

The Chemical Shift of Isotactic Poly(Methyl Methacrylate)

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ABSTRACT: The chemical shift contribution of the polar and the magnetic anisotropy effects due to the side chain carbonyl group is calculated for the methylene and the α -methyl protons of isotactic poly(methyl methacrylate) using 5_1 and 5_2 helical chain models. The contribution from the dyad monomeric units to the methylene protons gives larger magnetic shielding to the threo proton than the erythro proton, and that from the triad monomeric units to the α -methyl protons shifts the position of α -methyl protons slightly at higher field than the threo proton. This order of the chemical shifts calculated agrees with the observed order. The chemical shifts calculated on the two types of 5_1 models explain the observed values better than the 5_2 model.

KEY WORDS Chemical Shift / Polar Effect / Magnetic Anisotropy Effect / Poly(Methyl Methacrylate) / Conformation / NMR /

Since the high resolution nuclear magnetic resonance (NMR) method has been found useful in the study of the stereoregular configuration of poly(methyl methacrylate) (PMMA),¹⁻³ many reports have been published about the mechanism of polymerization of this polymer by quantitative analysis of the NMR spectrum based on the assignments of each signal of methylene and α -methyl protons. As for the isotactic poly(methyl methacrylate) (*i*-PMMA), the dyad methylene proton signals appear as an AB quartet with a relatively large chemical shift difference of 0.5-0.7 ppm depending upon solvents used. (A typical example of the NMR spectrum of a predominantly *i*-PMMA is shown in Figure 1, the α -methyl protons giving a strong isotactic peak at 8.74τ with two minor peaks at 8.91τ and 9.05τ due to heterotactic and syndiotactic triads, respectively, and the two meso methylene protons being nonequivalent to each other with a relative shift of about 0.5 ppm.) According to Bovey's definition⁴ of these two protons, the "erythro proton" is called the proton on the same side as the ester group in the planar zigzag chain model, whereas the "threo proton" is on the opposite side of the ester group as shown in Figure 2. In connection with the assignment of the two methylene protons in the NMR spectrum, the conclusion that the erythro proton appears at a lower magnetic field than the threo proton

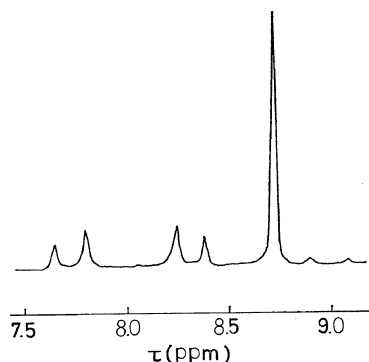


Figure 1. NMR spectrum of 6% solution in nitromethane of poly(methyl methacrylate) at 120°C (at 100 MHz).

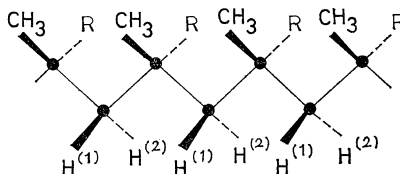


Figure 2. Structure of isotactic poly(methyl methacrylate): $\text{H}^{(1)}$, threo proton; $\text{H}^{(2)}$, erythro proton; R, COOCH_3 .

was first proposed by Bovey *et al.*^{4,5} on the basis of known facts about nuclear shielding in analogous small molecules, and was then proved clearly by Yoshino *et al.*⁶ based on the study of

polymers obtained by cis and trans β -deutero monomer. As for the α -methyl protons, the order of isotactic, heterotactic, and syndiotactic triads with an increasing magnetic field has not yet been assigned definitely from the view point of NMR, except for the suggestion by Ritchey *et al.*⁷ based on bond anisotropy. Therefore, it may be said that the validity of the assignment of each functional group in the NMR spectrum is not yet fully proved theoretically. In the case of small molecules, it is well known that the carbonyl group contributes effective chemical shift through the magnetic anisotropy effect and the polar effect called Buckingham effect. So it is plausible to suppose that the contribution is due to the carbonyl group in the case of PMMA. As is easily seen from the molecular structure of this polymer, the chemical shift contribution due to the carbonyl group may be larger on the methylene protons because of the neighbouring side groups than on the α -methyl protons. Though there would be some contributions from the bond anisotropy on these protons, we should like to report here as first approximations the contribution from the carbonyl group, assuming that both polar and magnetic anisotropy effects are dominant in the chemical shift of these protons. Because these effects depend upon the geometry of the molecule, it is necessary and significant to study the difference of the chemical shift of each functional group depending upon the stereoregular configuration and conformation of the chain polymer.

In this report we are mainly concerned with both methylene protons, erythro and threo protons, and also α -methyl protons of *i*-PMMA, assuming that the relative chemical shifts of these protons are predominantly contributed by the polar and the magnetic anisotropy effects due to the carbonyl group in the side chain. Then, in order to calculate the chemical shifts it is necessary to know the conformation of this polymer in solution. At present we have no detailed information about this particular conformation, but we may conjecture it from the suggestion that the helical conformation as in the solid state may sometimes exist locally in solution.^{6,9} Therefore, it may not be unreal to calculate the chemical shift on the basis of the model found in the solid state samples, although there are

some doubts about adopting the same molecular conformation as the solid state.

With reference to the conformation of *i*-PMMA, two helical forms, that is, 5_2 and 5_1 helices, are presented. The former type was suggested by Stroupe and Hughes¹⁰ based on the fiber period and the density in the solid state. However, D'Alagni *et al.*¹¹ proposed that the marked changes observed in the far ultra violet spectrum of *i*-PMMA with increasing temperature are related to the transition from the 5_1 to the 5_2 helix, which is probably in equilibrium within the same chain. Moreover, Liquori *et al.*¹² have shown that the Fourier transformation of the 5_2 helix previously proposed by Stroupe and Hughes¹⁰ was inconsistent with the intensity distribution of the fiber photographs of *i*-PMMA. Recently Tadokoro *et al.*¹³ have proposed a 5_1 helical model based on the conformational analysis, X-ray diffraction and infrared absorption method. In our studies of the conformation of *i*-PMMA, we have adopted three models, that is, two 5_1 helix models, model I and model II, and the 5_2 helix model proposed by Tadokoro *et al.*¹³ as the models for calculating the chemical shifts. In this report we should like to describe the general formulae to calculate the chemical shift of some protons in a helical chain molecule and the application of this method to the 5_1 and 5_2 helices of *i*-PMMA.

THEORY

As described earlier, we have assumed that these relatively large chemical shifts among the methylene and the α -methyl protons are mainly contributed by the polar and the magnetic anisotropy effects due to the carbonyl groups, although there may be some contribution of bond anisotropy. In calculating the chemical shift of any proton of a monomeric unit in a chain molecule, it is necessary to take into account the contribution of the neighboring monomeric units. Although it is necessary to calculate longer sequences to study the tetrad or pentad spectrum, we have used in the present theory the dyad and the triad models of the methylene and the α -methyl protons, respectively, in a helix molecule with a fixed position of the side chain, and calculated the resultant effect of both con-

tributions to the chemical shift of the methylene and the α -methyl protons of *i*-PMMA.

At first, the contribution of the polar effect due to the chemical shift of the carbonyl group can be calculated by the following Buckingham's formula.¹⁴

$$\delta_E = -2 \times 10^{-12} E_z - 10^{-18} E^2 \quad (1)$$

where E is the magnitude of the electric field at any proton influenced by the point charges or the electric dipole moment of the carbonyl group, and E_z is the component of this field in the direction of any specified C-H bond in the methylene or the α -methyl protons. In calculating E_z and E^2 we have used both methods of point charge and point dipole models, because the former is better at a short distance and the latter gives a simple approximation formula at a long distance.

In the point charge method, the point charge of the carbonyl group was calculated by the following equation.

$$q = \pm \frac{\mu}{r_{C=O}} \quad (2)$$

where the positive and the negative signs correspond to the carbon and the oxygen atoms respectively, μ denotes the observed permanent electric dipole moment (2.1–2.4 Debye units¹⁵) of the carbonyl group, and $r_{C=O}$ the bond length (1.22 Å¹⁶). Therefore, we can obtain *ca.* 2×10^{-10} esu for the value of q , and then calculate E_z and E by the use of the coordinates of atoms in the helical chain models.

In the point dipole approximation, we used the following equation¹⁷ for calculating E_z and E .

$$E = \frac{\mu \sqrt{3 \cos^2 \theta_E + 1}}{r_E^3} \quad (3)$$

where E is the magnitude of the electric field at the proton due to the point dipole of the carbonyl group, μ is situated at the middle point along the C=O bond, r_E is the distance from the point dipole to any specified proton, and θ_E the angle between the direction of the dipole moment and the vector r_E . The angle between E and μ can be easily calculated by the point dipole approximation, and then E_z can be evaluated on the basis of the molecular models.

Secondly, the contribution of the magnetic

anisotropy effect of the carbonyl group to the chemical shift δ_M can be written as follows,¹⁸

$$\delta_M = \frac{\sum_{i=1}^3 \Delta\chi_i (1 - 3 \cos^2 \theta_{M_i})}{3r_{M_i}^3} \quad (4)$$

where $\Delta\chi_i$ ($i = 1, 2,$ and 3) is the magnetic anisotropy of the carbonyl group, the adoption of 7.1, 1.4, and -9.5×10^{-30} cm³·sec⁻¹ as $\Delta\chi_1$, $\Delta\chi_2$, and $\Delta\chi_3$ by Pople,¹⁹ and θ_{M_i} is the angle between the direction of the anisotropy axis and the internuclear vector r_{M_i} (the vector from the nucleus at which the anisotropy exists to any specified proton) and $r_{M_i} = |r_{M_i}|$.

Now, to estimate the chemical shifts due to the polar and the magnetic anisotropy effects it is necessary to calculate E_z , E , r_{M_i} and θ_{M_i} . Therefore, if the coordinates of the atoms of *i*-PMMA could be determined, the values of E_z , E , r_{M_i} and θ_{M_i} are obtained and then the chemical shifts of the methylene and the α -methyl protons can be calculated. In Figure 3 we show a schematic structure of the *i*-PMMA molecule using labelled number (i) for each atom. b denotes the bond vector and φ the rotation angle about the main chain C-C bond.

Now, for the helical chain consisting of two kinds of skeletal members, *i.e.*, $-(\varphi_1 M_1 \varphi_2 M_2 -)_n$ where M_1 and M_2 are CH₂ and C(CH₃)COOCH₃, we can determine the internal rotation angle of the main chain by the use of the following equations proposed by Miyazawa.²⁰

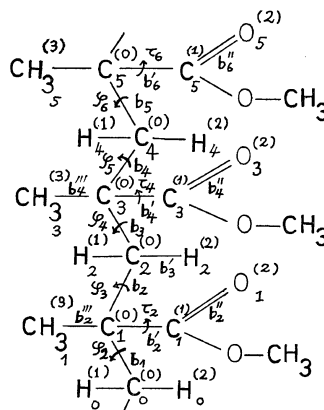


Figure 3. Representation and structure of isotactic poly(methyl methacrylate).

$$\cos\left(\frac{\theta}{2}\right) = \cos\left(\frac{\varphi_1}{2} + \frac{\varphi_2}{2}\right) \sin^2\left(\frac{\theta}{2}\right) - \cos\left(\frac{\varphi_1}{2} - \frac{\varphi_2}{2}\right) \cos^2\left(\frac{\theta}{2}\right) \quad (5-1)$$

$$d \sin\left(\frac{\theta}{2}\right) = 2r \sin\left(\frac{\varphi_1}{2} + \frac{\varphi_2}{2}\right) \sin^2\left(\frac{\theta}{2}\right) \quad (5-2)$$

where r is the bond length of the C-C bond, and d and θ are the helical parameters given by

$$d = \frac{t}{m} \quad (6-1)$$

$$\theta = \frac{2\pi n}{m} \quad (6-2)$$

where m is the number of repeating units and n the number of helical turns per fiber period t .

Let us introduce local systems of coordinates, linked to the bond of the chain in such a manner as shown in Figure 3. b_i denotes the skeletal bond vector which connects the $(i-1)$ th skeletal carbon atom C_{i-1} to the (i) th skeletal carbon (atom $(i = 1, 2, 3, \dots)$), and θ the angle between b_{i-1} and b_i , defined by $(\theta \text{ bond angle}) = 180^\circ$. The z_i axis is directed along the (i) th bond, the x_i axis lies in the plane of the $(i-1)$ th and the (i) th bonds, and the y_i axis completes a right-handed coordinate system. The internal rotation angle φ_i is chosen to be zero when the bond vectors b_{i-2} and b_i are in trans position, and its positive direction corresponds to the counter-clockwise rotation of these two vectors with

respect to each other. With the coordinate system so defined, the matrix that transforms the coordinates of a point in the $(i+1)$ th coordinate system into the (i) th coordinate system can be written as

$$T_{i+1}(\theta, \varphi) = \begin{bmatrix} -\cos \theta \cos \varphi_{i+1} & \sin \varphi_{i+1} & \sin \theta \cos \varphi_{i+1} \\ -\cos \theta \sin \varphi_{i+1} & -\cos \varphi_{i+1} & \sin \theta \sin \varphi_{i+1} \\ \sin \theta & 0 & \cos \theta \end{bmatrix} \quad (7)$$

Therefore, the transformation of the $(i+1)$ th coordinate $(x_{i+1}, y_{i+1}, z_{i+1})$ into the (i) th coordinate (x_i, y_i, z_i) is expressed as

$$r_i = T_{i+1}(\theta, \varphi) r_{i+1} \quad (8-1)$$

where

$$r_i = \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} \quad (8-2)$$

Thus, it can be shown that the transformation of the vector r_j of the (j) th coordinate into the (i) th one may be expressed as

$$b_j = T_{i+1}(\theta, \varphi) T_{i+2}(\theta, \varphi) \cdots T_{j-1}(\theta, \varphi) T_j(\theta, \varphi) \bar{r}_j \quad (9-1)$$

where

$$\bar{r}_j = \begin{bmatrix} 0 \\ 0 \\ r_j \end{bmatrix} \quad (9-2)$$

where r_j is the bond length of the (j) th bond.

Let us transform the coordinates of the atoms into the coordinate system linked to the bond $(i = 1)$. Thus, the coordinates of the (j) th carbon atom of the main chain are given by the component of the following vector.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = b_1 + b_2 + \cdots + b_j \quad (10-1)$$

where

$$b_j = T_2(\theta, \varphi) T_3(\theta, \varphi) \cdots T_j(\theta, \varphi) \bar{r} \quad (10-2)$$

The coordinates of the atoms of the side chain can be similarly calculated. The coordinates of the methylene protons bonded to the (j) th carbon atom of the main chain are given by the component of the following vector.

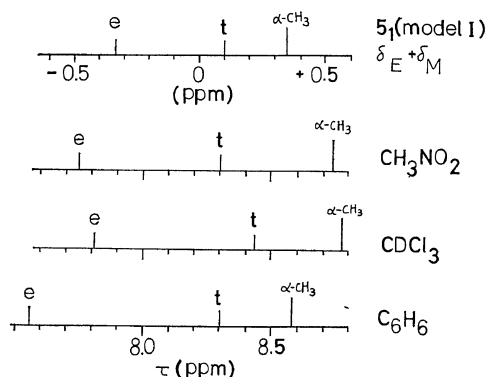


Figure 4. The calculated and the observed stick spectra of isotactic poly(methyl methacrylate). δ_E is calculated by the point charge method: e, erythro proton; t, threo proton.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = T_2(\theta, \varphi) T_3(\theta, \varphi) \cdots \\ T_{j+1}(\theta, \varphi) T_{j+2}(\theta, \varphi'_{C-CH_3}) \begin{bmatrix} 0 \\ 0 \\ r_{C-CH_3} \end{bmatrix} + \sum_{j=1}^{j+1} b_j \quad (12)$$

where φ'_{C-CH_3} may take either $\varphi + 120^\circ$ or $\varphi - 120^\circ$ and r_{C-CH_3} denotes the b and length between C and CH_3 .

The coordinates of the carbon atom of the carbonyl group bonded to the $(j+1)$ th carbon atom of the main chain are given by the component of the following vector.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = T_2(\theta, \varphi) T_3(\theta, \varphi) \cdots \\ T_{j+1}(\theta, \varphi) T_{j+2}(\theta, \varphi''_{C-C'}) \begin{bmatrix} 0 \\ 0 \\ r_{C-C'} \end{bmatrix} + \sum_{j=1}^{j+1} b_j \quad (13)$$

where $\varphi''_{C-C'}$ may take either $\varphi + 120^\circ$ or $\varphi - 120^\circ$, that is, $\varphi''_{C-C'} = \varphi'_{C-CH_3} \pm 120^\circ$ and $r_{C-C'}$ denotes the bond length between the carbonyl carbon atom of the side chain and the carbon atom of the main chain.

The coordinates of the oxygen atom of the carbonyl group bonded to the $(j+1)$ th carbon atom of the main chain are given by the component of the following vector.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = T_2(\theta, \varphi) T_3(\theta, \varphi) \cdots \\ T_{j+2}(\theta, \varphi'_{C-C}) T_{j+2}(\theta', \tau) \begin{bmatrix} 0 \\ 0 \\ r_{C=O} \end{bmatrix} + \sum_{j=1}^{j+2} b_j + b'_{j+2} \quad (14)$$

where θ' denotes the angle defined by $(\theta' + \angle C-C'=O) = 180^\circ$, τ the rotation angle which may be defined by $C_j C_{j+1} C'_{j+1} O_{j+1}$, $r_{C=O}$ the bond length of the C=O bond and b' the C-C' bond vector.

As mentioned above, we can calculate the coordinates of each atom in PMMA by using Eqs. 10 to 14 and then the values of E_z , E , r_{M_i} and θ_{M_i} . Thus, we may apply the theory developed above to the calculation of the chemical shifts for *i*-PMMA.

NUMERICAL RESULTS AND DISCUSSION

For calculating the chemical shifts of *i*-PMMA, we must first calculate the internal rotation angles of the main chain by using Eqs. 5-1 and 5-2 and then the coordinates of the atoms of *i*-PMMA. Here, for the internal rotation angle of the side chain we used parameters proposed by Tadokoro *et al.*¹³ The bond lengths and the bond angles used are shown in Table I.¹⁶ Then we calculated the chemical shifts of methylene and α -methyl protons of *i*-PMMA (5_1 helix models, model I and model II, and the 5_2 helix model) as follows;

Table I. Bond lengths and bond angles

C-C	1.54 (Å)
C=O	1.22
C-H	1.09
C-CH ₃	1.91
$\angle C-C-C$	114 (°)
$\angle C-C-C'$	114
$\angle C-C-H$	114
$\angle C-C-CH_3$	114
$\angle C-C'=O$	120

(i) 5_1 Helix (model I)

Substituting $t = 10.5 \text{ \AA}$, $m = 5$, $n = 1$, and $r = 1.54 \text{ \AA}$ into Eqs. 5-1 and 5-2, and transforming the obtained rotation angles according to our definition, we can obtain $\varphi_1 = 3^\circ$ and $\varphi_2 = -74.5^\circ$, where

$$\varphi_1 = \varphi_3 = \varphi_5 = \cdots = \varphi_{2n+1} \quad (16-1)$$

$$\varphi_2 = \varphi_4 = \varphi_6 = \cdots = \varphi_{2n} \quad (16-2)$$

The rotation angle $\varphi'_{C-H_2(1)}$ in the three proton $H_2^{(1)}$ is $\varphi'_{C-H_2(1)} = \varphi_3 + 120^\circ$, the rotation angle $\varphi'_{C-H_2(2)}$ in the erythro proton $H_2^{(2)}$ $\varphi'_{C-H_2(2)} = \varphi_3 + 240^\circ = \varphi_3 - 120^\circ$, the rotation angle φ'_{C-CH_3} in the α -methyl group $\varphi'_{C-CH_3} = \varphi_4 + 240^\circ = \varphi_4 - 120^\circ$, and the rotation angle $\varphi''_{C-C'}$ in the carbon atom of the carbonyl group of the side chain $\varphi''_{C-C'} = \varphi_4 + 120^\circ$. For the rotation angle (τ) of the side chain we used $+90^\circ$, proposed by Tadokoro *et al.*¹³ Substituting these values into Eqs. 10 to 15, we can obtain the coordinates of each atom. Then, we can calculate the values of δ_E , δ_M and $\delta_E + \delta_M$ as shown in Table II.

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Table II. The calculated chemical shifts of isotactic PMMA

Chemical Shift Model	$\delta_{\alpha\text{-CH}_3}$	δ_{threo}	δ_{erythro}	$\delta_{\text{threo}} - \delta_{\text{erythro}}$	$\delta_{\alpha\text{-CH}_3} - \delta_{\text{threo}}$
5_1 (model I)					
$\delta_{E'}^a$	-0.01	-0.04	-0.30	0.26	0.03
$\delta_{E''}^b$	-0.03	-0.07	-0.32	0.25	0.04
δ_M	+0.26	+0.14	-0.03	0.17	0.12
$\delta_{E'} + \delta_M$	+0.25	+0.10	-0.33	0.43	0.15
$\delta_{E''} + \delta_M$	+0.23	+0.07	-0.35	0.42	0.16
5_1 (model II)					
$\delta_{E'}$	-0.02	-0.05	-0.32	0.27	0.03
$\delta_{E''}$	-0.06	-0.11	-0.37	0.26	0.05
δ_M	+0.21	+0.11	-0.10	0.20	0.10
$\delta_{E'} + \delta_M$	+0.19	+0.06	-0.42	0.48	0.13
$\delta_{E''} + \delta_M$	+0.15	0	-0.47	0.46	0.15
5_2					
$\delta_{E'}$	-0.16	-0.20	-0.31	0.11	0.04
$\delta_{E''}$	-0.14	-0.28	-0.35	0.07	0.12
δ_M	+0.02	-0.06	-0.12	0.06	0.08
$\delta_{E'} + \delta_M$	-0.14	-0.26	-0.43	0.17	0.12
$\delta_{E''} + \delta_M$	-0.12	-0.34	-0.47	0.13	0.20

^a $\delta_{E'}$ is calculated by the point electric charge method.

^b $\delta_{E''}$ is calculated by the point dipole approximation.

(ii) 5_1 Helix (model II)

We used the parameters of the 5_1 helix (model I) for the rotation angles of the main chain except for the rotation angle of the side chain (τ), and -90° for the rotation angle (τ). Then we obtained the values of δ_E , δ_M and $\delta_E + \delta_M$ in the same manner as with the 5_1 helix (model I) as shown in Table II.

(iii) 5_2 Helix

Substituting $t = 10.5\text{\AA}$, $m = 5$, $n = 2$, and $r = 1.54\text{\AA}$ into Eqs. 5-1 and 5-2 and transforming the rotation angle according to our definition, we can obtain $\varphi_1 = 0^\circ$ and $\varphi_2 = -140^\circ$. For the rotation angle (τ) of the side chain we used -90° . Then we obtained the values of δ_E , δ_M , and $\delta_E + \delta_M$ as shown in Table II.

It is easily seen from Table II that the erythro proton appears at lower magnetic field than the threo proton in each of these three models, though there are some differences in the chemical shifts between the 5_1 and 5_2 models. So the assignment of the signals of both erythro and threo protons proved experimentally by Bovey *et al.*^{4,5} and Yoshino *et al.*⁶ agrees with our theoretical calculation based on the helical chain models. As for the 5_1 and 5_2 models, our results show

that the former models give larger chemical shifts between these two protons than the latter model. This is well in accordance with the observed values shown in Table III, which were obtained from the JNM 4H-100 spectrometer in nitromethane, deuterated chloroform, and benzene solutions. As for the 5_1 model I and model II, the calculated results show only a slightly difference and we cannot comment further about the selection of the models. The results in Table III also show that the α -methyl protons appear at higher field about 0.15–0.20 ppm than the threo proton through the three models. This order of the chemical shifts of erythro, threo and α -methyl protons located in an increasing field explains the observed order, but the differences between the calculated and observed values are slightly larger in the case of the α -methyl protons than the methylene protons. With reference to the discrepancies between the calculated and the observed values, there may be several factors in both theoretical and experimental origins. Theoretically, as mentioned briefly in the Introduction, there may be some contributions from the bond anisotropy due to the C-C bond, and further, there could be some

Table III. The observed chemical shifts of isotactic poly(methyl methacrylate)^a

Solvents	Temp. (°C)	$\tau_{\alpha\text{-CH}_3}$ (ppm)	τ_{threo} (ppm)	τ_{erythro} (ppm)	$\tau_{\alpha\text{-CH}_3} - \tau_{\text{threo}}$	$\tau_{\text{threo}} - \tau_{\text{erythro}}$
CH ₃ NO ₂	120	8.730	8.300	7.750	0.430	0.550
CDCl ₃	84	8.776	8.440	7.812	0.336	0.628
C ₆ H ₆	84	8.586	8.304	7.558	0.282	0.746

^a The observed values are compared with the calculated ones (5₁ model I) in Figure 4.

discrepancies from the idealized straight helical chain model if we imagine the flexible chain conformation of polymer molecules in solution. Experimentally the chemical shifts of these protons are found to depend on the type of solvent, especially the aromatic one, and it has been further observed that the chemical shifts change with the temperature even in nonpolar solvents like CCl₄.²¹ These results suggest that the chemical shifts of these protons in this molecule are influenced by the conformational changes of the chain molecule along the backbone, and there may be an "intrinsic" solvent effect properly related to the chain molecule and different from the usual meaning of "extrinsic" solvent effect. If we must consider the above factors in the calculation of the chemical shift of the polymer molecule in solution, it may perhaps be impossible to carry out a calculation theoretically. In spite of these difficult problems to be encountered in the future research, it may be considered to be significant that our calculation based on the helical chain model based on 5₁ helix of *i*-PMMA explains the validity of the assignment of the erythro and the threo protons, and the observed order of the chemical shifts of the methylene and the α -methyl protons. Further study is necessary to refine the calculation by taking into account in detail the bond anisotropy effect and other possible chain conformations.

In addition, it is shown in Table II that the point dipole approximation may apply for calculating δ_E in comparison with the point charge method.

CONCLUSION

We conclude that for *i*-PMMA two 5₁ helix models, model I and model II, explain the ob-

served values better than the 5₂ model and that the magnetic shielding calculated increases with the order of erythro, threo, and α -methyl protons, which is well in accordance with the order proposed by Bovey *et al.*^{4,5} and Yoshino *et al.*⁶ The same method can be applied to other polymer chains.

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