Conformations in partly ionized poly(methacrylic acid): 2. Unperturbed dimensions of syndiotactic chains*

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(Received 9 July 1979)

A rotational isomeric state model for the half-ionized syndiotactic polymethacrylate chain is described. The coupling of adjacent carboxylate groups by acid-salt hydrogen bonds suggests a model having a structural unit of 4 skeletal bonds. Energy calculations suggest that the skeletal bonds 1 and 2 between the coupled carboxylate groups adopt displaced *tt* locations at ~(–8°, –8°) and the carboxylate groups are rotated ~30° from the plane which bisects the skeletal angle at the C_α atom. The carboxylate rotations give rise to displacements of about 15° in the *t* and *g* states of bonds 3 and 4 although they do not affect the *gg* location which remains at (120°, 120°). Agreement between the computed characteristic ratio, C_∞, for the syndiotactic chain and the experimental value of ~15 for the half-ionized 'conventional chain' is obtained if the energies of *tg* and *gg* states in bonds 3 and 4 exceed *tt* by 1.0–1.5 kcal mol^{-1}. It is assumed that the unionized polyacid in aqueous solution is of similar conformational character to poly(methyl methacrylate) and has C_∞ = ~8. The computed dimensions of copolymers of unionized and ionized units prescribe a sigmoidal form for C_∞ vs. α over the range $0 < \alpha < 0.5$. It is suggested that hydrophobic interactions are not required to account for the conformational transformation.

INTRODUCTION

The conformational transition which is observed on progressive ionization of poly(methacrylic acid) is characterized by a sigmoidal form of the increase in chain dimensions with degree of ionization, α. As reported extensively in the literature, a 'coiled form' exists over the range $0 < \alpha <$ ~0.2 beyond which there is a more rapid increase in molecular dimensions with ionization and the greater part of the molecular expansion has occurred when the polyacid is 50% ionized. Added electrolyte suppresses chain dimensions over the full range of neutralization but even in the presence of high concentrations of electrolyte the conformational transition is still apparent in dilute solution viscosities[1]. This behaviour contrasts with that observed on ionization of poly(acrylic acid) where no such postponement of the molecular expansion occurs[2].

These observations have led to the postulation of various mechanisms for stabilization of the 'coiled form' including intramolecular hydrogen bonding[3] and hydrophobic bonding[4]. However, the experimental evidence that is available suggests that the 'coiled form' is not significantly more coiled in the presence of electrolytes or dilute acid than other structurally related polymethacrylates. The well-known dilute solution viscosity–molecular weight relationship of Katchalsky and Eisenberg[5] viz:

$$[\eta] = 6.6 \times 10^{-4} M^{0.50}$$

applies to solutions in 0.002 N HCl at 30°C in which ionization of the polyacid should be suppressed.

From the value of the exponent of M it may be assumed that the unionized polyacid assumes unperturbed dimensions. Application of the Flory–Fox relation[6] yields a value of 7.6 for the characteristic ratio $C_\infty = \langle r^2 \rangle / nl^2$ where $\langle r^2 \rangle_0$ is the unperturbed mean-square end-to-end distance of a chain of n bonds ($n \rightarrow \infty$) each of length l. Literature values[7] for characteristic ratios of poly(methyl methacrylate) in various solvents range between 7.3 and 8.0; values for poly(ethyl methacrylate) and poly(n-butyl methacrylate) are 7.6 and 7.9, respectively, in butanone/propanol mixtures at 23°C. Since only random fluctuations between local conformational states are necessary to account for the unperturbed dimensions of the non-aqueous polymers, the similar value for the unperturbed dimensions of unionized poly(methacrylic acid) in aqueous solutions suggests that the dimensions of this polymer may be accounted for in similar terms.

The apparent absence of a strong dependence of the unperturbed dimensions on the size of the substituent on the carboxylic side group is not unexpected from the conformational analysis of the poly(methyl methacrylate) chain by Sundararajan and Flory[9]. A principal factor in determining the conformational character of this chain is the accumulation of strong repulsive interactions of second order in all conformational states between the methylene or methyl groups and the carbonyl carbon atoms which are directly bonded to the C_α atoms*. These interactions result in large values for the skeletal bond angles at the methylene groups of about 122° while the skeletal angles at the C_α atoms remain essentially unstrained with values of about 110°.

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* Presented in part at 8th Europhysics Conference on Macromolecular Physics, Bristol, UK, 18–22 September 1978

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* The well-established practices of using the letter α to denote the degree of ionization and to label the carbon atom immediately bonded to a carboxyl group, C_α, have been adopted in this discussion. These unrelated uses of the same symbol should not be confused.

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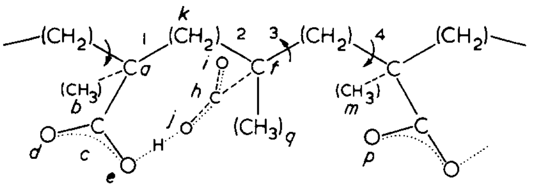

Figure 1 The 4-bond structural unit of the unperturbed syndiotactic polymethacrylate chain, $\alpha = 0.5$. Letters refer to particular atoms mentioned in the text

In Part 1 (ref 10) we have presented spectroscopic evidence for the formation of ionic hydrogen bonds between carboxylate groups across racemic dyads in partly ionized poly(methacrylic acid). In this paper are reported computations of conformational energies and unperturbed chain dimensions of half-ionized syndiotactic polymethacrylate chains. A 4-bond repeating unit incorporating an ionic hydrogen bond across one dyad is assumed. Computations of the dimensions of copolymer chains of these units with unionized units which are assumed to have similar conformational features to poly(methyl methacrylate) units are also discussed. These computations therefore describe the form of the change in dimensions with ionization over the range of α within the conformational transition in poly(methacrylic acid) is observed.

CONFORMATIONAL ENERGIES

Computational parameters and stereochemical conventions

The repeating unit of the half-ionized syndiotactic chain is shown in *Figure 1*. It comprises two racemic dyads. An ionic hydrogen bond couples carboxylate groups across the 1,2 dyad fixing the skeletal bonds in conformations close to *trans–trans* rotational states. However, hindered rotations are still possible about bonds 3 and 4. The 3,4 dyad is shown in the *trans–trans* state in *Figure 1*. The hydrogen bond is assumed to be symmetrical with the single negative charge delocalized across both carboxylate groups each oxygen atom bearing 0.25 of the electronic charge. Bond lengths and bond angles are given in *Table 1*. Data for lengths and angles between carbon atoms only are taken from those for poly(methyl methacrylate)[9] and data for the carboxylate side groups are taken from the review by Speakman[11] of acid–carboxylate hydrogen-bonded salts.

Conformational energies were computed at 5° intervals of the skeletal rotation angles for each dyad following the procedures adopted by Sundararajan and Flory[9]. Three-fold intrinsic torsional potentials given by $E_I = E_0(1 - \cos 3\phi)/2$ with barrier heights E_0 of 2.8 and 1.0 kcal mol^{-1} were assigned to rotations ϕ about the C—C bonds of the skeletal backbone and the C_α to carboxylate group (i.e. *a–c* in *Figure 1*), respectively. (The latter assignment may be somewhat high for the ionized side group. Eberson[12] considers that the C—C bond in the acetate ion should have very low barriers to rotation. If so, the 1,2 dyad may have a slightly lower energy than these computations suggest.) The non-bonded interaction energy was evaluated from the Lennard-Jones function,

$$E_{ij} = (A_{ij}/R_{ij}{}^{12}) - (B_{ij}/R_{ij}{}^{6})$$

for each pair of interacting atoms or groups having interatomic or intergroup distances R_{ij} given by the sum of the van der Waals radii. The B_{ij} were evaluated from the Slater–Kirkwood formula[13] using the atom or group polarizabilities and the effective numbers of electrons given in *Table 1* of ref 9. The carboxylate oxygens were assumed to be equivalent to the carbonyl oxygen of the ester group and the delocalized electron (one quarter to each oxygen atom) was ignored for this purpose. The A_{ij} were evaluated at the minimum value of E_{ij} (i.e. $A_{ij} = B_{ij}R_{ij}{}^6/2$). The Coulombic energy, E_c was estimated from the expression

$$E_c = \sum_i \sum_j (332\, \delta_i \cdot \delta_j / R_{ij} \cdot D) \text{ kcal mol}^{-1}$$

where δ_i and δ_j are the charges assigned to the oxygen atoms concerned. The assignment of 0.25 of electronic charge to each oxygen atom is probably a greatly over-simplified description of the charge distribution across the hydrogen bond and the uncertainty in the value of the effective dielectric constant D gives rise to further difficulties in obtaining accurate estimates of Coulombic interactions. However, these uncertainties do not affect the main conclusions to be drawn from this analysis of the essential conformational characteristics of the chain. A value of 3.5 was used for the effective dielectric constant as recommended by Brant *et al.*[14] for polypeptide systems. The energy of deformation in C_α—C—C_α skeletal angles was estimated from $V = F(\Delta\Theta)^2$ where F is half the force constant and $\Delta\Theta$ is the angular deformation in radians. Adopting the values for these parameters chosen by Sundararajan and Flory[9] for poly(methyl methacrylate) (F = 80 kcal mol^{-1} and C_α—C—C_α = 122°) an energy of 3.8 kcal mol^{-1} is contributed to the total energy in each dyad by skeletal angle deformation.

Following the convention adopted by Flory and coworkers[15] enantiomeric bonds are differentiated by viewing all bonds from the C_α atom towards the methylene group regardless of direction of progression along the chain. Thus we define a *d* bond as having the disposition of groups shown for bonds 1 or 2 in *Figure 1*. Bonds 3 and 4 are therefore represented as *l* bonds in *Figure 1*. A syndiotactic chain therefore comprises . . . *l* |*dd* |*ll* |*dd* |*l* . . . sequences where vertical lines denote C_α atoms. Positive rotations are clockwise about *d* bonds and anticlockwise about *l* bonds. The carboxylate side group rotation angle is zero when the oxygen atoms (*i* and *j*) are coplanar with the methyl group (*q*) and the C_α atom (*f*). We define a positive rotation of a side group with respect to a *d* skeletal bond as a clockwise rotation of the C_α—carboxyl carbon bond (*a* – *c*) and a positive side group rotation with respect to an *l* skeletal bond is given by an anticlockwise rotation of the corresponding bond. Thus hydrogen bond formation between adjacent carboxylate groups requires positive side group rotations with negative rotations of the intervening skeletal bonds 1 and 2, the latter being within the *trans–trans* domain.

Table 1 Geometrical parameters used in conformational energy calculations for the half-ionized polymethacrylate unit shown in *Figure 1*

Bond lengths (nm)		Bond angles (degrees)	
C_α–CH_2	0.153	CH_2–C_α–CH_2	110.0
C_α–CH_3	0.153	C_α–CH_2–C_α	122.0
C_α–CO_2	0.152	CH_2–C_α–CO_2	109.5
C$\overset{...}{-}$O	0.126	CH_2–C_α–CH_3	109.5
		C_α–C$\overset{...}{-}$O	117.5

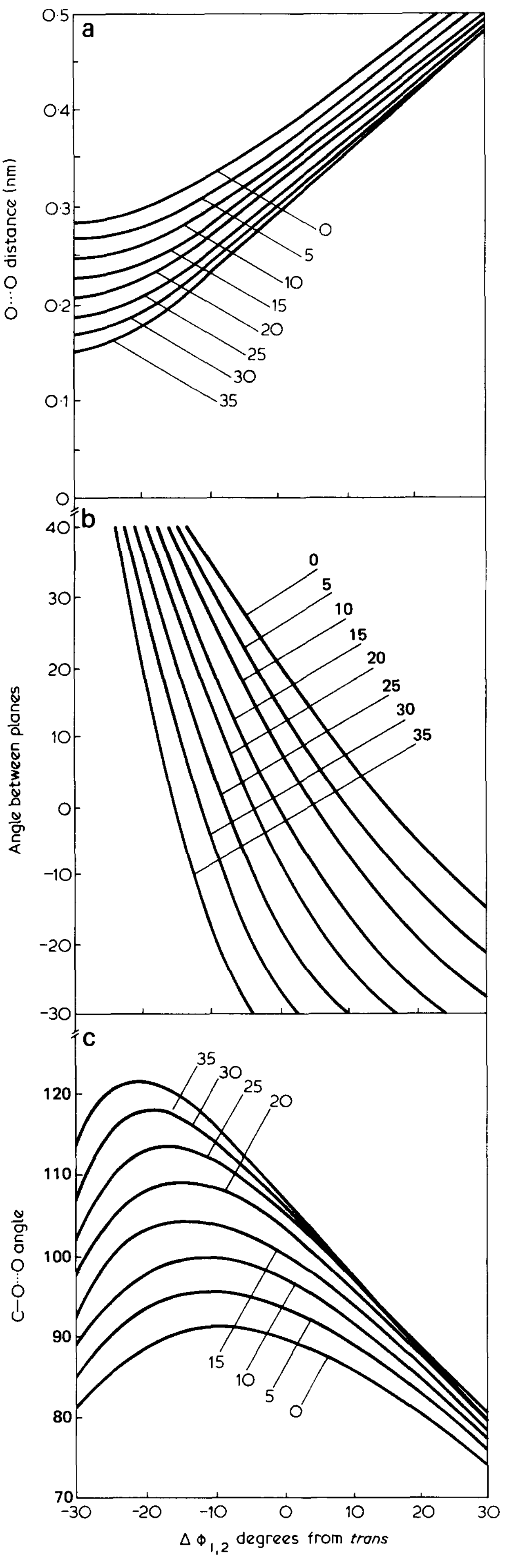

Figure 2 Optimum skeletal backbone and carboxylate rotation angles for the ionic hydrogen bond in the 1,2 dyad. (a) Oxygen—oxygen distances; (b) coplanarity (angle between planes defined by *cek* and *hjk* in *Figure 1*); (c) linearity (C—O ·········O angle is commonly ~114° in carboxylic acid—carboxylate hydrogen bonds[11]). The curves are labelled with carboxylate rotation angles

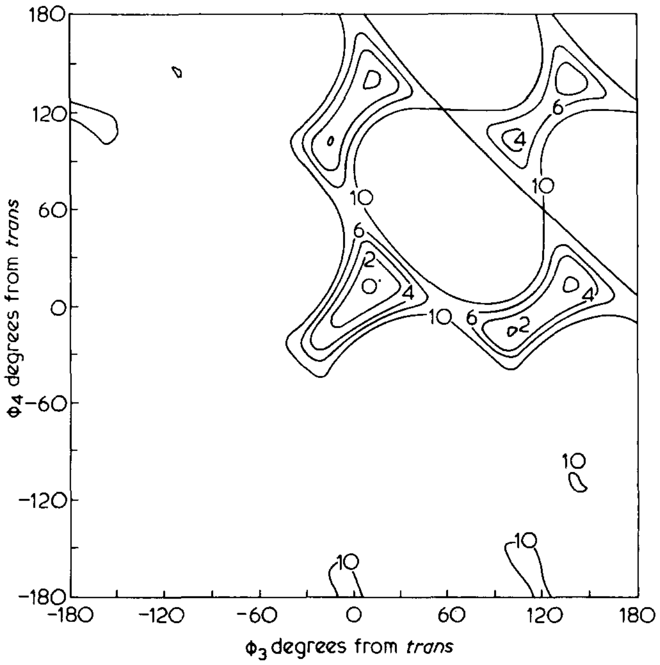

Figure 3 Conformational energies for a hypothetical racemic dyad with carboxylate rotation angles of 0° and 0.25 of electronic charge assigned to each oxygen atom. Minimum energy = 18.5 kcal mol^{-1}. The labels refer to contour heights (kcal mol^{-1}) above the minimum energy

Geometry of the ionic hydrogen bond

A model readily shows that coupling of adjacent carboxylate groups by a hydrogen bond is possible in the region of the low energy |*tt*| state of a racemic dyad[10]. According to Speakman[11] and McCoy[16] the oxygen ·········oxygen distance (*e*·········*j* in *Figure 1*) should be close to 0.245 nm and the carboxylate carbon and oxygen atoms (*c, d, e, h, i* and *j*) ideally should be coplanar. In this present case, coplanarity of all six atoms is not possible but if atoms *c, e, j* and *h* are coplanar the outer oxygens, *d* and *i* are only slightly displaced on opposite sides of the plane. Linearity of the hydrogen bond is also desirable and a measure of the linearity is obtained from the value of the angle C—O ·······O (*cej*). This angle commonly lies between 112° and 114° in the crystalline acid-salts reviewed by Speakman.

The effect of side group and backbone rotations on these three geometrical criteria is illustrated in *Figures 2a–c*. The rotation angles quoted apply to both side groups and both skeletal bonds within the dyad. The coplanarity of the hydrogen bond (*Figure 2b*) is measured by the closeness of approach to zero of the angle between the plane containing *hjk* and that containing *cek*. Thus the three geometric criteria are met reasonably well by side-group rotations of between 25° and 30° and backbone rotations of between −8° and −10°.

Conformational energy calculations

The energy map in *Figure 3* describes conformational energy minima for a dyad of a hypothetical syndiotactic chain in which each carboxylate group carries half an electronic charge and side group rotation angles are zero. Since

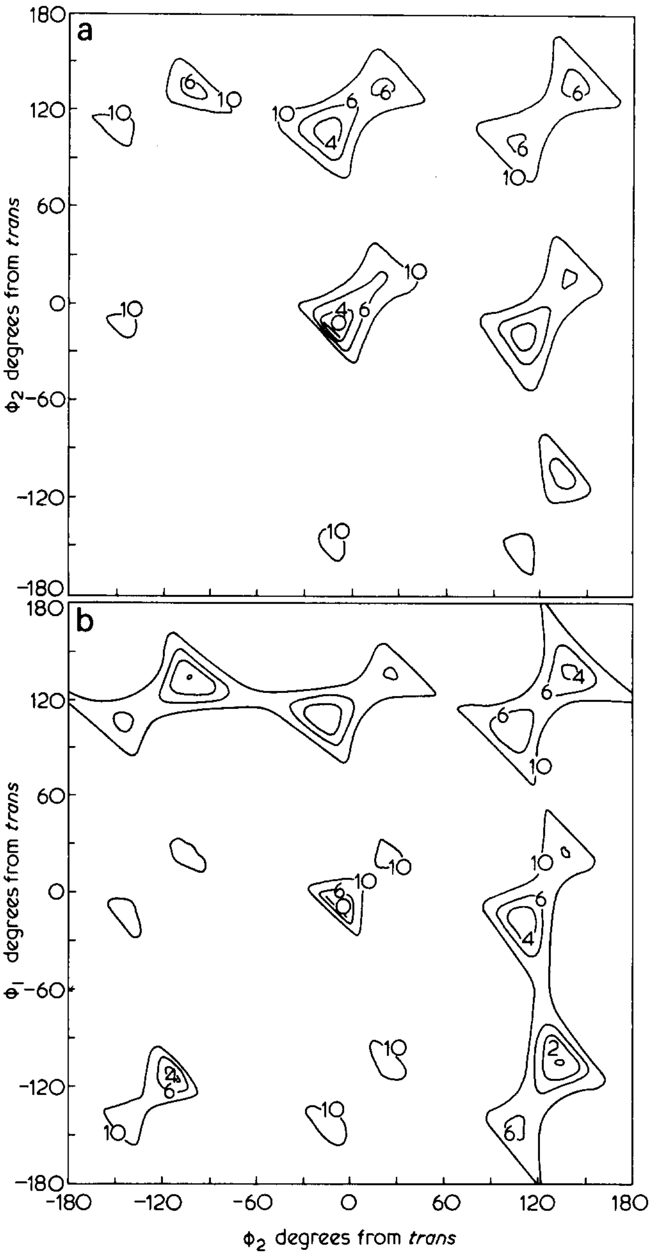

Figure 4 Conformational energies for the 1,2 dyad. (a) Carboxylate rotation angle = 20°; minimum energy = 16.0 kcal mol^{-1}; (b) carboxylate rotation angle = 30°; minimum energy = 17.6 kcal mol^{-1}. Oxygen–oxygen interactions have been disregarded for O······O distances between 0.24 and 0.25 nm and an energy contribution from the ionic hydrogen bond has not been included. The labels refer to contour heights (kcal mol^{-1}) above the minimum energy

the hydrogen bonding energy has not been included the energy map describes the 1,2 dyad or the 3,4 dyad.

The locations and shape of the domains of the energy minima are similar to those for the corresponding dyad of poly(methyl methacrylate)[9]. However the overall energy is higher in the ionized dyad. For zero side group rotation the increase is principally the result of two factors.

(i) Ionization causes changes in the C_α–C–O angles which bring about a decrease in the distance separating an oxygen atom and the methyl group attached to the same C_α (e.g. the $q \cdots j$ distance). Thus the distance of 0.270 nm separating the methyl and the carbonyl oxygen atom in the low energy side chain conformation of poly(methyl methacrylate) is reduced to 0.263 nm on ionization. Since both internuclear distances are well within the sum of their van der Waals radii (0.36 nm), ionization brings about an increase in the total energy from this source.

(ii) Ionization brings about an increase in the Coulombic energy principally in the region of the $|tt|$ minimum. However the separation of charges is greatest in the region of the $|gg|$ state (see *Figure 5* of Part 1) so that ionization effects a smaller increase in the energy of $|gg|$ states than $|tt|$ states with intermediate energy increases for $|tg|$ states. This assumes that for unperturbed chains the Coulombic interactions do not extend over more than six bonds along the chain. As pointed out by Sundararajan and Flory for poly(methyl methacrylate)[9], $\bar{g}$ conformations are inaccessible for side group rotations in the region 0° or 180° as a consequence of the severe overlaps between atoms of the carboxyl group and atoms bonded to the adjacent C_α atom.

Of particular interest are the shapes of the domains in the region of the energy minima. The *tg*, *gt* and *gg* states each have two minima located at displacements $\Delta\phi_1$, $\Delta\phi_2$ (or $\Delta\phi_3$, $\Delta\phi_4$ for zero side group rotations) of approximately ±15°, ±15° from rotation angles at zero or 120° which are adopted in the case of perfect staggering of tetrahedrally bonded atoms. Although the $|tt|$ state does not display two minima the computations suggest a trough of low energy on a diagonal extending from approximately (−15°, −15°) to (15°, 15°). The displacements from perfect staggering reduce the repulsive interactions between carbon atoms immediately bonded to each C_α atom on the same side of the plane defined by the two C_α atoms and the intervening methylene group of the dyad. For example in the $|tt|$ state, displacements of approximately ±15°, ±15° increase the internuclear separation of methyl group *m* to carboxyl carbon *h* from 0.28 to 0.31 nm. Similar increases are observed for corresponding adjustments in *tg*, *gt* and *gg* states.

However, considering the uncertainties in the computed energies, the approximate symmetry of the domains on each side of the locations for perfect staggering led Sundararajan and Flory to assign 0° and 120° to the *t* and *g* states in poly(methyl methacrylate). The same conclusions may be drawn from *Figure 3* for the hypothetical half-ionized polymethacrylate chain having zero carboxylate rotation angles.

Effect of carboxylate rotations on interactions within the 1,2 dyad

Figures 4a and *b* show the conformational energy as a function of rotation about bonds 1 and 2 in the region of the $|tt|$ minimum for side group rotations of 20° and 30°, respectively. In these energy maps, the total decrease in energy due to formation of the ionic hydrogen bond has not been taken into account. However, the repulsive interaction between the two oxygen atoms flanking the proton (*e* and *f*) which would arise in the absence of hydrogen bonding has been disregarded for oxygen ······oxygen separations of between 0.24 and 0.25 nm. For side group rotations up to ~20° there is a decrease in the minimum energy attributable at least in part to the decrease in the methyl–oxygen ($q \cdots j$) interaction (factor *i* discussed above). With further increase in rotation angle a rise in energy is apparent as the same oxygen atom (*j*) interacts with the methyl group *b* attached to the adjacent C_α atom. However, for side group rotations between 20° and 30° the minimum energy does not rise above its value at zero degrees. Thus the conclusions to be drawn from energetic considerations of interactions within the 1,2 dyad alone are in accord with the geometric analysis that the ionic hydrogen bond may form with side group rotations of between 25° and 30° and backbone rotations of between −8° and −10°.

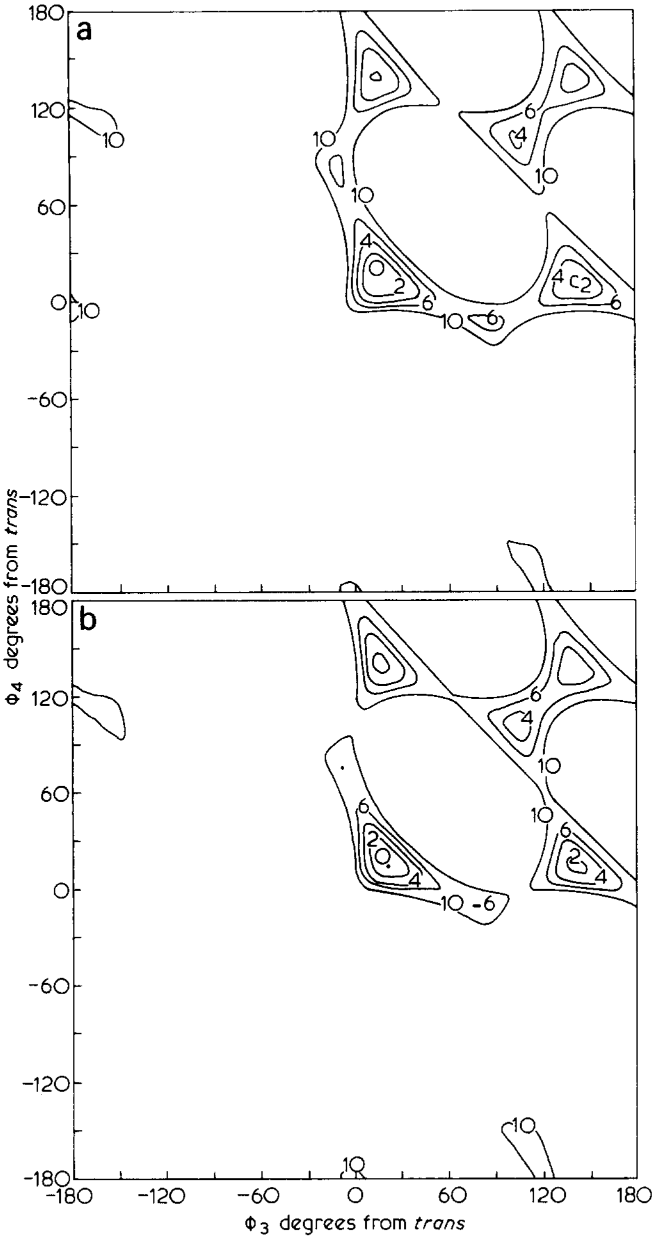

Figure 5 Conformational energies for the 3,4 dyad. (a) Carboxylate rotation angle = 20°; minimum energy = 18.2 kcal mol^{-1}; (b) carboxylate rotation angle = 30°; minimum energy = 18.8 kcal mol^{-1}. The labels refer to contour heights above the minimum energy

Effect of side group rotations on interactions within the 3,4 dyad

Figures 5a and *5b* show conformational energy maps for a racemic dyad having side group rotations of −20° and −30°, respectively. These maps therefore describe the changes in energy of the several conformational states of bonds 3 and 4 which are consequent upon hydrogen bond formation across the 1,2 dyad. Side group rotations increase the oxygen ·······methyl interaction (i······m and p······q) within the 3,4 dyad. As *Figure 5* shows their effect is to reduce the size of the $|tt|$, $|tq|$ and $|gt|$ domains and to shift the energy minima within these domains from the staggered conformations to locations at more positive angles. However, there is little change in the minimum energies or in the relative sizes of the $|tt|$ and $|tg|$ (or $|gt|$) domains. Statistical weights, σ, for $|gt|$ relative to unity for $|tt|$ are given by:

$$\sigma = Z_{gt}/Z_{tt}$$

where Z_{gt} and Z_{tt} are the partition functions obtained from summation of the Boltzmann factors of the energies in excess of the $|tt|$ minima at 5° intervals over each domain. The computed values of σ are approximately constant over the range of carboxylate rotation angles from 0° to −30°, increasing from 0.05 to 0.07.

The average conformational energy $\langle E_{tg}\rangle$ is given by:

$$\langle E_{tg}\rangle = Z_{tg}^{-1} \sum_{\phi_3,\phi_4} E_{\phi_3,\phi_4} \exp(-E_{\phi_3,\phi_4}/RT) \begin{cases} -60 < \phi_3 < 60; \\ \;\;60 < \phi_4 < 180; \end{cases}$$

With $\langle E_{tt}\rangle$ analogously defined, the relative conformational energy for the tg state, E_σ, is given by:

$$E_\sigma = \langle E_{tg}\rangle - \langle E_{tt}\rangle$$

The temperature, T, is 300K throughout. For carboxylate rotations between 0° and −30° the computations yield values between 1.7 and 1.6 kcal mol^{-1} for E_σ.

The mean energy weighted skeletal rotation angles within the $|tg|$ and $|gt|$ domains are given by:

$$\langle\phi_3\rangle = Z_{tg}^{-1} \sum_{\phi_3,\phi_4} \phi_3 \exp(-E_{\phi_3,\phi_4}/RT \quad \begin{cases} -60 < \phi_3 < 60 \\ -60 < \phi_4 < 180; \end{cases}$$

with $\langle\phi_4\rangle$ analogously defined. For side group rotations of −30°, the computations prescribe locations of (18°, 18°) for $|tt|$ and (115°, 140°) for the $|tg|$ state.

The $|gg|$ state, however, is essentially unaffected by carboxylate rotations and its average location remains at the staggered conformation. The decrease in size of the $|tt|$ and $|tg|$ domains means that the probability of $|gg|$ should increase in relation to the other states. The statistical weight for the $|gg|$ state, ψ, is given by:

$$\psi = Z_{gg}/Z_{tt}$$

and the computations suggest that ψ increases from 0.006 to 0.02 as the carboxylate group rotates from 0° to −30°. The corresponding changes in E_ψ are from 2.9 to 2.7 kcal mol^{-1}.

EXPERIMENTAL AND COMPUTED CHARACTERISTIC RATIOS

There is little experimental data in the literature relating to the unperturbed dimensions of aqueous polymethacylate systems. In *Figure 6*, the result of Katchalsky and Eisenberg[5] for the unionized polyacid is included with results of Noda, Tsuge and Nagasawa[17] for polymethacrylate systems in 0.1 M sodium bromide solutions having degrees of ionization, α, between 0.2 and 0.8. The tacticities of the samples were not specified but 'conventional' polyacid preparations are found to be highly syndiotactic. (The sample used in the spectrophotometric work reported previously[10] comprised 80% of racemic dyads). The results of Noda and coworkers were obtained by extrapolation of $[\eta]/M^{1/2}$ vs. $M^{1/2}$ in accord with the procedures of Stockmayer and Fixman[18]. The experiments described previously suggest that ionic hydrogen bonds should survive to their maximum concentrations in 0.1 M sodium bromide so that the extrapolated

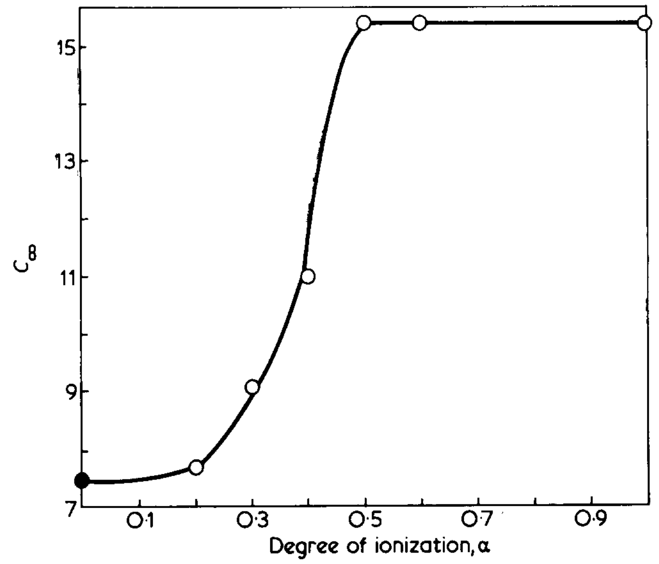

Figure 6 Experimental determinations of unperturbed dimensions of conventional polymethacrylate chains; ●, Katchalsky and Eisenberg[5] (30°C); ○, Noda, Tsuge and Nagasawa[17] (25°C)

values should correspond to the unperturbed dimensions of chains in which most carboxylate groups are involved in ionic hydrogen bonding. *Figure 6* reflects the form of the well documented variation of the reduced viscosity with degree of ionization particularly in high electrolyte concentrations[1] and of the corresponding changes in coild dimensions as measured by neutron scattering[19]. While these results are not representative of pure syndiotactic chains they should serve as a basis to test the proposed description of the conformational change on ionization of the syndiotactic polyacid.

Figure 6 suggests that the characteristic ratio increases sigmoidally from ~8 to about 15 over the range of α between zero and 0.5. We assume that, in theta conditions, the conformational character of the unionized polyacid may be described by a rotational isomeric state model essentially similar to that described by Sundararajan and Flory for poly(methyl methacrylate). Upon ionization, pairs of two-bond repeating units are converted into the four-bond structurally repeating units described above so that at half ionization the entire syndiotactic chain comprises such units.

Characteristic ratios were computed using the well-established methods developed by Flory and coworkers[15,20]. The unperturbed mean-square end-to-end distance $\langle r^2 \rangle_0$ for a chain of n bonds comprising the terminal bonds and x repeating units each of ξ bonds is given by

$$\langle r^2 \rangle_0 = 2Z^{-1} \mathscr{J}^* \mathscr{G}_0 \left(\prod_{K=1}^{x} \mathscr{G}_K^{(\xi)} \right) \mathscr{G}_n \mathscr{J}$$

Z is the conformational partition function; $\mathscr{G}_0$ and $\mathscr{G}$ are $\mathscr{G}$ matrices for the terminal bonds and $\mathscr{G}_K^{(\xi)}$ is the matrix product of the matrix for each bond within the Kth repeating unit, i.e.

$$\mathscr{G}_K^{(\xi)} = (\mathscr{G}_{\nu+1} \mathscr{G}_{\nu+2} \cdots\cdots \mathscr{G}_{\nu+\xi})$$

The formulations of $\mathscr{J}^*$, $\mathscr{J}$ and the $\mathscr{G}$(**U**,**T**) matrices and of the transformations **T** appropriate for syndiotactic chains are detailed in ref 15 and 20. Serial multiplication techniques were employed to yield characteristic ratios for chains of sufficient length to approximate the asymptotic values for infinite chains as indicated by the constancy of the results with successive doubling of the chain length to 8192 units.

In formulating statistical weight matrices for the unionized polyacid we assume that in aqueous solution this chain has similar conformational character to syndiotactic poly(methyl methacrylate). In this case $\xi = 2$ and following Sundararajan and Flory the two statistical weight matrices are formulated:

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \text{ and } \mathbf{U}'' = \begin{bmatrix} \beta & \gamma \\ \gamma & \gamma^2/\beta \end{bmatrix}$$

where **U**′ is the statistical weight matrix for skeletal bond pairs flanking an α carbon atom and **U**″ is for the dyad bond pair between successive α carbons. All first order interactions are included in the **U**″ matrix and $\bar{g}$ rotational states are excluded reducing the order of the **U** matrices to 2 x 2. The latter condition arises in poly(methyl methacrylate) from the severe interactions between ester oxygens and the groups bonded to the adjacent C_α atom when the ester side group is restricted to rotations of 0° or 180°. In adopting a similar 2 state model for the polyacid we assume that motions of the free acid side chains are similarly restricted as suggested by structural investigations[12]. (Side group rotations to ~60° may alleviate the interactions in the $\bar{g}$ state as noted above).

The foregoing analysis of the half-ionized chain ($\xi = 4$) shows that $\bar{g}$ states ($\phi \sim 240°$) are similarly inaccessible to bonds 3 and 4. However, in order to take full account of the lack of dependence on carboxylate side group rotations of the energy and mean skeletal bond rotation angle in the $|gg|$ state the latter is assigned to a discrete rotational state $|g^*g^*|$. Thus a model having 3 skeletal bond rotational states t, g and g^* is adopted. For non-zero values of the side group rotation angle, t and g states adopt discrete rotation angles $\Delta\phi$ and $120° + \Delta\phi$, respectively, whilst the g^* state remains at 120°. With bonds 1 and 2 fixed in *trans* locations by the ionic hydrogen bond, the statistical weight matrices for the half-ionized chain may be expressed:

$$\mathbf{U}_1 \begin{bmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} ; \mathbf{U}_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_3 = \begin{bmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \mathbf{U}_4 = \begin{bmatrix} 1 & \sigma & 0 \\ \sigma & 0 & 0 \\ 0 & 0 & \psi \end{bmatrix}$$

where σ is the statistical weight for $|tg|$ and $|gt|$ states of bonds 3 and 4 and ψ is the statistical weight for the $|g^*g^*|$ state. (Alternatively, since interdependence of rotational potentials about bonds 3 and 4 does not extend from one 4 bond unit to the next, the simplified computational methods normally employed for such chains[20] may be applied so that:

$$\mathbf{U}_1 = \mathbf{U}_2 = 1; \mathbf{U}_3 = [1 \ \ 1 \ \ 1]$$

with $\mathbf{U}_4$ formulated as before.)

Following Sundararajan and Flory, the dependence of chain dimensions on statistical weights were computed by varying E_σ and E_ψ at 300K according to

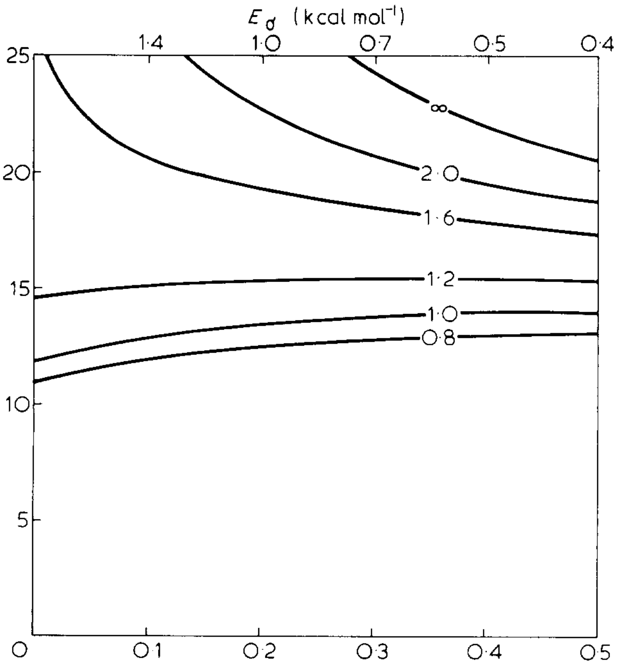

Figure 7 Computed characteristic ratios for syntiotactic polymethacrylate chains, $\alpha = 0.5$, with three rotational states of bonds 3 and 4; $\Delta\phi_{1,2} = -8°$ and $\Delta\phi_{3,4} = 15°$; curves are labelled with values of E_ψ (kcal mol^{-1}); $T = 300$K

$$\sigma = 1.0\exp(-E_\sigma/RT)$$

$$\psi = 1.6\exp(-E_\psi/RT)$$

with the pre-exponential factors suggested by the energy calculations remaining constant.

The unperturbed dimensions for chains having degrees of ionization between 0.0 and 0.5 were computed for representative chains of 400 bonds having random placings of 4 and 2 bond units. The sequences were determined by a random number generator and five representative chains were generated for each composition specified by w_4, the fraction of 4 bond units.

Calculations of chain dimensions

Figure 7 shows the dependence of the characteristic ratio for the half-ionized chain (consisting entirely of 4-bond units) on E_σ and E_ψ. $\Delta\phi_{1,2}$, the location of the $|tt|_{1,2}$ state is fixed at $(-8°, -8°)$ and the displacement $\Delta\phi_{3,4}$ for t and g states in bonds 3 and 4 is 15° with $|g^*g^*|_{3,4}$ remaining at 120°, 120°.

The displacements $\Delta\phi_{1,2}$ and $\Delta\phi_{3,4}$ have a marked effect on the conformational character of the chain. With zero displacements (discrete rotational states occupying locations corresponding to perfect staggering) a preference for *trans* conformations engenders relatively small chain dimensions as a consequence of the dissimilar skeletal bond angles at the methylene and C_α atoms. An increase in the probability of *gauche* states then tends to increase chain dimensions as the computations of Sundararajan and Flory illustrate in the case of poly(methacrylate) system. These features are assumed to be characteristic of the unionized syndiotactic poly(methacrylic acid) chain in the scheme presently considered. However, as *Figure 7* shows, the displacements $\Delta\phi_{1,2}$ and $\Delta\phi_{3,4}$ engender large chain dimensions when *trans* states are strongly favoured; an increase in the *gauche* population then brings about a decrease in chain dimensions.

As *Figure 6* shows, the experimental results of Noda *et al.* suggests a value of about 15 for the characteristic ratio of half-ionized 'conventional' poly(methacrylic acid). With E_σ and E_ψ assigned values of 1.6 kcal mol^{-1} and 2.7 kcal mol^{-1} (i.e. $\sigma = 0.07$; $\psi = 0.02$) as prescribed by the energy calculations, the computed dimensions are clearly too large for satisfactory agreement with experiment. However, the dimensions are sensitive to E_ψ and by reducing the latter by ~1.5 kcal mol^{-1} to 1.2 kcal mol^{-1} ($\psi = 0.20$) satisfactory agreement is obtained. In the region of interest the dimensions are less sensitive to E_σ although a similar decrease in this parameter also giving a value in the range 1.0 to 1.5 kcal mol^{-1} (σ lies in the range 0.1 to 0.2) is not incompatible with the experimental result. Reductions in the conformational energies of the corresponding *tg*, *gt* and *gg* states in the poly(methyl methacrylate) chain of approximately the same magnitude were found to be necessary by Sundararajan and Flory for agreement with experimental results. As suggested by the discussion above, the effect of these adjustments in the latter case is to raise the computed dimensions to an acceptable value. Thus, although limitations in the energy calculations are apparent, the adjustments required in each system are consistent. Sundararajan and Flory pointed out that more favourable weightings could be assigned to *gauche* conformations if bond angles were allowed to vary with conformation so as to minimize the energy.

A bond angle slightly smaller than 122° may be appropriate for the angle at the methylene group adjoining bonds 1 and 2 following a lowering in energy on formation of the ionic hydrogen bond. Computations of chain dimensions with the skeletal angle at the methylene group in the 1,2 dyad set at 120° while the corresponding angle in the 3,4 dyad remains at 122° are presented in *Figure 8*. As the

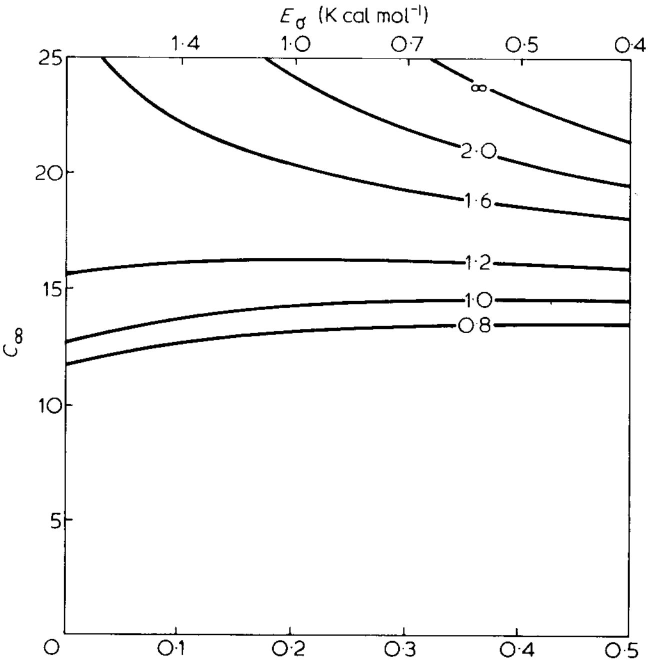

Figure 8 Computed characteristic ratios as in *Figure 7* except that the skeletal bond angle C_α—CH_2—C_α in the 1,2 dyad is reduced from 122° to 120°

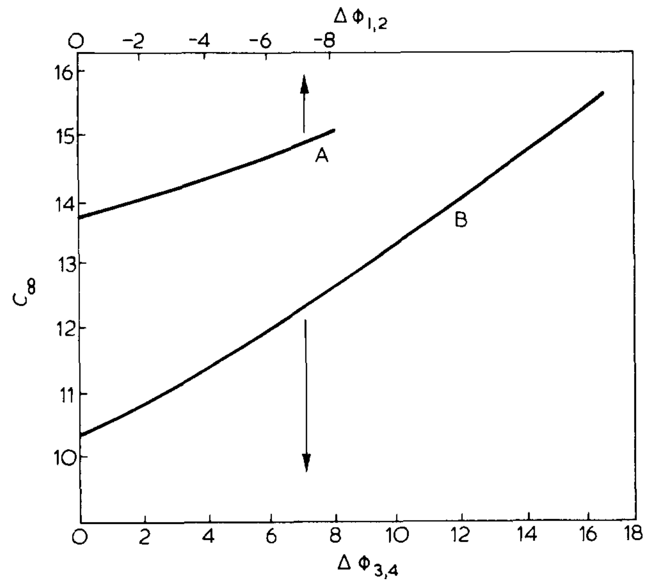

Figure 9 Computed characteristic ratios of syndiotactic polymethacrylate chains, $\alpha = 0.5$, with three rotational states; $\sigma = 0.1$ ($E_\sigma = 1.4$ kcal mol^{-1}), $\psi = 0.2$ ($E_\psi = 1.2$ kcal mol^{-1}). A, C_∞ vs. $\Delta\phi_{1,2}$ with $\Delta\phi_{3,4}$ fixed at 15°. B, C_∞ vs. $\Delta\phi_{3,4}$ with $\Delta\phi_{1,2}$ fixed at $-8°$

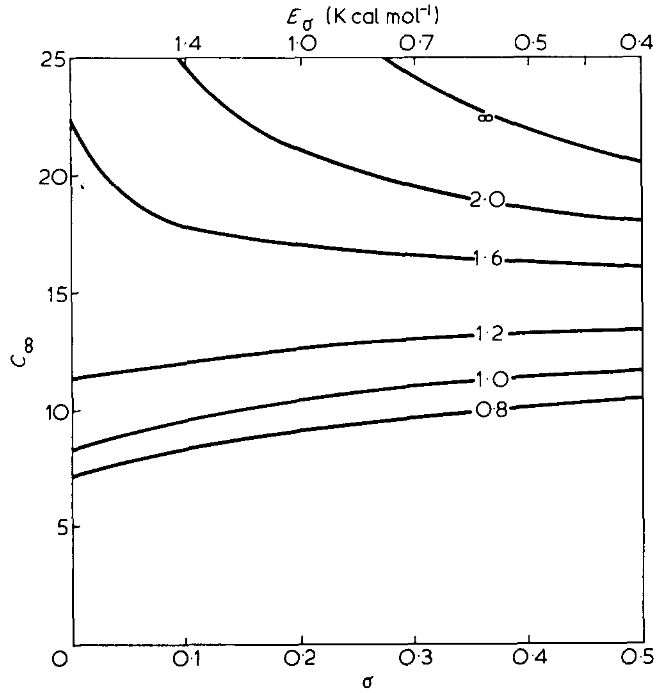

Figure 10 Computed characteristic ratios as in *Figure 7* but for two rotational states of bonds 3 and 4 (see text)

results show, this modification which supposes a net decrease in energy of ~3 kcal mol^{-1} does not bring about a significant change in the chain dimensions.

The influence of the displacements $\Delta\phi_{1,2}$ and $\Delta\phi_{3,4}$ on chain dimensions with the adjusted statistical weights maintained constant is shown in *Figure 9*. The displacement of rotational minima as a device for the enhancement of chain dimensions is clearly an important feature in the scheme presented here.

In view of the sensitivity of the chain dimensions to the $|g^*g^*|$ population it is of interest to explore the justification for the adoption of the 3 rotational state model which ensures that the rotational displacements $\Delta\phi_{3,4}$ are confined to $|tt|$, $|tg|$ and $|gt|$ states. Computations for a 2-state model are presented in *Figure 10*. In these computations the $|g^*g^*|$ state is abandoned and ψ becomes the statistical weight for the $|gg|$ state, the latter occupying the discrete rotational state (135°, 135°). The **U** matrices are reduced to order 2 x 2, $\mathbf{U}_4$ being formulated.

$$\mathbf{U}_4 = \begin{bmatrix} 1 & \sigma \\ \sigma & \psi \end{bmatrix}$$

Comparison of *Figure 10* with *Figure 7* shows that for given σ and ψ values the 2 state approximation gives significantly smaller dimensions and that the adoption of the 3 state scheme which takes due regard of the conformational analysis is justified.

Characteristic ratios for chains with degrees of ionization between zero and 0.5

Figure 11 shows the change in chain dimensions with composition denoted by the fraction of 4-bond units, w_4 and the degree of ionization, α. These quantities are related by:

$$w_4 = \alpha/(1-\alpha)$$

The statistical weights for the 2-bond units, $\gamma = 0.15$ and $\beta = 2$ are close to the values suggested for poly(methyl methacrylate) and give a characteristic ratio of ~8 for the unionized polyacid. For the four bond units, $\sigma = 0.1$, $\psi = 0.2$, $\Delta\phi_{1,2} = -8°$ and $\Delta\phi_{3,4} = 15°$. The bars indicate the range of results obtained within each set of 5 representative random chains of given composition. The conformational parameters are appropriate for the respective homopolymers so that this scheme should be most representative of the real system for values of w_4 approaching zero or unity. When unionized carboxylic acid functions precede or follow a hydrogen bonded dyad, displacements somewhat less in magni-

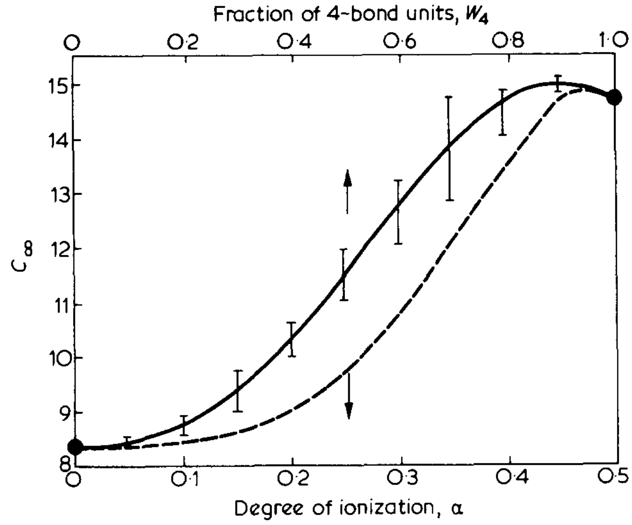

Figure 11 Computed characteristic ratios of syndiotactic polymethacrylate chains for degrees of ionization, α, between 0.0 and 0.5. The fraction of 4-bond units, $w_4 = \alpha/(1-\alpha)$; the sequence of 4-bond units was determined using a random number generator for chains of 400 units in length. Bars indicate the range of values obtained for each set of 5 chains for a given w_4 value. Statistical weights for 2 bond units: $\beta = 2.00$, $\gamma = 0.15$; statistical weights for 4-bond units $\sigma = 0.1$, $\psi = 0.2$

tude than $\Delta\phi_{3,4}$ should occur in the skeletal bonds of both preceding and following dyads. Nevertheless their effect should be similarly to enhance chain dimensions so that the approximation of discrete 4-bond and 2-bond structural units should not give rise to serious departures from the behaviour of the more realistic system. A plot having an initial steep gradient, for example, would not be expected from a more detailed analysis.

The form of the C_∞ *versus* α plot in *Figure 11* closely resembles that of *Figure 6* over the range $0 < \alpha < 0.5$. Experimental data for samples of pure syndiotactic polyacid would be desirable for closer comparison with the calculations. Furthermore, the assumption that the stability constant for the acid-salt hydrogen bond is so large that virtually all carboxylate groups should be coupled in a pure syndiotactic chain at the theta condition is only supported by experimental data for conventional polymer as described in Part 1.

Nevertheless, the results suggest that the sigmoidal form of the increase in chain dimensions with ionization is to be expected for predominantly syndiotactic chains in strong solutions of electrolyte where long range interactions are suppressed. The presence of attractive perturbing interactions such as hydrophobic forces or hydrogen bonds between acid functions which are well separated along the chain (so stabilizing a 'coiled state') are not required to account for the observations. The smaller dimensions at low α derive from the preference for *trans* skeletal conformations with average locations close to 0° in the unionized units. Comparison with the poly(methyl methacrylate) system[9] suggests that the conformational character of the isotactic polyacid (which may not form strong ionic hydrogen bonds[10] but which also shows a conformational transformation at about the same degree of ionization as the syndiotactic polyacid) should be quite similar in this respect.

Furthermore, if perturbing interactions are absent in high electrolyte concentrations it is difficult to explain their existence in solutions with low concentrations of supporting electrolyte in which coil dimensions are larger even over the range $0 < \alpha < 0.2$ (ref 1). In such solutions of partly ionized polymethacrylic acid) having any tacticity, the electrostatic energy for $\alpha < 0.1$ would need to offset the preference of the local interactions for $|tt|$ sequences in at least some dyads before more extended conformations could occur. As the rotational isomeric state models suggest, the latter states are preferred by ~1 kcal mol^{-1}.

The scheme described here is consistent with a preference for acid–water hydrogen-bonded interactions in the unionized system at ambient temperatures[21] rather than for acid–acid coupling between adjacent carboxyl groups. The possibility of preferred hydration of particular conformational states has not been considered here but the similarity of the unperturbed dimensions of the polyacid to other methacrylates in non-aqueous solutions[7,8] suggests that any such preference may be small. Acid–acid hydrogen bonding would require one carboxylic acid of the pair to adopt a conformation with the O–H bond *trans* to the carbonyl C=O bond. The latter conformation has an energy ~2 kcal mol^{-1} higher than the *cis* conformation[12]. However, non-aqueous solvents tend to promote both acid-salt and normal acid–acid hydrogen bonding. Eberson's[22] infra-red results suggest that intramolecular acid– acid hydrogen bonding occurs in racemic α,α' disubstituted succinic acids in methanol. In view of the report[23] of greater unperturbed chain dimensions of poly(methacrylic acid) in methanol than in aqueous solvents, it may be of interest to investigate the possiblity of acid–acid coupling across racemic dyads in this solvent.

CONCLUSIONS

The intrinsic viscosity data of Katchalsky and Eisenberg suggests that conventional poly(methacrylic acid) adopts unperturbed conformations in acidified dilute aqueous solutions at 30°C and that the coil dimensions are similar to those of poly(methyl methacrylate) chains ($C_\infty \sim 8$). The data of Noda *et al.* for ionized chains suggest an increase in the unperturbed dimensions to $C_\infty \sim 15$ at 50% ionization. We assume that a rotational isomeric state model similar to that for poly(methyl methacrylate) is appropriate for the unionized syndiotactic chain in aqueous solution in which the carboxylic acid functions are solvated by water molecules. For the half-ionized chain, a model having a 4 bond structural unit incorporating an ionic acid-salt hydrogen bond between adjacent carboxylate pairs is adopted. The computed dimensions of random copolymeric chains of unionized and ionized units are found to describe a curve of C_∞ vs. α which is in acceptable agreement with experimental results. It is concluded that hydrophobic bonding or hydrogen bonding between carboxylic acid functions well separated along the chain are not required to account for the dimensions of polymethacrylate chains in concentrated solutions of electrolyte where long-range electrostatic interactions are suppressed.

ACKNOWLEDGEMENTS

We acknowledge financial support for J. N. D. by a grant from the Science Research Council and we are grateful for computational facilities in the Department of Computing Services, University of Sheffield.

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