

A molecular model for viscometric and potentiometric irreversibility in isotactic poly(methacrylic acid)

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The energies of the accessible dyad states in isotactic poly(methacrylic acid) (PMAAI) are shown to be sensitive to the rotational states of the methyl and adjoining methylene groups, the individual hydrogen atoms of which must interdigitate to give low energy interactions across the dyad. Thus all-*trans* and all-*trans-gauche* sequences have low energies but mixed states are of high energy and interconversion takes place sequentially. The potentiometric irreversibility is traced to the inability of all-*trans* states to convert to *trans-gauche* states to promote ionization. The intervention of *gauche-gauche* states at intervals into *trans-trans* dyad sequences is of accessible energy and accounts for the observed irreversibility in viscometric titrations during which the chain dimension passes through a maximum on addition of alkali. The instability of PMAAI solutions at low degrees of ionization is also discussed.

(Keywords: isotactic poly(methacrylic acid); conformations; energies; irreversibility; computations; pH)

INTRODUCTION

In the previous paper¹, experimental evidence for significant potentiometric, spectrophotometric and viscometric irreversibility in titrations of isotactic poly(methacrylic acid) (PMAAI) solutions was presented. The influence of some multivalent ions on the irreversibility was also investigated and discussed in light of the local chain conformations expected for optimum association by the various ions. In this paper we present a molecular model for the preferred conformational states of PMAAI in strong solutions of 1:1 electrolyte in an attempt to account for our observations. Suter, Saiz and Flory² and others^{3,4} have pointed out the importance of optimum interdigitation of individual hydrogen atoms of interacting methyl and methylene groups on the low energy conformations of polyisobutene. We have here considered the PMAAI chain in similar detail rather than treating the methyl and methylene groups as spheres as in a previous study⁵ of syndiotactic poly(methacrylic acid) PMAAS.

COMPUTATIONAL PROCEDURES

Conventions for assigning rotational states

A dyad of PMAAI is shown in Figure 1 with the backbone rotation angles ϕ_{v-1} to ϕ_{v-2} in *trans* (0°) conformations. Enantiomeric bonds of PMAAI are differentiated using the stereochemical convention adopted by Flory and coworkers⁶. Each skeletal bond is viewed from the C_α atom towards the methylene group regardless of the direction of progress along the chain. A *d* bond has the $-\text{COOH}$ to which it is attached on the right and an *l* bond has the $-\text{COOH}$ on the left. The isotactic chain is then written $|d|d|d| \dots$ and the syndiotactic chain is $|d|l|d|l| \dots$ where a vertical bar denotes the position of the C_α atom. A *g* (*gauche*) state is obtained by a clockwise

rotation of a *d* bond through approximately 120° or the corresponding anticlockwise rotation of an *l* bond. A \bar{g} state corresponds to an anticlockwise rotation through approximately 120° of a *d* bond or the corresponding clockwise rotation of an *l* bond.

The carboxyl side group rotation angle ψ is zero when its oxygen atoms are coplanar with the methyl carbon atom C_{me} affixed to the common C_α atom and the carbonyl oxygen (O^*) is *cis* to the methyl group as shown in Figure 1. A positive rotation of the carboxyl group is a clockwise rotation about the $C_\alpha-C^*$ bond. The methyl side group rotation angle β is zero when a $C_{\text{me}}-\text{H}$ bond is coplanar with the carboxyl group when $\psi=0$ and a positive value of β is a clockwise rotation of the $C_\alpha-C_{\text{me}}$ bond.

Bond angles and bond lengths were assigned as in Table 1. Ignoring the outer methyl hydrogens the interatomic distances between each set of the remaining 11 atoms j and k in Figure 1 were computed for 5° incremental values of ϕ_v and ϕ_{v+1} (the rotation angles for bonds v and $v+1$). Interactions with the central methylene group were assumed to be independent of ϕ_v and ϕ_{v+1} and were not included in the computations. The non-bonded interactions across the unionized dyads for each ϕ_v and ϕ_{v+1} were computed as the sum of the Lennard-Jones potential energy E_{LJ} and the coulombic potential energy E_c for every $j \dots k$ interaction. Thus E_{LJ} is given by

$$E_{\text{LJ}} = \sum_j \sum_k (a_{jk}/x_{jk}^m - b_{jk}/x_{jk}^6)$$

where x_{jk} is the interatomic distance and a_{jk} and b_{jk} are constants. Two values of the exponent m were compared, i.e. $m=12$ as commonly assigned and $m=9$ as preferred by Lifson and coworkers⁷ in their investigations of carboxylic acid crystal structures. The b_{jk} were calculated using the Slater-Kirkwood equation⁸ with parameters

assigned¹² as in Table 2 and a_{jk} were obtained by minimization of the Lennard-Jones potential at the sum of the van der Waals radii for each $j \dots k$ interaction. Following the recommendations of Lifson and coworkers⁷ the Lennard-Jones constants a and b for the carboxylic hydrogen atom were set to zero.

The coulombic energy (kcal mol⁻¹) is given by

$$E_c = 332 \delta_j \delta_k / x_{jk} D$$

where δ_j and δ_k are the partial electronic charges assigned to atoms j and k and D is the dielectric constant. For all atoms except those of the -COOH group $\delta_j \delta_k$ were set to zero. The -COOH group was assumed to be electrically neutral and 3 sets of partial charges as in Table 2 were compared. The 'low' and 'high' values were from ab initio calculations reported by Hagler and Labicciarella⁹ and the 'intermediate' values were obtained from optimization procedures which gave best agreement with crystal lattice energies of hydrogen bonded carboxylic acids¹⁰. The dielectric constant was taken to be 3.5 for all states except *trans-cis* where the -COOH groups are at close range and a value of unity is assumed in this case.

Torsional potential energies were calculated according to

$$E_t = E_0(1 - \cos 3\phi)/2$$

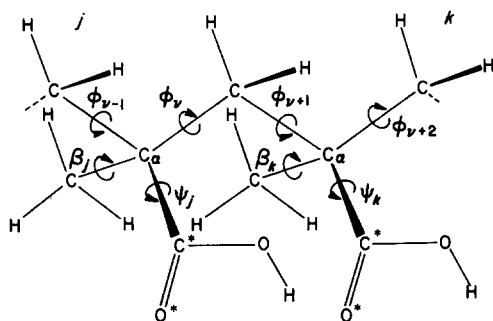


Figure 1 A meso dyad in the *trans-trans* (*tt*) conformation

Table 1 Bond lengths and unstrained bond angles

Bond length (Å)		Bond angle (degrees)	
C*=O*	1.23	C _α -CH ₂ -C _α	111.0
C*-O	1.29	C _α -C*=O*	121.0, 114.2 ^a
O-H	1.15	C _α -C*-O	116.0, 118.3 ^a
C-H	1.10	C*-O-H	110

Bond lengths not given in Table are 1.53 Å

Bond angles not given in Table are 109.5°

^a Values modified for hydrogen bonding

Data taken from refs. 2, 12 and 16

Geometry of carboxyl group also discussed by Housty, J. and Hospital, M. *Acta. Crystallogr.* 1965, **18**, 693 and Speakman, J. C., *Structure and Bonding* 1972, **12**, 141

Table 2 Non-bonded energy parameters

Atom	Van der Waals radius (Å) ^a	Effective no. of electrons ^a	Polarizability (Å ³) ^a	Partial charges ('low', 'medium', 'high') ^b
H (alkyl)	1.3	1	0.42	0
C	1.8	5	0.93	0
C*	1.8	5	1.23	0.32, 0.38, 0.74
O*	1.6	7	0.80	-0.29, -0.38, -0.58
O	1.6	7	0.80	-0.30, -0.38, -0.70
H (acid)	0	0	0	0.22, 0.38, 0.45

^a See ref. 12

^b See ref. 9

where E_0 is the torsional barrier height. For CH₂-C and C_{me}-C bonds E_0 was taken to be 2.8 kcal mol⁻¹ and for the C-C* bond a value of 1.0 kcal was assumed^{11,12}.

The bond angle C_{αj}-CH₂-C_{αk} was strained from its approximate tetrahedral unstrained value in order to minimize the non-bonded interactions. The strain energy was given by

$$E_s = F(\Delta\theta)^2/2$$

where F = the force constant (160 kcal mol⁻¹) and $\Delta\theta$ is the deformation in radians¹². In the *trans-cis* conformation the C_{mek}-C_{αk}-CH₂ (central) bond angle in each dyad was also increased by strain to alleviate the interaction between CH_{3k} and CH_{3j}, COOH_j. In this conformation this deformation, S , has no influence on interactions in the succeeding dyad but in the dyad in question angles CH₂-C_{αk}-CH_{2k} and CH₂-C_{αk}-C_k* were assumed to be reduced to approximately the same angle A given by

$$-\cos A = \sin 35.25 \cos (54.75 + S)$$

RESULTS AND DISCUSSION

Dyad energies

The locations and shapes of the energy domains of meso dyads which were computed using the 6-12 LJ potential function and the 'intermediate set' of partial charges on the carboxylic acid groups are sketched in Figure 2. The geometrical parameters for each conformational state are given in Table 3 and the computed energy minima for each LJ function and set of partial charges is given in Table 4. The energy map is symmetrical about the -180°, -180°---180°, 180° diagonal so that the domains not labelled or sketched are readily characterized from the data provided.

The minimum energies in Table 4 are lower by at least 4-5 kcal mol⁻¹ than for the corresponding states computed assuming spherical methylene and methyl groups⁵. Energy maps for the 6-9 LJ functions are similar to Figure 2 except that the domains sketched with the same energy contours are slightly larger in size. As Table 4 shows, the influence of choice of LJ function is not critical as far as the minimum energies of states A to F are concerned. Furthermore, the choice of set of carboxylic acid partial charges is of even less consequence for states A to F.

The data for states A, B, C, G and G' correspond to dyads within helical sequences of the same states. Since $g|g$ states are of intolerably high energy (see below) the $g|g$ state (Figure 3a) is flanked by rotations ϕ_{v-1} ,

$\phi_{v+2} = -20^\circ$ which is an average value for $|tt|$ or $|tg|$ states. Sequences of $t\bar{g}$ states in PMAAI are of high energy due to interactions of the carboxyls with the methyl or methylene groups on either flank. However, in a singular $t\bar{g}$ state with carboxyl k rotated through -60° (Figure 3b) the carboxyls are disposed as in the $|tt|$ state in a racemic dyad (PMAAS) and for a specific sequence in PMAAI such as $|t\bar{g}g\bar{g}|t\dots$ there are no high energy interactions between substituent groups. Such sequences involving \bar{g} could feature in distorted octahedral coordination with multivalent ions such as Cu^{2+} as tentatively proposed in the previous paper¹.

The possibility of intra dyad hydrogen bonding in $t\bar{g}$ states of PMAAI or $|tt|$ states of PMAAS is investigated in zone H where a carboxyl C-OH is rotated into the anti-planar conformation.

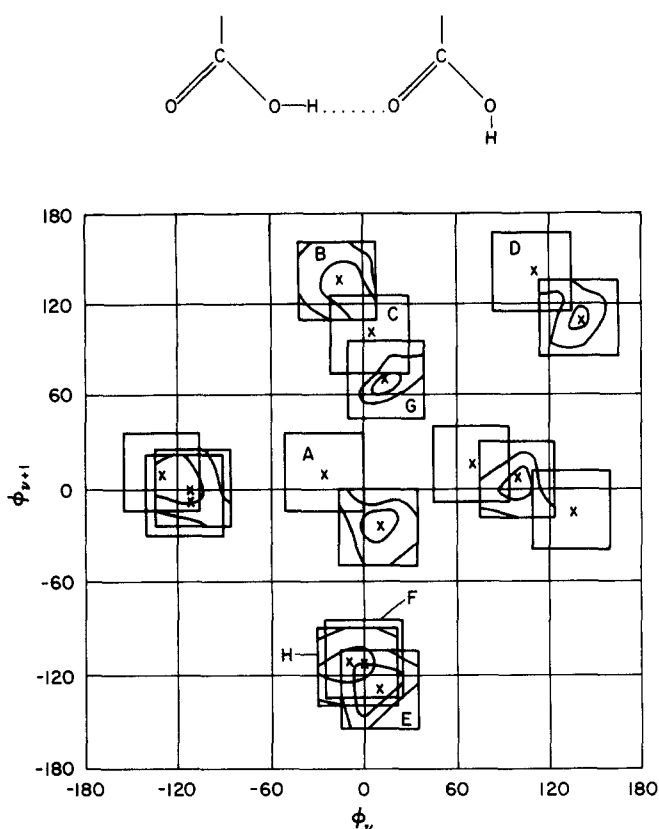


Figure 2 Conformational energy zones for the meso dyad (6-12 LJ function, 'medium' partial charges): x denotes position of energy minima. Contours refer to the frames on which they impinge and are 2 kcal and 10 kcal above their energy minima. Details of minimum energies and locations are given in Tables 3 and 4

Table 3 Locations^a of energy minima of conformational zones in PMAAI

Conformation zone	ϕ_{v-1}	ϕ_v, ϕ_{v+1}	ϕ_{v+2}	$\beta_{j,k}$	ψ_j, ψ_k	S	C_α	$\phi(\text{C}^*-\text{O})$	C^*	H
A	t_-t_+	10	-25, 10	-25	-3	0, 0	0	129	0	110
A	t_-t_-	-25	10, -25	10	3	0, 0	0	129	0	110
B	t_-g_+	135	-15, 135	-15	23	0, 0	0	129	0	110
C	t_+g_-	100	5, 100	5	12	0, 0	0	129	0	110
D	g_-g_+	-20	110, 140	-20	-5	0, 0	0	132	0	110
D	g_+g_-	-20	140, 110	-20	5	0, 0	0	132	0	110
E	t_+g_-	0	10, -130	10	8	0, -60	0	127	0	110
F	t_-g_+	0	0, -110	0	14	0, -60	0	129	0	110
G	$t\text{-cis}$	70	15, 70	15	22	118, 118	9	128	172	109
G'	$t\text{-cis}$	70	15, 70	15	22	-62, -62	9	128	180	131
H	$t\bar{g}$	0	-10, -110	24	25	23, -37	0	129	205	113

^aData given in degrees

The energy required for this modification is not included in Table 4 and is uncertain but estimates of 2-4 kcal mol⁻¹ have been made¹³. Also omitted from Table 4 is any contribution to stabilization of the various states by hydrogen bonding to solvent. While the solvation free energy is plausibly approximately the same for each of the 'free' states A-F, hydrogen bonding is likely to exclude some solvating capability. Thus a positive free energy contribution of several kcal mol⁻¹ from this source also is expected to render neutral hydrogen bonds in state H significantly less stable with respect to the 'free' states than the data in Table 4 imply. An ionic hydrogen bond at half ionization is not inconsistent with the dimensional changes of PMAAS during titration⁵ (see below) although there is no trace of a point of inflexion at half ionization in potentiometric (pH) titrations of PMAAS. However, the reports^{14,15} of larger unperturbed molecular dimensions of PMAAS in methanol may be related⁵ to a stronger unchanged intradyad interaction in this solvent.

The $|t\text{-cis}|$ state (G,G') also affords a geometric disposition of adjacent carboxyls for a carboxyl-carboxyl interaction centred on a small cation (Figure 3c). The energy of this state is lowered by increasing the $\text{CH}_2\text{-C}_\alpha\text{-Me}_k$ bond angle. This deformation is effected without consequence for the geometry of a succeeding dyad in the same trans-cis state so that a helical sequence of intradyad interactions is conceivable. Unlike the $|t\bar{g}|$ state the carboxyls in $|t\text{-cis}|$ become virtually coplanar with rotation $\psi_i = \psi_j$ as given in Table 3. For neutral H-bonds two possibilities are considered (G and G') in which the

Table 4 Energy minima^a of conformational zones in PMAAI

Conformation zone	6-12 LJ function			6-9 LJ function			
	Partial charges low	Partial charges medium	Partial charges high	Partial charges low	Partial charges medium	Partial charges high	
A	t_+t_- , t_-t_+	6.5	6.5	6.8	5.3	5.3	5.7
B	t_-g_+	6.0	6.0	6.1	5.2	5.2	5.3
C	t_+g_-	6.8	6.8	6.9	5.5	5.4	5.6
D	g_+g_- , g_-g_+	8.4	8.4	8.5	7.2	7.2	7.4
E	t_+g_-	5.0	4.9	5.1	4.1	4.1	4.3
F	t_-g_+	5.9	5.9	6.1	5.4	5.3	5.6
G	$t\text{-cis}$ H-bond	7.5	2.0	-1.4	5.8	-2.3	-8.9
G'	$t\text{-cis}$ H-bond	8.9	3.9	1.9	7.4	0.4	-3.7
H	t_-g_+ H-bond	3.0	-0.2	-0.6	-5.5	-8.5	-9.0

^aData given in kcal mol⁻¹; in *vacuo* energies; hydration and anti-planar carboxylic acid conversion in states G, G' and H not taken into account (see text)

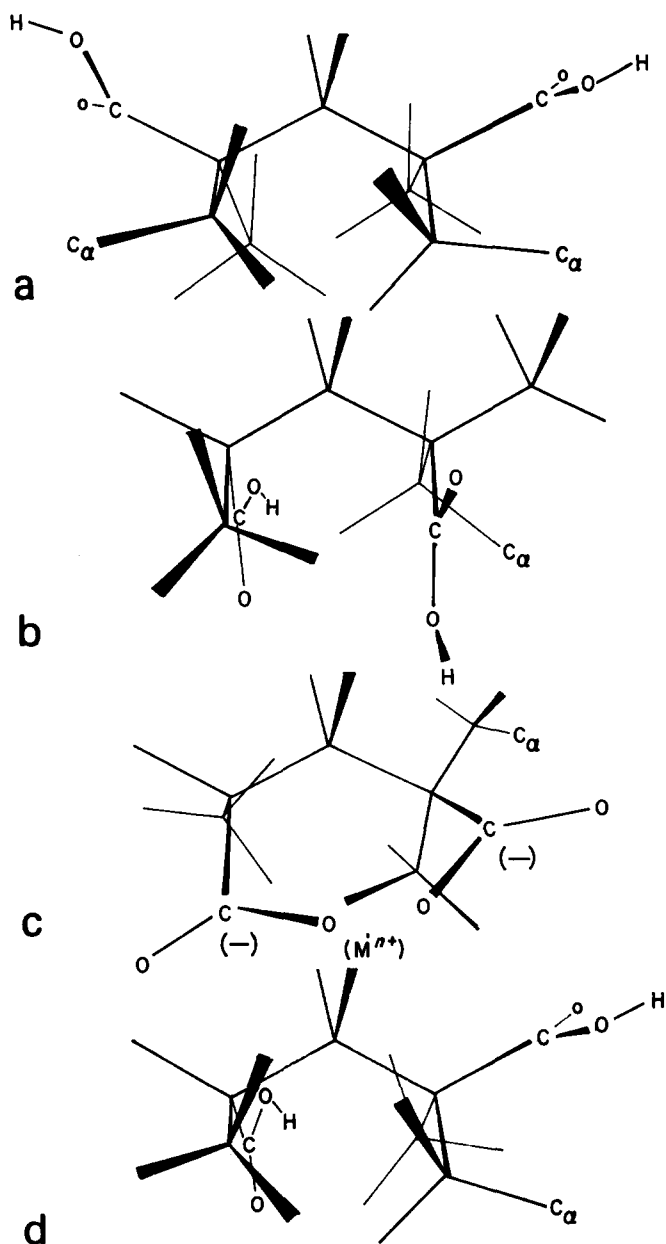


Figure 3 Sketches on meso dyad conformational states: (a) $|g-g_+|$ (D); (b) $|t-g_+|$ (F); (c) $|t-cis|$ (G); (d) $|t-g_+|$ (B)

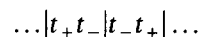
carboxyl rotations differ by 180° . Low *in vacuo* energies are computed for these states and the interdyad helical sequence of H bonds which may be envisaged for PMAAI is allowed a measure of plausibility by recognition of the similar catenated sequence in the crystal structure, of 1,1-cyclopropanedicarboxylic acid which also features an internal neutral hydrogen bond with intermolecular H-bond connections¹⁶. However, as reported in the previous paper¹, the spectrophotometric data are consistent with a simple ionization process of acid to carboxylate in PMAAI. Thus, the speculation¹⁷ that sequences of intramolecular neutral H-bonds may be responsible for potentiometric irreversibility in PMAAI is not supported experimentally. In addition to the positive energy contributions from conversion to the antiplanar carboxylic acid configuration and the forfeit of some hydration capability, the coplanar arrangement of carboxyls in *trans-cis* would require considerable cooperativity from neighbouring dyads. Nonetheless, although H-bonding may fail, the computations indicate

that state G is a plausible conformation in a stronger interaction between a small multivalent cation and a pair of chelating carboxyls. Such a possibility exists for the interaction of PMAAI with Cu^{2+} with molar ratios $[\text{COO}^-]:[\text{Cu}^{2+}]$ or 2:1 (ref. 1).

The $|tg|$ C state has a minimum energy of $0.8 \text{ kcal mol}^{-1}$ higher than that of the B state (Figure 3d) and a domain size below the 2 kcal contour of *ca.* $\frac{1}{4}$ that of the latter. From the summation of Boltzmann factors the probability of state C is estimated to be only *ca.* 5% of that of state B in unionized chains. This probability should be further reduced on full ionization in 1:1 electrolytes as the C state places the carboxyls at closer range. Thus further consideration of $|tg|$ is here confined to state B although state C gives a greater separation of alternate carboxyls and should have greater probability in the region of half-ionization of the chain.

Hydrogen interdigitation and the energies of mixed dyad sequences in unionized PMAAI

Mixed |tt| sequences. In Figure 4 the energy of a $|tt|$ dyad (A) in unionized PMAAI is plotted as a function of methyl rotation angle $\beta_j = \beta_k$. The shallowness of the curve in the region $\beta = 0$ suggests that a mixed sequence of dyads of each displaced state, i.e.



should interact at a common methyl with an energy which is not significantly greater than that for sequences of the same state $|t_+t_-t_+t_-|$. However, ionization of the chain in all-*trans* states should favour sequences of the same state since these lead to extended local conformations. Alternate carboxyls in such sequences are spaced at *ca.* 6.5 Å compared with only *ca.* 5 Å for the mixed dyad. However, as discussed in the previous paper, ionization of adjacent carboxyls in $|tt|$ PMAAI would engender prohibitively high electrostatic energies which could not be screened by solvent or by counterion condensation. Thus ionization of PMAAI up to 50% may occur reversibly in all *trans* sequences by conversion of alternate acid groups to carboxylates with randomly mixed $|tt|$ states having the greater probability at low degrees of ionization. Ionization above 50% of groups requires some conversion to *gauche* states.

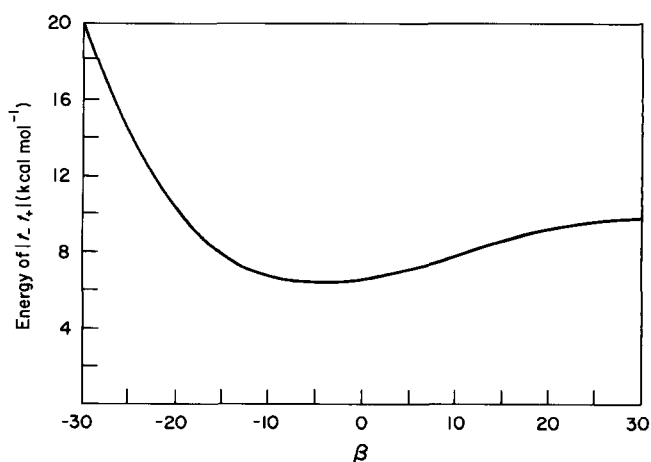
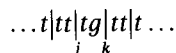


Figure 4 Energy of meso dyad in $|t-t_+|$ as a function of methyl rotation angle $\beta_j = \beta_k$ (6-12 LJ function, 'medium partial charges')

Mixed sequences involving g states

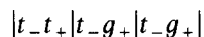
The lowest energy arrangement in $|tg|$ states in PMAAI requires appropriate interdigitation of the hydrogen atoms of a methyl and methylene group as shown in Figure 3d. The methylene k rotational state ϕ_{v+2} depends on the conformational state of the dyad succeeding (i.e. to the right as drawn) the dyad in question. In Figure 5 the energy of an unionized dyad with backbone rotations ϕ_v, ϕ_{v+1} assigned to those of state B ($-15^\circ, 135^\circ$) but with methyl rotation angle $\beta_j = \pm 3^\circ$, as required for $|tt|$ is plotted as a function of methylene k rotation angle ϕ_{v+2} .

These results suggest that the introduction of a solitary g state within an otherwise all-*trans* sequence



($\phi_{v+2} = -25$ or $+10$) must raise the energy of the $|tg|$ dyad by *ca.* 6 kcal to *ca.* 12 kcal mol⁻¹. Compromises, for example by allowing the methyl group to adopt higher values of β_j may alleviate the interaction in the $|tg|$ dyad but cause an accumulation of higher energy interactions in the preceding $|tt|$ dyads (see Figure 4).

The data suggest that if the preceding dyad is $|t_+t_-|$ ($\beta_j = +3$) and the succeeding one cooperatively converts to $|tg|$ ($\phi_{v+2} = -15$) the resulting sequence is of lower energy but still *ca.* 3 kcal mol⁻¹ above the $|tg|$ minimum energy giving the overall sequence probability of less than 1% of the $|tg|$ state as estimated from Boltzmann factors. In the alternative $|tt|$ state, i.e.



$\beta_j = -3$ and a higher energy interaction (*ca.* 11 kcal mol⁻¹) is predicted from Figure 5 (see Figure 6a).

Sequences involving



in polymethacrylate chains are of prohibitively high energy⁶ involving intolerable clashes between the

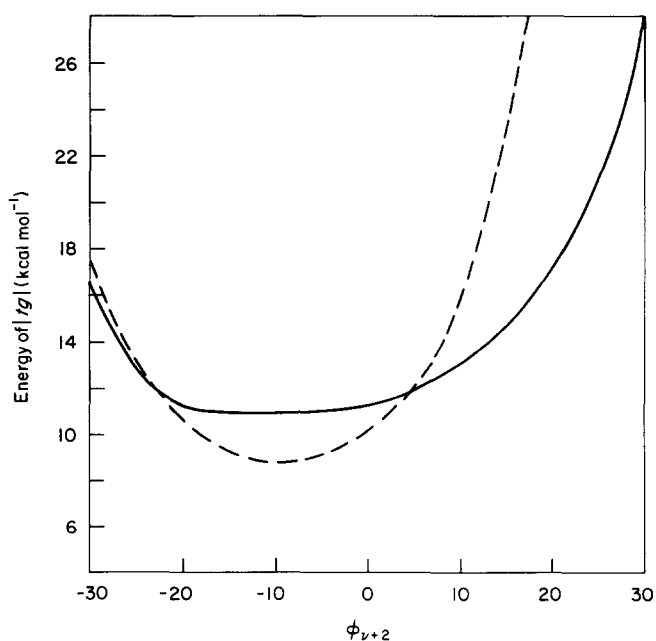


Figure 5 Energy of meso dyad in $|t_-g_+|$ as a function of methylene rotation angle ϕ_{v+2} . Broken line, methyl rotation, $\beta = 3^\circ$; solid line, methyl rotation $\beta = -3^\circ$ (6-12 LJ function 'medium' partial charges)

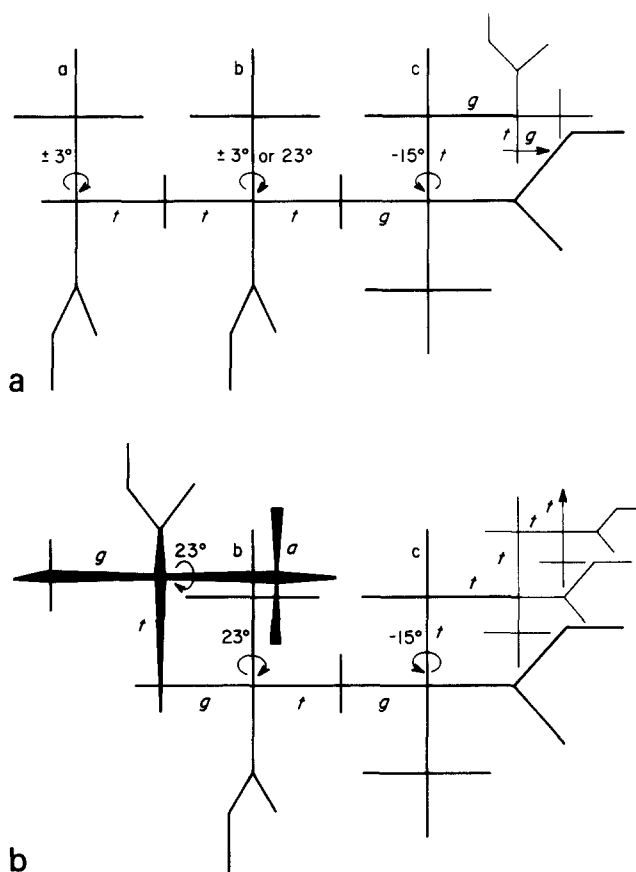
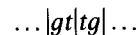


Figure 6 Schematic diagrams of PMAAI chain viewed from above in plane of skeletal backbone (displaced states not represented). (a) Showing conflicting rotational requirements of methyl b against methyl a and methylene c in a high energy $\dots |tt|tg| \dots$ sequence. (b) Showing methyl b free to interdigitate with methylene c in a $\dots g|tg|tg|tt| \dots$ sequence

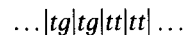
substituents appended to each C_α immediately flanking the central one.

Furthermore, reversals in helical pitch



must incur prohibitively high interactions at the common central methyl group for which each dyad has rotational requirements differing by 46° .

However, in sequences of $|tg|$ dyads, the methyl j groups are required to interdigitate only with methylenes k (to the right as drawn in Figure 6b). To the other side the methyls k are flanked by carboxyls which being planar are far less sensitive to the rotational state of the methyl. Thus if conversion to $|tg|$ occurs sequentially from the left, i.e.



the methyl j is free to conform to the interdigitation requirements of methylene k according to the state adopted by the first $|tt|$ dyad. Thus such a sequence, and its mirror image $tt|tt|gt|gt|$, apparently provides the only low energy route for $|tt| \rightarrow |tg|$ conversion which preferably commences at a terminus. Furthermore, if the conversion is to coincide with ionization of more than 50% of the carboxyls, i.e. ionization of an acid between two carboxylates appended to $|tt|tt|$, then a cooperative transition of a pair of groups at the interface between existing $|tg|$ and $|tt|$ sequences is required.

On the other hand, reversion from $|tg| \rightarrow |tt|$ also proceeds in the reverse low energy sequential manner to that described above. However, the deionization process is not confined to the interface between $|tg|$ and $|tt|$ sequences and may occur at any carboxylate. Furthermore the reversion to $|tt|$ does not require cooperativity between pairs of dyads at the interface but may proceed one dyad at a time. State A also gives rise to a greater separation of alternate carboxyls than state B which should favour state A at half-ionization.

The $|gg|$ state D requires optimum interdigitation of both $\text{CH}_2 \dots \text{CH}_2$ and $\text{CH}_3 \dots \text{CH}_3$ interactions. The computations were carried out for ϕ_{v-1} and $\phi_{v+2} = -20^\circ$ which should be compatible with either $\dots |gt|gg|tg| \dots$ or $\dots |tt|gg|tt| \dots$ sequences. However, while the optimum methyl rotations ($\beta = \pm 5^\circ$) are well matched for the latter sequence, the methyl rotation requirements for state D differ from those of B by $23 \pm 5^\circ$ and Figure 5 suggests interactions of at least 9 kcal mol^{-1} for a $|tg|$ dyad neighbouring a $|gg|$ dyad giving a total excess energy of more than 8 kcal mol^{-1} for a D state flanked by B states over that for pure B state sequences. Thus, the computations suggest that $|gg|$ can interrupt only *trans* sequences with a significant probability.

This analysis of PMAAI for which the difficulty in methyl ... methylene interdigitation in $|tg|$ states is a critical feature in accounting for the potentiometric irreversibility, is consistent with the absence of this phenomenon in PMAAS. In PMAAS $|tg|$ requires only methyl ... methylene interdigitation (cf. all-*trans* in PMAAI) while the methylene is opposed by the planar carboxyl which presents few interactive problems. However $|tg|$ is, in any case, less critical for full ionization of PMAAS as the $|t_+t_+|$ displaced state in the racemic dyad gives adequate separation of carboxylates.

Changes in molecular dimensions of PMAAI over the titration cycle

The changes in computed molecular dimensions of a model chain of PMAAI according to a scheme of the principal conformational sequences suggested by the discussions above are presented in Figure 7a. The model chain is 100 bonds in length and the sequences of mixed states were determined from random numbers. The conformational states were inserted as tetrads with rotational angles from Table 4, i.e. 'regular' $|t_+t_-|t_+t_-|$, random $|t_+t_-|$ or $|t_-t_+|$ etc. and $|g_-g_+|t_-t_+|$ (where $t_- = -20^\circ$ in the latter case). The computed dimensions are presented as $(\langle r^2 \rangle)^{3/2}$ so as to reflect the relative changes in the hydrodynamic volume. The computations are compared with the observed changes in specific viscosity of PMAAI. As discussed previously¹, the magnitude of η_{sp}/C is approximately the same in 1M and 3M electrolyte suggesting that long range electrostatic interactions are largely suppressed and the observed changes in viscosity have their origins in interactions between immediate neighbours.

After standing for a period greater than *ca.* 24 h at $\text{pH} > \text{ca.} 11$ the polyacid passes into solution and may be titrated with mineral acid to a point of inflexion in the potentiometric titration plot at $\text{pH} \sim 8$. At this point (P) the polyacid is fully ionized and exhibits its maximum reduced viscosity. Over the region PQ, corresponding to acid titration from fully ionized to half-ionized polyacid, a conformational transition from extended sequences of

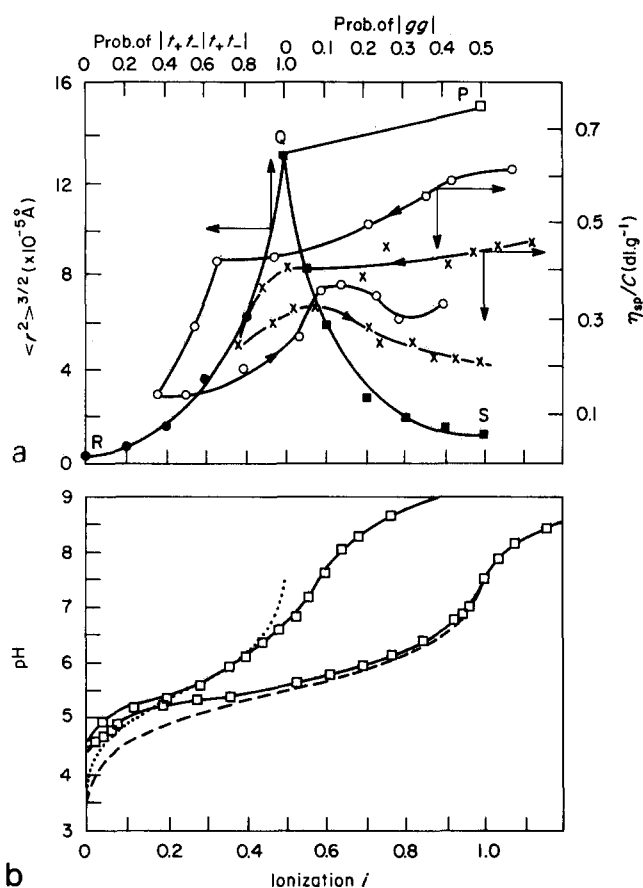


Figure 7 Changes of molecular dimensions and pH with degree of ionization, i , in solutions of PMAAI. (a) Computed average dimensions of 50 'Monte Carlo' chains of 100 bonds for: \square , 'pure' $|tg|$ helix; \bullet , all-*trans* chains as function of probability of sequences of the same displaced states; \blacksquare , $|t_+t_+|t_+t_+|$ with random placements of $|gg|$ states (r = end-to-end distance) (see text) experimental viscosity data for PMAAI in 1M NaCl. \times , 10°C ; \circ , 25°C ; (see ref. 1). (b) Calculated and experimental variation of pH with i . Dashed line, $\text{pH} = \text{pK} - \log_{10}[(1-i)/i]$ ($\text{pK} = 5.5$); dotted line, $\text{pH} = \text{pK} - \log_{10}[(0.5-i)/i]$ ($\text{pK} = 5.5$). PMAAI in 3 M NaCl (arrows indicate direction of titration—see ref. 1)

mainly $|tg|$ helices to all-*trans* states is envisaged. In the region of half-ionization these are presumed to be mostly regular $|tt|$ sequences giving maximum separation of the alternate charged carboxyls. From the previous discussion a chain of regular $|tt|$ and $|t_-g_+|$ states is either a once or twice 'broken rod' conformation and thus the average dimensions over a wide range of composition of these block sequences were computed¹⁸ to be close ($\langle r \rangle = 108 \text{ \AA}$) to that of the pure $|tg|$ helix ($\langle r \rangle = 115 \text{ \AA}$).

However, in experiments when the direction of titration is reversed at degree of ionization $i \geq \text{ca.} 0.4$ the degree of potentiometric irreversibility is low. This suggests that the transformation of states over $\text{P} \rightarrow \text{Q}$ does not proceed spontaneously in proportion to the extent of deionization but that the irreversible conversion to all-*trans* states occurs at a degree of ionization $i < 0.4$ as suggested by the viscometric data (at least at temperatures $\geq 25^\circ\text{C}$).

The collapse in the molecular dimensions over the region $\text{Q} \rightarrow \text{R}$ is interpreted as arising from the increasing proliferation of random sequences of both displaced $|tt|$ states in proportion to the extent of deionization of the polyacid. The smaller dimensions of random displaced $|tt|$ sequences arise from the alternation of the skeletal bond angles in polymethacrylates (see Table 3) so that for $\phi_v = \phi_{v+1} = 0^\circ$ the chain describes a closed loop within *ca.* 40 bonds. Figure 8 shows that the $|tt|$ displacements

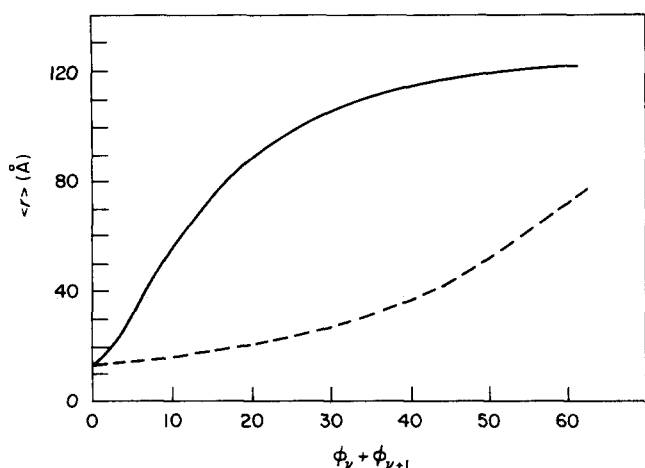


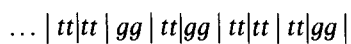
Figure 8 Average end-to-end distance of PMAAI chains of 100 bonds in all-*trans* conformations as a function of total displacement of minimum energy locations within each dyad. Solid line, regular sequences (...| t_+t_- | t_+t_- |...); dashed line, random sequences of each displaced state | t_+t_- | or | t_-t_+ |

suggested by the energy computations give rise to the maximum differences in dimensions for regular and random sequences.

The computed plot QS represents the interruption of the regular | t_+t_- | rodlike conformation with randomly placed | gg | states. The computations demonstrate the sensitivity of the molecular dimensions to | gg |; a low probability of | gg | at $i > 0.5$ is sufficient to account for the maximum in η_{sp}/C in the region of half-ionization.

The irreversibility in the viscometric data for $0 < i < 0.5$ is consistent with a low probability of | gg | into the 'trans rich' chain over the region $R \rightarrow Q$.

Inspection of representative sequences, e.g.



shows that while | gg | states allow the ionization of adjacent carboxyls their introduction into the otherwise all-*trans* chain does not allow the degree of ionization to increase above one carboxylate per tetrad ($i = 0.50$). However, the introduction of | gg | gives a greater choice in the distribution of charged groups along the chain and thus contributes to an increase in the entropy of the half ionized polyacid.

In Figure 7b experimental potentiometric data for PMAAI in 3 M NaCl is compared with calculated plots of

$$\text{pH} = \text{pK} - \log_{10}[(1-i)/i] \quad 0 < i < 1.0 \quad (1)$$

and

$$\text{pH} = \text{pK} - \log_{10}[(0.5-i)/i] \quad 0 < i < 0.5 \quad (2)$$

$$\text{for } \text{pK} = 5.5$$

The experimental data are described by equation (1) over the lower acid titration curve for $i > ca. 0.4$ where | tg | rich sequences are postulated. However, for $i < 0.4$ and on the upper (alkali titration) curve, the data are consistent with a transformation to all-*trans* states with potentiometric behaviour described by equation (2).

The stabilities of solutions of PMAAI and PMAAS at low degrees of ionization

The exponential form of the computed plot RQ is similar to the corresponding plot for the change in the

characteristic ratio $(\langle r^2 \rangle_0/nl^2)_{n \rightarrow \infty}$ for PMAAS computed by Davenport and Wright⁵ on the basis of various proportions of random | tt | dyads and regular | $tt|tt$ | tetrads. These workers proposed that the regular *trans* displacements in half-ionized tetrads of PMAAS arose from ionic hydrogen bonds across the racemic dyads. However, the maximum separation of alternate charged carboxylates as applied to the present discussion of PMAAI is equally applicable to PMAAS and leads to the same conclusion regarding the form of the computed plots for degrees of ionization $0 < i < 0.5$ for both polyacids. This form of plot reflects the well known form of the change in specific viscosity of PMAAS (which remains in solution at $i = 0$; see previous paper¹, Figure 5) and which has been commonly ascribed^{19,20,21} to stabilization of a coiled form of PMAA by intramolecular hydrophobic interactions. However, the intrinsic viscosity relationship of Katchalsky and Eisenberg²² for 'conventional' PMAA in θ conditions (0.002 M HCl at 30°C) viz.

$$[\eta] = 6.6 \times 10^{-4} M^{0.50} \text{ dl g}^{-1}$$

suggests chain dimensions similar to other random coil polymethacrylates in organic solvents²³. The computations of this work and of Davenport and Wright thus suggest that the form of the increase in dimensions can be explained by consideration of the local geometry of the chain rather than by intramolecular attractive forces. Hydrophobic interactions may have some stabilizing influence in certain states, for example in the | t_-g_+ | helix where the hydrocarbon material coalesces along the central axis of the structure. However, their negative contribution to the energy (estimated¹⁸ to be ca. 0.25 kcal per mol of dyad for | t_-g_+ |) is small in comparison with the magnitude of the largely repulsive interactions which are the dominating influence in the present interpretation of the behaviour of PMAAI.

The tendency for PMAAI to phase separate at low degrees of ionization is consistent with inter-strand association by $-\text{COOH} \cdots \text{HOOC}-$ hydrogen bonded dimerization at every carboxyl of each all-*trans* molecular strand as shown in Figure 9. The propagation of such a sequence of associations requires | tt | displaced rotations $\phi_v = -\phi_{v+1}$ (opposite signs in each strand) and small carboxyl rotations. However, both small adjustments to the minimum energy locations given in Table 4 are in

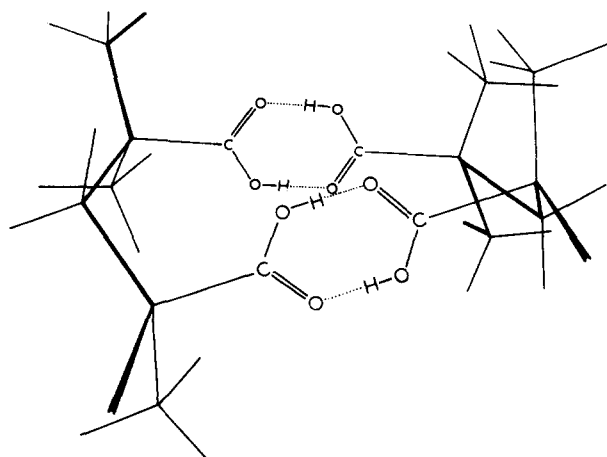


Figure 9 Proposed double strand structure of all-*trans* sequences in PMAAI to account for insolubility at low degrees of ionization

Molecular model for isotactic poly(methacrylic acid): S. M. Towlson and P. V. Wright

shallow energy wells and would be amply compensated by a fall in energy of approximately $7 \text{ kcal (mol of dyad)}^{-1}$ on hydrogen bonding. The resulting double strand helical sequence has all methyls to the outside and a much reduced capacity for hydration compared with the corresponding arrangement in PMAAS or with the single strand of PMAAI.

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