

Paramagnetically Shifted NMR Spectra and Conformation of Isotactic and Syndiotactic Poly(methyl methacrylate)s

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In a previous paper¹ we have reported that isotropic shifts (I.S.) induced in the NMR spectra of isotactic and syndiotactic poly(methyl methacrylate) (i- and s-PMMA) by tris(dipivalomethanato)europium(III) (shift reagent) are proportional to the amount of the shift reagent added in benzene solution. In the case of i-PMMA, the order of the magnitude of I.S. for each chemical group is as follows: $\text{CH}_2 > \alpha\text{CH}_3 > \text{OCH}_3$, while in the case of s-PMMA, $\alpha\text{CH}_3 > \text{CH}_2 > \text{OCH}_3$. These tendencies suggest that the shift is largely affected by the difference of conformations of the respective polymers in the solution. Thus, in this paper we try to propose possible conformations by comparing the observed values of I.S. with the values calculated for several kinds of conformations of these polymers. It is well known that isotropic proton resonance shifts caused by the shift reagent arise from two origins: namely, contact and pseudocontact interactions. For the proton shift of a σ -electron system, the pseudocontact mechanism predominantly contributes to the I.S. The pseudocontact

shift induced on the i th proton in a complex is generally given by²

$$\left(\frac{\Delta H}{H}\right)_i = f \cdot \frac{1 - 3 \cos^2 \theta}{r^3} \quad (1)$$

where f is a factor containing the g -tensor, temperature, etc., r is the distance between the magnetic nucleus considered and the rare earth ion, and θ is the angle between the r -vector and the principal molecular axis. As a monomer unit of PMMA contains two oxygen atoms, in carbonyl ($>\text{C}=\text{O}$) and the methoxy group ($\text{O}-\text{Me}$), it is necessary to decide how much the shift reagent coordinates to each oxygen atom. As the model compound of a side chain of PMMA, RCOOCH_3 ($\text{R}: \text{CH}_3\text{CH}_2-$, $(\text{CH}_3)_2\text{CH}-$, $(\text{CH}_3)_3\text{C}-$) was used and the I.S. of these compounds were measured in CCl_4 solution (25%) with a JNM-PS-100 NMR spectrometer (100 MHz) in the presence of $\text{Eu}(\text{DPM})_3$ (50 mg), as shown in Table I. The conformation of RCOOCH_3 coordinating to $\text{Eu}(\text{III})$ is assumed to occur in the same plane because of steric hindrance between

Table I. Geometric factors for $\text{Eu}(\text{III})-\text{>C}=\text{O}$ system (F) and $\text{Eu}(\text{III})-\text{OMe}$ system (F') and the observed chemical shifts in RCOOCH_3

Position	$F(r, \theta) = (1 - 3 \cos^2 \theta) / r^3$	$F'(r, \theta) = (1 - 3 \cos^2 \theta') / r'^3$	$\Delta\delta$ ppm (RCOOCH_3)		
			CH_3CH_2	$(\text{CH}_3)_2\text{CH}$	$(\text{CH}_3)_3\text{C}$
CH or CH_2	1.00	1.00	0.97	1.89	—
αCH_3	0.75	-0.45	0.63	1.28	0.68
OCH_3	0.66	5.05	0.91	1.74	0.99

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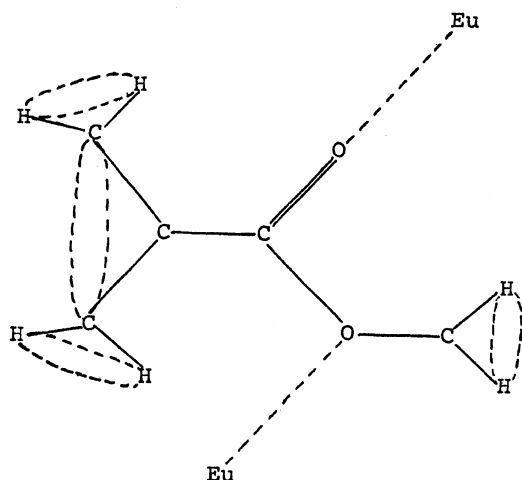


Figure 1. Assumed conformation of $(\text{CH}_3)_2\text{CHCOOCH}_3$ in the coordination of Eu(III) .

C—H: 1.10 (Å), C—C: 1.54, C=O: 1.22, C—OMe: 1.36, O—CH₃: 1.46, C—CO: 1.44, Eu—O: 2.8, $\angle\text{CCC}$: 109.5°, $\angle\text{CCH}$: 109.5°, $\angle\text{CCO (Eu)}$: 102°, $\angle\text{COC}$: 115°, $\angle\text{COEu}$: 122.5°.

the shift reagent and each group of RCOOCH_3 , as shown in Figure 1. The coordination number of Eu(III) to each oxygen in RCOOCH_3 can be decided by comparing the observed value of I.S. (Table I) with the calculated value of the pseudocontact shift, which is obtained from the geometric factor $((1 - 3 \cos^2 \theta^2)/r^3)$ for RCOOCH_3 coordinated to Eu(III) . The calculation of the geometric factor was carried out as follows: the expression for the pseudocontact shift (ΔH_{obs}^i) for RCOOCH_3 was modified as

$$\Delta H_{\text{obs}}^i = f\{F(r, \theta)\alpha + F'(r, \theta)(1 - \alpha)\} \quad (2)$$

where $F(r, \theta)$ and $F'(r, \theta)$ are geometric factors

Table II. Coefficients of linear combination between $\text{Eu(III)}-\text{>C=O}$ and $\text{Eu(III)}-\text{OMe}$ coordinations estimated from chemical shifts in RCOOCH_3

R	CH_3CH_2	$(\text{CH}_3)_2\text{CH}$	$(\text{CH}_3)_3\text{C}$
α	0.09	0.06	0.08

for the $\text{Eu(III)}-\text{>C=O}$ system and the $\text{Eu(III)}-\text{OMe}$ system, respectively, and α is a fraction of the former system. The relative values of $F(r, \theta)$ and $F'(r, \theta)$ are shown in Table I. Substituting the values in Table I into eq 2, we obtained the values of α given in Table II. From the values of α in Table II it is concluded that only one complex of $\text{Eu}-\text{OMe}$ exists for every ten complexes of $\text{>C=O}-\text{Eu}$. The fact that the electron density of the oxygen atom in >C=O (calculated by CNDO/2 method) is larger than that of OMe, as shown in Figure 2, also shows that this result is reasonable. From these results, we are ready to calculate the geometric factors for the $\text{PMMA}-\text{Eu}$ systems. For *i*-PMMA we calculate the geometric factor using the conformations of 5_1 helix which were proposed by Tadokoro, *et al.*³, 5_2 helix, and 3_1 (*T, G*); for *s*-PMMA, the *T-T* and *T-cis* conformations are taken into consideration. The bond lengths and the bond angles used are shown in Table IIIa for *i*- and *s*-PMMA and the internal rotation angles are shown in Table IIIb.

i-PMMA

Comparing the calculated values of the I.S. with the experimental ones, as shown in Table IVa, we concluded that the calculated values for 5_1 helix agree well with the experimental

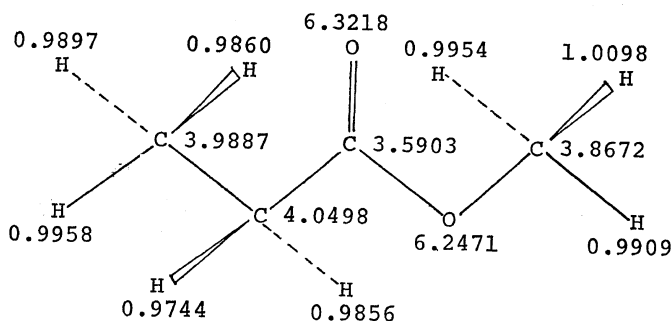
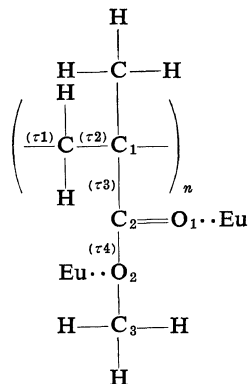


Figure 2. Calculated electron densities on each atom in $\text{C}_2\text{H}_5\text{COOCH}_3$.

Table III. (a) The bond lengths and the bond angles for isot. and synd. PMMA used in calculation

C—H	1.10(Å)	$\angle C C C$	109.5°
C—C	1.54	$\angle C C H$	109.5
C ₁ —C ₂	1.44	$\angle C_1 C_2 O_1(Eu)$	120.0
C ₂ —O ₁	1.22	$\angle C_1 C_2 O_2$	115.0
C ₂ —O ₂	1.36	$\angle C_2 O_2 C_3$	115.0
O ₂ —C ₃	1.43	$\angle O_2 C_3 H$	109.5
Eu—O	2.80	$\angle C_2 O_2 Eu$	122.5

**Table III.** (b) The internal rotation angles for isot. and synd. PMMA used in calculation

Isot. PMMA	τ_1	τ_2	τ_3	τ_4
5 ₁ model	-3°	74.5°	-90°	-90°
5 ₂ model	0°	140°	-90°	-90°
3 ₁ (T·G)	0°	60°	-90°	-90°
Synd. PMMA				
T·T	0°	0°	-90°	0°
T·cis	0°	180°	-90°	0°

Table IV. (a) Observed values and the relative values calculated on the assumption that only one complex of Eu—OME exists for every ten complexes of >C=O—Eu

Model	Isot. PMMA				Synd. PMMA			
	3/1	5/1	5/2	obsd	T·T	T-cis	T·T + T-cis	obsd
αCH_3	1.64	1.50	1.65	1.57	3.98	0.64	1.56	1.78
CH ₂	2.06	1.91	2.84	1.80	-0.36	0.42	0.22	1.61
OCH ₃	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Table IV. (b) Observed values and the relative values calculated on the assumption that only the complex of >C=C—Eu exists

Model	Isot. PMMA				Synd. PMMA			
	3/1	5/1	5/2	obsd	T·T	T-cis	T·T + T-cis	obsd
αCH_3	1.23	1.94	2.27	1.57	2.90	0.99	1.78	1.78
CH ₂	1.68	2.17	3.55	1.80	1.60	1.77	1.70	1.61
OCH ₃	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

values. This conformation is consistent with the S_1 helical model which Tadokoro, *et al.*³, have proposed based on the conformational analysis, X-ray diffraction, and infrared absorption method, and which one of the authors⁴ has obtained by the study of the NMR chemical shift of this polymer.

s-PMMA

In the case of *s*-PMMA, we calculated the geometric factors for the complex of the $>C=O$ system alone, as well as the complex of $Eu-OMe+>C=O-Eu$. Because of the steric hindrance the complex formation of $Eu-OMe$ is more difficult than the complex formation of $>C=O-Eu$.

The calculated values for the $T \cdot T$, $T-cis$, and $T \cdot T + T-cis$ conformations of *s*-PMMA and the observed values are tabulated in Table IV. In this Table IVa the calculated results disagree with those observed. Now we consider the contribution of the complex of $>C=O-Eu$ system only.

In Table IVb, the calculated values for $T \cdot T$

and $T-cis$ are far from the observed ones. Thus, as one of the possible conformations of *s*-PMMA, the structure containing both forms (1 : 1) of the $T \cdot T$ (planar zigzag) and $T-cis$ in a chain is considered.

The calculated values for this model agree well with the observed values, as shown in Table IV b. In conclusion we can say that in benzene solution the isotactic PMMA has a S_1 helical conformation, and the syndiotactic PMMA has the 1 : 1 mixture of $T \cdot T$ and $T-cis$ conformations.

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