Conformational Characteristics of Poly(methyl acrylate)

D. Y. Yoon, U. W. Suter, P. R. Sundararajan, and P. J. Flory*

Department of Chemistry, Stanford University, Stanford, California 94305.

Received June 16, 1975

ABSTRACT: Conformational energies of meso and racemic dyads of poly(methyl acrylate) have been computed as functions of skeletal bond rotations, the planar ester group being oriented perpendicular to the plane defined by the two adjoining skeletal bonds. Solvent interactions affect the relative energies of various conformations, as found for polystyrene. The conformational energy surfaces are similar to those for polystyrene, and the same two-state scheme with trans and gauche states at $\varphi_t = 10°$ and $\varphi_g = 110°$ is applied. The first-order statistical weight parameter is given by $\eta = 1.0(\pm 0.1)\exp(-E_\eta/RT)$ where the preexponential factor is evaluated from the computed conformational energy surfaces. Similarly, the second-order parameters that represent $CH_2 \cdots CH_2$, $CH_2 \cdots R$, and $R \cdots R$ interactions, respectively, are $\omega = 1.3(\pm 0.1)\exp(-1600/RT)$, $\omega' = 1.4(\pm 0.1)\exp(-1600/RT)$, and $\omega'' = 1.2(\pm 0.1)\exp(-E_{\omega''}/RT)$. The energies E_η and $E_{\omega''}$, being affected by solvent interactions, cannot be reliably estimated from energy calculations. Agreement with experimental dimensions of the PMA chain and stereochemical equilibria in the dimeric and trimeric oligomers requires that $E_\eta = -300 \pm 100$ cal mol^{-1} and $E_{\omega''} = 1500 \pm 300$ cal mol^{-1}. Calculated values of the NMR-coupling parameter ΔJ for oligomers and for isotactic PMA are consistent with experimental results.

The configurational characteristics of the poly(methyl acrylate) (PMA) chain, wherein the substituent group $COOCH_3$ is planar and, hence, resembles phenyl in its spatial requirements, may be expected to resemble those of the polystyrene chain treated in the preceding paper.[1] Severe steric interactions in the $\bar{g}$ conformation, corresponding to those occurring in polystyrene, likewise preclude its occurrence, as may be established by examination of a model. The smaller size and thickness of the $COOCH_3$ group compared with phenyl may be expected to introduce minor quantitative differences, however. First, steric interactions between substituents in the meso;tt state are smaller than in polystyrene and can be diminished further by minor adjustments of the rotations φ_i and φ_{i+1}. Thus, a larger value of ω'' may be expected. Second, the dependence of the interactions between solvent and polymer should vary to a lesser degree with conformation than in polystyrene.

In order to quantify these predictions and to acquire a fuller understanding of the interactions in PMA chains, we have carried out conformational energy calculations using conventional empirical functions cited in the preceding papers.[1,2] In recognition of the limitations of the energy calculations, we again rely on them principally to define the accessible regions of conformational space and their shapes. The estimated energies are adjusted within reasonable ranges as required to achieve agreement with experimental results on the chain dimensions of conventional, radical-polymerized, atactic PMA and on stereochemical equilibria.

Conformational Energies

Geometrical Data and Calculation Methods. Bond lengths and bond angles, assumed to be fixed at the same values in all conformations, are given in Table I.

The ester group was taken to be planar with the $O-CH_3$ bond trans to $C^\alpha-C^*$ (see Figure 1), as is indicated by an abundance of experimental evidence on various esters.[4] Rotation of the ester group around the $C^\alpha-C^*$ bond is specified by the angle χ measured relative to the conformation in which the bond $C^*=O^*$ is cis to $C^\alpha-H$. Infrared spectra of low molecular analogs of PMA show the plane of the ester group to be normal to the plane defined by the skeletal bonds flanking the C^α atom, with the carbonyl bond cis to the $C^\alpha-H$ bond,[5] i.e., with $\chi = 0°$. Although steric impingements in the several conformations of the PMA dyad doubtless induce minor displacements, χ is considered below to be restricted to this value in all conformations. As was shown for the poly(methyl methacrylate) (PMMA) chain,[6] the assignment of the ester group to the alternative conformation, $\chi = 180°$, in which the ester bond C^*-O is cis to $C^\alpha-H$, raises the energy only about 0.2 kcal mol^{-1}, the increase being about the same in all conformations. Hence, configurational averages would be affected negligibly by arbitrary choice of $\chi = 180°$, or by permitting access to both conformations.

As in the preceding papers,[1,2] a threefold intrinsic torsional potential having a barrier of 2.8 kcal mol^{-1} was assigned to each skeletal C–C bond. The Lennard-Jones 6–12 potential was employed for nonbonded pairs of atoms in the manner previously described. The methyl group in the side chain was approximated by a spherical domain of fixed size.[6] The parameters for different atoms and groups are listed in Table II.

Following Brant et al. Coulombic interactions were assessed by assigning partial charges to the atoms. Bond moments of 0.74 D for C–O and 2.3 D for C=O were used. A value of 3.5 was chosen for the effective dielectric constant.

As discussed in detail for the polystyrene chain,[1] changes in the exposure of the planar substituent in different conformations imply significant variations in solvent–polymer interactions. Accordingly, the 6–12 potential energy function was truncated in the manner there described[1] at a suitably chosen distance σ beyond which the interaction energies for all pairs i,j were fixed at their values for $r_{ij} = \sigma$.

Results of Energy Calculations. Conformational energies calculated for a meso dyad, differences in solvent–polymer interactions being ignored by taking $\sigma = \infty$, are represented in Figure 2 as functions of the skeletal bond rotational angles φ_i and φ_{i+1}; see Figure 1. Contours are drawn at the energies quoted in kcal mol^{-1} relative to the minimum for the racemic;tt state (Figure 3). For the meso dyad as represented in Figure 1, the angle φ_i is measured in the right-handed sense and φ_{i+1} in the left-handed sense.[2]

Energies were computed at intervals of 5° in φ_i and φ_{i+1} within ranges of ±40° of each of the minima, and at intervals of 20° elsewhere. The conformational energy surface for the meso dyad of PMA resembles closely that for polystyrene; compare Figure 2 with Figure 2 of ref 1. This is an obvious consequence of the similar geometry of the respective substituents; both are planar and comparable in size. Thus, the tg and gt minima occur at 0,115° and at 115,0°, respectively; the gg conformation is separated into a pair of minima at 115,75° and at 75,115° and the tt minimum is displaced to 15,15°. As in polystyrene, the low energy of the tt minimum is likewise attributable to the attractions between the pairs of substituents juxtaposed in this confor-

Table I
Geometrical Parameters[3]

Bond	Length, Å	Bond angle	Angle, deg
C—C	1.53	$\angle CC^{\alpha}C$	112
		$\angle C^{\alpha}CC^{\alpha}$	114
C^{α}—C*	1.52	$\angle CC^{\alpha}C^*$	112
C—H	1.10	$\angle CC^{\alpha}H$	107
		$\angle C^{\alpha}CH = \angle HCH$	110
C*—O	1.36	$\angle C^{\alpha}C^*O$	114
C*—O	1.22	$\angle C^{\alpha}C^*O^*$	121
O—(CH_3)	1.45	$\angle C^*O(CH_3)$	113

Table II
Parameters Used in Energy Calculations

Atom or group	van der Waals radius, Å	Effective no. of electrons	Polarizability, Å^3
C	1.8	5	0.93
C (carbonyl)	1.8	5	1.23
O (ester)	1.6	7	0.70
O* (carbonyl)	1.6	7	0.84
H	1.3	0.9	0.42
CH_3	2.0	7	1.77

mation. The $\bar{g}$ conformation imposes severe steric overlaps between atoms of the ester group and the groups bonded to the adjacent C^{α} atom. These interactions, analogous to those occurring in polystyrene, were discussed in detail for the PMMA chain.[6] Hence, the $\bar{g}$ domains have been eliminated from Figure 2 (and also from Figure 3), and are disregarded in the following treatment.

The conformational energy surfaces computed using the truncated Lennard-Jones potential with $\sigma = 3.9$ and $\sigma = 5.0$ Å are scarcely distinguishable from Figure 2, apart from changes in the differences between the energies for the several minima. The computations for PMA closely parallel those for polystyrene in these respects.

Figure 3 shows the conformational energy surface for the racemic dyad computed for $\sigma = \infty$ in the manner stated above for the meso dyad. Again, the energy surface for the racemic dyad corresponds closely to that for polystyrene; see Figure 4 of the preceding paper.[1] The tt minimum occurs at 0,0°, the gg minimum at 105,105°, and the gt and tg minima at 90,10° and 10,90°, respectively. The locations of the minima and the shapes of their domains are likewise little affected by allowance for solvent–polymer interactions through the device of taking $\sigma = 3.9$ and 5.0 Å in separate computations.

The mean locations $\langle\varphi_i\rangle,\langle\varphi_{i+1}\rangle$ of each of the major dyad conformations were evaluated in the manner described for polystyrene.[1] The results of these computations carried out for several values of σ at $T = 300$ K are presented in Table III. The results are quite insensitive to the value of σ, in accordance with the similar findings for polystyrene.[1]

Statistical Weight Matrices

Adopting the scheme set forth for polystyrene in the preceding paper,[1] we may approximate the averaged conformations listed in Table III by combinations of the two rotational isomeric states located at $\varphi_t = 10°$ and $\varphi_g = 110°$. The statistical weight matrix $\mathbf{U}'$ for the pair of bonds flanking the C^{α} atom and $\mathbf{U}_m''$ and $\mathbf{U}_r''$ for the pair of bonds within the meso and racemic dyads, respectively, may be represented by eq 2–4 of the preceding paper.[1]

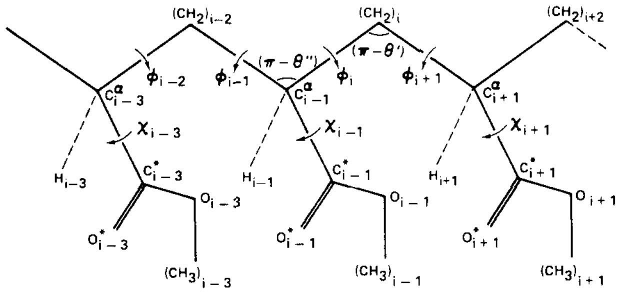

Figure 1. A portion of the isotactic poly(methyl acrylate) chain in the all-trans conformation.

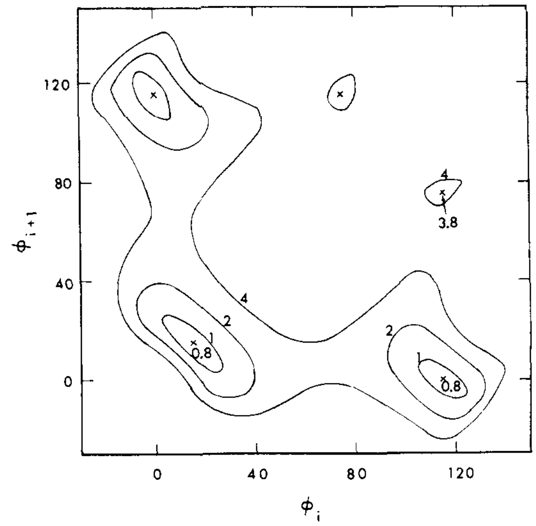

Figure 2. Conformational energy contours for a meso dyad; solvent interactions ignored; ester group rotations fixed at $\chi = 0°$. Locations of minima are denoted by × and the energy contours are labeled in kcal mol^{-1} relative to the energy minimum of the racemic;tt conformation. The torsional angles φ_i and φ_{i+1} are measured in the right- and left-handed senses, respectively.

Partition functions z_{ζ}, the average energies $\langle E_{\zeta}\rangle$, and the preexponential factors α_{ζ} for each conformation relative to the racemic;tt state computed according to the procedure described for polystyrene (see eq 5 of the preceding paper) are presented in Table IV for $\sigma = 3.9$ Å and $\sigma = \infty$, the temperature being 300 K. For $\sigma = 5.0$ Å, the results differ imperceptively from those for $\sigma = \infty$, and, hence, are omitted in Table IV.

The marked changes in values of z_{ζ} and of $\langle E_{\zeta}\rangle$ with σ on the one hand, and the slight dependence of α_{ζ} on σ on the other, duplicate the findings for polystyrene[1] and reaffirm that the major effects of the solvent–polymer interactions occur in the alteration of the relative energies of the several conformations; the energy surface surrounding a given minimum is little affected. The solvent–polymer interactions, of course, should depend on the size of the substituent of the vinyl polymer as well as on its geometry. This is clearly manifested in the fact that for PMA the energy $\langle E_{\text{meso;tt}}\rangle$ relative to $\langle E_{\text{racemic;tt}}\rangle$ changes from 0.76 kcal mol^{-1} for $\sigma = \infty$ to 1.38 kcal mol^{-1} for $\sigma = 3.9$ Å (see Table IV), whereas for polystyrene the corresponding relative energies $\langle E_{\text{meso;tt}}\rangle$ are 0.91 and 2.61 kcal mol^{-1}, respectively (see Table III of the preceding paper[1]). The smaller change in $\langle E_{\text{meso;tt}}\rangle$ for PMA is attributable to the somewhat smaller dimensions of the $COOCH_3$ group compared to phenyl.

The values of ξ, ξ_0, and E_{ξ} for each of the four statistical

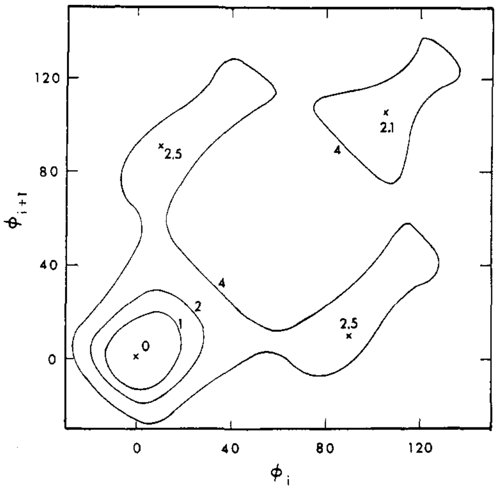

Figure 3. Conformational energy contours for a racemic dyad; solvent interactions neglected. For the racemic;*dd* dyad, φ_i and φ_{i+1} are measured in the right-handed sense, and for the racemic;*ll* dyad, in the left-handed sense.

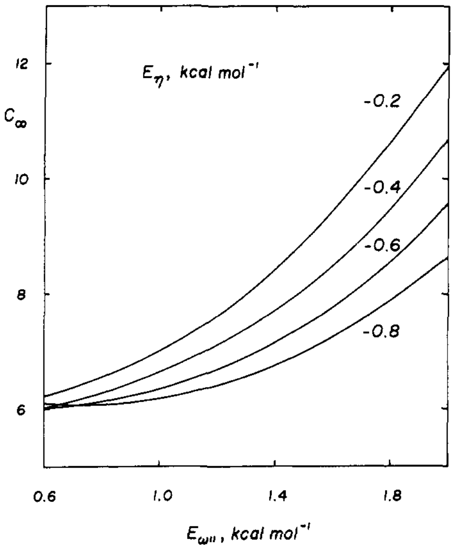

Figure 4. Dependence of C_∞ on E_η and $E_{\omega''}$ for isotactic PMA at T = 300 K; φ_t = 10° and φ_g = 110°.

weights η, ω, ω', and ω'' were calculated from the quantities z_ξ and $\langle E_\xi \rangle$ in Table IV in the same manner as in the first paper of this series.[2] The parameters ξ_0 and E_{ξ_0} thus obtained are presented in Table V. The dependence of these parameters on σ parallels the corresponding results for polystyrene.[1] The energies E_η and $E_{\omega''}$ depend strongly on σ, while E_ω and $E_{\omega'}$ and the preexponential factors η_0, etc., are little affected. The following rounded values of these quantities have been chosen: $E_\omega = E_{\omega'} = 1.6$ kcal mol^{-1}, $\eta_0 = 1.0$, $\omega_0 = 1.3$, $\omega_0' = 1.4$, $\omega_0'' = 1.2$. These values approximate those found for polystyrene.[1] Accordingly, the statistical weights are represented by

$$\omega \approx 1.3 \exp(-800/T) \quad (1)$$

$$\omega' \approx 1.4 \exp(-800/T) \quad (2)$$

$$\omega'' \approx 1.2 \exp(-E_{\omega''}/RT) \quad (3)$$

$$\eta \approx 1.0 \exp(-E_\eta/RT) \quad (4)$$

We infer from the energy calculations that the plausible ranges for E_η and $E_{\omega''}$ are: $-1.2 < E_\eta < -0.4$, $0.6 < E_{\omega''} < 1.8$, in kcal mol^{-1}.

Table III
Averaged Conformations $\langle \varphi_i \rangle$, $\langle \varphi_{i+1} \rangle$ at T = 300 K

	$\langle\varphi_i\rangle,\langle\varphi_{i+1}\rangle$, deg		
	σ = 3.9 Å	σ = 5.0 Å	$\sigma = \infty$
Meso;tt	17,17	17,17	17,17
Meso;tg	3,112	3,111	2,112
Meso;gg	92,92	93,93	92,92
Racemic;tt	7,7	4,4	4,4
Racemic;gg	105,105	105,105	105,105
Racemic;tg	20,92	21,94	19,92

Table IV
Partition Functions, Average Energies, and Preexponential Factors for the Respective Conformations[a,b]

State	z_ξ	$\langle E_\xi \rangle$, kcal mol^{-1}	α_ξ
	σ = 3.9 Å		
Meso;tt	0.11	1.38	1.16
Meso;tg	0.66	0.14	0.83
Meso;gg	0.011	2.81	1.21
Racemic;tt	1.0	0	1.0
Racemic;tg	0.040	2.09	1.36
Racemic;gg	0.098	1.35	0.95
	$\sigma = \infty$		
Meso;tt	0.32	0.76	1.17
Meso;tg	0.28	0.73	0.95
Meso;gg	0.003	3.72	1.41
Racemic;tt	1.0	0	1.0
Racemic;tg	0.018	2.62	1.51
Racemic;gg	0.027	2.22	1.12

[a] All values are relative to the racemic;tt state. [b] The calculations were carried out for a temperature of 300 K.

Equations 1–4 were employed in the following calculations, $E_{\omega''}$ and E_η being adjusted within the stated limits as required to achieve agreement with experiments.

Characteristic Ratios

Limiting values of the characteristic ratio C_∞ were calculated using the matrix generation procedures (see eq 10–15 of the preceding paper). Rotational states were taken at φ_t = 10° and φ_g = 110°. The statistical weight parameters were evaluated according to eq 1–4 for a temperature of 300 K. In Figure 4 values of C_∞ for isotactic PMA are plotted against $E_{\omega''}$ for the several values of E_η indicated. Characteristic ratios calculated for syndiotactic PMA are plotted against E_η in Figure 5. For the same values of E_η and $E_{\omega''}$, the characteristic ratios for isotactic and for syndiotactic PMA are very close to those for polystyrene (compare Figures 6 and 7 of the preceding paper[1]). This follows from the fact that other parameters are nearly the same. Explanations of the effects of E_η and $E_{\omega''}$ on C_∞ for polystyrene[1] are, therefore, immediately applicable to PMA.

Characteristic ratios C_∞ for PMA are plotted in Figure 6 against the stereochemical composition expressed by the fractions w_m of meso dyads for the several values of E_η and $E_{\omega''}$ indicated. At intervals of 0.2 in w_m over the atactic range, ten chains of 200 units were generated by Monte Carlo methods, their stereochemical configurations being assigned according to Bernoullian statistics. The curves connect the averages for each such set of ten chains. Values

Table V
Energies and Preexponential Factors Associated with the Statistical Weights

	Energies in kcal mol^{-1}			
σ, Å	E_η	E_ω	$E_{\omega'}$	$E_{\omega''}$
3.9	−0.67	1.64	1.60	1.56
∞	−1.11	1.63	1.64	0.89
	Preexponential factors			
	η_0	ω_0	ω_0'	ω_0''
3.9	1.04	1.32	1.43	1.19
∞	0.96	1.27	1.44	1.20

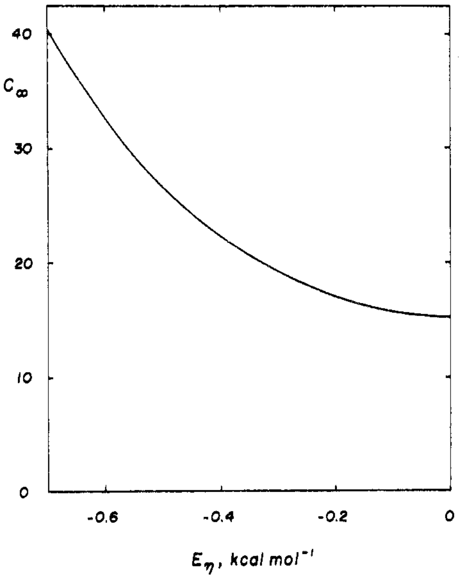

Figure 5. Dependence of C_∞ on E_η for syndiotactic PMA at T = 300 K; φ_t = 10° and φ_g = 110°.

of C_∞ for the stereoregular polymers are taken from Figures 4 and 5.

PMA prepared by radical polymerization is about 50% isotactic according to the NMR studies of Matsuzaki et al.[8] Experimental results[9-11] on chain dimensions of atactic PMA thus prepared give $C_\infty \approx 8.4 \pm 0.5$. Numerical calculations show that a value of E_η in the range −0.4 to −0.1 kcal mol^{-1} is required in order to yield a characteristic ratio consistent with these experimental results, assuming that $w_m = 0.5 \pm 0.1$ and that $E_{\omega''}$ is within the limits stated above.

Stereochemical Equilibrium in Oligomers of PMA

The equilibria between the diastereomers of 2,4-dimethoxycarbonylpentane (x = 2) and between those of 2,4,6-trimethoxycarbonylheptane (x = 3) were calculated according to previous methods.[12] In Figure 7 the fraction f_m of meso dyads in the dimer at equilibrium at 25°C is plotted as a function of $E_{\omega''}$ for several values of E_η. The fractions F_I, F_H, and F_S of isotactic, heterotactic, and syndiotactic triads, respectively, in the trimer at stereochemical equilibrium at 25°C are plotted in Figure 8 against $E_{\omega''}$ for the values of E_η indicated. All parameters used in these calculations were evaluated according to eq 1–4.

Experimental values for the equilibrium compositions of the diastereomers of the dimeric and trimeric homologs at T = 25°C in methanol as reported by Clark[13] are: $f_m = 0.45_5 \pm 0.01$ for x = 2; and $F_I = 0.19_8 \pm 0.01$, $F_H = 0.50_9 \pm 0.01$ and $F_S = 0.29_3 \pm 0.01$ for x = 3. The result for f_m when x = 2 requires that $E_\eta \leq -0.3$ kcal mol^{-1} for values of $E_{\omega''}$ within the plausible range, which is covered in Figure 7. The results for x = 3 require that $E_\eta \leq -0.2$ kcal mol^{-1}. Consistency of the calculated values with the experimental data within the limits of its accuracy imposes strong restrictions on $E_{\omega''}$ once a value for E_η is chosen. Calculated values for dyad and triad compositions at stereochemical equilibrium are listed in Table VI. Agreement between cal-

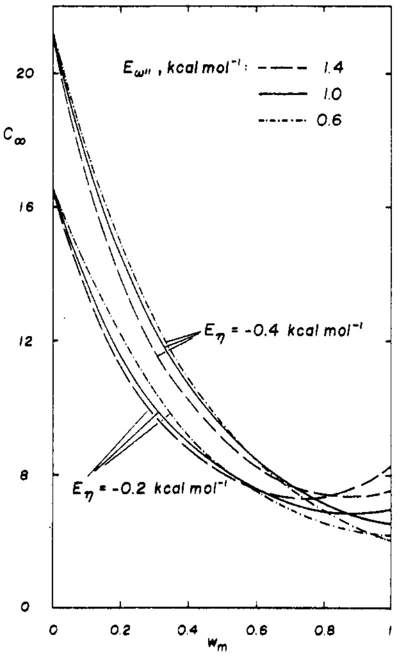

Figure 6. Characteristic ratios calculated for Monte Carlo chains of 200 units for the combinations of E_η = −0.2 or −0.4, and $E_{\omega''}$ = 0.6, 1.0, or 1.4 in kcal mol^{-1}; T = 300 K; φ_t = 10° and φ_g = 110°.

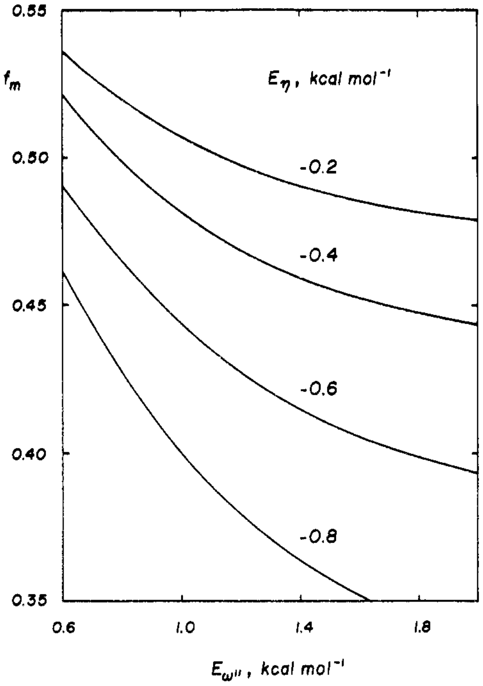

Figure 7. Fraction f_m of meso dyads in the dimer (x = 2) at stereochemical equilibrium as functions of E_η and $E_{\omega''}$ in kcal mol^{-1}; T = 25°C.

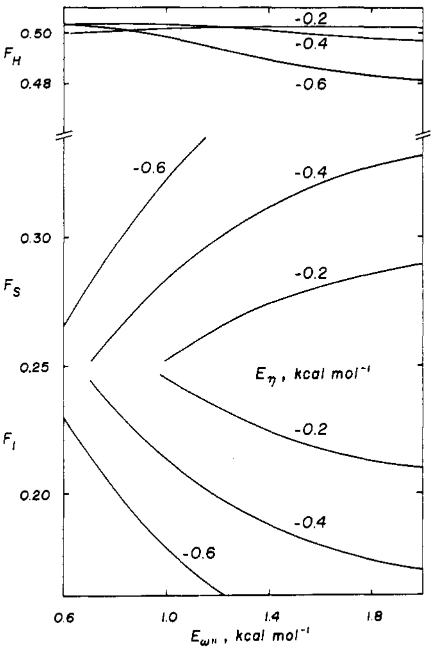

Figure 8. Fractions F_I, F_H, and F_S of isotactic, heterotactic, and syndiotactic triads for the trimer ($x = 3$) at stereochemical equilibrium, respectively, as functions of E_η and $E_{\omega''}$; $T = 25$°C.

Table VI
Calculated Dyad and Triad Compositions at Stereochemical Equilibrium at 25°C[a]

E_η[b]	$E_{\omega''}$[b]	f_m ($x = 2$) (0.455 ± 0.01)[c]	F_I ($x = 3$) (0.198 ± 0.01)[c]	F_S ($x = 3$) (0.293 ± 0.01)[c]
−200	800	0.520	0.261	0.238
	1200	0.498	0.233	0.265
	1600	0.486	0.218	0.281
	2000	0.479	0.209	0.290
−400	800	0.499	0.233	0.263
	1200	0.470	0.199	0.299
	1600	0.453	0.180	0.321
	2000	0.444	0.170	0.333
−600	800	0.466	0.201	0.296
	1200	0.428	0.162	0.344
	1600	0.405	0.140	0.373
	2000	0.394	0.129	0.390

[a] Calculated with parameters from eq 1–4. [b] Energies in cal mol^{-1}. [c] Experimental values from ref 13 are given in parentheses.

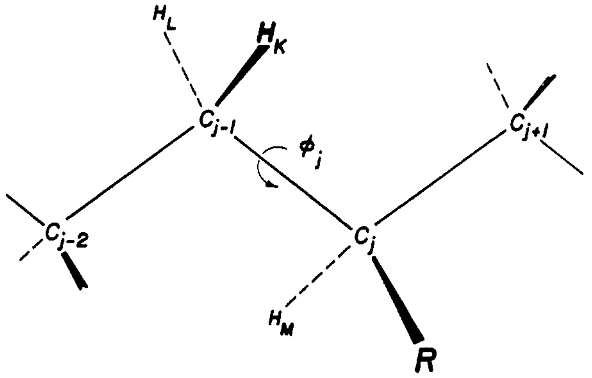

Figure 9. Designations of methine and methylene protons of PMA.

culated and experimental values occurs for $E_{\omega''} \approx 1000$ cal mol^{-1} at $E_\eta = -600$ cal mol^{-1}, for $E_{\omega''} \approx 1400$ cal mol^{-1} at $E_\eta = -400$ cal mol^{-1}, and for $E_{\omega''} > 2000$ cal mol^{-1} at $E_\eta = -200$ cal mol^{-1}.

The limitations imposed on E_η by the experimental results on chain dimensions of atactic PMA, as discussed in the preceding section, together with the restrictions stated above, suggest that $-0.3 \geq E_\eta \geq -0.4$ kcal mol^{-1}. This value is in agreement with all experimental data on chain dimensions discussed above. From the values in Table VI we conclude that $E_{\omega''} = 1.5 \pm 0.3$ kcal mol^{-1}.

NMR Coupling Constants

Experimental data on the vicinal coupling constants in the proton magnetic resonance spectra of 2,4-dimethoxycarbonylpentane and 2,4,6-trimethoxycarbonylheptane are available from the work of Doskočilová et al.[14] Results are reported for the isotactic polymer by Yoshino et al.[15] and Matsuzaki et al.[16]

The quantity deduced directly from the proton NMR spectra is the difference ΔJ between the conformationally averaged vicinal coupling constants for pairs of protons that are anti and syn, i.e., $\Delta J = \langle J_{\text{anti}} \rangle - \langle J_{\text{syn}} \rangle$. Two protons are syn if they lie on the same side of the backbone plane in the all-trans conformation, and anti if they lie on opposite sides.[17] With the methine and methylene protons labeled as in Figure 9, $J_{\text{anti}} = J_{\text{KM}}$ and $J_{\text{syn}} = J_{\text{LM}}$. If the configuration of the methine group carrying H_M were reversed by interchanging R and H_M, then $J_{\text{anti}} = J_{\text{LM}}$ and $J_{\text{syn}} = J_{\text{KM}}$. In keeping with the usual procedure in such circumstances,[17,18] we assume that J depends only on the dihedral angle τ_φ between the two protons in question. In the foregoing two-state scheme, the vicinal coupling constant J_{anti} averaged over all conformations of C–C bond j is[19]

$$\langle J_{\text{anti}} \rangle_j = p_{\text{t},j} J_{\text{anti,t}} + p_{\text{g},j} J_{\text{anti,g}} = p_{\text{t},j}(J_{\text{anti,t}} - J_{\text{anti,g}}) + J_{\text{anti,g}} \quad (5)$$

where $J_{\text{anti,t}}$ and $J_{\text{anti,g}}$ are the coupling constants in the trans and gauche state, respectively, and $p_{\text{t},i}$ and $p_{\text{g},i}$ are the corresponding a priori probabilities.[20] For $\varphi_\text{t} = 10°$ and $\varphi_\text{g} = 110°$, the dihedral angles between the anti protons are $\tau_{\text{anti,t}} = 170°$ and $\tau_{\text{anti,g}} = 70°$. Analogously we write

$$\langle J_{\text{syn}} \rangle_j = p_{\text{t},j}(J_{\text{syn,t}} - J_{\text{syn,g}}) + J_{\text{syn,g}} \quad (6)$$

Then

$$\Delta J = p_{\text{t},j}(\Delta J_\text{t} - \Delta J_\text{g}) + \Delta J_\text{g} \quad (7)$$

where $\Delta J_\text{t} = J_{\text{anti,t}} - J_{\text{syn,t}}$ and $\Delta J_\text{g} = J_{\text{anti,g}} - J_{\text{syn,g}}$. With $\varphi_\text{t} = 10°$ and $\varphi_\text{g} = 110°$, it follows that $\Delta J_\text{g} = -\Delta J_\text{t}$ and

$$\Delta J = \Delta J_\text{t}(2p_{\text{t},j} - 1) \quad (8)$$

The ΔJ_t can be evaluated from the Karplus equations[21] or otherwise.[14,17,18]

In Table VII experimental results from the indicated sources are compared with calculations according to eq 8 with $\Delta J_\text{t} = 10$ Hz.[14,17,18] The probabilities were calculated by methods previously described.[20] Statistical weights were obtained from eq 1–4 with $E_\eta = -0.3 \pm 0.1$ kcal mol^{-1}, and $E_{\omega''} = 1.5 \pm 0.3$ kcal mol^{-1}. For $x = 3$ the observed and calculated quantities are the mean values for C–C bonds 2 and 3, or 4 and 5 in the case of a symmetric triad. For the unsymmetric triad mr, the dyad of reference is marked with an asterisk in Table VII. The agreement between experiment and calculations is satisfactory, in view of the experi-

Table VII
NMR Coupling Parameter $\Delta J = \langle J_{\text{anti}} \rangle - \langle J_{\text{syn}} \rangle$

x	Stereo-configuration	T, °C	ΔJ, Hz		$10^2 \mathrm{d}\Delta J/\mathrm{d}T$, Hz K^{-1}	
			Exptl	Calcd	Exptl	Calcd
2	m	26	1.0[a,d]	0.6 ± 0.5		
	r	20	3.6[a,e]	4.2 ± 1.3	−2.8	−1.5 ± 0.4
3	mm[h]	26	1.6[a,d]	0.9 ± 0.6		
	m*r[h,i]	26	1.0[a,d]	0.8 ± 0.5		
	r*m[h,i]	26	5.0[a,d]	6.2 ± 1.0		
	rr[h]	26	3.8[a,d]	5.4 ± 0.8	−1.2	−0.9 ± 0.2
∞	$(\mathrm{m})_\infty$	25	1.3[b,e]			
		25	1.9[b,f]	1.9 ± 0.6		
		25	2.5[b,g]			
		140	1.2[c,d]	2.2 ● 0.8		

[a] D. Doskočilová, S. Sýkora, H. Pivcová, B. Obereigner, and D. Lim, *J. Polym. Sci., Part C*, 23, 365 (1968). [b] T. Yoshino, Y. Kikuchi, and J. Komiyama, *J. Phys. Chem.*, 70, 1059 (1966). [c] K. Matsuzaki, T. Uryu, A. Ishida, and M. Takeuchi, *J. Polym. Sci., Part C*, 16, 2099 (1967). [d] In *o*-dichlorobenzene. [e] In chloroform. [f] In methyl formate. [g] In benzene. [h] In the trimer the mean values for C–C bonds 2 and 3 (or 4 and 5) are listed. [i] An asterisk denotes the dyad that gives rise to the ΔJ in the heterotactic trimer.

mental inaccuracies and the simplifications employed above.

Acknowledgment. This work was supported by the National Science Foundation, Grant No. DMR-73-07655 A01.

References and Notes

(1) D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8**, 776 (1975).
(2) U. W. Suter and P. J. Flory, *Macromolecules*, **8**, 765 (1975).
(3) H. J. M. Bowen and L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions", The Chemical Society, London, 1958.
(4) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933); R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936); J. M. O'Gorman, W. Shand, and V. Schomaker, *J. Am. Chem. Soc.*, **72**, 4222 (1950); J. K. Wilmshurst, *J. Mol. Spectrosc.*, **1**, 201 (1957); R. F. Curl, *J. Chem. Phys.*, **30**, 1529 (1959).
(5) S. Dirlikov, J. Štokr, and B. Schneider, *Collect. Czech. Chem. Commun.*, **36**, 3028 (1971).
(6) P. R. Sundararajan and P. J. Flory, *J. Am. Chem. Soc.*, **96**, 5025 (1974).
(7) D. A. Brant, W. G. Miller, and P. J. Flory, *J. Mol. Biol.* **23**, 47 (1967).
(8) K. Matsuzaki, T. Uryu, A. Ishida, T. Ohki, and M. Takeuchi, *J. Polym. Sci., Part A-1*, **5**, 2167 (1967).
(9) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).
(10) K. Karunakaran and M. Santappa, *J. Polym. Sci., Part A-2*, **6**, 713 (1968).
(11) H. Matsuda, K. Yamano, and H. Inagaki, *J. Polym. Sci., Part A-2*, **7**, 609 (1969).
(12) P. J. Flory, *J. Am. Chem. Soc.*, **89**, 1798 (1967).
(13) H. G. Clark, *J. Polym. Sci., Part C*, **16**, 3455 (1968).
(14) D. Doskočilová, S. Sýkora, H. Pivcová, B. Obereigner, and D. Lím, *J. Polym. Sci., Part C*, **23**, 365 (1968).
(15) T. Yoshino, Y. Kikuchi, and J. Komiyama, *J. Phys. Chem.*, **70**, 1059 (1966).
(16) K. Matsuzaki, T. Uryu, A. Ishida, and M. Takeuchi, *J. Polym. Sci., Part C*, **16**, 2099 (1967).
(17) T. Moritani and Y. Fujiwara, *J. Chem. Phys.*, **59**, 1175 (1973).
(18) F. A. Bovey, F. B. Hood III, B. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).
(19) H. S. Gutowsky, G. G. Belford, and P. B. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).
(20) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969, Chapter III.
(21) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

Electric Transport for Aqueous Solutions of Sodium Alginate and Sodium Polygalacturonate

Fred M. Tuffile and Paul Ander*

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079.
Received March 31, 1975

ABSTRACT: The electrical conductances and transport numbers were determined in aqueous solutions at 25° for sodium alginate and sodium polygalacturonate at several concentrations. The measurements indicated that the sodium polygalacturonate has a greater degree of dissociation than does the sodium alginate even though the latter has a smaller charge density. Measurements of the conductances of aqueous sodium chloride solutions of these polyelectrolytes at several concentrations of simple salt and of polyelectrolyte resulted in higher conductances for the sodium polygalacturonate solutions over the whole concentration range. A comparison of the electrophoretic mobilities at 0°C for both polyelectrolytes resulted in higher values obtained with the sodium polygalacturonate. The data were correlated with Manning's theory of polyelectrolyte solutions.

Ionic polysaccharides of both plant and animal origin appear to be of lesser interest for study than proteins and nucleic acids, yet they are of importance in all living matter. With our interest in the interaction of small ions with polyelectrolytes, we report the results of electric transport at 25° obtained using the sodium salts of alginic acid and polygalacturonic acid in aqueous solution with and without NaCl present and the electrophoretic mobilities at 0°C of both polyelectrolytes in NaCl. It was of interest to compare the solution properties of sodium alginate (NaAlg) and sodium polygalacturonate (NaPGal) because they are stereoisomers with different spacings of their pendant carboxyl groups.[1-5] Alginic acids are linear copolymers of D-mannuronic acid and L-guluronic acid[6-9] and their x-ray patterns have been studied.[10,11] Polygalacturonic acid is a linear homopolymer of D-galacturonic acid derived from pectins.[12] It has been shown that pectic acid and sodium pectates of different origin have the same distance per pyranose unit.[1,2]

Experimental Section

Materials. The sodium alginate sample used in this study was a gift of the Kelco Co. This material, KNLV-6573, although of high purity, was further purified by the method described by Haug and Smidsrod.[13,14] The purification process involved three successive ethanol (95%) precipitations. The amount of calcium or magnesium in the samples was determined using a Techtron AA4 Atomic Absorption Spectrophotometer. The purification reduced the concentration of Ca^{2+} and Mg^{2+} ions to less than 0.05%. The sodium