Conformational Characteristics of Poly(methyl acrylate). 2. Calculations

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ABSTRACT: The simplified two-rotational-state scheme previously used for PMA is not able to predict satisfactory values for its dipole moment. A more realistic scheme with four rotational states is introduced which allows for the distinguishing between different interactions for different orientations of the ester group lateral to the chain. Values of dimensions, dipole moments, stereochemical equilibria, and NMR coupling constants calculated using this scheme are in agreement with experimental results. However, this scheme fails to reproduce the experimental variation of dipole moment with temperature. A possible justification for this discrepancy is suggested.

The conformational characteristics of the poly(methylacrylate) (PMA) chain have been studied by Flory and co-workers.[1] Following the general theory of rotational isomeric states,[2,3] they computed conformational energies of meso and racemic dyads as a function of skeletal bond rotations. The results of this calculation allowed them to use a very simplified scheme with two rotational states trans (t) and gauche (g), at rotational angles $\phi = 10, 110°$, respectively. Theoretical values of dimensions, stereochemical equilibria, and NMR coupling constants thus obtained are in excellent agreement with experimental data.

However, this scheme fails when applied to calculate dipole moments of the same polymer. The reason for this failure stems from its inability to take into account different allowed orientations of the ester group lateral to the chain.

There is experimental evidence that the ester group is planar with the bond O–CH$_3$ trans to the C$^\alpha$–C*,[4-8] the whole group being placed at the bisector plane of the skeletal bond angle at C$^\alpha$. Still, there is a degree of rotational freedom over the C$^\alpha$–C* bond (angle χ on Figure 1) which, also according to experimental results, is allowed to have two different orientations, one that places the O* cis relative to the H lateral on the chain and the second one that places these two atoms trans; we will give the value $\chi = 0$ to the cis orientation and $\chi = \pi$ to the trans one.

Flory and co-workers[1] used the average between these two orientations of the ester group. This simplification is quite reasonable for all the magnitudes they calculated since the only difference between these two orientations is a slight variation in the statistical weight parameters. However, the situation changes when the dipole moment is calculated, because the dipole moment for the repeating unit is located in the ester group plane; when the contribution of two consecutive units in the t conformation is considered, the result changes drastically according to the relative orientations of the ester groups in these units; if the ester groups have the same orientation ($\chi_1 = \chi_2$), both dipole moments are almost parallel, and they reinforce each other; on the other hand, if they have opposite orientation ($\chi_1 = 0$ and $\chi_2 = \pi$, or vice versa), the dipole moments are almost opposite, and they cancel each other out.

Therefore, averaging over the two values of χ is not allowed for dipole moment calculations; the two orientations must be considered separately. This separation requires expansion of the scheme of calculation to four rotational states as will be shown below.

Table I
Parameters Used for Nonbonded Interactions

atom or group	radius,[a] Å	b	polarizability, Å^3
C	1.8	5	0.93
C*	1.8	5	1.23
O	1.6	7	0.70
O*	1.6	7	0.84
H	1.3	0.9	0.42
CH$_3$	2.0	7	1.77

[a] van der Waals. [b] Effective number of electrons.

Energy Calculations

(a) Energetic and Geometrical Parameters. Nonbonded interactions were computed, using the Lennard-Jones potential $E_{ij} = (a_{ij}/r_{ij}^{12}) - (b_{ij}/r_{ij}^{6})$. The b_{ij} constants were evaluated according to the Slater–Kirkwood formula[9] from atom or group polarizabilities, α_i, and the effective number of electrons, N_i. Table I shows the values used for these parameters together with the adjusted van der Waals radii.[3,10] The a_{ij} constants were assigned as to minimize the energy when the distance r_{ij} is set equal to the sum of van der Waals radii for the interacting groups. Methyl groups were treated as spherical domains, since the position of their H atoms depends on rotation over three bonds of the side chain and the error introduced by misadjusting these rotations even by a few degrees is larger than the error implied in this substitution.

Rotational energy was computed, using a threefold intrinsic potential with a barrier of 2.8 kcal/mol over the C–C$^\alpha$ bonds[1] and a twofold potential with a barrier of 0.5 kcal/mol over the C$^\alpha$–C* bonds.[11]

An energy $E(\theta) = A(\Delta\theta)^2$ was assigned to the deformation of the valence angle at CH$_2$, where $\Delta\theta$ is the difference from the used value to the tetrahedral angle; a value of 80 kcal mol^{-1} rad^{-2} was used for the A constant.[12]

Dipole moment interactions were computed by assigning partial charges to the atoms involved[10] to reproduce the experimental dipole moment for the repeating unit (see below). A value of 3.5 was used for the effective dielectric constant.

The geometrical parameters used on the calculations are presented in Table II. Some preliminary calculations

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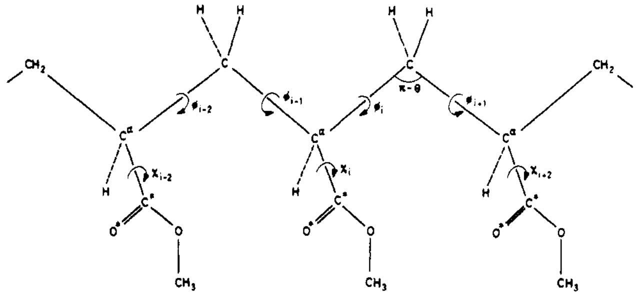

Figure 1. A portion of the isotactic PMA chain in the all-trans conformation.

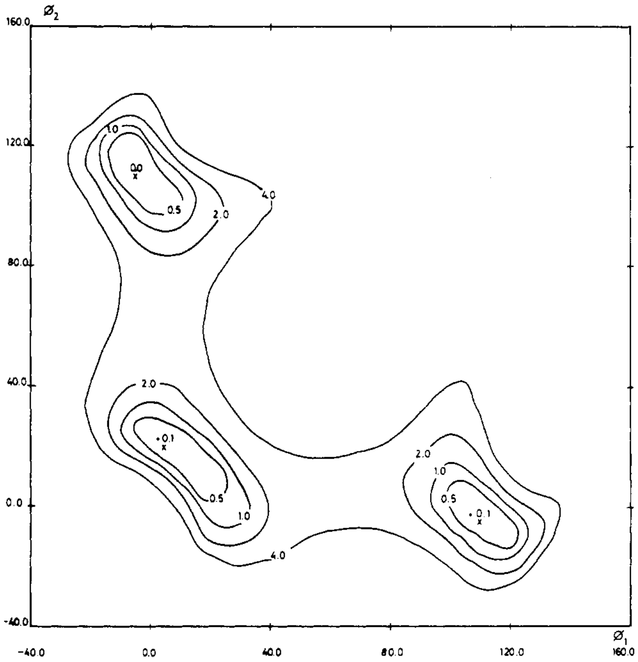

Figure 2. Conformational energy contours for a meso$_{\pi\pi}$ dyad calculated as a function of skeletal bond rotations ϕ_i and ϕ_{i+1}; solvent interactions were ignored. Locations of minima are denoted by ×, and the energy contours are labeled in kcal mol^{-1} relative to the lowest energy minimum ($E_{\min}$ = −1.13 for ϕ_i = −5, ϕ_{i+1} = 110°).

Table II
Geometrical Parameters

bond	bond length, Å	bond angle	angle, deg
C-C$^\alpha$	1.53	CC$^\alpha$C	112
C$^\alpha$-C*	1.52	CC$^\alpha$C*	109.5
C$^\alpha$-H	1.10	C$^\alpha$C*O*	121
C*-O*	1.22	C*C$^\alpha$H	109.5
C*-O	1.36	C$^\alpha$C*O	114
O-(CH$_3$)	1.45	C*O(CH$_3$)	113

carried out in order to optimize the value of the valence angle at CH$_2$ indicate that the energy is minimum when this angle is approximately 114°; this value will be used henceforth.

(b) Results. Calculations were carried out for meso and racemic dyads allowing for χ = 0 or π orientations in each of the ester groups. Figures 2 and 3 show the results of these calculations for meso$_{\pi\pi}$ and racemic$_{0\pi}$, respectively, and the subscripts refer to orientation of the ester groups (values adopted for the angle χ).

Partition functions (Z), average energies ($\langle E\rangle$), and average angles ($\langle\phi\rangle$) were evaluated for a region of ±40° over each minimum at intervals of 5° in ϕ_1 and ϕ_2. Results are summarized in Table III; the values for 0–π conformations are identical with the π–0 ones and are omitted.

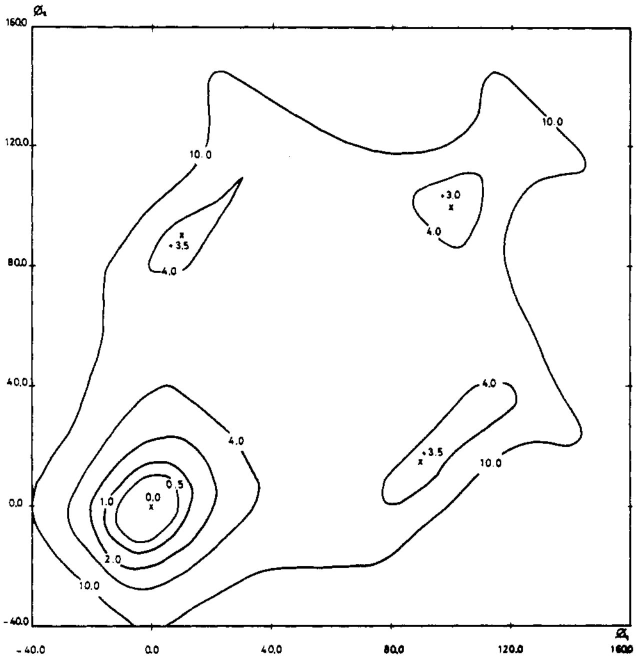

Figure 3. Conformational energy contours for a racemic$_{0\pi}$ dyad. Energy contours are in kcal mol^{-1} relative to $E_{\min}$ = −2.97 found for ϕ_1 = 0, ϕ_2 = 0°. See the legend for Figure 2.

Table III
Results of Energy Calculations[a]

isomer	$\langle E\rangle$	$\langle\phi_1\rangle$	$\langle\phi_2\rangle$	10^2Z
racemic t_0t_0	0	1.1	1.0	100
racemic t_0g_0	2.9	19.5	99.2	0.8
racemic g_0t_0	3.0	98.5	19.6	0.6
racemic g_0g_0	2.3	108.4	109.4	2.0
racemic $t_\pi t_0$	−0.3	0.7	0.3	163.0
racemic $t_\pi g_0$	2.8	20.1	99.4	1.0
racemic $g_\pi t_0$	3.1	98.8	19.8	0.6
racemic $g_\pi g_0$	2.3	108.9	109.9	2.1
racemic $t_\pi t_\pi$	0.0	0.4	0.4	96.3
racemic $t_\pi g_\pi$	3.4	20.3	99.8	0.4
racemic $g_\pi t_\pi$	3.5	98.9	20.4	0.3
racemic $g_\pi g_\pi$	2.8	109.7	110.8	1.0
meso t_0t_0	1.2	14.6	14.2	14.4
meso t_0g_0	0.7	−1.2	111.4	29.5
meso g_0t_0	0.8	110.4	−1.4	23.4
meso g_0g_0	4.3	97.8	100.3	0.0
meso $t_\pi t_0$	1.1	14.5	12.2	14.7
meso $t_\pi g_0$	1.2	−1.4	111.8	13.6
meso $g_\pi t_0$	1.3	110.1	−0.6	10.4
meso g_0g_π	4.8	96.9	101.3	0.0
meso $t_\pi t_\pi$	1.7	15.6	15.1	6.3
meso $t_\pi g_\pi$	1.1	−0.8	115.5	14.6
meso $g_\pi t_\pi$	1.3	110.4	−1.0	11.6
meso $g_\pi g_\pi$	4.8	97.8	100.5	0.0

[a] Subscripts refer to ester group orientation. Energies in kcal mol^{-1} relative to racemic t_0t_0. Angles in degrees. T = 300 K.

The average values ϕ = 10 and 110° will be used for trans and gauche states, respectively.

Statistical Weight Matrices

As has been pointed out before, consideration of two different orientations of the ester group separately requires the expansion of the scheme of calculation to four rotational states; each of Flory's states[1] is divided into two different ones depending on the position of the ester group. A statistical weight parameter ρ is introduced to represent the difference between χ = π and 0 states. With this separation, the required statistical weight matrices are as follows.

Table IV
Average Energies and Preexponential Factors Obtained from the Energy Calculation $p = P_0 \exp(-\langle E_p \rangle/RT)$

p parameter	$\langle E_p \rangle$, kcal mol^{-1}	P_0
η	−0.8	0.97
ω	2.8	0.25
ω'	2.2	1.05
ω''_i	1.2	1.06
ω''_d	1.1	0.94
ρ	0.5	1.07

U′ Matrix. This matrix represents bonds like $i - 1$ and i in Figure 1; there is only one ester group for these two bonds, and therefore 0–π or π–0 states are forbidden; these elements must be set equal to zero. The required matrix with states written in the order $t_0 t_\pi g_0 g_\pi$ may then be expressed by

$$\mathbf{U}' = \begin{vmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{vmatrix}$$

U″ Matrices. They represent bonds like i and $i + 1$ in Figure 1; there are two ester groups and therefore the orientations 0–π and π–0 are allowed. The factor ρ representing the stability of π vs. 0 states must be introduced indistinctly either in rows or in columns but not in both of them, otherwise we are counting it twice. In all our calculations, it will be introduced in columns, and then the required matrices may be expressed as follows:

$$\mathbf{U}''_m = \begin{vmatrix} \omega''_i & \rho\omega''_d & 1/\eta & \rho/\eta \\ \omega''_d & \rho\omega''_i & 1/\eta & \rho/\eta \\ 1/\eta & \rho/\eta & \omega/\eta^2 & \rho\omega/\eta^2 \\ 1/\eta & \rho/\eta & \omega/\eta^2 & \rho\omega/\eta^2 \end{vmatrix}$$

$$\mathbf{U}''_r = \begin{vmatrix} 1 & \rho & \omega'/\eta & \rho\omega'/\eta \\ 1 & \rho & \omega'/\eta & \rho\omega'/\eta \\ \omega'/\eta & \rho\omega'/\eta & 1/\eta^2 & \rho/\eta^2 \\ \omega'/\eta & \rho\omega'/\eta & 1/\eta^2 & \rho/\eta^2 \end{vmatrix}$$

Two different values of the ω'' parameter are introduced on meso tt states: ω''_i for conformations in which both ester groups have the same orientation and ω''_d for conformations having different orientations of these groups. This distinction is not needed for the other states because of the large separation between ester groups in these conformations.

Comparison of these matrices with the results of Table III by following standard procedures[1,2] leads to evaluation of all the statistical weight parameters. Unfortunately, this evaluation is somehow hindered by the inaccuracy of energy calculations. (This inaccuracy is reflected, for instance, in the fact that racemic t_0t_0 and $t_\pi t_0$ states, which are supposed to have the same interactions, appear with different values in Table III.) The parameter E_η can be evaluated by comparing the energies of r-g_0g_0, r-$g_\pi g_0$, m-t_0g_0, m-$t_\pi g_0$, m-g_0t_0, or m-$g_\pi g_0$ with r-t_0t_0 (taking this last state as the zero of energies); this comparison gives values of E_η ranging from −0.7 to −1.3 kcal/mol; we choose the value −0.8 kcal/mol as the most representative. Once the value of this parameter has been selected, the remaining energies can be evaluated in the same way. The parameter E_ρ can be determined by comparison of $\pi\pi$ with 00 or π0 states; its values range from 0.0 to 0.6 kcal/mol. Once the energies have been selected, the same procedure may be used for assigning the preexponential factors. We take the average values listed in Table IV and use the energies as adjustable parameters to be optimized by comparison of calculated and experimental results of several magnitudes, as is shown below.

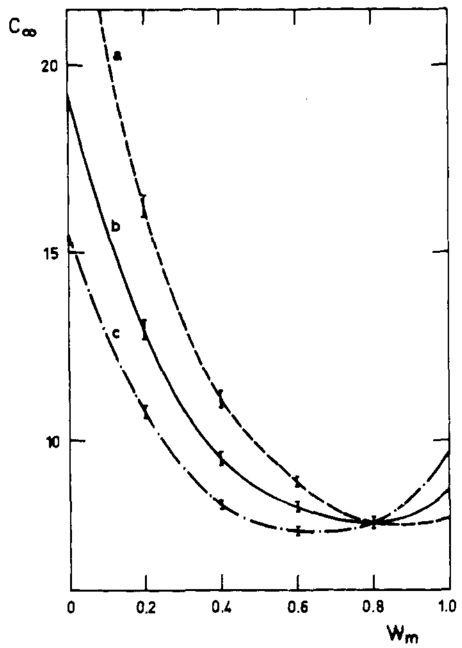

Figure 4. Dependence of C_∞ on W_m, the fraction of meso dyads, for three values of E_η. Curve (a) $E_\eta = -0.5$; curve (b) $E_\eta = -0.3$; and curve (c) $E_\eta = -0.1$. $E_\omega = 2.8$; $E_{\omega'} = 2.2$; $E_{\omega''_i} = 1.6$; $E_{\omega''_d} = 1.0$; $E_p = 0.3$; $T = 300$ K. All energies are in kcal mol^{-1}.

Calculation of Polymer Magnitudes

(a) Characteristic Ratio. The ratios $C_n = \langle r^2 \rangle_0 / nl^2$, where l is the C–C bond length, were evaluated according to Flory's procedure.[13] Twenty Monte-Carlo chains consisting of 100 dyads ($n = 200$) were generated with Bernoullian distributions of meso and racemic centers; the values of C_n were extrapolated to infinite n by plotting C_n against $1/n$; the projected increase of C_n beyond $n = 200$ amounted to about 2% of its limiting value. The average C_∞ values are plotted in Figure 4 against the fraction W_m of meso dyads for the several values of E_η indicated; vertical lines represent the standard error in calculations.

Experimental results[14-16] on chain dimensions of PMA prepared via radical polymerization give $C_\infty \simeq 8.4 \pm 0.5$. The PMA thus prepared is about 50% isotactic, according to the studies of Matsuzaki et al.[17]

The only energetic parameter that modifies appreciably the results of C_∞ is E_η, and as could be seen from Figure 4, an energy $E_\eta = -0.3$ to -0.5 kcal/mol is needed in order to yield a value of C_∞ consistent with the experimental data.

(b) Dipole Moment. The ratios $D_x = \langle \mu^2 \rangle_0 / x\mu^2$, where $x = n/2$ is the degree of polymerization and μ_0 is the dipole moment of the repeating unit, were computed by the same chain generation procedure as that explained for C_n. Both module and orientation of μ_0 are needed for this calculation.

The module is not a critical parameter since it changes little the D_∞ results. La Fevre's experimental value for methyl propionate in benzene solution at 25 °C[18] has been used as μ_0.

Unfortunately, the assignation of orientation is not so straightforward as that of the module. Curl's measurements of methyl formate in the gas phase yield a dipole moment[19] of 1.77 ± 0.03 D located in the plane of the ester group with an orientation defined by an angle $\gamma \simeq 40°$ between the dipole moment vector and the C*=O* bond. On the other hand, Le Fevre's results[18] for methyl esters

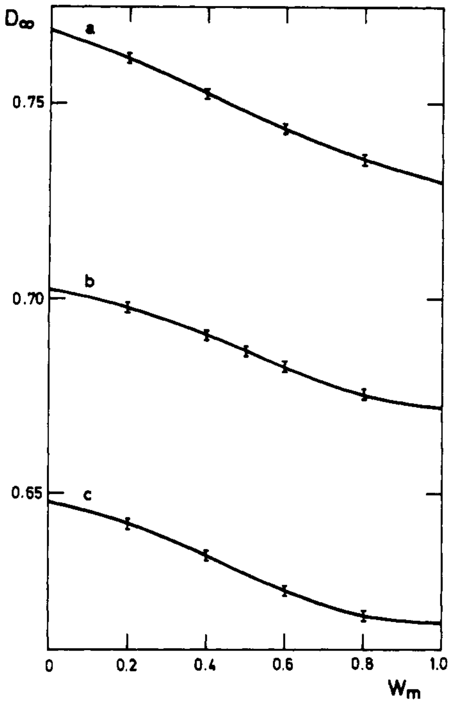

Figure 5. Variation of D_∞ with W_m for three values of μ_{CH}. Curve (a) μ_{CH} = 0.3 D; curve (b) μ_{CH} = 0.4 D; and curve (c) μ_{CH} = 0.5 D. E_η = −0.3 kcal mol^{-1}; γ = 40°. All other parameters are as those in Figure 4.

$RCOOCH_3$ in benzene solution at 25 °C are $\mu = 1.80 \pm 0.03$ D for R = H, CH_3, CH_2CH_3, and $CH(CH_3)_2$. The dipole moment of these molecules can be expressed as the resultant of two contributions, μ_e from the ester group and μ_R from the R group; this second contribution can be evaluated from the tabulated values of the C–H bond dipole moments, $\mu_{CH} \simeq 0.4$ D.[20] For all of these molecules, the vectors μ_e and μ_R are almost perpendicular for any orientation of the R group, and the module of μ_e is much greater than the one of μ_R; therefore $\mu = \mu_e + \mu_R \simeq \mu_e$ for all of these compounds, which is in agreement with experimental results. By similarly decomposing the dipole moment of the PMA repeating unit into μ_e and μ_R, we find that the vectors μ_e from the ester group and μ_{CH} from the CH bond lateral to the backbone are nearly in opposite directions when the ester group has the cis orientation (they make an angle of 169°), whereas μ_e and μ_{CH} are almost in the same direction (at an angle of 11°) if the ester group has the trans orientation. Therefore the dipole moment of the repeat unit is different for cis (μ_{cis}) and trans (μ_{trans}) orientations of the ester group; if there is a different probability for the occurrence of these two orientations (measured by ρ), the overall dipole moment for the repeating unit is $\mu_0 = (\mu_{cis} + \rho\mu_{trans})/(1 + \rho)$. We use an orientation γ = 40° and a value μ_{CH} = 0.4 D[20] in all of our calculations and adjust the μ_e module for each ρ value to give μ_0 = 1.76 D in accordance with Le Fevre's result for methyl propionate.[18] The dipole moment of the CH_2 group was not included in this treatment, since it is nearly perpendicular to μ_e because of the distortion of chain geometry (both in valence and rotational angles); therefore, it modifies almost equally the value of μ_{cis} and μ_{trans}; its only effect is a slight change in the μ_0 value to which D_∞ is not sensitive.

According to experimental dipole moment measurements,[21-24] $D_\infty = 0.67 \pm 0.01$ for atactic samples with W_m = 0.5.

Calculated values of D_∞ are sensitive to μ_{CH} and to a much less extent to E_ρ and $E_{\omega''_d}$. Figure 5 shows the results of D_∞ calculated with three different values of μ_{CH}. As can be seen from this figure, agreement between theoretical and experimental results of D_∞ occurs for $\mu_{CH} \simeq 0.4$ D.

Table V
NMR Coupling Constants ΔJ

			ΔJ, Hz		$10^2(\mathrm{d}\Delta J/\mathrm{d}T)$, Hz K^{-1}	
x	config	T, °C	exptl (ref)	calcd	exptl	calcd
2	m	26	1.0 (26)	0.7		
	r	20	3.6 (26)	4.3	−2.8	−1.4
3	mm^a	26	1.6 (26)	0.9		
	$m{*}r^a$	26	1.0 (26)	0.8		
	$r{*}m^a$	26	5.0 (26)	6.4		
	rr^a	26	3.6 (26)	5.5	−1.2	−0.9
∞	$(m)_\infty$	25	1.9 (27)[b]	2.0		
		140	1.2 (28)	2.5		

[a] In the trimer, the mean values for CC bonds 2 and 3 are listed; an asterisk denotes the dyad for which ΔJ was calculated in the heterotactic trimer. [b] Averaged over results for several solvents.

(c) Stereochemical Equilibrium in Oligomers of PMA. Standard methods[1,2] were used to evaluate the fractions of meso (f_m) and racemic (f_r) diastereomers of (2,4-dimethoxycarbonyl)pentane (x = 2) and the fractions of isotactic (F_I), heterotactic (F_H), and syndiotactic (F_s) diastereomers of (2,4,6-trimethoxycarbonyl)heptane (x = 3). Experimental values of these parameters measured in methanol at 25 °C are:[25] $f_m = 0.45_5 \pm 0.01$; $F_I = 0.19_8 \pm 0.01$, $F_H = 0.50_9 \pm 0.01$, and $F_S = 0.29_3 \pm 0.01$.

Calculated values of these fractions are sensitive to E_η; agreement between theoretical and experimental results is achieved with E_η = −0.3 to −0.5 kcal/mol. By using E_η = −0.3 and the "most likely value" for all of the other parameters (see Table VI), the following results are obtained at 25 °C: $f_m = 0.48_6$, $F_I = 0.21_6$, $F_H = 0.50_3$, $F_S = 0.28_1$.

(d) NMR Coupling Constants. Vicinal coupling constants in the proton magnetic nuclear resonance spectra of PMA oligomers are given by[1]

$$\Delta J = \Delta J_t(2p_{tj} - 1)$$

Calculated values of ΔJ are sensitive to E_η in all cases and to E_ω in meso dyads. Table V shows the result of calculations using the "most likely value" for all the parameters together with experimental results for this magnitude.

Discussion

Separation of the two possible orientations in the ester group requires the use of four rotational isomers and the consideration of two more energetic parameters (E_ρ and the splitting of $E_{\omega''}$ into $E_{\omega''_i}$ and $E_{\omega''_d}$). All of these modifications have a small incidence in dimensions, stereochemical equilibria, and NMR coupling constant calculations, but they drastically change the results of dipole moment calculations rendering them in agreement with experimental data.

The sensitivity of calculated magnitudes to each of the parameters used has been checked in the following way: The set of values that gives the best fit for all the magnitudes was evaluated and will be referred to as the "most likely value". The value of each one of the parameters was slightly changed keeping constant all the others, and the variation thus introduced in the magnitudes was calculated; these variations expressed as d(magnitude)/d(parameter) are summarized on Table VI. As can be seen from this table, E_η is the most critical parameter for all of the magnitudes except D_∞, for which μ_{CH} is the dom-

Table VI
Variation of Calculated Magnitudes with Parameters Used in the Calculation (Variations are Expressed as 10^2 d(magnitude)/d(parameter))

	parameter ("most likely value" *a*)									
	θ (114°)	E_η (−0.3)	E_ω (2.8)	$E_{\omega'}$ (2.2)	$E_{\omega''_i}$ (1.6)	$E_{\omega''_d}$ (1.0)	E_ρ (0.3)	γ (40°)	μ_{CH} (0.4 D)	T (300 K)
C_∞ [b]	10.4	−539.0	1.0	−4.5	−5.0	−8.0	0.0	0.0	0.0	−0.5
D_∞ [b]	0.07	2.0	0.0	0.0	−4.0	6.9	10.2	0.3	−59.3	−0.01
f_m	0.0	14.8	−0.03	1.0	−1.4	−1.7	−0.5	0.0	0.0	0.02
F_I	0.0	18.9	−0.02	0.8	−1.6	−2.3	−0.4	0.0	0.0	0.03
F_S	0.0	−18.3	0.02	−1.0	1.6	2.4	0.4	0.0	0.0	−0.03
$\Delta J(m)$	0.0	−115.0	0.0	0.0	−55.0	−65.0	−20.0	0.0	0.0	0.4
$\Delta J(r)$	0.0	−1325.0	0.0	15.0	0.0	0.0	0.0	0.0	0.0	−1.4
$\Delta J(mm)$	0.0	−140.0	0.0	0.0	−60.0	−125.0	−20.0	0.0	0.0	0.6
$\Delta J(mr)$	0.0	−100.0	0.0	0.0	−60.0	−70.0	−20.0	0.0	0.0	0.5
$\Delta J(rm)$	0.0	−920.0	0.0	25.0	15.0	20.0	5.0	0.0	0.0	−1.2
$\Delta J(rr)$	0.0	−810.0	0.0	15.0	0.0	0.0	0.0	0.0	0.0	−0.9
$\Delta J(m_\infty)$	0.0	−160.0	0.0	0.0	−60.0	−100.0	−10.0	0.0	0.0	0.5

[a] Energies in kcal mol^{-1}. [b] Averages over 20 chains with $W_m = 0.5$.

inant one followed by E_ρ. The dependence of D_∞ on μ_{CH} and E_ρ is reasonable. μ_{CH} is placed on the side of the chain backbone; for the most stable states of a dyad (meso *tg* or *gt* and racemic *tt*), the two lateral CH bonds have nearly opposite directions, and their dipole moments almost cancel each other; the larger this contribution is (i.e., larger μ_{CH} value), the smaller the dipole moment for the whole chain will be, since we keep μ_0 constant. On the other hand, the value of E_ρ governs the stability of $\chi = \pi$ vs. $\chi = 0$ orientations of the ester group and therefore the reinforcement or cancellation of dipole moments from two consecutive units.

Variation of magnitudes with temperature is shown in the last column of Table VI. The calculated values for $\Delta J(r)$ and $\Delta J(rr)$ are in satisfactory agreement with experimental measurements (see Table V).

As for the experimental variation of D_∞ with temperature, Kotera et al.[23] give values of D_∞ at 20 and 50 °C; according to their results, D_∞ increases about 5% from 20 to 50 °C. Our own results[24] show a transition at 35 °C; D_∞ increases slightly from 20 to 30 °C, then decreases by about 30% from 30 to 35 °C, and finally increases again. The net variation from 20 to 50 °C is a decrease of about 1%. The calculated values of D_∞ are insensitive to temperature (the obtained change of -10^{-4} K^{-1} obtained is much smaller than the inaccuracy of calculation). This insensitivity of D_∞ to temperature could be due to the use of an inadequate expression for the temperature variation of energetic parameters; in fact, if we use p as any one of the parameters appearing in **U**″ matrices, the variation of D_∞ with temperature may be expressed by

$$\frac{dD_\infty}{dT} = \sum_p \left(\frac{dD_\infty}{dE_p} \frac{dE_p}{dp} \frac{dp}{dT} \right)$$

$$p = \omega, \omega', \omega''_d, \text{etc.}$$

If, as usual, we take

$$p = p_0 \exp(-E_p/RT) \tag{1}$$

which amounts to saying that the preexponential factors and the averaged energies do not vary with T, this expression reduces to:

$$\frac{dD_\infty}{dT} = \sum_p \left(-\frac{E_p}{T} \frac{dD_\infty}{dE_p} \right) \tag{2}$$

according to the results of Table VI. The contributions of E_η, E_ω, $E_{\omega'}$, $E_{\omega''_i}$, $E_{\omega''_d}$, and E_ρ to the variation of D_∞ with T are 2.0×10^{-5}, 0, 0, 2.1×10^{-4}, -2.3×10^{-4}, and -1.0×10^{-4} K^{-1}, respectively, and they compensate each other. However, if the variation of parameters with temperature were of a different form, D_∞ could be more sensitive to temperature.

A statistical weight parameter is evaluated as a ratio of two partition functions, and therefore it represents an equilibrium constant between the state for which we are calculating it and the state we take as a reference. In this sense, a statistical weight may be expressed by

$$p = \frac{z_p}{z_0} = k_p = \exp(-\Delta G^\circ{}_p/RT) = \exp(\Delta S^\circ{}_p/R)\exp(-\Delta H^\circ{}_p/RT) \tag{3}$$

This equation is transformed into eq 1 by writing P_0 instead of the entropic term and $\exp\{-E_p/RT\}$ instead of the enthalpic one; this second term contains an explicit dependence of p on temperature. However, ΔS° *does depend on T*, and therefore p_0 is temperature dependent, and eq 2 must be corrected.

In fact, the experimental variation of D_∞ with T can be thus explained; if we assume ρ to be more sensitive to T, so that it could reach unity in the vicinity of 35 °C, then the value of D_∞ will be minimum because the above-mentioned cancellation between $\chi = 0$ and π orientations will be maximum and will increase either by increasing or decreasing T as ρ goes away from unity and one of the orientations dominates the second one.

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Circular Dichroism and Conformational Equilibrium of Homopoly-L-peptides with Alkyl Side Chains in Concentrated Sulfuric Acid

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ABSTRACT: Differences have been observed between the CD spectrum of poly-L-alanine (PA) and those of poly-L-leucine (PL), poly-L-valine (PV), and poly-L-isoleucine (PI) in 95.2% sulfuric acid and are attributed to short-range conformational order which is absent in PA and present in PL, PV, and PI. PA exhibits a CD spectrum characterized by a single negative band with the maximum at 195 nm, consistent with the conformation of an expanded random coil. PL, PV, and PI show in addition to a negative band centered around 197 nm a less intense positive band with the maximum slightly below 220 nm. The polymers appear to be essentially completely O protonated in sulfuric acid, so this positive band cannot be attributed to $n-\pi^*$ transitions of nonprotonated peptide groups. On the basis of a comparison with the CD spectra for a series of L-isoleucine oligomers in sulfuric acid, it is proposed that this positive band derives from the interaction of electronic transitions below 220 nm of the protonated peptide groups and that it reflects the presence of short, conformationally regular sequences in the polymer chains.

The relationship between the conformational equilibrium and the CD pattern for polypeptides with protonated peptide groups in strong acid solvents is still unclear. Some authors[2-6] consider polypeptides in backbone-protonating solvents to have the conformation of a random coil, and more specifically[4] that of an expanded one. Tiffany and Krimm[7] assert that under these conditions polypeptides should favor the extended helix (EH) conformation. This disagreement reflects different conformational interpretations[8] of the CD spectrum that is typical for fully ionized poly(L-glutamic acid)[9] or poly-L-lysine[9,10] in aqueous solution. CD spectra of this type, with a large negative band slightly below 200 nm and a weak positive band near 220 nm, have also been found for all synthetic poly-L-peptides investigated so far, when strongly protonating solvents, such as sulfuric acid[3-5] or methanesulfonic acid,[3,6] have been employed. Among the polypeptides which in sulfuric acid give CD spectra of this type, there are[5] poly-L-leucine (PL) and poly-L-valine (PV). However, in trifluoroacetic acid solution, PL and PV show no evidence of a positive CD band around 220 nm,[11] nor do either poly-L-alanine (PA)[11,12] or poly-L-isoleucine (PI).[11] These polypeptides have alkyl lateral chains, and protonation may occur only in the main chain. Furthermore, the lateral chains contain no chromophore which would contribute to the CD in the 185–250-nm region. On these grounds, these polypeptides seemed more suitable than others for a study of the relationship between the CD pattern and the conformational equilibria of protonated polypeptides. With this intent, we have undertaken a CD, UV, and NMR spectroscopic study of PA, PL, PV, and PI, using concentrated, aqueous sulfuric acid as solvent. Since it was expected that similar observations of oligomeric peptides of increasing chain length would greatly assist in the interpretation of particular spectral properties of these polypeptides, a series of oligo-L-alanines and oligo-L-isoleucines was also investigated. In this paper, we report and discuss the results obtained.

Experimental Section

Materials. The samples of PA and PL used in this study were purchased from Myles-Yeda Ltd. The degree of polymerization ($\bar{n}$) of the sample of PA, according to the specifications, was 46. The samples of PV ($\bar{n}$ = 19) and of PI ($\bar{n}$ = 20) were synthesized by the NCA method using *n*-butylamine as the initiator. The details of the synthesis of the sample of PI have been reported elsewhere.[13] The $\bar{n}$'s of these samples were determined from the NMR spectra of trifluoroacetic acid solutions by measuring the ratio of the NH_3^+ end group to the peptide NH proton resonance areas. The $\bar{n}$ of the commercial sample of PL, not specified, was also investigated by NMR and estimated to be at least 50.

The Boc- and MeO-protected oligopeptides Boc-Ala$_n$-OMe and Boc-Ile$_n$-OMe (n = 2–6) were prepared in a stepwise fashion using equivalent, conventional solution methods. The synthetic procedures used are those described for the L-isoleucine oligomers in ref 13. All oligopeptides were found to be pure by thin-layer chromatographic criteria and gave correct elemental analyses.

HCl·H-Ala-OMe and HCl·H-Ile-OMe were Fluka products.

Concentrated sulfuric acid, Merck "pro analysi", with an acid content of 95.2% by weight (base titration) and trifluoroacetic

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