unchanged for the polymers prepared from cis and trans deuterated monomers (Table II). The peaks at τ 8.35, 8.38, and 8.44 were assigned to the rrm, mrm, and rrr tetrads, respectively. The rrm tetrad, in principle, should appear as a doublet corresponding to the two possible heterosteric structures. Such a doublet has been observed in the spectra of poly(vinyl chloride)[10,23] and poly(propylene-*cis*- and -*trans-1,2,3,3,3-d*$_5$).[12] On the other hand, the spectra of poly(methyl methacrylate)[24] at 220 MHz and deuterated poly(methyl and -ethyl methacrylate) as well as deuterated poly(isopropyl acrylate)[25] at 100 MHz show only a slightly broadened singlet for the rrm tetrad. Our observations of deuterated poly(vinyl methyl ether) at 100 and 220 MHz also indicate only a singlet for the rrm tetrad.

Figure 3c illustrates the tetrads observed for an atactic polymer of poly(vinyl-α,*cis*-β-d_2 methyl ether) prepared with PF_5 catalyst at $-60°$. From Table I it may be seen that the heterotactic content for this material is very high, which means that the block lengths are very short.[26] For this polymer we expect, and find, a higher proportion of mrm and rmr tetrads than is found for the more stereoregular polymers, *viz.* Figures 3a and 3b.

From Figure 3 it is obvious that there is extensive overlap between the racemic tetrads and the upfield meso portion. The appearance of racemic peaks upfield from a mean value between the meso absorptions is similarly observed for the decoupled spectrum of poly(vinyl methyl ether)[2,4] as well as for the dimer model compound of racemic 2,4-dimethoxypentane.[21]

The tetrad assignments made in this study were confirmed by two independent methods. First, the observed triad mole fractions were found to agree satisfactorily with those calculated from the tetrads. These calculations were carried out using the relationships derived by Frisch, Mallows, and Bovey[27]

$$\text{rr} = \text{rrr} + {}^1/_2(\text{rrm}) \tag{1}$$

$$\text{mr} = \text{mmr} + 2(\text{rmr}) = \text{rrm} + 2(\text{mrm}) \tag{2}$$

$$\text{mm} = \text{mmm} + {}^1/_2(\text{mmr}) \tag{3}$$

The comparison is shown in Table I. Second, the tetrad–tetrad correlation[27] (eq 4) was tested and, for

$$[(\text{mmr}) + 2(\text{rmr})] - [(\text{rrm}) + 2(\text{mrm})] = 0 \tag{4}$$

eleven different spectra of polymers prepared under various conditions, it was found to hold to a mean deviation of 0.018. Other tetrad assignments were considered, but were ruled out on the basis of the above triad and tetrad tests.

Experimental Section

Monomers. The synthesis of vinyl-α,*cis*-β-d_2 methyl ether (I) and vinyl-α,*trans*-β-d_2 methyl ether (II) has been described elsewhere.[28] Monomer was usually contained in a sealed, calibrated ampoule and dried over small pieces of calcium hydride for at least 24 hr. Further purification was performed by allowing the monomer to stand over a freshly prepared sodium mirror for at least 48 hr. The sodium mirror was carefully formed by distilling sodium metal on the inside wall of a Pyrex glass ampoule which had been previously flamed out and dried overnight on a high-vacuum-line manifold at 10^{-5} Torr. Transfer of monomer to the sodium mirror ampoule was made by slowly distilling the monomer through a break-seal which had been broken by means of a glass-enclosed iron magnet. The empty monomer ampoule and break-seal were then melted off at the constriction.

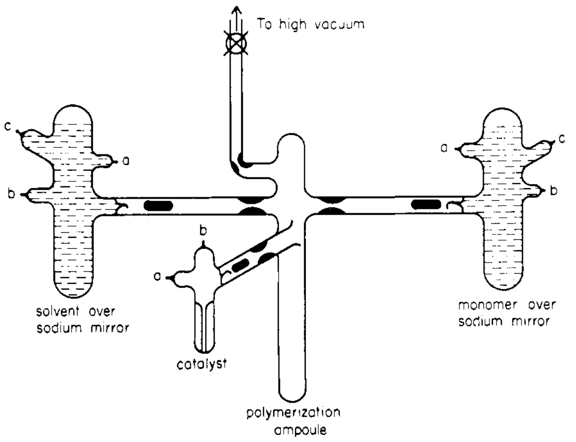

Figure 4. Polymerization apparatus: a, previously connected to high-vacuum manifold; b, previous entry for reagents; c, previous entry for distilled sodium mirror.

Solvents. Toluene and hexane (spectrophotometric grade) were dried first over calcium hydride for 24 hr and then over a freshly prepared sodium mirror for 48 hr before use. The solvents were handled in all-glass systems on a high-vacuum line with the usual precautions.

Catalysts. Commercial grade $BF_3 \cdot OEt_2$ (yellow to brown color) was vacuum distilled under nitrogen. The colorless fraction boiling between 52 and 53° at 20 mm was collected. The $BF_3 \cdot OEt_2$ was further purified over calcium hydride[29] and distilled three times *in vacuo*, the center cut being taken each time. The calculated amount of catalyst was thereafter distilled into a calibrated capillary tube connected to a break-seal and melted off from the main portion of the vacuum line.

Phosphorus pentafluoride catalyst was generated by pyrolysis of *p*-chlorobenzene diazonium hexafluorophosphate (Ozark Mahoning Co., Tulsa, Okla.). The calculated amount of freshly recrystallized diazonium salt was first introduced into a catalyst break-seal under a flow of dry nitrogen, sealed, and dried under high vacuum overnight. The break-seal containing the dry diazonium salt was then melted off the vacuum line, fitted with a glass enclosed magnetic bar, and subsequently fused onto a polymerization ampoule.

Polymerizations. All polymerizations were carried out under high vacuum in an apparatus illustrated in Figure 4. The system was dried overnight at 10^{-5} Torr with intermittent flaming. Solvent (1.0 ml) and monomer (0.25 ml) were sequentially distilled into the polymerization ampoule and mixed thoroughly after the respective break-seals were broken. The monomer–solvent solution was frozen with

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liquid air, and catalyst was introduced. PF_5 catalyst (0.01 mol %) was generated by pyrolysis of the diazonium salt precursor by heating the catalyst ampoule to 155–160°.[30,31] Initiation with $BF_3 \cdot OEt_2$ catalyst (1.0 mol %) was carried out by slowly distilling the etherate complex into the polymerization ampoule, while simultaneously cooling the polymerization ampoule with liquid air. When the condensation of either catalyst in the polymerization ampoule was completed, the empty catalyst, solvent, and monomer ampoules were melted off at the constrictions. The polymerization ampoule, with the contents still frozen at liquid air temperature, was melted off from the vacuum line manifold and placed in a cold temperature bath maintained at −60°. Polymerization was allowed to proceed for 24 hr. The ampoule was then opened and the polymerization was terminated with cold ammoniacal methanol. The polymer was recovered by precipitation in a small volume of warm (35°) distilled water. The precipitated polymer was collected and dissolved in a minimum volume of methanol and the precipitation procedure was again repeated. The polymer was finally dissolved in benzene, filtered through a sintered glass filter, freeze-dried, then further dried under high vacuum overnight. In one instance, the polymerization was terminated at approximately 50% conversion and the unpolymerized monomer was collected and checked by nmr for racemization of the β-CHD. Racemization was not observed.

Nmr Analysis. The freeze-dried polymer was dissolved in $CDCl_3$ (10–15% w/v), filtered through a small sintered glass filter into Royal Imperial nmr tubes, and 2% tetramethylsilane (TMS) was added. The spectra were obtained on a Jeolco 100-MHz spectrometer operated at ambient temperature. $CDCl_3$ was found to be the best solvent for resolution of tetrad absorptions at room temperature. Polymer spectra obtained in aromatic solvents such as chlorobenzene showed poorer triad[3] and tetrad resolution and broadened peaks; even at higher temperatures (100–150°) spectral resolution in aromatic solvents was not as good as in $CDCl_3$ at 37°. Deuterium spin decoupling of the polymers was not attempted. For most deuterated polymer systems the nmr resolution[8,18,22] is adequate to distinguish all tetrads.

Spectral Calculations. The resolution of the nmr curves into individual component peaks was performed with a curve resolution program on an IBM 1620 computer equipped with a CalComp plotter.[15] The experimental curve was digitized at sufficiently narrow intervals along the frequency scale, usually 0.5 Hz, by recording its intensity values (on an arbitrary scale) for each interval. Each spectral peak was identified with an estimated peak position, height, and width at half-height. These parameters were then optimized by fitting the calculated sum curve to the experimental curve, using a linear combination of Gaussian and Cauchy functions to describe each component peak. The best results were obtained with a 40:60 combination of the two functions. The goodness of fit, R, was evaluated from

$$R = \left\{ \frac{\sum_{i=1}^{n} (f_{o_i} - f_{c_i})^2}{\sum_{i=1}^{n} f_{o_i}^2} \right\}^{1/2}$$

where f_{o_i} and f_{c_i} are the observed and calculated sum curve intensities, respectively, for the ith data point. The area under each peak was subsequently obtained by numerical integration with the same program. The triad and tetrad line widths at half-height were found to range between 4.20 and 6.14 Hz. However, the heterotactic line width, in all cases, was found to be about 1 Hz greater than either the syndiotactic or isotactic.

Acknowledgment. We wish to acknowledge the courtesy of Dr. F. A. Bovey and the Bell Telephone Laboratories in the exploratory use of the 220-MHz spectrometer on these samples. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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