are nine distinct branching possibilities (A, B, or C branching from A, B, or C), as many as nine additional kinetic constants would be required to specify the system, not considering whatever constants are necessary to describe the branching mechanism.

**2. Nearest Neighbor Effects.** In the model, the stability of any link was assumed to be independent of the presence and type of neighboring links. If, however, the effect of a given linkage extends beyond this linkage, then additional constants are necessary. For a terpolymer, in the case of an A–A linkage, for example, the following scission constants need to be included: $k_{aaaa}$, $k_{aaab}$, $k_{aaac}$, $k_{baab}$, $k_{baac}$, $k_{caac}$. A total of 36 constants would be required for complete description of the system.

**B.** Two major simplifications were made in the derivation of eq 15–20. The first was that the effect of penultimate and ante-penultimate units was negligible, the second assumed constant feed ratios of monomers ($f_i$). If the first assumption is invalid, alternate treatments are available.[18] If the second is invalid (as, for example, in a batch or semibatch process), then eq 15–20 may be integrated numerically to give appropriate values of $f_{ii}$.

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[18] E. Merz, T. Alfrey, and G. Goldfinger, *J. Polymer Sci.*, **1**, 75 (1946).

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# Line Width of Nuclear Magnetic Resonance High Resolution Spectra of Vinyl Polymers

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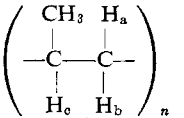
ABSTRACT: The line widths of high resolution nmr spectra of vinyl polymers were studied with particular reference to isotactic polypropylene. It was observed, by deuterium decoupling experiments, that for polypropylene it is the coupling constants through several bonds that mainly determine the broadening of the lines. By eliminating them, we obtained spectra with resonance line widths of the same order of magnitude as observed on small organic molecules.

Let us consider a nondeuterated vinyl polymer in solution. The nmr spectrum of this solution generally does not exhibit well-resolved lines. In the presence of suitable solvents, the widths of the resonance lines can be decreased by increasing the temperature and decreasing the concentration. However, even in the best circumstances, at high temperature, the width of the resonance lines of a polymer ranges from a minimum of 1 to several cycles per second. The purpose of this research is to establish why the bands undergo this residual broadening.

A resonance signal may be broadened as a result of several reasons: I, insufficient average of magnetic dipole–dipole interactions in the solutions, due to relatively slow motion of the chains;[1] II, excessive viscosity of the solutions;[1] III, spectra that are not completely of the first order, with consequent broadening of the experimental bands, which are actually multiple;[2] IV, small long-range coupling constants; and V, not sufficiently rapid exchange among the various conformers so that the same proton may be situated in magnetically nonequivalent surroundings.

It was shown that the line width of a polymer in solution is independent of the molecular weight of the polymer,[1-3] so the viscosity of the solution will not be considered here. Nevertheless, we operated under experimental conditions such that the solution might flow on the test tube walls. If a polymer is not sterically pure, its spectrum consists of the superimposition of the spectra of various components,[4] owing to the presence of different types of tetrads and pentads that may give partly superimposed bands; thus an artificial broadening of the lines is created, due only to the poor resolution of spectrometers. To exclude this difficulty, we mainly used isotactic polypropylene because this polymer can be obtained sterically pure.[5,6]

**Isotactic Polypropylene.** Products A–E have been studied. All isotactic polymers considered were high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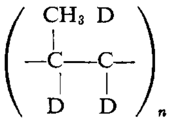
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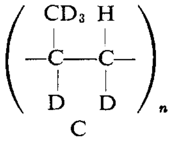
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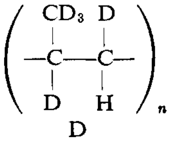
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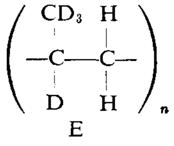
E

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[1] F. A. Bovey, G. V. D. Tiers, and G. Filipovich, *J. Polymer Sci.*, **38**, 73 (1959).

[2] P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

[3] A. Odajima, *J. Phys. Soc. Japan*, **14**, 777 (1959).

[4] F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).

[5] A. Zambelli, A. L. Segre, M. Farina, and G. Natta, *Makromol. Chem.*, in press.

[6] A. Zambelli, private communication.

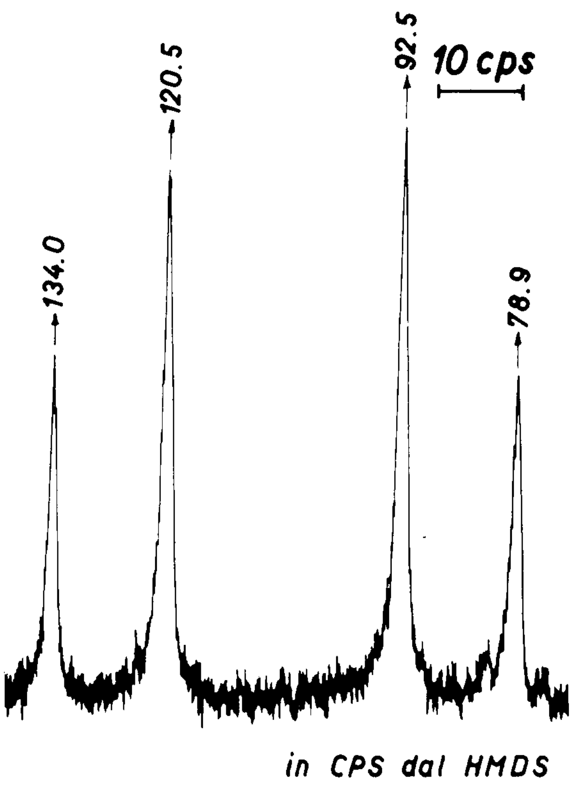


Figure 1. Spectrum of isotactic polypropylene-2,3,3,3-$d_4$ sample E.

molecular weight heptane residues, whose intrinsic viscosity, measured in tetralin at 135°, ranged between 3 and 5 (100 cm$^3$/g). The widths of the lines forming the spectrum of polymer A are, respectively, $CH_3$ $\simeq 1$ cps, $H_a \simeq 2$ cps, $H_b \simeq 2$ cps, and $H_c > 3$ cps. The coupling constants of this polymer are $|J_{AB}| = 13.5$, $J_{AC} \simeq 7$ cps, $J_{BC} \simeq 6$ cps, and $J_{HC-CH_3} = 6.5$ cps. The spectrum of polymer B consists of a singlet having width greater than 2 cps. This broadening may be easily explained by considering the vicinal coupling constant $J_{CD-CH_3}$.

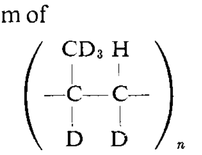
$$J_{CD-CH_3} = \frac{\gamma_D}{\gamma_H} J_{CH-CH_3} = (0.154)(6.5) = 1 \text{ cps}$$

Deuterium was then decoupled. The D-decoupled singlet has a band width less than 0.5 cps; this value may be fully compared with those found in small organic molecules. Cause V, therefore, does not seem to be present. This example, however, does not distinguish between the causes of broadening I, III, IV. In fact, from wide nmr line studies,[7] we know that the methyl group, at the spectrum-running temperature, rotates far faster than the nmr observation time. Therefore it does not supply information on I. Moreover, the broadening of the methyl doublet of sample A can be easily understood by III.

Let us now consider the spectrum of polymer E; it is a spectrum of the AB type which, decoupled from deuterium (Figure 1), shows band widths of the order of 1 cps. This polymer supplies us with precise information, since cause III cannot be present in a spectrum of the AB type. Therefore the broadening of the bands from less than 0.5 (small organic molecules) to 1 cps may be only due to I, IV, or V. The spectra of polymers C and D consist of singlets having width higher than 3 cps. However, under conditions of D decoupling, the width of these singlets is <0.6 cps (Figure 2). Considering that in polymers C and D only cause IV of line broadening has been completely excluded, if line broadening were due to I or V, this broadening should be still present. The fact that this does not occur, except to a very small extent, indicates that long-range coupling is the predominant cause of line broadening in polypropylene. The extreme sharpness of the backbone protons in high molecular weight isotactic polypropylene, obtained under these conditions, and with this type of deuterated polymers, shows that all the motions are fast compared with the nmr observation time. This sharpness of peaks raises the signal-to-noise ratio to such an extent that we observed the $C^{13}$ side bands for polymer D. The $J_{C^{13}-H} = 124.4 \pm 0.5$ cps is quite in agreement with the data obtained on ethane (126 cps) and cyclohexane (123 cps).[8] Moreover, the observation of this band, which is 0.56% of the main signal, reveals the limit of sensitivity to impurities present and indicates that *the steric purity of isotactic polypropylene is higher than 99.5%*.[9]

After these results, which show that the broadening of resonance signals in isotactic polypropylene is mainly due to the presence of long-range coupling constants, we studied other polymers in order to check whether this conclusion might be extended.

**Syndiotactic Polypropylene.**[10] We ran the spectra of syndiotactic polypropylene under the same experimental conditions as for the isotactic ones. The D decoupled spectrum of



$$\left( \begin{array}{cc} CD_3 & H \\ | & | \\ -C- & C- \\ | & | \\ D & D \end{array} \right)_n$$

shows a singlet having width <0.6 cps and other small bands originating from steric impurities. This result confirms that, even in syndiotactic polypropylene, all motions are fast in comparison with the nmr observation time. This behavior is completely different from what was observed on polymethyl methacrylate,[11] but since in this polymer line widths are very broad, we think that the results may be compared only on suitably deuterated samples.

**Polyvinyl Chloride.** We ran D-decoupled spectra of a high molecular weight polyvinyl chloride-$\beta,\beta$-$d_2$ in pentachloroethane at 150° (Figure 3). The spectrum shows that the three syndiotactic pentads are unresolved; the four heterotactic pentads are resolved

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(7) J. G. Powles, *Polymer*, 1, 219 (1960).

(8) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution N.M.R. Spectroscopy," Vol II, Pergamon Press Ltd., London, 1966, p 1012.

(9) We note in addition that we succeeded in detecting the isotopic impurities of the methyl group, which can be estimated to be 1.5%, since the isotopic purity of the monomer was evaluated as 99.5% on the whole by mass spectrometry. Now if we suppose a random distribution of the isotopic impurities, 1.5% of the methyl group will contain one proton.

(10) A. Zambelli, G. Natta, and I. Pasquon, *Polymer Symp., Part C*, **4**, 411 (1963).

(11) S. Brownstein and D. M. Wiles, *Can. J. Chem.*, **44**, 153 (1966).

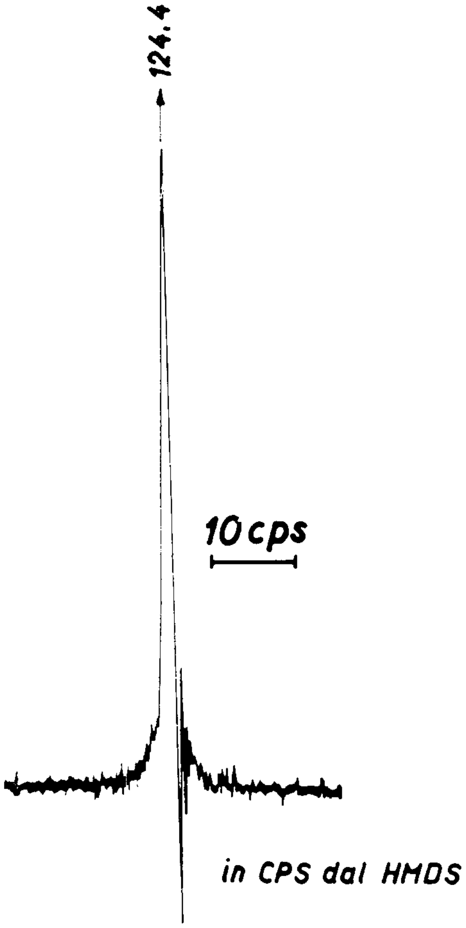

Figure 2. Spectrum of isotactic polypropylene-1,2,3,3,3-$d_5$ sample D.

only two by two; the three isotactic pentads do not superimpose and yet have a line width of $\simeq$1 cps.[4,12] Therefore, also in nonsterically pure PVC polymer the single bands (that is, without superposition) are much more sharp than those usually observed. This residual broadening can originate from different causes, for instance superposition of heptads, long-range coupling between the different pentad protons, or causes I or V.

**Polyethylene.** The spectrum of undeuterated linear polyethylene is a singlet with a 0.7 cps width. Now, if the V effect were present in the completely deuterated polymer containing a small amount (5%) of protons, a smaller width, in D-decoupling conditions, due to the absence of geminal coupling would be found.[13,14] We do not observe any difference between the line width of the two polymers. We may conclude that at 150° all motions of polyethylene are rapid in comparison with the nmr observation time.

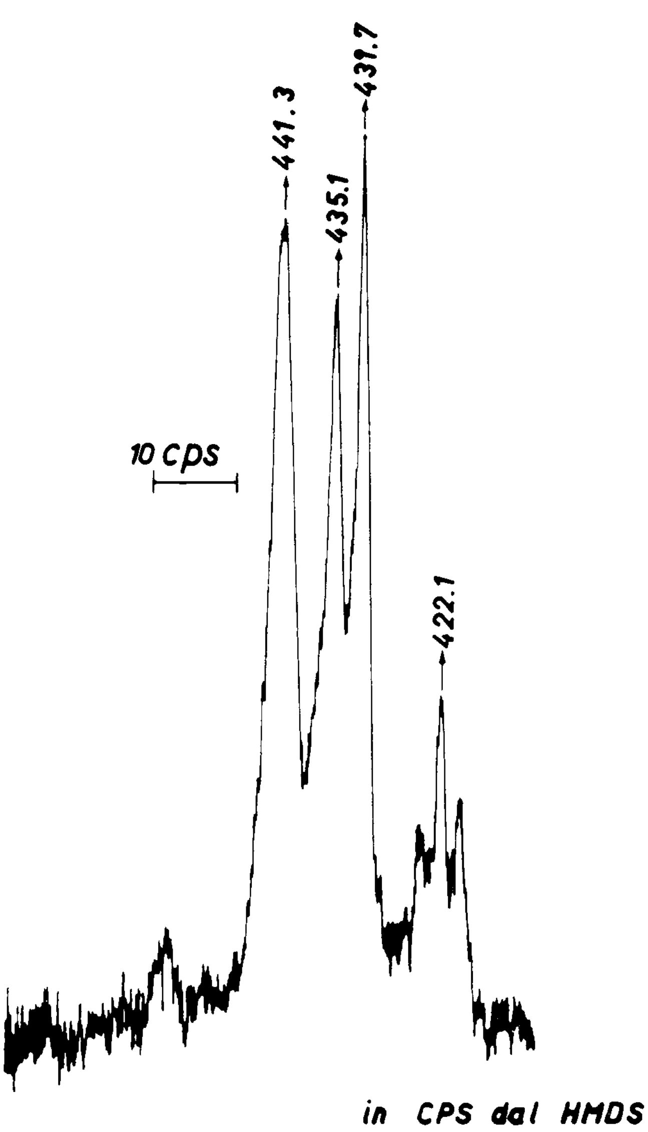

Figure 3. Spectrum of polyvinyl chloride-$\beta,\beta$-$d_2$.

### Experimental Section

All spectra of polypropylenes and polyethylenes were run at 150° in *o*-dichlorobenzene solution, using HMDS as internal standard. The spectra of PVC-$\beta,\beta$-$d_2$ were run in pentachloroethane at 150°. We used a Varian HA 100 spectrometer, operating in frequency sweep conditions. The experiments of deuterium decoupling were performed with the SB 60 NMR Specialities decoupler, locked with a Hewlett-Packard Model 4204 A oscillator. All samples were in $N_2$ atmosphere. Line widths were measured in cycles per second, on a 50-cps scale, at half-height, without any correction.

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(12) (a) L. Cavalli and G. Carraro, private communication; (b) F. A. Bovey, F. P. Hood, E. W. Anderson, and R. C. Kornegay, *J. Phys. Chem.*, **71**, 312 (1967); (c) T. Yoshino and J. Komiyama, *J. Polymer Sci.*, **A2**, 5221 (1964).

(13) S. Alexander, *J. Chem. Phys.*, **37**, 971 (1962).

(14) R. J. Kurland, M. B. Rubir, and W. B. Wise, *ibid.*, **40**, 2426 (1964).