Pentad Conformations in Vinyl Polymers and the Nuclear Magnetic Resonance Spectrum of Methine Protons in Polystyrene

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ABSTRACT: Conformational probabilities are calculated for pentads situated in vinyl chains of varying stereochemical composition according to the rotational isomeric state model with neighbor dependence. The average conformational probabilities are strongly dependent upon the severity of steric repulsions between groups separated by four bonds, and hence on the average stereochemical composition of the vinyl chain as a whole. The nmr spectra of methine protons in deuterated polystyrene and in the oligomers, 2,4-diphenylpentane and 2,4,6-triphenylheptane, are treated on the premise that proximity of a phenyl group attached to the neighboring α-carbon atom is the principal determinant of the chemical shift, and that the chemical shift is proportional to the incidence of conformations which place phenyl in apposition to H. The calculations are in qualitative accord with spectra reported for the oligomers, and frequencies observed in the spectrum of atactic polystyrene-d_7 are partially identified. Calculations further indicate that chemical shifts of the pentads should depend appreciably on the stereochemical configurations of dyads nearby. Hence, both the location and breadth of the resonance for a given pentad will depend on its stereochemical environment, *i.e.*, on the "tacticity" of the chain in which it is situated.

Recently we have treated the chemical shifts of the methylenic protons in atactic polypropylene by first singling out those conformations having a major effect on the magnetic environment of the proton in question, and then calculating the time-averaged occurrence, or probability $p_{\zeta\eta}$, of each such conformation. This probability depends[1,2] not only on the stereochemical character of the dyad in question; it depends in marked degree on the character of adjoining dyads, *i.e.*, on the character of the tetrad within which the methylene group is centered, and also on more remote dyads. This "long range" dependence of the conformation probability $p_{\zeta\eta}$ is a consequence of the severe conformational constraints generally prevalent in vinyl chains. Such effects are most pronounced in predominantly isotactic chains. The resonances associated with a racemic dyad in a predominantly isotactic chain consequently may be spread over a considerable frequency range owing to statistical variations in the stereochemical character of surrounding units.[1,2] The difficulties thus arising elude circumvention by resorting to higher resolution in the hope of separating resonances for stereochemical multiplets of higher order; the number of such resonances increases in greater profusion than the narrowing of the individual resonances with specification of the stereochemical configuration over a sequence of greater length.

In consequence of the circumstances outlined above, the nmr frequencies associated with a given multiplet depends on the average tacticity of the chain as a whole, and the resonances for atactic polymers are spread over a much wider range of frequency than are those for the main dyad in a predominantly stereoregular chain. These predictions[1] are well confirmed[2] by the spectra published by Zambelli and Segre[3] for atactic polypropylene. Moreover, it was possible, from conformational statistical analysis,[2] to identify the principal resonances discernible in the spectra for the atactic polymer.

More recently Segre, Ferruti, Toja, and Danusso[4] have reported 100-MHz spectra of isotactic and of atactic (free radical polymerized) polystyrene-d_7, the proton in both instances being in the α position. Six poorly resolved peaks were found for the atactic polymer compared with one (as expected) for the predominantly isotactic chain. The α-proton spectrum of atactic polystyrene covers a greater frequency range than that for the β protons in polypropylene. Yet, as Segre, *et al.*,[4] point out, the breadth of the identifiable peaks for the atactic polystyrene exceeds the breadths of the peaks observed for atactic polypropylene.[3] The former of these observations is apparently related to the greater magnetic shielding offered by the phenyl group. The latter we believe to be due to the larger size of the phenyl group compared with methyl (*i.e.*, to the smaller value to be assigned to the steric parameter ω; *cf.* the following). The conformational correlations consequently are transmitted over a greater range of units in polystyrene than in polypropylene.

In this paper we treat the conformational probabilities within various pentads in vinyl chains with particular reference to the conformations affecting the methine protons in polystyrene. We present a preliminary analysis of the chemical shifts for oligomers of polystyrene and for the atactic polymer.

Theory

The theory of the configurational statistics of vinyl chains,[5,6] as simplified by recent revisions,[1,6] is employed for the following analysis. Skeletal bonds will be viewed in the direction from CHR to CH_2, or, rather to CD_2 for the deuterated polystyrene specifically of interest here. A Newman diagram for the *trans* con-

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[1] P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 315 (1969).

[2] P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 327 (1969).

[3] A. Zambelli and A. L. Segre, *Polymer Lett.*, **6**, 473 (1968).

[4] A. L. Segre, P. Ferruti, E. Toja, and F. Danusso, *Macromolecules*, **2**, 35 (1969).

[5] P. J. Flory, J. E. Mark, and A. Abe, *J. Amer. Chem. Soc.*, **88**, 639 (1966).

[6] P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969, Chapter VI.

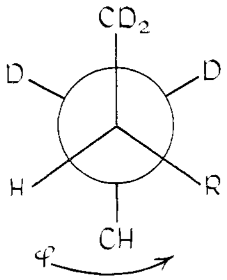

Figure 1. The Newman projection of a skeletal bond in deuterated polystyrene viewed from CHR to CD_2. The arrow indicates the direction of rotation of the group (CHR) at the near end of the bond for a right-handed rotation. The rotation angle φ is assigned positive values for rotation in this right-handed sense when the asymmetric center CHR has the stereochemical configuration represented in this diagram. The *trans* state shown in assigned $\varphi = 0$.

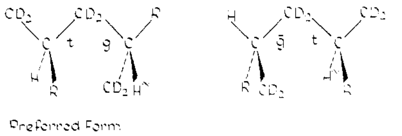

Figure 2. The two conformations of a *meso* dyad in which the methine proton H* is apposed to R (phenyl). The $\bar{g}t$ form is subject to a severe steric overlap of CD_2 with R.

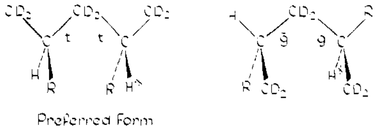

Figure 3. The two conformations of a racemic dyad in which the methine proton H* is apposed to *R*. Steric repulsion between the two CD_2 groups disfavors the $\bar{g}g$ conformation.

formation of such a bond is shown in Figure 1. A right-handed rotation φ about the skeletal bond will be reckoned as positive if the stereochemical configuration is that shown in Figure 1. For the enantiomorphic form, obtained by interchanging R and H in Figure 1, φ is to be reckoned in the opposite sense; *i.e.*, it is to be taken positive for left-handed rotations.[1,6] Three states may be distinguished: *trans* (*t*) at φ_t, *gauche* (*g*) at φ_g, and *gauche bar* $\bar{g}$ at $\varphi_{\bar{g}}$. Under the foregoing convention on the sign of φ, the values of these rotation angles, including their signs, are invariant to mirror reflection and hence take on the same values for corresponding conformers of the enantiomorphs; φ_g will be positive and $\varphi_{\bar{g}}$ negative. The rotational states may be taken symmetrically at $\varphi_t = 0°$, $\varphi_g = 120°$, and $\varphi_{\bar{g}} = -120°$. More realistically, we may expect φ_t to be a little greater than, and φ_g to be a little less than, these values (the displacements being on the order of 10°).[5-7] These are matters of little concern in the present discussion.

In harmony with previous conventions,[1,6] we assign statistical weights of η, 1, and τ for the "first-order" interactions associated with the respective states *t*, *g*, and $\bar{g}$. In the first of these CH is *syn* to R (see Figure 1), in the second it is *syn* to CH_2, and in the third it is subject to *syn* interactions with both R and CH_2. For polystyrene at ordinary temperatures[8] $\eta \approx 1.5$ and τ probably is less than unity. The precise value of τ is unimportant (*cf.* the following).

All steric interactions of "second order" involving pairs of groups CH, CD_2, and R separated by four bonds will be accorded the same statistical weight ω, which we may safely assume to be <0.05 for polystyrene[8] having the comparatively large substituent $R = C_6H_5$, or C_6D_5 in the polymers to be discussed. The several kinds of second-order interactions may readily be distinguished[8] and calculations could have been carried out on this basis. Experimental evidence presently available would not warrant this refinement, however.

The required statistical weight matrices for vinyl chains are[1,5,6]

$$\mathbf{U}' = \begin{bmatrix} \eta & 1 & \tau \\ \eta & \omega & \tau \\ \eta & 1 & \tau\omega \end{bmatrix} \tag{1}$$

for the first skeletal bond of a dyad,[9] and

$$\mathbf{U}''_m = \begin{bmatrix} \eta\omega & 1 & \tau\omega \\ \eta & \omega & \tau\omega \\ \eta\omega & \omega & \tau\omega^2 \end{bmatrix} \tag{2}$$

$$\mathbf{U}''_r = \begin{bmatrix} \eta & \omega & \tau\omega \\ \eta\omega & 1 & \tau\omega \\ \eta\omega & \omega & \tau\omega^2 \end{bmatrix} \tag{3}$$

for the second; the former matrix (eq 2) is for a *meso* dyad and the latter for a racemic one. Rotational states are indexed in the order *t*, *g*, and $\bar{g}$;[1,8] those for the preceding bond are indexed on the rows and those for the bond in question on the columns. The same parameter ω is used to represent all steric interactions between groups separated by four bonds. These vary in severity. Most of them involve the phenyl group, which is comparatively large. Hence, the appropriate mean value for ω should be small.

The phenyl group is subject to a large induced ring current in a magnetic field; *i.e.*, its diamagnetic susceptibility is large, and likewise the anisotropy of its susceptibility. Proximity of a phenyl group to a proton and the orientation of the former with respect to the vector leading from it to the proton may be expected to have the overriding effect on the chemical shift. Accordingly, we consider those conformations in which the methine proton is "shielded" by a phenyl group. For a given methine proton, there are two such conformations for a *meso* dyad and likewise two for a racemic dyad. These are shown in Figures 2 and 3, respectively. The proton considered is marked with an asterisk in each instance. One of the alternative conformations in each figure is free of second-order steric overlaps and is labeled as a "preferred conformation." Other preferred conformations in which H* is not apposed to R, *i.e.*, to C_6D_5, are of no interest and have not been included in Figures 2 and 3. The second conformation in each figure is subject to a

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(7) Y. Fujiwara and P. J. Flory, *Macromolecules*, to be submitted.

(8) A. D. Williams and R. J. Flory, *J. Amer. Chem. Soc.*, **91**, 3111 (1969).

(9) We omit the factor τ^* from the 1,1 element of U′ inasmuch as its value must closely approximate unity for polystyrene.[8]

second-order overlap of such severity as to diminish greatly the probability of its occurrence.

In each of the preferred conformations in Figures 2 and 3, the phenyl group is constrained by steric interactions of its *ortho* hydrogens and carbons to assume an orientation about the C–R bond with its plane perpendicular to the plane defined by the adjoining skeletal bonds.[10] Consequently, H* is located in a direction perpendicular to the plane of the phenyl group and at a distance of 2.5 Å from the plane. The situation of H* relative to phenyl is equivalent for both the *meso* and the racemic dyads in their preferred conformations, p''_{tg} and p''_{tt}, respectively.

In the nonpreferred conformations shown in Figures 2 and 3, the phenyl group probably is rotated *ca.* 60° from the line connecting H* and the phenyl group. Of course, the precise angle of tilt of the phenyl group depends on the value of $\Delta\varphi$ (see above)[5–7] and other details of the conformations. In any event, this is a matter of little concern since the occurrence of the nonpreferred conformations is comparatively rare.

In Figures 2 and 3, we have shown only interactions with substituents to the left of the proton H* whose resonance is under consideration. Corresponding interactions of H* with R of the succeeding dyad must of course be counted as well. If that dyad is *meso*, the relevant conformations are *gt* (preferred) and $t\bar{g}$ (nonpreferred). These obviously are equivalent to those for the preceding dyad illustrated in Figure 2. If the succeeding dyad is racemic, then the relevant conformations affecting H* are *tt* and $g\bar{g}$.

In compliance with implications of the foregoing considerations, we define a quantity ϵ representing the expected number of appositions of neighboring phenyl groups with respect to a given methine proton H* in the manner described above. This expectation is of course a time averaged, or equilibrium, quantity. It affords a measure of the predicted chemical shielding of the specified proton. If the *k*th and (*k* − 1)st dyads, *i.e.*, the dyads preceding and following $(\mathrm{CHR})_k$, respectively, are both *meso*, then

$$\epsilon_{mm;\,k} = p''_{tg;\,k} + p''_{gt;\,k+1} + p''_{\bar{g}t;\,k} + p''_{t\bar{g};\,k+1} \qquad (4)$$

Similarly, for a syndiotactic triad

$$\epsilon_{rr;\,k} = p''_{tt;\,k} + p''_{tt;\,k+1} + p''_{\bar{g}g;\,k} + p''_{g\bar{g};\,k+1} \qquad (5)$$

and for a methine proton in a heterotactic triad

$$\epsilon_{mr;\,k} = p''_{tg;\,k} + p''_{tt;\,k+1} + p''_{\bar{g}t;\,k} + p''_{g\bar{g};\,k+1} \qquad (6)$$

Of course, the various conformation probabilities p'' depend on the stereochemical configurations of other nearby dyads. In the adoption of ϵ as a measure of the chemical shift (*cf.* the following), we shall ascribe the same chemical shift to preferred and to nonpreferred conformations, the less favorable orientation of the phenyl group in the latter notwithstanding.[11] Since the latter conformations occur infrequently, any error thus introduced will have only a negligible effect on the resulting calculations at their present state of refinement.

Conformational probabilities $p''_{\alpha,\beta}$ that the pair of skeletal bonds comprising a given dyad, *i.e.*, the bonds separating two consecutive asymmetric centers CHR, are in states designated α and β, respectively, were calculated by methods given previously.[1,2,12,13] Thus, for dyad *k* in a vinyl chain consisting of *x* units, and therefore $x - 1$ dyads, we have[1,13]

$$p''_{\alpha\beta;\,k} = Z^{-1}\mathbf{J}^*\left(\prod_{h=1}^{k-1}\mathbf{U}^{(2)}{}_h\right) \times (\mathbf{U}'\mathbf{U}''_{\alpha\beta;\,k})\left(\prod_{k+1}^{x-1}\mathbf{U}^{(2)}{}_h\right)\mathbf{J} \qquad (7)$$

where $\mathbf{U}_h{}^{(2)}$ denotes the statistical weight matrix for the *h*th dyad of the chain. It is given by

$$\mathbf{U}^{(2)}{}_m = \mathbf{U}'\mathbf{U}''_m \qquad (8)$$

if this dyad is *meso*, and by

$$\mathbf{U}^{(2)}{}_r = \mathbf{U}'\mathbf{U}''_r \qquad (9)$$

if it is racemic; $\mathbf{U}''_{\alpha\beta;\,k}$ represents the matrix for the second bond of the *k*th dyad, with all elements except $\mathbf{U}_{\alpha\beta}$ replaced by zero; **J** is the column with all elements equal to unity and **J*** is the row [100]; the configurational partition function *Z* is given by

$$Z = \mathbf{J}^*\left(\prod_{1}^{x-1}\mathbf{U}^{(2)}{}_h\right)\mathbf{J} \qquad (10)$$

Equation 7 may serve also for the calculation of the sum of the probabilities of occurrence of any combination of conformations within the *k*th unit. All that is required is to retain those elements $\mathbf{U}_{\alpha\beta}$ in $\mathbf{U}''_k$ for the conformations to be included, all other elements being made zero.

Numerical Calculations of Conformation Probabilities. The results of calculations of the sums of the probabilities of the preferred conformations for *meso* and racemic dyads in a variety of situations are presented in Table I. In each instance the calculations were carried out for the pentad sequence designated in the first column, this sequence being adjoined on either side by isotactic chains of 50 *meso* dyads (columns two and three) or by syndiotactic chains of 50 racemic dyads (columns four and five). The second dyad of the pentad, marked by an asterisk in the first column of the table, is the one to which the calculations refer. If it is *meso* (*m*), then the quantities recorded represent $p''_{tg} + p''_{gt}$; if it is racemic (*r*), they represent $p''_{tt} + p_{g\bar{g}}$. The entries are presented in three groups: in the first group the central triad of the pentad is isotactic, in the second it is syndiotactic, and in the third it is heterotactic.

These calculations and all which follow have been carried out with $\eta = 1.5$ and $\tau = 0.5$, except where noted otherwise. Two values of ω were used as indicated in Table I. Increase in the lengths of the ad-

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[10] A. E. Tonelli, Ph.D. Dissertation, Stanford University' 1968.

[11] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[12] R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **50**, 4165 (1969).

[13] See ref 6, Chapter III.

TABLE I

PROBABILITIES OF PREFERRED CONFORMATIONS OF DYADS IN VARIOUS PENTADS SITUATED IN ISOTACTIC AND IN SYNDIOTACTIC CHAINS[a]
($\eta = 1.5, \tau = 0.5$)

	Isotactic chain		Syndiotactic chain	
Pentad	$\omega = 0.01$	$\omega = 0.05$	$\omega = 0.01$	$\omega = 0.05$
*mm*mm*	0.930	0.835	0.964	0.860
*rm*mm*	0.974	0.886	0.973	0.883
*mm*mr*	0.960	0.857	0.968	0.868
*rm*mr*	0.977	0.894	0.975	0.888
*rr*rr*	0.984	0.925	0.984	0.926
*mr*rr*	0.984	0.924	0.984	0.926
*rr*rm*	0.986	0.932	0.985	0.930
*mr*rm*	0.985	0.929	0.985	0.929
*mm*rm*	0.980	0.906	0.979	0.902
*rm*rm*	0.990	0.943	0.988	0.936
*mm*rr*	0.969	0.878	0.975	0.888
*rm*rr*	0.984	0.928	0.985	0.930
*mr*mm*	0.988	0.938	0.987	0.936
*rr*mm*	0.985	0.929	0.986	0.931
*mr*mr*	0.974	0.886	0.976	0.891
*rr*mr*	0.979	0.902	0.978	0.899

[a] The dyad considered is denoted by an asterisk in the first column. For those cases in which this dyad is *meso*, the quantities tabulated in succeeding columns represent $p''_{tg} + p''_{gt}$; for racemic dyads the quantities tabulated are $p''_{tt} + p''_{gg}$.

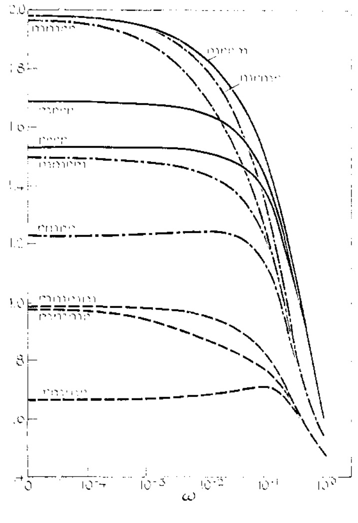

Figure 4. Expected number ε if appositions of C_6H_5 (or C_6D_5) to the central methine proton of the indicated pentads plotted as functions of log ω when the pentad is situated between sequences of 50 *meso* isotactic dyads, $\eta = 1.5$ and $\gamma = 0.5$.

joining stereoregular sequences beyond 50 units had no perceptible effect on the results. Hence, they may be construed to be representative of the indicated pentads situated within chains of infinite length.

Each dyad has accessible to it two preferred conformations as opposed to seven conformations subject to second-order steric repulsions. Yet, as the calculations in Table I demonstrate, the former dominate the latter overwhelmingly for $\omega = 0.01$. An increase in ω to 0.05 raises the proportion of the nonpreferred

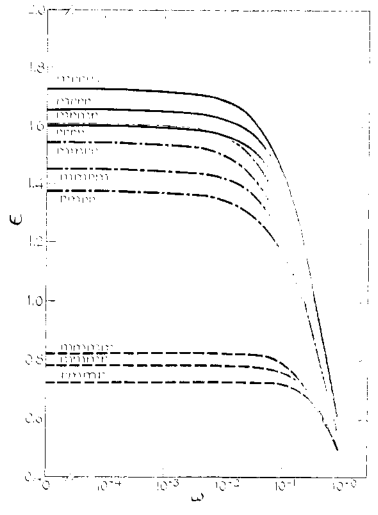

Figure 5. Expectations ε for the central methine proton of the indicated pentads when situated between racemic (syndiotactic) sequences of 50 units, plotted as functions of ω, $\eta = 1.5$ and $\tau = 0.5$.

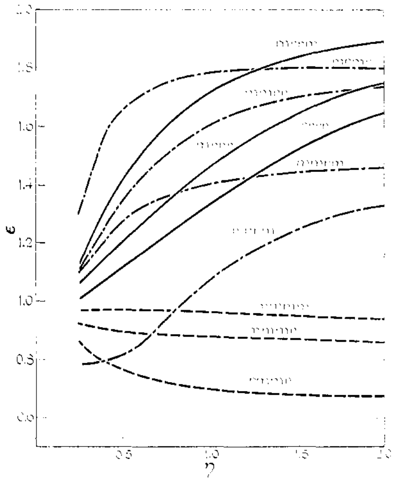

Figure 6. Expectations ε as funcions of η for the indicated pentads situated between isotactic sequences of 50 units, $\omega = 0.01$ and $\tau = 0.5$.

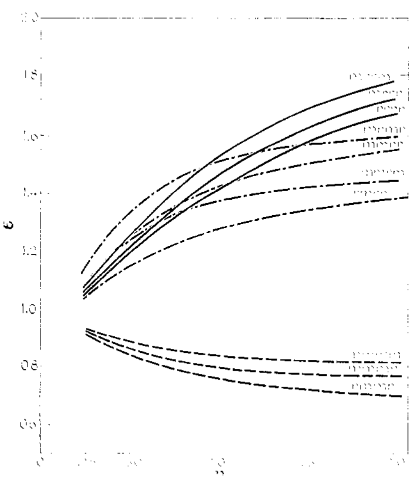

Figure 7. Expectations ε as functions of η for the indicated pentads situated between 50-unit syndiotactic sequences; $\omega = 0.01$ and $\tau = 0.5$.

conformations substantially. Nevertheless, they remain in minority in all cases. These results confirm and extend previous calculations which were confined to tetrads and shorter sequences.[1,2] Only one of the seven nonpreferred conformations contributes to ϵ, whereas one of the two preferred conformations for each dyad juxtaposes phenyl to H*. Thus, the contributions of nonpreferred conformations to ϵ are disproportionately smaller than the combined incidences for all seven of them, as recorded in Table I, might suggest.

In Figures 4–7 we show values of ϵ, calculated according to eq 4–10 for the central protons H* in pentads of the stereochemical configurations indicated,

$$\text{-CHRCD}_2\text{CHRCD}_2\text{CH*RCD}_2\text{CHRCD}_2\text{CHR-}$$

each such pentad being situated between stereoregular sequences of 50 dyads. Calculations for pentads in which the central triad is isotactic (*mm*) are shown by dashed curves, those for racemic triads (*rr*) are shown by solid curves, and those for heterotactic triads (*rm* or *mr*) by dot–dash curves.

The dependence on ω is shown in Figures 4 and 5, the former for the indicated pentads bounded by isotactic (*meso*) sequences of 50 units on either side, and the latter for pentads correspondingly situated within syndiotactic chains. Values of ϵ are lowest for the isotactic triads and largest for syndiotactic triads, except in the atypical range of $\omega > 0.10$. Their dependences on ω are in the same order. Heterotactic triads differ considerably, depending on the pentad in which they are situated, but in general values of ϵ for them display intermediate behavior. The dependence on ω is smaller for the pentads situated in syndiotactic than for those in isotactic chains, as expected.[1,2]

The effect of η is explored in Figures 6 and 7 for isotactic and for syndiotactic chains, respectively, with $\omega = 0.01$ in both cases. Isotactic triads are comparatively insensitive to η. Greater effects are evident for syndiotactic and heterotactic triads.

Calculations not reproduced here showed the effect of τ to be very small. The greatest change from $\tau = 0$ to 1.0 was only about 3%.

The dependence of the expectation ϵ for various pentads on the average stereochemical composition of the adjoining sequences of dyads is shown in Figures 8 and 9. Each point represents the average $\bar{\epsilon}$ for 20 Monte Carlo chains comprising two sequences of 50 dyads, one on either side of the pentad specified, the sequences being generated[1,2,5,6] subject to an *a priori* probability f_r that a dyad is racemic, this probability being independent of the stereochemical character of the neighboring dyad. In several instances calculations were carried out for 100 Monte Carlo chains. Neither the value of $\bar{\epsilon}$ nor the standard deviation from $\bar{\epsilon}$ (see below) was materially affected by the choice of a larger sample. Similar procedures have been applied previously[2] to the calculation of conformational probabilities for tetrads embedded in atactic chains of average stereochemical composition f_r. Increasing the lengths of the sequences of 50 dyads had no perceptible effect on the results; *i.e.*, those given may be considered to be representative of infinite chains.

As in previous studies[1,2] of effects of the stereochemical environment on conformational probabilities, influences are greatest in the isotactic region (small f_r). Dependence on the average stereochemical environment, expressed by f_r, is greater for heterotactic (dash–dot curves) than for either isotactic (dashed curves) or syndiotactic triads (solid curves). Curves for pentads in each category (isotactic, syndiotactic, and heterotactic) converage with increase in f_r. Of course, the dependence on f_r and the differences for various pentads decrease with increase in ω, as comparison of Figure 9 with Figure 8 shows.

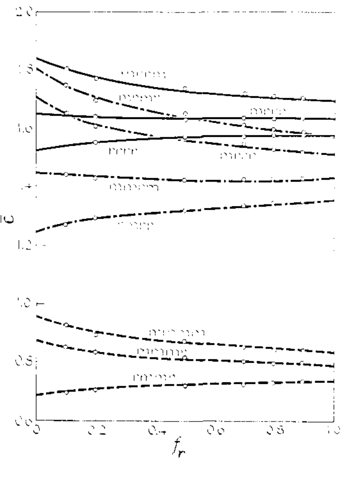

Figure 8. Average expectations $\bar{\epsilon}$ for various pentads as functions of their stereochemical environments denoted by f_r, the *a priori* probability that a given dyad external to the pentad is racemic. Each point is the average for 20 "Monte Carlo" chains consisting of the indicated pentad bounded on either side by a sequence of 50 dyads generated subject to the probability f_r given on the abscissa. $\omega = 0.01$, $\eta = 1.5$, and $\tau = 0.5$.

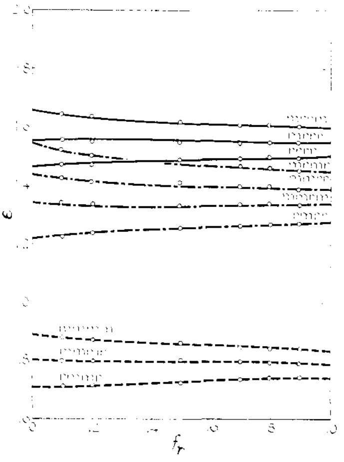

Figure 9. Average expectations $\bar{\epsilon}$ for chains generated as in Figure 8, but with ϵ calculated taking $\omega = 0.05$. As in Figure 8 and elsewhere, $\eta = 1.5$ and $\tau = 0.5$.

Standard deviations of the values of ϵ for the 20 Monte Carlo chains generated to obtain the average $\bar{\epsilon}$ for each point on three of the curves in Figure 8 ($\omega = 0.01$) are plotted against f_r in Figure 10. As in the similar analysis of conformations of the bonds adjoining methylenic protons,[1,2] the fluctuations are greatest for chains which are mainly isotactic, *i.e.*, near $f_r = 0.20$. Standard deviations in ϵ for all pen-

Table II

Standard Deviations of ϵ for Sets of 20 Monte Carlo Chains Generated with $f_r = 0.20$, $\eta = 1.5$, and $\tau = 0.5$

Pentad	$\sqrt{(\epsilon - \bar{\epsilon})^2}$ $\omega = 0.01$	$\omega = 0.05$
mmmm	0.0359	0.0202
rmmr	0.0148	0.0097
mmmr	0.0387	0.0163
rrrr	0.0166	0.0103
mrrm	0.0436	0.0202
mrrr	0.0250	0.0134
mrmr	0.0781	0.0343
rmrr	0.0341	0.0185
mmrr	0.0889	0.0330
mmrm	0.0374	0.0199

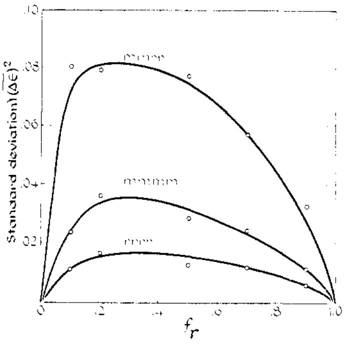

Figure 10. Standard deviations $\sqrt{(\epsilon - \bar{\epsilon})^2}$ for each of the sets of 20 Monte Carlo chains employed in the calculations for three of the curves in Figure 8 ($\omega = 0.01$), plotted against f_r.

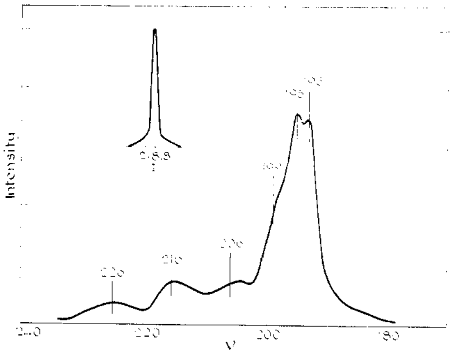

Figure 11. Nmr spectrum of isotactic (inset) and atactic polystyrene-d_7 as observed in o-dichlorobenzene at 160° by Segre, Ferruti, Toja, and Danusso.[4] The six frequencies ν, indicated in cycles per second on the diagram, are values reported by these authors.

tads in chains of composition $f_r = 0.20$ are given in Table II. They are largest for the pentads *mrmr* and *mmrr* formed from heterotactic triads. The indicated variations in ϵ must cause the proton resonances associated with the various pentads to be correspondingly broadened.

Estimation of Chemical Shifts and the Nmr Spectrum of Polystyrene and Its Oligomers. According to calculations of Johnson and Bovey,[11] the chemical shift of a proton at a distance of 2.6 Å from C_1 of the benzene ring, and in the approximate direction of the normal to the plane of the ring, should be about 0.5 ppm when account is taken of possible rotary fluctuations of the benzene ring in polystyrene. Hence, we take the chemical shift for the central proton in a given pentad to be

$$\tau = \tau_0 + 0.50\epsilon \tag{11}$$

in parts per million, or

$$\nu = \nu_0 - 50\epsilon \tag{12}$$

in cycles per second at 100 MHz, the usual sign convention being adopted.

Application of eq 11 and the foregoing methods to analysis of the nmr spectra of the dimeric and trimeric oligomers, 2,4-diphenylpentane[14,15] and 2,4,6-triphenylheptane,[16] is summarized in Table III. The isotactic, syndiotactic, and heterotactic trimers are denoted by I, S, and H, respectively, in the second column. The experimental results quoted in the last column are from measurements carried out in CCl_4 at 20° by Doskočilová and Schneider[14] and by Lím, Kolinský, Petránek, Doskočilová, and Schneider.[16] Observed values given in parentheses are rough estimates from the curves published by the latter workers.[16] Choosing τ_0 arbitrarily in such manner as to optimize agreement with the observations, we take

$$\tau = 7.25 + 0.50\epsilon \tag{13}$$

in parts per million, or

$$\nu = 275 - 50\epsilon \tag{14}$$

in cycles per second at 100 MHz. Calculated values of τ in the penultimate column of Table III were obtained, using eq 13, from the ϵ's calculated for $\omega = 0.01$.

The spectrum of the methine protons in atactic deuterated polystyrene[4,17] determined by Segre, *et al.*,[4] in o-dichlorobenzene at 160° is represented in Figure 11, the curve having been smoothed to remove "noise." The frequencies identified by these authors are indicated in the figure. Also shown in the inset is their spectrum for the isotactic polymer. It exhibits a single line at $\nu = 218.8$ cps; its width at half-height is reported to be 1.1 cps. If we take $\eta = 1.5$, $\omega = 0.01$ and $f_r = 0$ for the isotactic polymer, then ϵ calculated for the *mmmm* pentad identified with this peak is 0.956. Ten per cent of racemic units ($f_r = 0.10$) would only lower this figure to 0.93 (see Figures 4 and 8). If, however, we choose $\omega = 0.05$, then the values calculated for ϵ for the *mmmm* pentad are 0.89 and 0.87 for $f_r = 0$ and 0.10, respectively. For the calculations presented below, we have chosen arbitrarily to adopt 0.95 as the value of ϵ appropriate for the pentad whose resonance was observed by Segre, *et al.*,[4] at 218.8 cps for their isotactic polymers. It follows from eq 12 that $\nu_0 = 267$ cps in o-dichlorobenzene at 160°. A

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(14) D. Doskočilová and B. Schneider, *J. Polym. Sci., Part B*, 3, 213 (1965).

(15) F. A. Bovey, F. P. Hood, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, 42, 3900 (1965).

(16) D. Lím, M. Kolinský, J. Petránek, D. Doskočilová, and B. Schneider, *J. Polym. Sci.*, 4, 645 (1966).

(17) S. Brownstein, S. Bywater, and D. J. Worsfold, *J. Phys. Chem.*, 66, 2067 (1963).

TABLE III

CHEMICAL SHIFTS FOR DIMERIC AND TRIMERIC OLIGOMERS OF POLYSTYRENE (IN CCl_4 AT 20°)

	ϵ			τ	
Compounds	$\omega = 0$	$\omega = 0.01$	$\omega = 0.05$	Calcd ($\omega = 0.01$)	Obsd[a]
Dimer *meso*	0.50	0.49	0.47	7.50	7.4[a]
racemic	0.69	0.68	0.65	7.59	7.6[a]
Trimer I—center	0.67	0.67	0.67	7.59	(7.5)[c]
I—end	0.67	0.65	0.60	7.58	(7.5)[c]
S—center	1.53	1.51	1.42	8.01	7.9[b]
S—end	0.76	0.75	0.70	7.63	(7.6)[c]
H—center	1.23	1.20	1.14	7.85	(7.7)[d]
H—*m*-end	0.59	0.58	0.54	7.54	(7.7)[d]
H—*r*-end	0.82	0.80	0.75	7.65	(7.7)[d]

[a] Doskočilová and Schneider.[14] [b] Numerical value quoted by Lím, *et al.*[16] [c] From spectra of Lím, *et al.*[16] Subject to an uncertainty of ±0.1 ppm. [d] Same as footnote *c* but subject to an uncertainty of ±0.2 ppm.

value of $\epsilon = 0.90$ for the pentad resonance they observed would yield $\nu_0 = 264$ cps. The difference is not significant in comparison with other uncertainties, including especially those associated with the value of $\sigma \approx 0.50$ and with the neglect of secondary shielding effects.[18] Hence, without commitment concerning the probable value of f_r for the isotactic polymer, and especially without implying prejudice for a particular value of ω, we adopt the former estimate of ν_0. Accordingly, we take

$$\nu = 267 - 50\epsilon \qquad (15)$$

for polystyrene-d_7 in dichlorobenzene at 160°.[19]

Vertical lines in Figure 12 represent mean frequencies for the indicated pentads calculated according to eq 15 using average values ϵ computed by the Monte Carlo methods described above, with $\omega = 0.01$, $\eta = 1.5$, $\tau = 0.5$, and $f_r = 0.50$ (see Figure 8). The heights of these lines are doubled for asymmetric pentads, as required for inclusion of the other member of each such pair. Line widths were then assigned on the basis of the equation

$$\delta\nu = 1/2\pi T'_{2;\,\mathrm{app}} = 1/2\pi T'_2 + \sigma\sqrt{(\epsilon - \bar{\epsilon})^2} \qquad (16)$$

where $T'_{2;\,\mathrm{app}}$ is the apparent relaxation time, and T'_2 is the actual relaxation time. We take $(2\pi T'_2)^{-1} = 1.1$ cps from the quoted width of the line for isotactic polystyrene reported by Segre, *et al.*,[4] and $\sigma = 50$ cps as above. The line width $\delta\nu$ is then calculated from the standard deviation for the relevant Monte Carlo chains, 20 in number, generated with $f_r = 0.50$. For convenience, the shape of each line is taken to be Lorentzian; this assumption is of course quite arbitrary. The curve drawn in Figure 12 is the sum of the Lorentzian curves calculated in this manner for each resonance.

By comparing Figure 11 with Figure 12, we may conclude that the resonances reported by Segre, *et al.*,[4] at 226 and 216 cps are due to pentads whose central triads are isotactic (*mm*). Those at 206 and 199 cps probably are mainly due to heterotactic triads, and the more intense peaks observed at 195 and 193 cps represent combinations of syndiotactic and heterotactic tetrads. These identifications are tentative. There is no assurance that the atactic polymer investigated by them consisted of equal numbers of *meso* and racemic dyads and that these were distributed at random, as we have assumed in our calculations. The stereochemical composition must affect *the locations* as well as the widths of the various pentad resonances, as we have repeatedly emphasized. Qualitative agreement of the calculated curve with that observed experimentally has nevertheless been realized. The correspondence is clearly sufficient to support the premise that the chemical shifts are principally determined by the incidence of those conformations in which the relevant methine proton H* is shielded by the phenyl groups attached to the adjoining asymmetric centers.

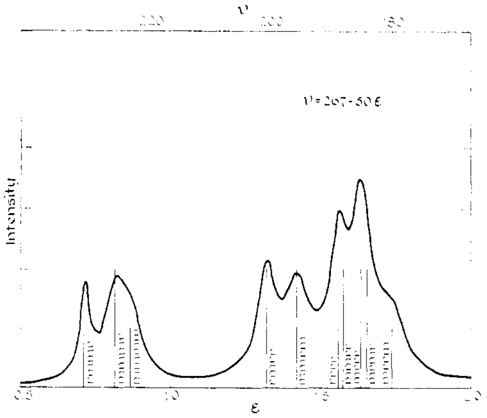

Figure 12. Nmr spectrum calculated for methine protons in atactic polystyrene-d_7 with $f_r = 0.50$, $\omega = 0.01$, $\eta = 1.5$, and $\tau = 0.5$. The vertical lines represent mean frequencies calculated for the indicated pentads. The curve represents the sum of intensities calculated assuming each to be Lorentzian in shape and of breadth determined according to eq 16.

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(18) Adoption of $\epsilon = 0.90$ yields a calculated spectrum for the atactic polymer which is in somewhat better agreement with the observed spectrum than our Figure 12. We are not prepared at present to attach significance to improvement gained in this manner; it is overshadowed by the uncertainty in the value of σ.

(19) The small difference between eq 14 and 15 may be attributed to differences in temperature and solvent.