f_r. This appears to be a reflection of the pronounced effect, when $\omega = 0$, of a decrease in length of the isotactic sequence adjacent to the racemic dyad.

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Conformations of Tetrads in Vinyl Polymers and Nuclear Magnetic Resonance Spectra of the Methylenic Protons

P. J. Flory and Y. Fujiwara

Department of Chemistry, Stanford University, Stanford, California 94305.

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ABSTRACT: The environment of a methylenic proton in a vinyl polymer is affected in major degree by the occurrence of the conformation *gt* for the pair of main-chain bonds preceding the methylene group, and similarly by the *tg* conformation for the following bond pair. These conformations are suggested as being of overriding importance in determining the nmr chemical shifts of the methylenic protons in polypropylene in which the substituent CH_3 resembles CH_2. Probabilities of these conformations are calculated for the several kinds of tetrads situated either in stereoregular chains or in atactic chains generated for various dyad compositions. The probabilities depend on the stereochemical configurations of dyads comprising the sequences adjoining the tetrad, and on this account the proton nmr resonances for tetrads of given character may be distributed over a range of frequencies (*ca.* 0.05 ppm) commensurate with the displacement (0.05–0.10 ppm) of their mean position from the resonances of tetrads of other kinds. The proton nmr spectra of poly(1,2,3,3,3-propylenes-d_5) are interpreted on this basis. The breadth of the range of resonances for racemic dyads in various stereochemical situations may obscure their detection in predominantly isotactic chains.

Rotations about the two skeletal bonds within a dyad —CHR—CH_2—CHR— of a vinyl chain determine the locations of the substituent groups R with respect to the methylenic protons. If the dyad is *meso*, the preferred conformations are g^+t and its mirror image tg^-, or *gt* and *tg* in the terminology introduced in the preceding paper (I).[1] In each of these equivalent conformations the methylenic hydrogen atom H* in Figure I-1 is *syn* to both R groups; the other methylenic hydrogen atom H is *syn* to one of the R groups only. If $\omega \ll 1$, as is usually the case, then this conformational pair is overwhelmingly preferred over all others.[1] This preference, expressed by values of $p_{gt}'' + p_{tg}''$ near unity according to calculations presented in the preceding paper,[1] is little affected by the stereochemical configurations of neighboring dyads. It follows that the chemical shielding of the respective methylenic hydrogens *by the substituents R* should be about the same for all *meso* dyads, irrespective of the stereochemical configurations of neighboring dyads of the chain.

The methylene protons of a racemic dyad are equivalent (if symmetries of neighboring dyads are ignored; *cf.* the following), but the environments differ for the two preferred conformations, *tt* and *gg*. In the former conformation, both protons of the methylene group of the racemic dyad are in situations corresponding to that of *one* of the *meso* protons (H in Figure I-1) when the *meso* dyad is in either of its preferred conformations. In the *gg* conformation, the two racemic protons are situated like the other proton (H* in Figure I-1) of the *meso* dyad. The distances between the respective protons and the pendant R and CH_2 groups in the two kinds of dyads (*meso* and racemic) are the same in these corresponding situations, and the directions of bonds CH—R and CH—CH_2 relative to the methylenic C—H bond are also equivalent. Hence, the space-averaged magnetic shielding of the protons by these groups in the corresponding situations should be approximately the same. (This equivalence may be vitiated if the substituent R is nonsymmetric about the CH—R bond axis, and in particular if its magnetic susceptibility tensor is not cylindrically symmetric with respect to this axis. Such effects are assumed to be small for the kinds of R groups of main interest.) On this basis, the chemical shift for the (equivalent) methylenic protons of a racemic dyad should be intermediate between those for the nonequivalent protons of the *meso* dyad. Its location within this range should depend on the proportions p_{tt}'' and p_{gg}'' of the two conformers. These proportions are strongly influenced by the stereochemical configurations of neighboring dyads, and this influence may persist over a considerable range of units[1] if $\omega \ll 1$. Hence, if the anisotropy of the magnetic shielding tensor for R differs markedly from that of the group, CH_2, which it replaces in the *gauche* (*g*) conformation, then the chemical shift for the methylenic protons of a racemic dyad must depend on the stereochemical configurations of neighboring dyads.[2]

Connections between chemical shifts and chain configuration cannot be interpreted solely on the foregoing limited basis, however. Effects of groups further removed from the dyad must be taken into account as well. Consider the preferred conformations shown in Figure 1 for a *meso* dyad and adjoining bonds. These conformations may be designated $g(tg)_m$ and $(gt)_m g$, respectively, the conformations of the pair of bonds

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(1) P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 315 (1969), designated I in this paper.

(2) P. J. Flory and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **88**, 2873 (1966).

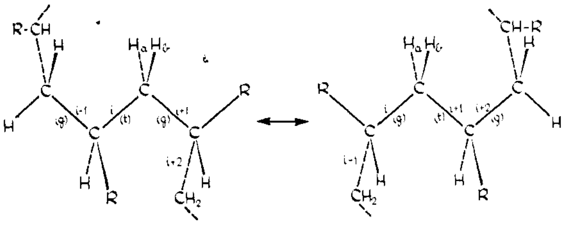

Figure 1. Preferred conformations for a *meso* dyad and adjoining bonds.

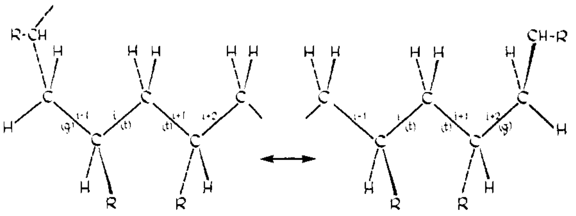

Figure 2. The *trans,trans* conformation for a racemic dyad with one or the other of the adjoining bonds *gauche* (g).

within the dyad being enclosed in parentheses and the character of the dyad being indicated by the subscript m. (In the former g may be identified with g^-, and in the latter with g^+.) Each places a CH group close to the methylene proton designated H_a; the distance of separation between atom centers of C and H_a is about 2.7 Å. The protons H_a and H_b correspond to H* and H in Figure I-1.[3] The disfavored conformations $\bar{g}t$ and $t\bar{g}$ place the respective CH groups in similar locations relative to H_b, rather than to H_a. They are of rare occurrence in chains of interest, and may therefore be neglected for purposes of the following discussion. The conformation $g(tt)_m g$ would place both of the CH groups in proximity to H_a; in a sense it is a hybrid of the two conformations shown in Figure 1. It is disfavored, however, owing to steric repulsion between the R groups. The conformations $t(gt)_m t$ and $t(tg)_m t$, in which neither CH group impinges on H_a, do not entail major steric overlaps and therefore must be taken into account. The extent to which these latter conformations occur depends upon the stereochemical configurations of neighboring dyads. If the *meso* dyad in question occurs as a nonterminal member of an isotactic sequence, either of these conformations may mark the junction of right- and left-handed helical sequences. Proximity of racemic dyads enhances the probability of occurrence of these conformations, as explained in the preceding paper.[1]

Conformations in which CH groups separated by three bonds from the methylene group of a racemic dyad are apposed to one or the other of the methylenic protons in the same manner as above are shown in Figure 2. Unlike the analogous conformations for the *meso* dyad shown in Figure 1, each proton of the methylene group is approached by a CH group in one or the other conformation. In recognition of their intrinsic indistinguishability, the methylene protons of the racemic dyad are not labeled by subscripts.[3] Other conformations free of major steric conflict are $g(tt)_r g$ and $t(tt)_r t$. Both protons are in contact with CH groups in the former; neither is thus affected in the latter. The relative occurrence of these several conformations will depend on the stereochemical configurations of neighboring dyads. This dependence can be partially comprehended by considering the central (racemic) dyad in the tetrads *rrr*, *rrm* and *mrm*, and the application to them of the conformational rules cited in the preceding paper.[1] Although the two methylenic protons of a racemic dyad are identically equivalent in a completely syndiotactic chain, or when considered in relation to the asymmetric center of the dyad alone (as in Figure 2), it is to be noted that the protons of the central dyad in *rrm* (or *mrr*) are nonequivalent. They may be nonequivalent also in the other tetrads if account is taken of the configurations of more remote dyads.

Whereas assignment of a *gauche* conformation to one of the bonds *within* a dyad replaces CH_2 by R in the position *syn* to both methylenic protons, the conformations illustrated in Figures 1 and 2 bring a CH group into close contact with one of these protons without displacing an intramolecular neighboring group. Solvent is displaced instead. The effect of the former conformations on the shielding of the proton in question depends on the magnetic anisotropy of R compared to CH_2; the effect of the latter depends on the magnetic anisotropy of CH (and to some extent on neighboring groups as well) compared with the solvent molecules displaced.

The criterion for the latter kind of neighbor relationship depicted in Figures 1 and 2 is the occurrence of the gt conformation for the two bonds preceding a methylene group (*i.e.*, the bond pair flanking the first CHR group of the dyad), or of the tg conformation for the two following bonds. This criterion applies irrespective of the stereochemical form of the dyad, or of its neighbors. The probability of occurrence of these conformations depends in marked degree, however, on the stereochemical configuration of the dyad in question and of others nearby in the chain. Because of the very strong influence of adjoining dyads, it is appropriate to examine the occurrence of gt and tg conformations for the stated bond pairs in various tetrads —CHR—CH_2—CHR—CH_2—CHR—CH_2—CHR—. Calculations to this end are presented below. Their bearing on nmr spectra, with special reference to polypropylene, is discussed.

Numerical Calculations

Calculations in Figures 3 and 4 have been carried out according to eq I-40′, the statistical weight matrices being given by eq I-9, 10, and 15. Values of $\eta = 1.0$ and $\tau = 0.5$ have been used throughout. Calculations relevant to the methylene group of a *meso* dyad are presented in Figure 3. The solid curves represent p_{gt}' for the bond pair flanking the —CHR— group preceding this methylene, which occupies the central dyad of the tetrad (comprising three dyads) enclosed in parenthe-

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[3] Asterisks were applied to certain of the protons in the several diagrams in Figure I-1 and I-2 of the preceding paper for the purpose of differentiating conformations, and in particular to differentiate the two kinds of proton environments there considered. In keeping with current practice, we use subscripts a and b in this paper to differentiate *distinguishable protons*, irrespective of the conformation of the dyad. The proton H_a corresponds to H* of the *meso* dyad in Figure I-1, but in other circumstances the two schemes do not correspond. The methylene protons of the racemic dyad in Figure 2 do not carry subscripts inasmuch as they are indistinguishable (apart from possible differentiations based on the stereochemical configurations of neighboring dyads; *cf.* the following).

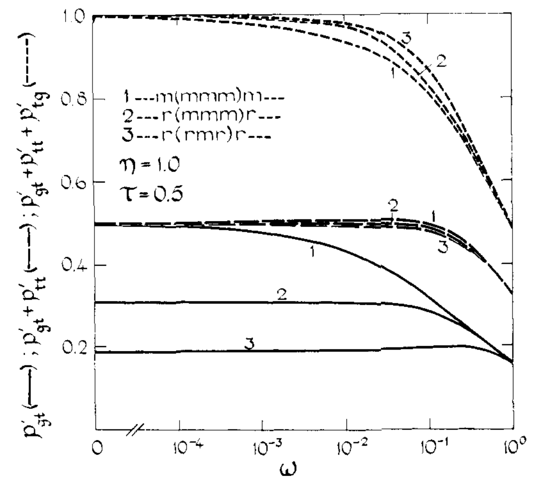


Figure 3. Conformation probabilities, plotted against log ω, for the bond pair preceding the methylene group of a *meso* dyad situated in various tetrads as indicated. The length of the chain is infinite.

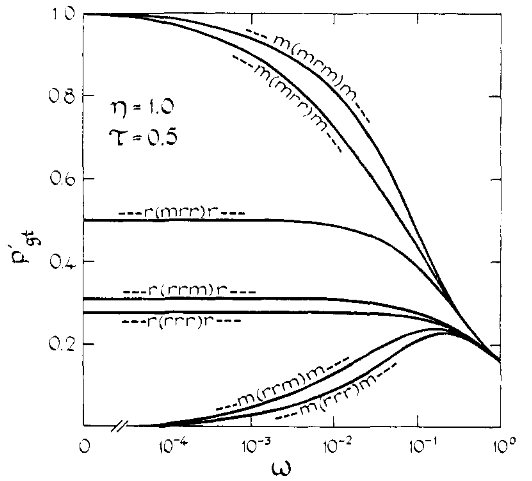


Figure 4. The conformation probability p_{gt}' for the pair of bonds preceding the methylene group of a racemic dyad in the various tetrads indicated, plotted against log ω, for infinite chains.

ses in the key given in the figure. In other words, p_{gt}' refers to the junction between the first and second dyads of the tetrad in parentheses. Sequences preceding and following the tetrad sequence are indefinitely long, stereoregular, and of the stereochemical characters indicated in each instance. Thus, the uppermost solid curve represents p_{gt}' for the pair of bonds preceding the methylene group of a *meso* dyad in an all-*meso* (or isotactic) chain. For such a dyad, $p_{gt}' = p_{tg}' = {}^1/_2$ when $\omega = 0$. Presence of a racemic dyad in the preceding sequence of dyads raises the possibility of a *tt* conformation, even at $\omega = 0$, for the bond pair considered. The influence is greater the nearer the racemic dyad is to the *meso* dyad. Thus, for $\cdots r(mmm)r \cdots$, curve 2, the incidence of the *gt* conformation is diminished on this account. It is reduced further for $\cdots r(rmr)r \cdots$, curve 3, in which the *meso* dyad is isolated in an otherwise racemic chain. These effects of the stereochemical configurations of adjoining dyads follow from the rules governing preferred conformations cited in I. The influence of racemic dyads, as manifested by the ordinates for the solid curves 2 and 3 for small values of ω, depend of course on the value assigned to η.

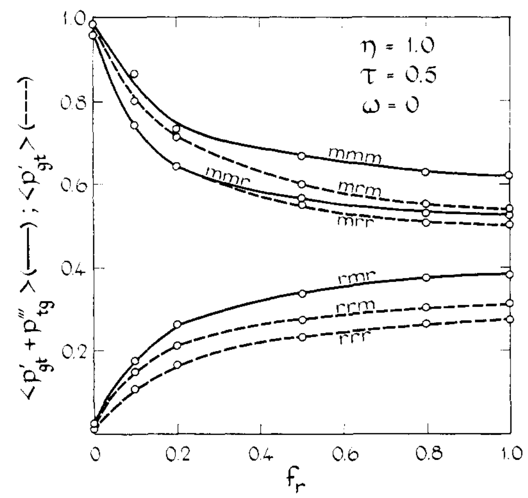


Figure 5. Conformation probabilities for bond pairs preceding (p') and following (p''') the central methylene group of the indicated tetrads, each such tetrad being situated between atactic sequences of 50 units preceding and 50 units following the tetrad. The average fraction f_r of racemic dyads in these sequences is plotted on the abscissa. Each point for $0 < f_r < 1.0$ represents the average for 100 Monte Carlo chains whose atactic sequences were generated for the specified value of f_r. Values at $f_r = 0$ and 1.0 are unique for the specified structure and have been calculated by exact methods.[1] Calculations carried out with $\omega = 0$.

The long dashed curves in Figure 3 represent $p_{gt}' + p_{tt}'$, and the short dashed curves represent the sum, $p_{gt}' + p_{tt}' + p_{tg}'$, of all of the preferred conformations for the pair of bonds preceding the CH_2 group of a *meso* dyad in the various situations. Differences between these curves represent values of p_{tt}' and of p_{tg}'. For $\omega < 0.10$, the preferred conformations predominate. The solid curves, representing p_{gt}', are the ones of primary interest. They also serve to define the probabilities relevant to the conformation (*gt*)*g* in Figure 1, in which the —CHR— group following the central dyad is juxtaposed to the methylene hydrogen H_a of the dyad. Designating this probability p_{tg}''', we observe that $p_{gt}' = p_{tg}'''$ for symmetrical stereochemical sequences like those treated in Figure 3.

In Figure 4, conformation probabilities p_{gt}' are plotted as functions of ω for racemic dyads in various tetrads situated between infinite stereoregular sequences as indicated. Using the all-racemic chain for comparison, we observe that insertion of a single *meso* dyad on the right-hand side of the central racemic dyad has little effect on p_{gt}'. A single *meso* unit to the left raises p_{gt}' appreciably. Effects of long sequences of *meso* units are more dramatic. When on the left-hand side, they raise p_{gt}' causing it to reach unity at $\omega = 0$; when on the right, they lower it to zero in the same limit. When the racemic dyad is isolated within an otherwise isotactic chain, $p_{gt}' = 1.00$ for $\omega = 0$, as noted in I. In analogy to the connection cited above, $p_{gt}' = p_{tg}'''$ for racemic dyads in symmetrical environments of neighboring dyads. This equality does not hold for nonsymmetric tetrads such as *mrr* and *rrm*. These tetrads are in fact identical; they differ only in orientation. *Their methylene protons differ*, however, and for this reason it is

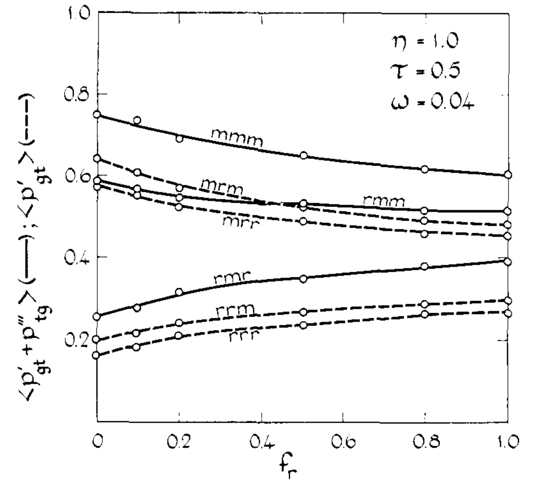


Figure 6. Averages of results for Monte Carlo chains (see legend for Figure 5) plotted against the average composition. Calculations carried out with $\omega = 0.04$.

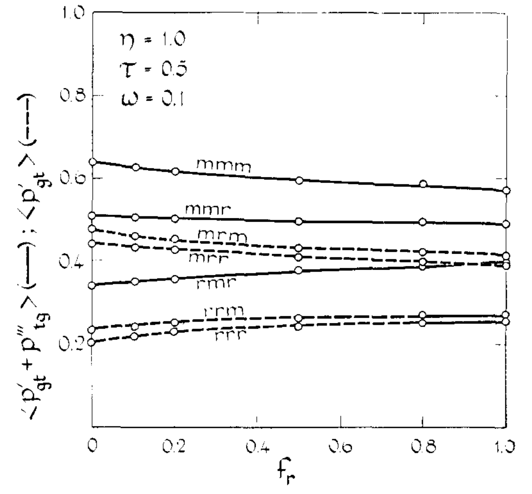


Figure 7. Averages of results for Monte Carlo chains (see legend for Figure 5) plotted against the average composition. Calculations carried out for $\omega = 0.10$.

convenient to maintain a distinction, albeit an artificial one, between them. We observe that $(p_{gt}')_{mrr} = (p_{tg}''')_{rrm}$ which follows from the identity of *mrr* to *rrm*.

As is clear from comparison of Figure 4 with 3, the effects of the stereochemical configurations of neighboring units on p_{gt}' for a central racemic dyad are greater than for a *meso* dyad. Once again the wide variations in p_{gt}' for small values of ω can be correlated with the conformation rules for vinyl chains. These marked differences for different tetrads are moderated by an increase in ω, for reasons discussed in detail in I.

Calculations for tetrads situated in Monte Carlo chains of various tacticities denoted by f_r, the *a priori* probability of occurrence of a racemic dyad, are summarized in Figures 5–7. Calculations were carried out in the manner described in the preceding paper,[1] eq I-30 being used for this purpose. Tetrads of the characters designated in Figures 5, 6, and 7 were situated between Monte Carlo sequences of 50 units each. One hundred chains were generated for a given value of f_r; the points in these figures are averages for such sets of chains. The ordinates in these figures represent the expectation values for the number of "contacts" occurring between one of the methylenic protons of the central dyad and either or both of the CH groups separated from it by three bonds on either side. For a *meso* dyad, only the proton H_a in Figure 1 is susceptible to such contacts brought into effect by $\cdots g(t\cdot\cdot)\cdots$ and $\cdots(\cdot\cdot t)g\cdots$ conformations considered. With references to this proton, the incidence of juxtaposition of the CH group preceding the *meso* dyad is measured by p_{gt}', and juxtaposition of the CH group of the following dyad by p_{tg}'''. Their sum, whose average is shown by solid lines for central dyads which are *meso* in Figures 5–7, represents the total effect on proton H_a.

Each of the methylenic protons of a racemic dyad is eligible for such contacts (see Figure 2). One of them is accessible to the CH group of the preceding dyad, the other to that of the following dyad. We therefore plot $\langle p_{gt}'\rangle$ as the ordinate for those tetrads whose central dyads are racemic in order to express the mean effect on one proton. These curves are shown by dashed lines in Figures 5–7. In symmetrical situations, $\langle p_{gt}'\rangle = \langle p_{tg}'''\rangle$; hence, the ordinate in such cases represents the effect on *each* of the two equivalent protons. When the tetrad is nonsymmetric, as in *rrm* tetrads, the protons are nonequivalent and $\langle p_{gt}'\rangle \neq \langle p_{tg}'''\rangle$. However, $\langle p_{tg}'''\rangle_{rrm} = \langle p_{gt}'\rangle_{mrr}$, from which it follows that $\langle p_{gt}'\rangle_{rrm}$ represents the average effect on one of the methylenic protons of *rrm* (alias *mrr*) and $\langle p_{gt}'\rangle_{mrr}$ the effect on the other. Both of the methylenic protons may be represented therefore by plotting $\langle p_{gt}'\rangle$ separately for tetrads designated *mrr* and *rrm*. As noted above, these tetrads are identical; the two curves so labeled in Figures 5 and 6 represent the respective nonequivalent protons of the central racemic dyad in a tetrad of this character.

Results in Figure 5 have been calculated for $\eta = 1.0$, $\tau = 0.5$, and $\omega = 0$; those in Figures 6 and 7 have been calculated for the same values of η and τ, but with $\omega = 0.04$ and 0.10, respectively. Results at the boundaries of the diagrams, *i.e.*, at $f_r = 0$ and 1, closely approximate values taken from the curves in Figures 3 and 4 for the same tetrads situated within *infinite* stereoregular sequences; small differences occur owing to the finite lengths of the chains represented in figures. The strong dependence of average conformation probabilities on the character of the tetrad previously found for $f_r = 0$ and 1 obtains as well over the intermediate range of f_r; the differences are most marked at $f_r = 0$, however. That the conformation probabilities depend also on configurations of dyads beyond the tetrad is shown by their dependences on f_r. This dependence is most marked for small values of f_r. The latter observation corroborates results reported in the preceding paper[1] showing the constraints imposed by isotactic sequences to be of longer range than those of syndiotactic sequences, which enjoy a greater latitude in the configurations accessible to them. An increase in ω diminishes the magnitude of the effects of the stereochemical configurations of neighboring dyads. This is evident from comparison of Figures 6 and 7 with 5, both as regards the differences for the various tetrads and the changes with the *a priori* probability f_r, which characterizes the stereochemical environment of the tetrad.

Large variations occurred in the values of p' and p''' for individual Monte Carlo chains amongst the sets of

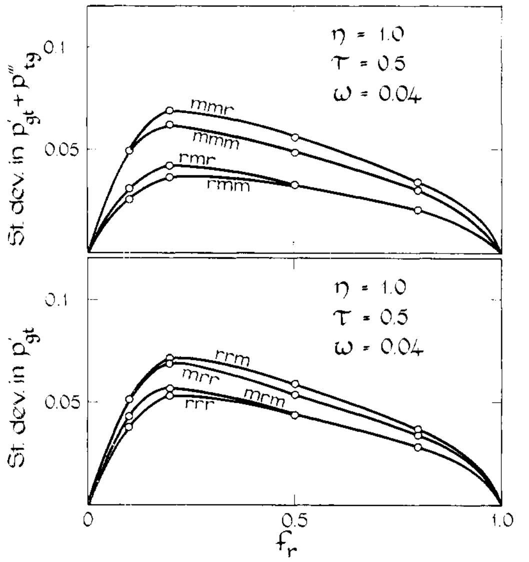


Figure 8. Standard deviations for each set of 100 Monte Carlo chains used to obtain the average values represented by the points in Figure 6. The upper diagram represents tetrads whose central dyad is *meso;* the lower diagram represents those in which it is racemic.

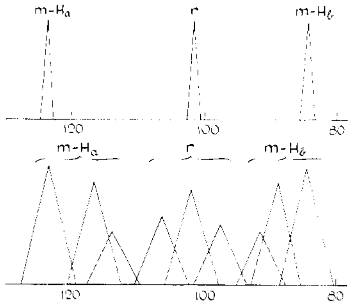


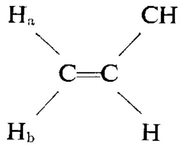
Figure 9. Diagrammatic representation of the 100 MHz, deuteron decoupled nmr spectra reported by Segre[7] and by Zambelli and Segre[8] for polypropylenes-d_5 in *o*-dichlorobenzene at 135°. The upper diagram combines the spectra for the stereoregular polymers; the outermost peaks represent the isotactic polymers from the *cis* and *trans* monomers, respectively, and the central peak is for the syndiotactic polymer from either monomer. The lower diagram similarly combines the spectra for atactic polymers from the *cis* and *trans* monomers. Relative heights and half-widths of peaks approximate the spectra reported by Segre[7] and by Zambelli and Segre.[8]

100 that yielded the averaged results presented in Figures 5–7. These variations reflect the degree of dependence of the average conformation on the stereochemical configurations of other dyads in the vicinity of the tetrad considered. The standard deviations plotted against f_r in Figure 8 for the case $\omega = 0.04$ are indicative of the magnitude of this variation. They are commensurate in fact with the departures of the conformation probabilities from their values for the stereoregular chains at $f_r = 0$ and 1.0. In keeping with this generalization, the standard deviations are greatest for stereochemical compositions in the range $0.1 < f_r < 0.3$, *i.e.*, for polymers approaching the isotactic limit, where the change in conformation probability with composition is greatest (see above). Standard deviations (not shown) for the cases $\omega = 0$ and 0.10 follow similar trends. They are larger, of course, for $\omega = 0$ and smaller for 0.10 in conformity with the dependences of the conformation probabilities on f_r. Similar manifestations of the effect of the variability of stereochemical environment in atactic chains on the average conformation have been discussed in the preceding paper.[1]

The implications of these results with respect to the magnetic anisotropy of the shielding afforded by the environments of the methylene protons and the associated chemical shifts observed in their nmr spectra are straightforward. To the extent that the shielding is altered by replacement of solvent by CH adjacent to a methylenic proton, the chemical shift should differ for different tetrads, and it should depend on the stereochemical configurations of neighboring dyads over a range dependent upon the value of ω. Stereochemical configurations of sequences of higher orders, *viz.*, of hexads, octads, etc., should be considered. To avoid the obvious complexities of proceeding in this manner, we have resorted above to characterization of the "environment" of the tetrad by the *a priori* probability f_r. We may infer that the chemical shifts will not only differ for the several kinds of tetrads (and for nonequivalent methylenic protons in these tetrads); they should depend also on f_r. Moreover, for a given value of f_r, the statistical variation in the environments of individual tetrads should cause the chemical shifts to be correspondingly distributed. Line broadening to a large degree is to be expected on this account.

Nmr Spectra of Polypropylene

Zambelli, Segre, Farina, and Natta[4] have reported an elegant series of experiments on the nmr spectra of isotactic, syndiotactic, and atactic polypropylenes prepared from *cis*- and *trans*-1,2,3,3,3-propylene-d_5. These spectra confirm earlier deductions[5,6] from infrared spectra showing polymerization by Ziegler–Natta catalysis to occur exclusively by *cis* addition of the monomer. If the β protons of propylene are labeled as shown below



then the one remaining proton of the deuterated *cis* isomer is H_a and that of the *trans* isomer is H_b. Polymerization by *cis* addition yields *meso* units in which the respective protons H_a and H_b occur as shown in Figure 1. Inasmuch as no similar correspondence holds for the protons of a racemic dyad, they are shown without subscripts in Figure 2. Even if the methylenic protons of the racemic dyad are rendered nonequivalent by the asymmetry of neighboring dyads (see above), each of them will nevertheless be populated equally by H_a and H_b. Consider, for example, the tetrads *mrr* and *rrm* generated by *cis* addition of three molecules of pro-

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(4) A. Zambelli, A. L. Segre, M. Farina, and G. Natta, *Makromol. Chem.*, **110**, 1 (1967).

(5) G. Natta, M. Farina, and M. Peraldo, *Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis. Mat. Nat.*, **25**, 424 (1958); *Chim. Ind.* (Milan), **42**, 255 (1960).

(6) T. Miyazawa and T. Ideguchi, *J. Polym. Sci., Part B*, **1**, 389 (1963).

pylene in left-to-right succession in both. The protons H_a and H_b are distinguishable but their roles are reversed in the two tetrads. The tetrads are equivalent, of course, and they must occur with equal frequency in a long chain. The assertion above is thus proved. Its generalization to longer sequences is obvious.

Proton magnetic resonances of isotactic and syndiotactic poly(1,2,3,3,3-propylene-d_5)'s determined in *o*-dichlorobenzene at 135–150° at 100 MHz are depicted in the upper portion of Figure 9, which is a schematic representation of results of Zambelli, *et al.*,[4] and of Segre.[7] The isotactic from the *cis* monomer showed only the resonance marked *m*-H_a; the polymer from the *trans* monomer showed only *m*-H_b. The syndiotactic polymers from each monomer yielded the same resonance *r*. The three resonances are combined in a single diagram in the figure. With deuteron decoupling, their half-widths are *ca.* 0.5 cps at 100 MHz according to Segre.[7] The widths are so represented in the upper diagram of Figure 9. Their positions have been adjusted to the locations reported by Zambelli and Segre[8] for a temperature of 135°.

Deuteron decoupled spectra for the corresponding "atactic" polymers, obtained by Zambelli and Segre[8] at 135°, are represented schematically in the lower diagram of Figure 9. Observed heights and half-widths are reproduced approximately by the corresponding dimensions of the peaks in the figure. The triplet on the left is observed only for the polymer prepared from the *cis* monomer, and that on the right only for the polymer from the *trans* monomer; both yield the triplet in the center, with the overlapping peaks occurring at identical positions within limits of observation. The respective triplets are thus identified unambiguously with the protons indicated in the lower diagram of Figure 9.

The combined intensities of one of the *meso* triplets (H_a for the polymer from *cis*-propylene-d_5, or H_b for the polymer from the *trans* isomer) exceed slightly those for the racemic triplet. A crude estimate of intensities from peak heights in the spectra of Zambelli and Segre[8] indicates a ratio of about 0.55–0.45 for *meso* and racemic dyads in the atactic polymers. There is no assurance that the distribution of *m* and *r* dyads is random (*i.e.*, Bernoullian). In fact, the intensities of the main peaks, which, in confirmation of the tentative assignments of Zambelli and Segre, will be identified with *mmm* and *rrr* tetrads (*cf.* the following), suggest a tendency favoring perpetuation of dyads of the same kind. The sums of intensities of subsidiary peaks in each triplet exceed the intensity of the major triplet, however, from which it follows that the perpetuation tendency is not large. Specifically, the occurrence of long stereoblocks of *m* and of *r* dyads is not indicated.

The magnetic anisotropy of the substituent, CH_3, in polypropylene should differ little from that of the CH_2 group. Hence, a bond rotation from *trans* to *gauche* within a given dyad, whereby CH_2 is replaced by CH_3 as the *syn* neighbor to the methylene protons, may be assumed to have only a minor effect on the chemical shift. Greater effects may be expected to be associated with the *gt* and *tg* conformations of the pairs of bonds respectively preceding and following the CH_2 group. Not only is the intramolecular environment of the methylenic proton markedly affected by occurrence of these conformations; the proximity and average orientation of the surrounding solvent may be affected as well. The magnetic anisotropy of the solvent, *o*-dichlorobenzene, used in the experiments described above is large, and the molecule is nonsymmetric in shape. Hence, difference in solvent shielding experienced by the several kinds of methylenic protons may have contributed appreciably to their respective chemical shifts shown in Figure 9. Regardless of the relative importance of the intramolecular arrangement of bonds and groups on the one hand and of the external influence of the proximity and orientation of solvent molecules on the other, it is obvious that the local conformation of the chain is the primary determinant.

A given methylenic proton of the polypropylene chain may occur in one or another of three primary situations defined as follows.

(i) Neither the proton nor its partner of the same methylene group is neighbored by a CH group of an adjoining dyad. Preferred conformations presenting this situation are $t(gt)_mt$, $t(tg)_mt$, $t(tt)_rt$, and $t(gg)_rt$.

(ii) The proton is neighbored by a CH group from one of the adjoining dyads but its partner is not. Preferred conformations in this category are $t(gt)_mg$, $g(tg)_mt$, $g(tt)_rt$, and $t(tt)_rg$.

(iii) The proton considered is not neighbored by CH as above, but its partner is. The relevant conformations are the same as for ii.

The local environment of the designated methylenic proton is very nearly the same in each of the conformations within a given category specified above. The major differences between conformations of a given category merely entail interchanges of CH_2 and CH_3 groups; the effects of such interchanges are presumed to be small. Hence, we may expect similar chemical shifts to be applicable to each conformation of a given category. On this basis, we let ν_0 represent the chemical shift for a proton which occurs in situations i where it is not subject to the consequences attending proximity of a CH group; $\delta\nu_a$ will represent the chemical shift relative to ν_0 for a proton which, like H_a of the *meso* dyad in Figure 1, is subject to situation ii; and $\delta\nu_b$ will represent the chemical shift for a proton which, like H_b in Figure 1, is subject to the influence of a CH group apposed to its partner, and hence sufficiently close to affect also the proton in question. We further assume the effects denoted by subscripts a and b to be additive. Thus, in the favorable conformation $g(tt)_rg$ each methylenic proton is subject to an a and to a b conformational environment. Similar circumstances arise in various disfavored conformations. For example, in $g(tt)_mg$ one methylenic proton is contacted by both of the CH groups of the adjoining dyads; chemical shifts $\nu_0 + 2\delta\nu_a$ and $\nu_0 + 2\delta_b$ are ascribed to these respective protons according to the present scheme and the assumption of additivity. The disfavored conformations involving *t* and *g* states are included in following calculations; those involving $\bar{g}$ states are not. Disregard of the latter is justified if $\tau\omega$ is sufficiently small.

Making the further assumption of complete exchange averaging over all eligible conformations, we have for the chemical shift of a given proton

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(7) A. L. Segre, *Macromolecules*, **1**, 93 (1968).

(8) A. Zambelli and A. Segre, *Polym. Lett.*, **6**, 473 (1968).

$$\Delta\nu = \nu_0 + p_a\delta\nu_a + p_b\delta\nu_b \qquad (1)$$

where p_a and p_b are the respective expectations, at equilibrium, of conformations in which the proton is subject to the designated environments. For the respective methylenic protons of a *meso* dyad

$$\left.\begin{aligned}\Delta\nu_{m;a} &= \nu_0 + (p_{gt}' + p_{tg}''')\delta\nu_a\\ \Delta\nu_{m;b} &= \nu_0 + (p_{gt}' + p_{tg}''')\delta\nu_b\end{aligned}\right\} \qquad (2)$$

and for the protons of a racemic dyad

$$\left.\begin{aligned}\Delta\nu_{r;1} &= \nu_0 + p_{gt}'\delta\nu_a + p_{tg}'''\delta\nu_b\\ \Delta\nu_{r;2} &= \nu_0 + p_{gt}'\delta\nu_b + p_{tg}'''\delta\nu_a\end{aligned}\right\} \qquad (3)$$

Subscripts 1 and 2 distinguish the two protons of a racemic dyad, which as noted earlier, are equally populated by protons H_a and H_b of the monomer. If the racemic dyad is symmetrically situated with respect to its neighbors, the protons are equivalent, $p_{gt}' = p_{tg}'''$, and we have for both of them

$$\Delta\nu_r = \nu_0 + p_{gt}'(\delta\nu_a + \delta\nu_b) \qquad (4)$$

For the stereoregular polypropylenes, Zambelli and Segre[8] report $\Delta\nu_{m;a} = 123.5$ cps, $\Delta\nu_{m;b} = 84.4$ cps, and $\Delta\nu_r = 101.6$ cps, all measured at 100 MHz in *o*-dichlorobenzene at 135°. In consideration of the similarity in size of the substituent, CH_3, to CH_2, we take $\eta = 1.0$. Information on the proper values for τ and ω is meager;[9] τ may be assumed to be less than unity, but greater than 0.1 and ω to be in the range 0.01–0.10 at 135°. For the tentative calculations that follow, we take $\tau = 0.5$ and $\omega = 0.04$. Results obtained are fairly insensitive to the precise values assigned to η and τ, but the admissible range of ω introduces an appreciable uncertainty. According to the calculations in Figure 6, we have, for the stated values of the statistical weight parameters, $p_{gt}' + p_{tg}''' = 0.75$ for the *meso* sequence at $f_r = 0$, and $p_{gt}' = p_{tg}''' = 0.27$ for the racemic sequence at $f_r = 1.0$. It follows from eq 2 and 4 that $\nu_0 = 95.6$, $\delta\nu_a = 37.1$, and $\delta\nu_b = -14.9$, all in cycles per second. Frequencies calculated according to eq 2 and 3 for atactic polymers with $f_r = 0.50$, the foregoing values of the parameters being used, are given in the second column of Table I. Conformational probabilities p_{gt}' and p_{tg}''' used in these calculations were taken from Figure 6 at $f_r = 0.50$. The results are precariously dependent on the departure of $\Delta\nu_r = 101.6$ cps for the syndiotactic polymer from the mean, 104.0 cps, of $\Delta\nu_{m;a}$ and $\Delta\nu_{m;b}$. If this small difference were to vanish, the patterns calculated for the triplets would be altered drastically. Errors arising from inaccuracy in the observed difference probably exceed those from arbitrariness in the choices of statistical weight parameters.

Observed frequencies for the atactic polymers are listed in the third column of Table I. The peak of highest frequency (lowest field) of the observed racemic triplet is suggested as representing the two protons *rrm*;1 and *mrm*. This identification may account for the observation of three instead of four peaks for racemic tetrads. The order of the observed frequencies is well reproduced by the calculations; the absolute values are inaccurately represented, however. Quantitative agreement could not have been expected in view of the assumptions involved. The agreement could be improved by taking account of the nonrandom occurrence of *m* and *r* dyads. Thus, the evident preference (see above) for perpetuation of dyads of the same character causes the averages for *mmm* and *rrr* tetrads in the actual chains to resemble the stereoregular polymers more closely than is implied by our calculations carried out on Monte Carlo chains in which *m* and *r* dyads were permitted to succeed one another without bias by the stereochemical character of predecessors. A further marginal improvement would be achieved if account were taken of the probable departures of the "stereoregular" polymers from perfect stereoregularity. These departures, probably on the order of 5–10% in f_r,[10] affect the values assigned to ν_0, $\delta\nu_a$ and $\delta\nu_b$. Such refinements are unwarranted in view of uncertainties in the stereoregularities of the "isotactic" and "syndiotactic" polymers and in the sequence distribution of *m* and *r* dyads that obtain therein.

TABLE I

COMPARISON OF CALCULATED NMR SPECTRA FOR α PROTONS OF POLYPROPYLENE WITH EXPERIMENTAL RESULTS OF ZAMBELLI AND SEGRE[8]

Tetrad; proton	$\Delta\nu_{calcd}$,[a] cps	$\Delta\nu_{obsd}$,[a] cps	Relative abundance Calcd	Relative abundance Obsd
mmm; a	119.8	123.3	0.29	0.24
mmr; a	115.3	118.4	0.22	0.21
rmr; a	108.4	113.6	0.04	0.10
rrm; 1 *mrm*	109.9 109.4	106.3	0.15	0.14
rrr	101.8	101.7	0.20	0.19
rrm; 2	98.1	97.6	0.10	0.12
rmr; b	90.5	91.5	0.04	0.11
mmr; b	87.7	88.6	0.22	0.21
mmm; b	85.9	84.4	0.29	0.23

[a] Nmr frequency shifts at 100 MHz.

The qualitative agreement of calculated frequencies with the observed spectra lends support to the premise that conformations *gt* and *tg* for bonds pairs preceding and following, respectively, the methylene group are principal determinants of the chemical shifts. It should not be construed as confirmatory of the particular values chosen for the statistical weight parameters.

Also included in Table I are the abundances of various tetrads in the atactic polymers, calculated assuming Markoffian chains with dependence on first neighbors only. The conditional probabilities used in these calculations are

$$q(m|m) = 1 - q(r|m) = 0.73$$

$$q(r|r) = 1 - q(m|r) = 0.67$$

these values having been chosen to yield *a priori* probabilities $f_m = 1 - f_r = 0.55$ (see above). In accordance with the interpretation given of the frequencies, we combine the *a priori* probabilities for protons *rrm*;1 and *mrm*. The observed values given in the last column are

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(9) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969, Chapter VI.

(10) P. J. Flory, J. E. Mark, and A. Abe, *J. Polym. Sci., Part B*, **3**, 973 (1965); *J. Amer. Chem. Soc.*, **88**, 639 (1966).

crude estimates[11] from the peak heights in the spectra of Zambelli and Segre.[8] Like the calculated values, they are normalized to unity (one proton) for the combined abundances of racemic plus *meso* H_a or *meso* H_b. The order of these observed intensities is correctly reproduced by the calculations, and this concurrence supports the identifications of the frequencies within the three multiplets. To be sure, the assumption of simple first neighbor dependence governing the distribution of dyads is *ad hoc*, and may be substantially in error. It offers improvement over the assumption of a random distribution of dyads, however, and the observed intensities appear to be compatible with it.

Discussion

Regardless of the precise details of intramolecular magnetic shielding and the effects of solvent molecules nearby, it is clear that the conformation of a vinyl polymer (of specified stereochemical structure) plays the decisive role in determining its nmr spectrum. Detailed study of the situations of the methylene protons in polypropylene chains having various stereochemical configurations suggests that the time-averaged occurrences of the various conformations specified by rotations about skeletal bonds which are first and second neighbors of the methylene group should be principally important. Differences in these averages over these conformations for the various tetrads (and sequences of higher order as well) are believed to be mainly responsible for the differences in the resonances they exhibit. The stereochemical configuration of a dyad well removed from the methylene group may affect its resonance(s), but the effect is indirect, being transmitted from one unit to the next in consequence of the strong neighbor correlations of conformations. Magnetic shielding necessarily is of short range in the sense of actual distances. The dependence of the nmr spectra on the stereochemical configurations of dyads some number of units away from the one considered is long range in a topological sense, and its mode of action is conformational.

The calculations presented above on the nmr spectra of atactic polypropylenes-d_5 offer a satisfactory account of the observed spectra in crude approximation, and, in combination with estimated intensities, support the identifications of individual peaks with various tetrads. Of greater importance is the occurrence of shifts in the positions of the nmr peaks with stereochemical configurations of neighboring dyads. Such displacements were predicted by Flory and Baldeschwieler.[2] They are as great as 9 cps at 100 Mc for atactic polymers at midrange of stereochemical composition (*i.e.*, at $f_r \approx 0.5$). Moreover, the separate peaks for the respective tetrads are greatly broadened. Their half-widths are 4–5 cps; *i.e.*, broadening is commensurate with the displacements of the separate peaks for a given dyad proton, and this is in harmony with predictions from the Monte Carlo calculations above (see Figure 8).

Natta and coworkers[4,12] have criticized the conclusions reached by one of the present authors and his collaborators[10] to the effect that isotactic polymers of propylene, *n*-butene-1, styrene, etc., are stereoirregular to an appreciable degree. These conclusions[10] were reached primarily on the basis of the configurational behavior of isotactic vinyl polymers in dilute solution, and also in the bulk state as manifested in stress–temperature coefficients for amorphous networks. It was suggested that small percentages of racemic dyads, *e.g.*, less than 5–10%, probably would not be detected in the nmr spectra. The contention of Natta and coworkers that less than 2% could be detected[5,7] rests on the presumption that the peak comprising the resonances for racemic dyads in predominantly isotactic chains is of a breadth comparable to that (±0.5 cps[7,8]) observed for the syndiotactic polymer. Our calculations emphasize the untenability of this assumption. The resonances associated with a given kind of tetrad should vary considerably depending on the configurations of surrounding dyads; and their variation must be manifested in the width of the peak observed for resonances associated with that tetrad. These predictions are fully confirmed by the nmr spectra of the atactic polypropylenes.[8] Not only do the resonances differ for the several tetrad protons; they are markedly broadened as well.

The calculations in Table I, like the spectra reported by Zambelli and Segre,[8] pertain to atactic polymers in the middle range of dyad composition where $f_r \approx 0.5$. In the isotactic range, *e.g.*, for $f_r \approx 0.1$, the shifts in frequency for the racemic protons, *rrm*;1, *mrm*, and *rrm*;2, must increase. The resonance for *rrr* must of course vanish in intensity for small f_r. Moreover, the ranges of the former resonances should be greater at $f_r \approx 0.1$ than at $f_r \approx 0.5$, according to calculations of which those in Figure 8 are representative. Hence, these peaks may be further broadened as the polymer becomes increasingly isotactic within this range. The minimum percentage of them which may be detected in the nmr spectrum must be correspondingly increased. A tenfold reduction in the sensitivity of the nmr method for detection of racemic dyads is easily foreseeable as a consequence of the broadening of the range of the resonances as f_r decreases from ≈ 1.0 to ≈ 0.1. We suggest that the failure of Zambelli, Segre, Farina, and Natta[4] to detect resonances for racemic dyads in their isotactic polypropylenes-d_5 can reasonably be attributed to the broadened range of these resonances combined with their low concentration in polymers for which f_r may be in the vicinity of about 0.1. It is to be noted that the sensitivity of the nmr method is not enhanced by greater resolution (for a given signal-to-noise ratio) when the resonances are distributed over a range of frequencies.[13]

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(11) That the intensities estimated from the observed nmr spectra, and given in the last column of Table I, are subject to a large error is demonstrated by their failure to adhere to the intensity sum rule $(mmr) + 2(rmr) = (mrr;\ 1) + (mrr;\ 2) + 2(mrm)$ enunciated by Frisch, Mallows, and Bovey, *J. Chem. Phys.*, **45**, 1565 (1966). Although the spectra do not admit of more refined estimates, revision to comply with the foregoing sum rule would improve agreement with our calculations.

(12) G. Natta and P. Corradini, *Makromol. Chem.*, **110**, 291 (1967).

(13) The high degree of crystallinity often observed for isotactic polymers does not assure a high degree of stereoregularity. Instances of contradiction of such an assumed connection are well documented. See, for example, I. W. Bassi, G. Dall'Asta, U. Campigle, and E. Strepparola, *Makromol. Chem.*, **60**, 202 (1963); S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatadi, *J. Polym. Sci., Part B*, **4**, 65 (1966); and K. C. Ramey and D. C. Lini, *ibid., Part B*, **5**, 47 (1967). Structural irregularities evidently can be incorporated in the crystalline regions in some manner, not altogether clear, as we have endeavored to point out previously.[9]

If, as Natta and coworkers[4,12] believe, isotactic polymerization proceeds from catalytic sites each of which preferentially generates asymmetric centers of one kind, *d* or *l*, then the residual racemic dyads must occur in pairs · · · *mrrm* · · · in a predominantly isotactic chain.[1,14] The racemic resonances are then divided equally between *rrm;* 1 and *rrm;* 2, in the notation of Table I. One of these occurs upfield and the other downfield from the frequency characteristic of the racemic dyad in a syndiotactic polymer. Both will be broadened, and shifted as well, compared to the resonance for the predominantly syndiotactic polymer. Since the resonances for the racemic dyad are divided between two peaks, the limits of detection must be correspondingly raised.

In conclusion, the detailed analyses of chain conformation in relation to stereochemical configurations presented in this paper, together with the confirmatory nmr results of Zambelli and Segre,[8] show beyond reasonable doubt that small proportions of racemic dyads in predominantly isotactic chains of vinyl polymers such as polypropylene may easily escape detection by nmr spectroscopy. High degrees of stereoregularity should not be inferred from the absence of detectable resonances attributable to racemic dyads.

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[14] This mechanism is implausible for atactic polymers for which $f_r \approx 0.5$.

Preferential Orientation and Strain–Dichroism of Polymer Chains

P. J. Flory and Y. Abe

Department of Chemistry, Stanford University, Stanford, California 94305.

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ABSTRACT: A general theory of dichroism induced by strain in polymeric networks is developed by adaptation of methods recently published for treating strain birefringence. It is generally applicable to dichroic bands associated with any specified conformation involving sequences of one or more consecutive bonds. The transition dipole moment is introduced in the local framework of the skeletal bonds associated therewith. Possible differences in transition moments for various conformations and repeat units are taken into account without difficulty. Numerical calculations for polymethylene chains show *gauche* (*g*) bonds, rather than *trans* (*t*), to be more favorably oriented with respect to the chain vector **r**. The *g* bond in the *tgt* conformation for three consecutive bonds undergoes a comparatively high orientation; the *t* bond in *gtg* is preferentially oriented transverse to **r**. Orientations of other symmetry axes for various conformations are calculated, and the results are found to be in qualitative accord with the dichroic ratios observed for amorphous polyethylene by Read and Stein.

Dichroism induced by strain in polymers reflects preferential orientation of the transition dipole moment for absorption of radiation of given frequency. The transition moments for various absorption processes differ in their orientations with respect to the chain skeleton, and a given absorption may be contingent upon the occurrence of a specific backbone conformation. It is not surprising, therefore, that the strain-induced orientations indicated by dichroic measurements at various frequencies differ markedly, as Read and Stein[1] have shown. The sign and magnitude of the orientation indicated by the dichroic ratio may be expected to depend on the direction of the transition dipole with respect to the local bond structure and conformation. Elucidation of the relationship requires a detailed accounting of the configurational statistics of the chain as a whole.

Methods[2-4] developed for the treatment of strain birefringence can be adapted to the interpretation of strain–dichroism, as one of us has pointed out.[4] Both depend on quantities which can be expressed as second-order tensors. Rigorous treatment of strain–dichroism on this basis is presented here. Calculations carried out for various absorptions in the infrared spectrum of polymethylene chains are included as well. The results of these calculations are illustrative of the connection between preferential orientation of a transition moment and (a) its specification within a reference frame affixed to the local structure, and (b) the skeletal conformation required for occurrence of the absorption process.

Theory

Let $\mathbf{m}_i$ be the transition moment for the absorption of electromagnetic radiation at a frequency ν by skeletal bond i, or by groups associated therewith. Further, let $\boldsymbol{\varepsilon}_i$ be the dyadic representation of $\mathbf{m}_i\mathbf{m}_i$. Then the absorbance (and the extinction coefficient) for radiation with polarization vector parallel to $\mathbf{m}_i$ will be proportional to ϵ_i = trace $\boldsymbol{\varepsilon}_i = m_i^2$, where m_i is the scalar magnitude of $\mathbf{m}_i$. For random orientation of bond i with respect to the incident radiation, the absorbance will be proportional to $\bar{\epsilon}_i = \epsilon_i/3$.

The absorbance of the molecule as a whole may be formulated as the appropriate tensor sum over the $\boldsymbol{\varepsilon}_i$ associated with the skeletal bonds comprising the chain. In the evaluation of this sum, account must be taken of differences in transition moments, as embodied in the $\boldsymbol{\varepsilon}_i$, for various bonds or repeat units of the chain; for

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[1] B. E. Read and R. S. Stein, *Macromolecules*, **1**, 116 (1968).

[2] K. Nagai, *J. Chem. Phys.*, **40**, 2818 (1964); **47**, 2052 (1967).

[3] P. J. Flory, R. L. Jernigan, and A. E. Tonelli, *ibid.*, **48**, 3822 (1968).

[4] P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., Chapter IX.