

The Chemical Shifts of Poly(vinyl chloride) and Its Model Compounds

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ABSTRACT: The proton chemical shifts of *meso* and *racemic* 2,4-dichloropentanes (DCP) were calculated by taking into account the diamagnetic shielding, bond anisotropy and polar effects, using preferred conformations of *TG* and *G'T* forms for *meso* DCP, and *TT* and *GG* forms for *racemic* DCP. The *TT* form was found to be more stable than the *GG* one by 1.97 kcal/mol. It is predicted theoretically that the anti methylene proton would appear at higher field than the syn proton. Also the orders of the excess charges of the *2p* electrons and the total charges on the carbon atoms of *meso* and *racemic* DCP's coincide with the order of the observed C-13 chemical shifts of those DCP's.

The proton chemical shifts of poly(vinyl chloride) (PVC) were calculated assuming the preferred conformations, $(TG)_n$ and $(G'T)_n$ for isotactic PVC and $(TT)_n$ for syndiotactic PVC. The calculated chemical shifts of *racemic* methylene and isotactic methine protons appear at a higher field than the *meso* methylene and syndiotactic methine protons, respectively. As for the isotactic PVC the anti proton appears at higher field than the syn proton just as for DCP.

KEY WORDS Poly(vinyl chloride) / Dichloropentane / Chemical Shift / Conformation / Extended Hückel Method /

The proton NMR spectrum of poly(vinyl chloride) (PVC) in solution has long been studied for the stereochemical structure of this polymer, sometimes using decoupling and selective deuteration techniques.¹⁻¹⁶ Recently Heatley,¹⁶ *et al.*, have studied the vicinal coupling constants of PVC, using a 220-MHz NMR spectrometer and have suggested that in thermodynamically good solvents, the isotactic dyads are in approximate equilibrium between the conformations which result in a 3_1 helix, whereas syndiotactic dyads are probably in a planar zigzag structure. Also, as the model compounds of PVC, the molecular structure of *meso* and *racemic* 2,4-dichloropentanes (DCP) and isotactic, heterotactic and syndiotactic 2,3,6-trichloroheptanes have been studied by infra-red and NMR methods¹⁷⁻²⁴ and it has been proposed that the *TG* and *G'T* forms are preferred for *meso* DCP, whereas the preferred form for *racemic* DCP are predominantly *TT*, and also *GG* with some probabilities. Flory, *et al.*,²⁵ have pointed out the existence of less-favoured conformations. However, these may be almost ignored in our discussion described

below.

As described above, the molecular structures of DCP and PVC have been studied in detail, but the relationship between the chemical shifts and molecular structures of these compounds have been scarcely studied theoretically. In this paper the calculation of the proton and C-13 chemical shifts of these model compounds in their preferred conformations are described.

At first, in the cases of DCP's the extended Hückel theory²⁶ was applied to calculate the total electron energies, the total net charges and the excess charges of *2p* electrons. Then the proton chemical shifts of these compounds were calculated by taking into account the contributions from diamagnetic shielding, magnetic anisotropy and polar effects, and were compared with the observed ones. Also the C-13 chemical shifts were calculated and compared with the observed results.

On the basis of these calculations of the model compounds, the proton chemical shifts of isotactic and syndiotactic PVC's were calculated by taking into account the contributions from the

bond anisotropy and polar effects, and compared with the observed results.

THEORETICAL

For the molecules (DCP and PVC) under consideration, the proton shielding constant σ_H for a proton A can be calculated approximately by a sum of the following terms^{27,33} neglecting the ring current effect,

$$\sigma_H = \sigma_H^{\text{dia}} + \sigma_H^{\text{para}} + \sum_{B(\neq A)} \sigma_{AB} + \sigma_E \quad (1)$$

where σ_H^{dia} is the diamagnetic shielding term on the specified proton, σ_H^{para} the paramagnetic contribution on the proton, σ_{AB} the neighbour anisotropy effect arising from locally induced currents on the atom B's other than A in the molecule, and σ_E the polar effect arising from the electric field due to any polar group in the molecule.

The value of σ_H^{dia} is given by the well-known formula²⁸

$$\sigma_H^{\text{dia}} = (e^2/3mc^2) \sum_i \langle r_i^{-1} \rangle \quad (2)$$

where e is the electron charge, m the mass of the electron, C the velocity of light, $\langle r_i^{-1} \rangle$ is the mean value of $1/r_i$, r_i the distance between i -th electron and the nucleus, and the summation is done over all the electrons on the atom considered. This gives immediately a linear correlation with the electron density around the proton as follows²⁸

$$\sigma_H^{\text{dia}} = k\rho \quad (3)$$

where ρ is the electron density on the proton and we used 17.8 ppm²⁷ as the value of k .

The paramagnetic term σ_H^{para} is neglected as usually due to the small contribution to the proton chemical shift.²⁷

The neighbour anisotropy term σ_{AB} can be estimated as follows²⁹

$$\sigma_{AB} = \frac{\Delta\chi_B}{3r_{AB}^3} (1 - 3 \cos^2 \theta) \quad (4)$$

where $\Delta\chi_B (= \chi_B^{\parallel} - \chi_B^{\perp})$ is the magnetic anisotropy of the B atom and θ is the angle between the anisotropy axis and the internuclear vector r_{AB} . However we used the following equation³⁰ of the magnetic anisotropy of the X—Y bond in-

stead of eq 4 because of the difficulties in directly estimating on the neighbour anisotropy effect in long chain molecules

$$\sigma_{X-Y} = \frac{\Delta\chi_{X-Y}}{3r^3} (1 - 3 \cos^2 \theta_M) \quad (5)$$

where $\Delta\chi_{X-Y}$ is the magnetic anisotropy of the X—Y bond, r the distance between any specified nucleus and the magnetic anisotropy $\Delta\chi$, and θ_M the angle which the direction of r makes with the X—Y bond. Here we assume the point dipole to be located at the midpoint along the X—Y bond. We took into account the magnetic anisotropies of the C—C and C—Cl bonds, but neglected $\Delta\chi_{C-H}$ because of its small contribution.³⁰ So far, various values for $\Delta\chi_{C-C}$ are reported, but the most reliable value is not known at present. For the comparison we used for $\Delta\chi_{C-C}$ both values of $5.5 \times 10^{-30} \text{cm}^3$ ³⁰ and $9.1 \times 10^{-30} \text{cm}^3$,³¹ and used $5.0 \times 10^{-30} \text{cm}^3$ ³² for $\Delta\chi_{C-Cl}$.

The value of σ_E is estimated by the Buckingham's equation³³

$$\sigma_E = -1.48 \times 10^{-12} \frac{q}{R^2} E_z - 0.74 \times 10^{-18} E^2 \quad (6)$$

where R is a distance between any specified proton and an atom (X) bonded to it, q the charge on the atom (X), and E_z is the component of a uniform electric field E in the bond direction of any specified proton. E_z and E were estimated from the charge distributions obtained by the extended Hückel method as described below.

Generally the chemical shift of a particular molecule is affected by the surrounding molecules, which may be of the same or different species, as in the liquid state or a solvent respectively. However it is theoretically very difficult to estimate exactly the solvent effect on polymer molecules. Thus we neglected the solvent effect in a first approximation.

The net charge distributions and the total electron energies of the $TG(G'T)$ form for *meso* DCP are calculated by the extended Hückel theory.²⁶ In this calculation the various Coulomb integrals (H_{rr}) are taken as the appropriate valance-state ionization potential for the particular atomic orbital under consideration that is, $H_{rr}(H_{1s}) = -13.6 \text{ eV}$, $H_{rr}(C_{2s}) = -21.43 \text{ eV}$, $H_{rr}(C_{2p}) = -11.42 \text{ eV}$, $H_{rr}(Cl_{3s}) = -25.26 \text{ eV}$ and

$H_{rr}(Cl_{3p}) = -15.09 \text{ eV}$,³⁴ where in $H_{rr}(X_Y)$, X and Y denote any atomic symbol and the electron orbital state of atom X, respectively. The resonance integral (H_{rs}) is taken as follows.

$$H_{rs} = \frac{K}{2}(H_{rr} + H_{ss})S_{rs} \quad (7)$$

where the K is a constant which was assigned a value of 1.75²⁶ and S_{rs} is the overlap integral. The Slater's effective nuclear charges used for H, C, and Cl atoms are 1.1, 3.25 and 6.10, respectively. In this calculation, the iteration is performed until the total electron energy of molecule under consideration converges.

The rotational isomeric states of *trans* (T), and two *gauches* (G and G') are defined as occurring at the rotational angles 0°, 120° and 240°, respectively, by the clockwise rotation around the C—C bond as expressed in the Newman projection. The C—C, C—H and C—Cl bond length³⁵ used are set to 1.54, 1.10 and 1.69 Å, respectively, and each of the C—C—C, C—C—H and C—C—Cl bond angles used is set to 109°28'.

RESULTS AND DISCUSSION

Meso and Racemic 2, 4-Dichloropentanes

The net charge distributions and the total electron energies of the TG form for *meso* DCP, and the TT and GG forms for *racemic* DCP calculated by the extended Hückel theory are shown in Figure 1, where one of the methyl protons was assumed to take the *trans* position against the central carbon atom, and the net charges on the three hydrogen atoms of the methyl group were averaged taking into account its free rotation. As shown in Figure 1 the total electron energy of the TT form in *racemic* DCP is 1.97 kcal/mol lower than the GG form. This value is in well accordance with that of 1.7—2.3 kcal/mol by the van der Waals and electrostatic interaction,¹⁹ and of 1.5 kcal/mol by NMR.²¹ Moreover, the total electron energies of *meso* and *racemic* DCP's show that *racemic* DCP is much more stable than *meso* DCP. This is in close agreement with the results calculated by McMahan, *et al.*,²¹ assuming Lennard—Jones type interactions between nonbonded atoms.

Using these results and, eq 1, 3, 5, and 6, the proton magnetic shielding constants of DCP's

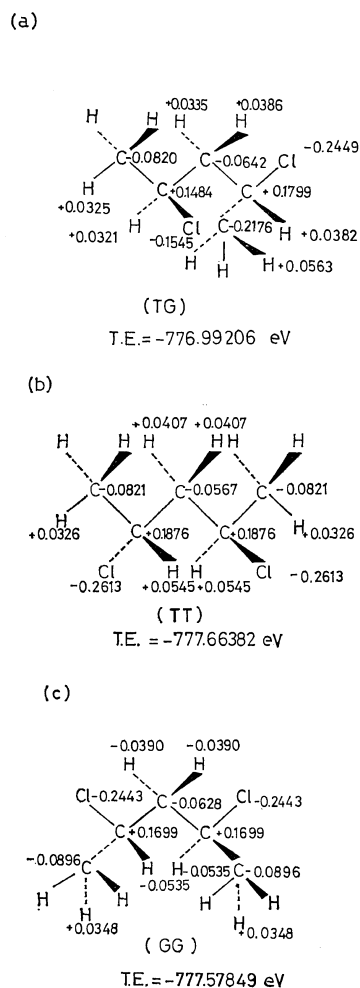


Figure 1. The charge distributions and total electron energies (T.E.) of 2,4-dichloropentanes. (a) *meso*, TG; (b) *racemic*, TT; (c) *racemic*, GG.

are estimated and tabulated in Tables I and II, in which the magnetic shielding constant for the methyl group is averaged on the three methyl protons and the values in the bracket are those obtained by using $9.1 \times 10^{-30} \text{ cm}^3$ as $\Delta\chi_{C-C}$. We calculated E and E_z with the point dipole approximation. The dipole moment of the C—Cl bond used was 1.72 Debye unit (D) which was averaged over all values calculated by the charge distribution of the preferred conformation. The chemical shifts (σ_{AV}) of each proton were averaged for the preferred conformations using the following equations.

Table I. The calculated proton chemical shifts of *meso* 2,4-Dichloropentane

	Averaged over the preferred <i>TG</i> and <i>G'T</i> conformations (at room temp) (ppm)				
	CH ₃	anti	CH ₂	syn	CH
σ^{dia}	17.009	17.203		17.112	17.175
$\sigma_{\text{C-C}}^{\text{a}}$	-0.293 (-0.486)	-0.583 (-0.965)		-0.782 (-1.294)	-0.598 (-0.989)
$\sigma_{\text{C-Cl}}$	-0.009	-0.071		+0.103	-0.370
σ_{E}	-0.204	-0.341		-0.409	-1.790
σ_{Proton}	16.503 (16.310)	16.208 (15.826)		16.029 (15.517)	14.417 (14.026)
$\Delta\sigma_{\text{Proton}}^{\text{b}}$		0.295 (0.484)	0.179 (0.309)		1.612 (1.491)

^a $\sigma_{\text{C-C}}$, $\Delta\chi_{\text{C-C}}=5.5 \times 10^{-30}\text{cm}^3$; (), $\Delta\chi_{\text{C-C}}=9.1 \times 10^{-30}\text{cm}^3$.

^b $\Delta\sigma$'s denote difference between the CH₃ and CH₂, the anti and syn protons, and the CH₂ and CH, respectively.

Table II. The calculated proton chemical shifts of *racemic* 2,4-dichloropentane

	Preferred conformation						Averaged over the preferred <i>TT</i> and <i>GG</i> conformations (at room temp) (ppm)		
	<i>TT</i> (ppm)			<i>GG</i> (ppm)			CH ₃	CH ₂	CH
	CH ₃	CH ₂	CH	CH ₃	CH ₂	CH			
σ^{dia}	17.219	17.076	16.831	17.179	17.106	16.848	17.218	17.076	16.831
$\sigma_{\text{C-C}}^{\text{a}}$	-0.318 (-0.526)	-0.484 (-0.801)	-0.634 (-1.049)	-0.220 (-0.364)	-0.667 (-1.094)	-0.485 (-0.802)	-0.314 (-0.521)	-0.490 (-0.779)	-0.629 (-1.040)
$\sigma_{\text{C-Cl}}$	+0.090	-0.071	-0.248	-0.051	+0.101	-0.404	+0.085	-0.066	-0.253
σ_{E}	-0.177	-0.354	-1.645	-0.396	-0.409	-1.687	-0.184	-0.355	-1.647
σ_{Proton}	16.814 (16.606)	16.167 (15.850)	14.304 (13.889)	16.512 (16.368)	16.137 (15.704)	14.272 (13.955)	16.805 (16.598)	16.165 (15.876)	14.302 (13.891)
$\Delta\sigma_{\text{Proton}}^{\text{b}}$		0.647 (0.756)	1.863 (1.961)		0.375 (0.664)	1.865 (1.749)		0.640 (0.722)	1.863 (1.985)

^a $\sigma_{\text{C-C}}$, $\Delta\chi_{\text{C-C}}=5.5 \times 10^{-30}\text{cm}^3$; (), $\Delta\chi_{\text{C-C}}=9.1 \times 10^{-30}\text{cm}^3$.

^b $\Delta\sigma$'s denote the differences between the CH₃ and CH₂, and the CH₂ and CH, respectively.

$$\sigma_{\text{av}} = \sum X_i \sigma_i \quad (8)$$

$$X_i = e^{-\Delta E_i/RT} / \sum e^{-\Delta E_i/RT} \quad (9)$$

where σ_i and X_i are the chemical shift and fraction of the i -th preferred conformation, $\Delta E_i = E_i - E_0$, E_0 being the energy of the conformation taken as the reference state and E_i the energy of the i -th preferred conformation. The sum is taken over all the important conformers. R and T are the gas constant and absolute temperature, respectively.

From Tables I and II it was found that the polar effect contributes predominantly to the relative chemical shift difference as compared with the other terms and the contribution of the diamagnetic terms to the relative chemical shift difference is very small.

Table III. The observed proton chemical shifts of *racemic* and *meso* 2,4-dichloropentanes (at 20°C and 60 MHz)^a

	Chemical shift (ppm)			
	CH ₃	CH ₂		CH
		A	B	
<i>Racemic</i>				
$\sigma_{\text{Proton}}^{\text{obs}}$	8.57	8.11		5.81
$\Delta\sigma_{\text{Proton}}^{\text{obs}}$		0.46	2.30	
<i>Meso</i>				
$\sigma_{\text{Proton}}^{\text{obs}}$	8.49	8.05	7.75	
$\Delta\sigma_{\text{Proton}}^{\text{obs}}$		0.44	0.30	1.82

^a The reference is TMS. $\Delta\sigma$'s denote the differences between the CH₃ and CH₂, the anti and syn protons, and the CH₂ and CH, respectively.

The Chemical Shifts of DCP and PVC.

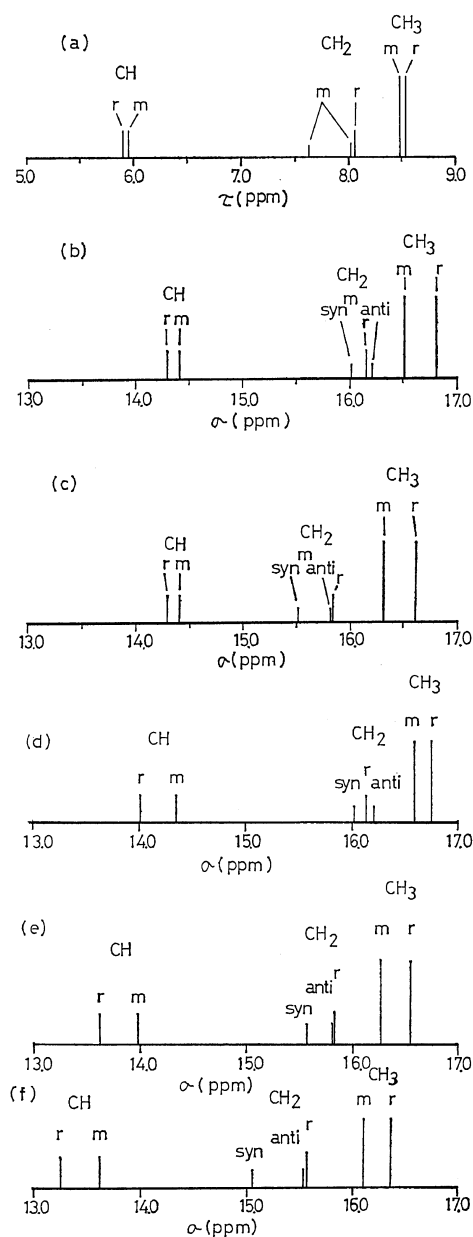


Figure 2. The stick spectra of 2,4-dichloropentanes: (a) observed²⁰; (b) calculated, $\Delta\chi_{C-C} = 5.5 \times 10^{-30} \text{ cm}^3$, $\Delta\chi_{C-Cl} = 5.0 \times 10^{-30} \text{ cm}^3$, and $\mu_{C-Cl} = 1.72D$; (c) calculated, $\Delta\chi_{C-C} = 9.1 \times 10^{-30} \text{ cm}^3$, $\Delta\chi_{C-Cl} = 5.0 \times 10^{-30} \text{ cm}^3$, and $\mu_{C-Cl} = 1.72D$; (d) calculated $\Delta\chi_{C-C} = 5.5 \times 10^{-30} \text{ cm}^3$, $\Delta\chi_{C-Cl} = 5.0 \times 10^{-30} \text{ cm}^3$, and $\mu_{C-Cl} = 1.86D$; (e) calculated, $\Delta\chi_{C-C} = 9.1 \times 10^{-30} \text{ cm}^3$, $\Delta\chi_{C-Cl} = 5.0 \times 10^{-30} \text{ cm}^3$, and $\mu_{C-Cl} = 1.86D$; (f) calculated, $\Delta\chi_{C-C} = 12.0 \times 10^{-30} \text{ cm}^3$, $\Delta\chi_{C-Cl} = 5.0 \times 10^{-30} \text{ cm}^3$, and $\mu_{C-Cl} = 1.86D$.

The chemical shifts of *meso* and *racemic* DCP's observed by Tincher²⁰ are shown in Table III. For a clear comparison of the observed results with the calculated ones, we showed these results in terms of the stick spectra in Figure 2. It was found that the order of the CH_3 , CH_2 , and CH protons in *meso* and *racemic* DCP's is consistent with the observed one, and the anti proton appears at higher field than the syn proton in *meso* DCP. The *racemic* CH_3 , CH_2 , and *meso* CH protons appear at higher fields than the *meso* CH_3 and CH_2 protons, and the *racemic* CH protons, respectively. When both of the calculated results (b) and (c) are compared with the observed ones (a), the appearance of the order of the methylene protons is better explained by (c) than by (b). This means that greater than $5.5 \times 10^{-30} \text{ cm}^3$ is better value for $\Delta\chi_{C-C}$ in this case. On the other hand, as for the difference in chemical shift between CH and CH_2 protons, both of (b) and (c) are not good. Because of the larger polar effect due to μ_{C-Cl} , the chemical shift of CH proton should be sensitive to the value of μ_{C-Cl} . Then the difference in the values for calculated chemical shift between CH and CH_2 protons which was smaller than the observed value will be improved by adjusting the value of μ_{C-Cl} . The value of μ_{C-Cl} to obtain the plausible values of difference in the chemical shift between the CH and CH_2 protons of *racemic* DCP was found to be $1.86D$, where in this calculation the electric charge, μ_{C-Cl}/r_{C-Cl} , instead of μ_{C-Cl} was changed as the parameter, r_{C-Cl} being the bond length between the C and Cl atoms. The spectrum (d) was obtained by using $5.5 \times 10^{-30} \text{ cm}^3$ as $\Delta\chi_{C-C}$. The calculated chemical shifts of CH_2 protons don't coincide with the observed ones. In the spectra (e) and (f) using $9.1 \times 10^{-30} \text{ cm}^3$ and $12.0 \times 10^{-30} \text{ cm}^3$ as $\Delta\chi_{C-C}$, respectively, the calculated chemical shifts of *meso* and *racemic* CH_2 protons become close to the observed ones. Thus the magnitude of $\Delta\chi_{C-C}$ plays an important role for the chemical shifts of the CH_2 protons. As for $\Delta\chi_{C-Cl}$, the deviation of $\Delta\chi_{C-Cl}$ from $5.5 \times 10^{-30} \text{ cm}^3$ did not give the large influence on the chemical shift in comparison with the case of $\Delta\chi_{C-C}$. As shown in Figure 2(d)–(f) the agreement between the calculated and observed chemical shifts $\delta(\text{CH}_2-\text{CH})$ was improved by using $1.86D$ as the value

of μ_{C-C1} ; but with this better agreement the difference in the values for calculated chemical shifts between the *meso* and *racemic* protons of CH_3 or CH group are much larger than the observed values. These discrepancies would be partly attributable to our model based on the isolated molecule, and the neglect of the effect of the medium or solvent and so on. Further improvements will be necessary.

Recently the C-13 chemical shifts of *meso* and *racemic* DCP's were measured^{36,37} and it was found that each carbon nuclei of *meso* DCP appears at a higher field than those of *racemic* DCP. Yonezawa, *et al.*,³⁸ have shown theoretically that the shielding constant of carbon nuclei in saturated hydrocarbons is roughly proportional to the excess charge of the $2p$ electrons. Thus the total net charges and the excess charges of the $2p$ electrons of DCP calculated above are shown in Table IV together with the observed C-13 chemical shifts reproduced from our previous paper.³⁷ The calculated results showing that each *meso* carbon appears at higher field than a *racemic* carbon, agree with the observed results. To show clearly these relationships, the chemical shifts plotted against the total net charges and the excess charges of the $2p$ electrons are shown in Figure 3, where the reference signal is $^{13}CH_3OH$. It is found that

Table IV. The total net charges, excess (or deficient) charges of $2p$ electrons on the carbon atoms, and C-13 chemical shifts for *meso* and *racemic* 2,4-dichloropentanes

	Total net charge ^a	Excess (or deficient) charges of $2p$ electrons ^a	C-13 chemical shift ^b (ppm)
<i>Meso</i>			
CH_3	-0.1498	+0.0489	+23.60
CH_2	-0.0642	+0.1160	-2.20
CH	+0.1642	+0.1589	-6.55
<i>Racemic</i>			
CH_3	-0.0823	+0.1149	+22.60
CH_2	-0.0569	+0.1231	-2.32
CH	+0.1871	+0.3038	-7.65

^a Averaged by the preferred conformations. The minus and plus signs denote the excess and deficient charges, respectively.

^b The chemical shifts are in parts per million up field from $^{13}CH_3OH$.

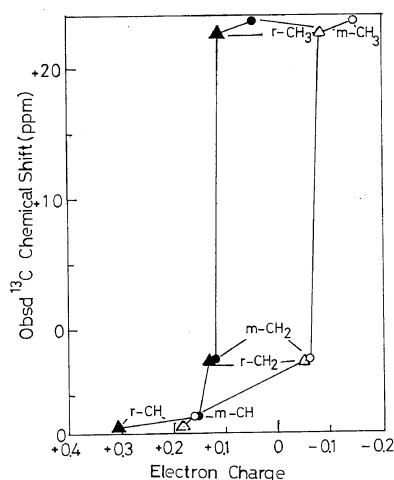


Figure 3. The C-13 chemical shifts versus the total charges (\circ , *meso* and \triangle , *racemic*) and excess charges of $2p$ electrons (\bullet , *meso* and \blacktriangle , *racemic*) on the carbon atoms.

the chemical shift appears at a higher field with increasing the total net charge or the excess charges of the $2p$ electrons, though there is not a linear relationship between them. As for the causes of the discrepancy it may be suggested that Yonezawa, *et al.*,³⁸ derived a linear relationship between the C-13 chemical shift and the excess charge of the $2p$ electrons taking into account only the diamagnetic and paramagnetic terms, but did not consider the magnetic anisotropy of the C—C bonds. Another weak point may be considered in our calculation based on the extended Hückel theory. The improvements of these points will be necessary in future.

Proton Chemical Shifts of Isotactic and Syndiotactic PVC's

The unique character which characterizes a linear polymer from a simple molecule is the diversity of the stereospecific conformations and configurations of the former. Usually, the temperature dependence of the chemical shifts of a small molecule in solution can be attributed mainly to the solvent effect, but that of a linear polymer includes the change of conformation of a polymer chain together with the above effect. The latter could be referred to as an "intrinsic" effect, which should be treated separately from the "external" solvent effect, *i.e.*, the commonly used solvent effect.³⁹

In the system under consideration it may be safely said that PVC does not form a π -complex with solvent and therefore the "external" solvent effect neglected as a first approximation. Here, we will be concerned with only the "intrinsic" solvent effect. The following factors as the "intrinsic" solvent effect are considered: σ_H^{dia} , σ_H^{para} , σ_{AB} and σ_E . It is necessary to calculate σ_H^{dia} when discussing the absolute value of the total shielding, but for a discussion of only the chemical shift difference between the isotactic and syndiotactic polymers, σ_H^{dia} neglected due to the small difference between σ_H^{dia} 's of the corresponding *meso* and *racemic* DCP's. Also σ_H^{para} neglected as well as in the case of DCP. The calculation of σ_{AB} was approximated by the point dipole method as well as in the case of DCP. σ_E was calculated by the Buckingham's equation (eq 6) and the same values of μ_{C-Cl} were used as in the case of DCP.

At present we cannot prepare isotactic PVC and it has been reported that polymerization of vinyl chloride under special conditions yields highly syndiotactic PVC,⁴⁰ but its NMR spectrum has not been measured because of its poor solubility. Thus we will be concerned with and discuss the chemical shifts of isotactic and syndiotactic polymers on the basis of those of the corresponding sequences in atactic polymer.

Isotactic PVC

The chemical shifts of a polymer molecule with any specified preferred conformation will be changed by the following factors: (i) the number of monomer units near any specified atom, (ii) the deviation ($\Delta\varphi$) from *trans* and *gauche* locations, 0° and 120° respectively, and (iii) the values of $\Delta\chi_{C-C}$, $\Delta\chi_{C-Cl}$ and μ_{C-Cl} .

At first the dependence of the chemical shifts of the CH_2 and CH protons of isotactic PVC on the number of monomer units (n) contributed by the magnetic anisotropies of the C—C and C—Cl bonds, and polar effects, using $(TG)_n$ as the conformation are shown in Figures 4 and 5, where for example the four-monomer unit model for the CH_2 is defined as follows; that is, in order to calculate the chemical shifts of the i -th CH_2 we took into account the contributions from the $i-2$ th to the $i+4$ th carbon atoms in this model (Figure 6). In this calculation, we

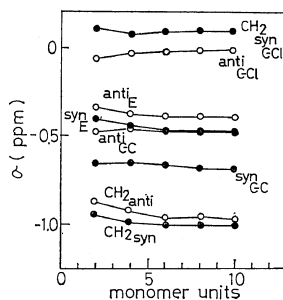


Figure 4. The dependence of the chemical shifts of the CH_2 protons in isotactic PVC on the number of monomer units and the contributions of the C—Cl and C—C bond anisotropies and the polar effect to them: \circ , anti proton; \bullet , syn proton. σ_{XY} is the chemical shift of the X proton due to the Y bond or polar effect.

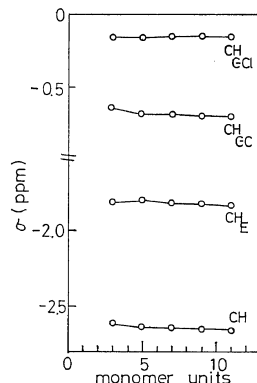


Figure 5. The dependence of the chemical shifts of the CH in isotactic PVC on the number of monomer units and the contributions of the C—Cl and C—C bond anisotropies and the polar effect.

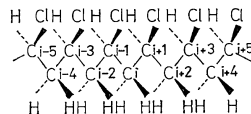


Figure 6. The notation of the structure of poly(vinyl chloride).

used the same values of $\Delta\chi_{C-C}$, $\Delta\chi_{C-Cl}$ and μ_{C-Cl} (1.72D) as the case of DCP. Each proton shift seems to approach a constant value at about four or five monomer units. Therefore the chemical shifts of this polymer may be discussed by a relatively short sequence in a chain. And also

as expected from the case of DCP, the polar effect contributes predominantly to the chemical shift of the CH proton. As for the CH₂ protons the anti proton appears at higher field than the syn proton as well as the case of *meso* DCP and both $\Delta\chi_{C-C}$ and polar effect contribute predominantly to the chemical shift.

Hereafter we will be concerned with only the 4—5 model for comparison with the observed data of tetrad and pentad tacticities as described below, where the 4—5 model is defined as follows; the numbers of monomer units being taken into account the CH₂ and CH are four and five monomer units, respectively.

So far it has been pointed by studies⁴ on conformational analysis that the preferred locations of the rotational angles of the *T* and *G* conformations in the various polymer chains deviate slightly from the positions at $\varphi_t=0^\circ$ and $\varphi_g=120^\circ$, respectively. According to these reports, we have studied the chemical shifts of polypropylene⁴² and results have supported that the small deviation ($\Delta\varphi$) of *T* and *G* from 0° and 120° , respectively, are reasonable in explaining the chemical shift of polypropylene. Thus the dependence of the proton chemical shift of isotactic PVC on the rotational angle deviation ($\Delta\varphi$) were calculated using the 4—5 model of isotactic PVC, and typical results are compared with the observed ones as shown in Figure 7(a)—(d). The rotational angles are varied in the stable direction of the conformational energy on the basis obtained in the case of polypropylene.⁴² Then it was found that the anti proton appears at higher field than the syn proton in the range from $\Delta\varphi=0^\circ$ to 20° , and the chemical shift difference between both protons decreases with increasing $\Delta\varphi$ and becomes closer to the observed value. Although the CH proton appears at lower field than the CH₂ protons, the agreement of the calculated results with the observed ones is not sufficiently quantitative. In these calculations the difference between both results calculated by 5.5×10^{-20} and $9.1 \times 10^{-30} \text{cm}^2$ as $\Delta\chi_{C-C}$ was small. As the magnitude of μ_{C-C1} contributes largely to the chemical shift of the CH proton, we calculated the chemical shift by changing the magnitude of μ_{C-C1} . A closer agreement with the observed values is shown in Figure 7(e) and (f), where the more suitable value of μ_{C-C1} was

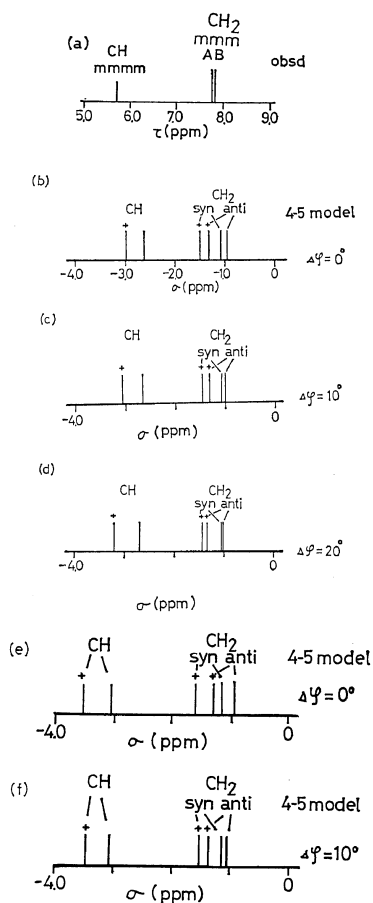


Figure 7. The stick spectra of isotactic poly(vinyl chloride): (a) observed¹⁶ in pentachloroethane, at 140°C (220 MHz); (b)—(d) calculated, $\mu_{C-C1}=1.72D$; (e) and (f) calculated, $\mu_{C-C1}=1.84D$. \downarrow , $\Delta\chi_{C-C}=5.5 \times 10^{-30} \text{cm}^2$; \uparrow , $\Delta\chi_{C-C}=9.1 \times 10^{-30} \text{cm}^2$.

$1.84D$. This value of μ_{C-C1} is nearly equal to that ($1.86D$) of DCP. The difference in chemical shift between the anti and syn protons at $\Delta\varphi=10^\circ$ is in better agreement with the observed results than those at $\Delta\varphi=0^\circ$.

Syndiotactic PVC

The preferred conformation of syndiotactic PVC, may be considered from the results of its model compound that a planar zigzag and $\{(TT)(GG)(TT)\}_n$ forms are preferable. However, the former is much more stable than the latter. Therefore we calculated the chemical shift of only the planar zigzag form. At first the dependence of the chemical shifts on the number

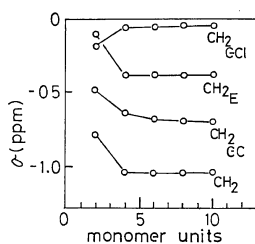


Figure 8. The dependence of the chemical shifts of the CH_2 protons in syndiotactic PVC on the number of monomer units and the contributions of the C—Cl and C—C bond anisotropies and the polar effect.

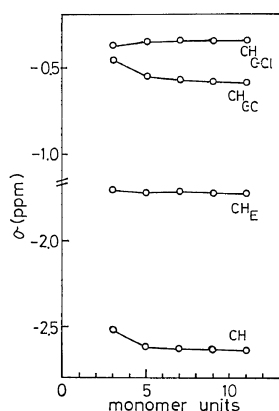


Figure 9. The dependence of the chemical shifts of the CH proton in syndiotactic PVC on the number of monomer units and the contributions of the C—Cl and C—C bond anisotropies and the polar effect.

of monomer units is shown in Figures 8 and 9, where $\varphi_t = 0^\circ$. Each proton chemical shift seems to approach a constant value at about four or five monomer units and the polar effect contributes predominantly to the chemical shift of the CH proton as well as in the case of isotactic PVC. The n dependence of the chemical shift of the CH_2 protons is larger than that of the CH proton. With the CH_2 protons, both $\Delta\chi_{\text{C-C}}$ and the polar effect contribute predominantly to the chemical shift as well as in the case of isotactic PVC. The $\Delta\varphi$ dependence of the chemical shift of the planar zigzag form is shown using the stick spectrum in Figure 10(b)—(d) together with the observed one (a), where the same values of $\Delta\chi_{\text{C-C}}$, $\Delta\chi_{\text{C-Cl}}$ and $\mu_{\text{C-Cl}}$ (1.72D) were used

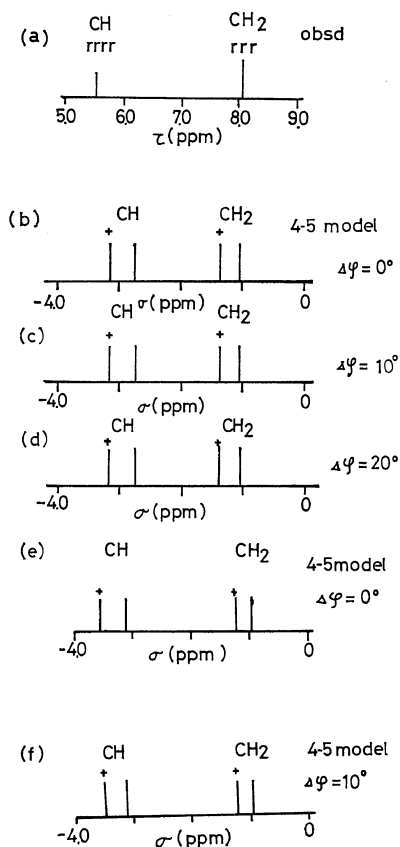


Figure 10. The stick spectra of syndiotactic poly(vinyl chloride): (a) observed¹⁶, in pentachloroethane, at 140°C (220 MHz); (b)—(d) calculated: $\mu_{\text{C-Cl}} = 1.72D$; (e) and (f) calculated, $\mu_{\text{C-Cl}} = 1.84D$. \downarrow , $\Delta\chi_{\text{C-C}} = 5.5 \times 10^{-30}\text{cm}^3$; \uparrow , $\Delta\chi_{\text{C-Cl}} = 9.1 \times 10^{-30}\text{cm}^3$.

as in the case of DCP. The rotational angle deviated from $\varphi_t = 0^\circ$ as in the case of isotactic PVC. The chemical shifts of the CH_2 and CH protons of 4—5 model change only slightly to higher field with increasing of $\Delta\varphi$. However the difference in the calculated chemical shift between the CH_2 and CH protons is too small, as compared with the observed results. As aforementioned, this discrepancy could be improved by using a larger value of $\mu_{\text{C-Cl}}$ (1.84D), which contributes largely to the chemical shift of the CH proton. These results are shown in Figure 10(e) and (f). The agreement between the calculated and observed results is better than (b) and (c). The $\Delta\varphi$ and $\Delta\chi_{\text{C-C}}$ dependences of the chemical shift are small. The difference in the

chemical shift between the CH₂ and CH protons depends predominantly on the value of μ_{C-C1} .

Some typical calculated chemical shifts of isotactic and syndiotactic PVC's are shown in Figure 11, selected from Figures 7 and 10 in order to compare with the observed results. Figure 11(a) shows the observed spectrum.¹⁶ In Figure 11(b), $\Delta\varphi=0^\circ$ and $1.84D$ was used as μ_{C-C1} . The signals of the anti and *racemic* CH₂ protons respectively tend to overlap with each other. In Figure 11(c), $\Delta\varphi=10^\circ$ and $1.84D$ was used as μ_{C-C1} . Each signal of the anti and *racemic* CH₂ protons is separated from each other. The stick spectrum 11(c) is more reasonable than the spectrum 11(b) in comparison with the observed spectrum 11(a). In the spectrum 11(d) $\Delta\varphi=10^\circ$ and 0° were used for isotactic and syndiotactic PVC's respectively. The anti and *racemic* CH₂ protons more separate from each other than in spectrum 11(c) and is close to the observed results. It is found that $\Delta\varphi$ plays an important role for the chemical shift of PVC as well as in the case of polypropylene.⁴²

From the results described above it could be

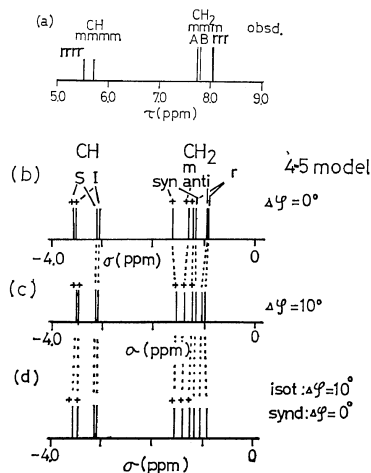


Figure 11. The stick spectra of poly(vinyl chloride): (a) observed¹⁶, in pentachloroethane, at 140°C (220 MHz); (b) calculated, $\mu_{C-C1}=1.84D$ (\downarrow , $\Delta\chi_{C-C}=5.5 \times 10^{-30}\text{cm}^3$, \uparrow , $\Delta\chi_{C-C}=9.1 \times 10^{-30}\text{cm}^3$, $\Delta\varphi=0^\circ$); (c) calculated, $\mu_{C-C1}=1.84D$ (\downarrow , $\Delta\chi_{C-C}=5.5 \times 10^{-30}\text{cm}^3$, \uparrow , $\Delta\chi_{C-C}=9.1 \times 10^{-30}\text{cm}^3$, $\Delta\varphi=10^\circ$); (d) calculated, $\mu_{C-C1}=1.84D$ (\downarrow , $\Delta\chi_{C-C}=5.5 \times 10^{-30}\text{cm}^3$, \uparrow , $\Delta\chi_{C-C}=9.1 \times 10^{-30}\text{cm}^3$, $\Delta\chi_{C-C1}=5.0 \times 10^{-30}\text{cm}^3$, $\Delta\varphi=10^\circ$ for isotactic PVC, $\Delta\varphi=0^\circ$ syndiotactic, PVC).

interpreted theoretically that the signal of *racemic* CH₂ appears at higher field than that of syndiotactic CH. These results coincide with the results of DCP shown above.

As shown above the chemical shifts of isotactic and syndiotactic PVC's were calculated separately from each other and the influence of the isotactic placement in atactic PVC was not taken into account. Thus for discussing the chemical shifts of PVC in more detail we must take this effect into account and the "external" solvent effect neglected in this paper.

CONCLUSION

Above results are conclusively summarized as follows;

- It was predicted from the calculated chemical shifts using the preferred conformations that the anti proton of the CH₂ in *meso* DCP and isotactic PVC together appears at higher field than the syn proton. The calculated results that the CH₂ and CH in *racemic* DCP or syndiotactic DCP together appear at higher and lower fields than those in *meso* DCP or isotactic PVC respectively, coincide with the observed results. Also the calculated result that the CH₃ in *racemic* DCP appears at higher field than that of *meso* DCP coincides with the observed results.
- From comparison of the calculated and observed proton chemical shifts in DCP and PVC it was found that the polar effect predominantly contributes to the chemical shift.
- Every carbon nuclei in *meso* DCP appears at higher field than corresponding one in *racemic* DCP both theoretically and experimentally.
- The *TT* form in *racemic* DCP is more stable than the *GG* form by 1.97 kcal/mol. This value compares reasonably with other data.

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REFERENCES

1. U. Johnsen, *J. Polym. Sci.*, **54**, 56 (1961).
2. F. A. Bovey and G. V. D. Tiers, *Chem. Ind.* (London), 826 (1962).
3. R. Chûjô, S. Satoh, T. Ozeki and E. Nagai, *J. Polym. Sci.*, **61**, 512 (1962).
4. W. C. Tincher, *ibid.*, **62**, 5148 (1962).
5. F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).
6. S. Satoh, *J. Polym. Sci., Part A*, **2**, 5221 (1964).
7. W. C. Tincher, *Makromol. Chem.*, **85**, 20 (1965).
8. T. Yoshino and K. Komiyama, *J. Polym. Sci., Part B*, **3**, 311 (1965).
9. O. C. Böckman, *ibid., Part A*, **3**, 3399 (1965).
10. B. Schneider, J. Štokr, D. Doskočilova, M. Kolinsky, S. Sykora, and D. Lim, Preprint, International Symposium Makromolekular Chemistry Prague, 1965, 1966, p 599.
11. J. Bargon, K.-H. Hellwege, and U. Johnsen, *ibid.*, **95**, 187 (1966).
12. K. C. Ramey, *J. Phys. Chem.*, **70**, 2525 (1966).
13. S. Enomoto, M. Asahina, and S. Satoh, *J. Polym. Sci., Part A-1*, **4**, 1373 (1966).
14. F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *J. Phys. Chem.*, **71**, 312 (1967).
15. U. Johnsen and K. Kolbe, *Kolloid-Z.*, **221**, 64 (1967).
16. F. Heatley and F. A. Bovey, *Macromolecules*, **2**, 241 (1969).
17. R. Shimanouchi and M. Tasumi, *Spectrochim. Acta*, **17**, 755 (1961).
18. D. Lim and M. Kolinsky, *J. Polym. Sci.*, **53**, 173 (1961).
19. T. Shimanouchi, M. Tasumi, and Y. Abe, *Makromol. Chem.*, **86**, 43 (1965).
20. D. Doskočilova, *J. Polym. Sci., Part B*, **2**, 421 (1964).
21. P. E. McMahon and W. C. Tincher, *J. Mol. Spectrosc.*, **15**, 180 (1965).
22. T. Shimanouchi, *Pure Appl. Chem.*, **12**, 287 (1966).
23. Y. Abe, M. Tasumi, T. Shimanouchi, S. Satoh, and Chûjô, *J. Polym. Sci., Part A-1*, **4**, 1413 (1966).
24. D. Doskočilova, J. Štokr, B. Schneider, H. Pivcova, M. Kolinsky, J. Petranek, and D. Lim, *ibid., Part C*, 215 (1967).
25. P. J. Flory and A. D. Williams, *J. Amer. Chem. Soc.*, **91**, 3118 (1969).
26. R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
27. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw Hill Book Co., Inc., New York N. Y., 1957, Section 7.4.
28. W. E. Lamb, *Phys. Rev.*, **60**, 817 (1941).
29. H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).
30. A. A. Bothner-By and C. Naar-Colin, *Ann. New York Acad. Sci.*, **70**, 833 (1958).
31. I. Ando and A. Nishioka, Preprint of the 10th Symposium on NMR, Tokyo, 7 (1971).
32. T. Schaefer and T. Yonemoto, *Can. J. Chem.*, **42**, 2318 (1964).
33. A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
34. H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953); H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).
35. L. Pauling, "Nature of Chemical Bond", Cornell University Press, New York N. Y., 1960.
36. C. J. Carman, A. R. Tarpley, and J. H. Goldstein, *J. Amer. Chem. Soc.*, **93**, 2864 (1971).
37. Y. Inoue, I. Ando and A. Nishioka, *Polymer J.*, **3**, 246 (1972).
38. T. Yonezawa, I. Morishima and H. Kato, *Bull. Chem. Soc. Japan*, **39**, 1398 (1966).
39. I. Ando and A. Nishioka, *Polymer J.*, **1**, 288 (1970).
40. T. Shimanouchi, *Kobunshi (High Polymers)*, **15**, 776 (1966).
41. P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience Pub., New York N. Y., 1969, Chapter VI.
42. I. Ando and A. Nishioka, *Polymer J.*, **2**, 161 (1971).