

# Potentiometric and conformational irreversibility in isotactic poly(methacrylic acid) and the effects of multivalent cation binding

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Significant potentiometric (pH), viscometric and spectrophotometric irreversibility in titrations of isotactic poly(methacrylic acid) in 1:1 electrolytes are reported. The effect is most pronounced at degrees of ionization  $i > 0.5$  and in stronger electrolyte solutions but is absent in the syndiotactic polyacid. The molecular basis of the irreversibility is discussed in terms of the interdigitation requirements of methyl and methylene hydrogen atoms in various conformational states. Diammoniummethane and  $\text{Ca}^{2+}$  ions are found to reduce potentiometric irreversibility by assisting proton release at  $i > 0.5$  but  $\text{Cu}^{2+}$  ions assist proton release at  $i < 0.5$  and promote the higher pH pathway at  $i > 0.5$ .

(Keywords: poly(methacrylic acid); titrations; irreversibility; pH; u.v.; viscosity; ion binding)

## INTRODUCTION

In a previous short communication<sup>1</sup> we reported the observation of extensive potentiometric (pH) hysteresis in isotactic poly(methacrylic acid) (PMAAI). This followed an earlier report by Leyte *et al.*<sup>2</sup> who observed a small degree of potentiometric hysteresis in titrations of PMAAI but not in solutions of the syndiotactic polyacid (PMAAS). A more detailed study of the PMAAI system<sup>3</sup> has shown that our previously reported results were complicated by certain agents, most notably aluminium, which was extracted from borosilicate glass during preparation of the polyacid by alkaline hydrolysis of isotactic poly(trimethylsilylmethacrylate) according to the method of Aylward<sup>4</sup>. Following the hydrolysis in glass vessels PMAAI precipitated from alkaline solutions above pH7 was found to contain varying quantities of aluminium whereas that precipitated below pH7 was obtained as the pure polyacid. This method of preparation was chosen in preference to the method commonly employed<sup>2,5</sup> which involves treatment of isotactic poly(methyl methacrylate) with concentrated  $\text{H}_2\text{SO}_4$ . The more facile alkaline hydrolysis of the polysilylester yields spectroscopically pure material.

The influence of aluminium on potentiometric and viscometric behaviour of poly(carboxylic acids) solutions is found to be considerable but a report of this work is reserved for a separate publication. In this paper we report on results of an investigation of irreversible phenomena in pure PMAAI in solutions of 1:1 electrolytes alone and in the presence of certain multivalent cations.

## EXPERIMENTAL

### Preparation of polyacids

Following the procedures described by Aylward<sup>4</sup>, trimethylsilylmethacrylate was polymerized using butyl

lithium catalyst in toluene solution. The polymer was recovered by removal of toluene under reduced pressure and then hydrolysed as a 1% solution by reflux for several hours in 3M NaOH. Ideally, the hydrolysis should be carried out in an inert vessel. The polyacid was recovered in fractions by progressive neutralization with HCl. All material precipitated above pH7 was discarded. Material precipitated below pH7 was filtered, washed with further acid and distilled water and the fine powder dried under vacuum at 60°C. Neutron activation elemental analysis showed that silicon and aluminium were absent from these fractions; the absence of trace metals was also confirmed by atomic absorption spectroscopy. Isotactic poly(acrylic acid) was prepared by the same procedure using trimethylsilylacrylate as monomer.

<sup>13</sup>C n.m.r. spectra of 15% solutions of PMAAI in NaOH compared favourably with the spectra reported by Schaefer<sup>6</sup> and the samples were estimated to have >90% isotactic triads. The <sup>13</sup>C n.m.r. spectra also confirmed the absence of trimethylsilyl residues indicating that hydrolysis of the ester was complete.

Syndiotactic poly(methacrylic acid) PMAAS was prepared by irradiation of a 30% solution of methacrylic acid in isopropanol at 195 K using a <sup>60</sup>Co source. The total dose of radiation was 2.6 Mrad. The polyacid was purified by successive dissolution in methanol and precipitation in petroleum ether. The PMAAS, as a fine powder, was finally dried under vacuum. The <sup>13</sup>C n.m.r. indicated that the material had >80% syndiotactic triads.

Both PMAAI and PMAAS gave infra-red spectra which compared favourably with published spectra<sup>5</sup>. Assuming the intrinsic viscosity relationship of Katchalsky *et al.*<sup>7</sup> for conventional PMAA in a  $\theta$  solvent ( $[\eta] = 6.6 \times 10^{-4} M^{0.5} \text{ dl gm}^{-1}$ ), a molecular weight of ca. 50 000 is indicated for the PMAAI sample from dilute solution viscosity data in 1–3 M NaCl. The PMAAS sample was estimated to have a molecular weight of ca. 200 000.

Potentiometric and spectrophotometric titrations

Solutions of PMAAI and PMAAS were prepared by allowing accurately weighed quantities of the powdered materials to stand at ambient temperature in 0.1 M or 1 M NaOH solutions so as to give solutions of 1 to  $4 \times 10^{-3}$  M carboxylate concentrations throughout the titrations. The solutions were then titrated using 1 M and 0.01 M HClO<sub>4</sub> and 0.01 M NaOH (HCl was used when spectroscopic data was not required). All titrations were carried out in a nitrogen atmosphere at ambient temperature using an EIL type 1160 combination electrode with an EIL 7050 pH meter. The solutions were circulated from the titration flask through a u.v. silica cell mounted in a Perkin Elmer 330 UV-visible spectrometer using a peristaltic pump. The reference cell contained pure degassed distilled water and the trace was checked for zero deflection from the baseline throughout the spectral range using polymer-free solutions before all experiments. The degree of ionization,  $i$ , is given to good approximation by,  $i = (b + 10^{-\text{pH}})/a$  where  $a$  is the total carboxylate concentration and  $b$  is the net concentration of added base.

Viscometric titrations

Viscometric titrations were performed using an Ubbelohde suspended level viscometer incorporating a 0.4 mm diameter capillary. The viscometer was modified so as to allow a mini pH electrode and a 2 ml microburette to be inserted into the viscometer reservoir. The viscometer was also connected to a gas line to allow the experiments to be conducted in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Potentiometric titrations

Potentiometric titrations for PMAAI in 0.1 M, 1 M and 3 M electrolyte are shown in Figures 1 and 2. Corresponding data for PMAAS in 1 M electrolyte are also shown in Figure 1. The latter plot is typical of all data obtained on the syndiotactic polyacid in the present work. In the same concentration of 1:1 electrolyte it is a stronger acid than the isotactic polyacid, as previously reported<sup>5</sup>, and there is no evidence for potentiometric irreversibility.

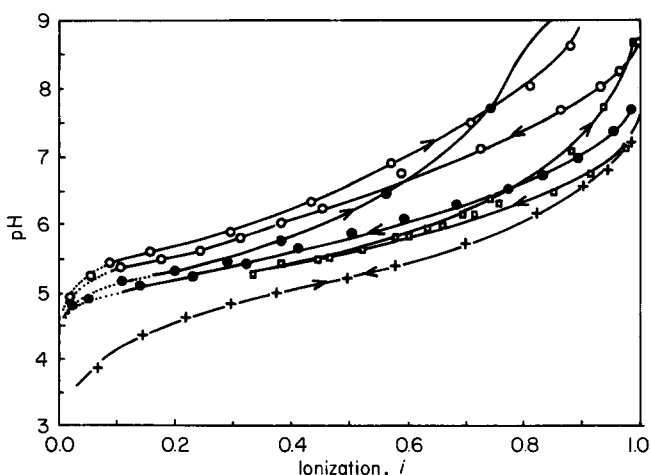


Figure 1 pH versus degree of ionization  $i$ , for PMAAI in 0.1 M NaClO<sub>4</sub>, ○; 1 M NaClO<sub>4</sub>, ●; 1 M NaCl (10°C), □; for PMAAS in 1 M NaClO<sub>4</sub> (20°C), +; carboxyl concentration  $\sim 2 \times 10^{-3}$  M in all experiments. Arrows indicate direction of addition of titrant; dotted lines indicate observation of phase separation

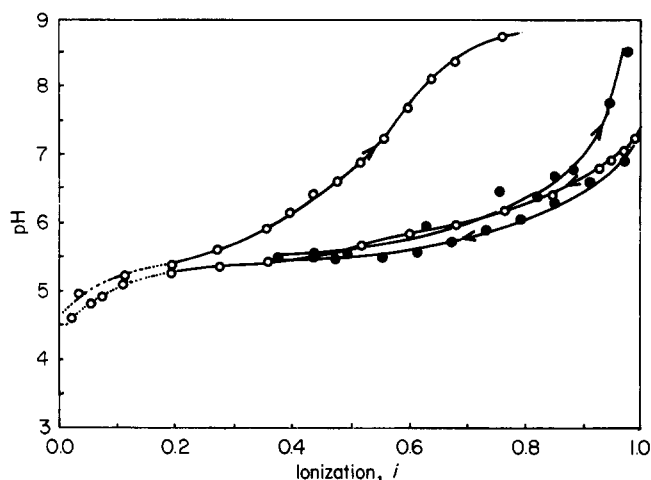


Figure 2 pH versus degree of ionization  $i$ , for PMAAI in 3 M NaCl: ● denotes a run in which direction of titration was reversed at  $i \sim 0.4$  and titrant was added slowly during a viscometric titration (see Figure 5); dotted lines indicate observation of phase separation. Carboxyl concentration  $\sim 2 \times 10^{-3}$  M

In contrast, PMAAI shows varying degrees of potentiometric irreversibility. The areas inside the hysteresis loops are greater in stronger electrolyte solutions. The effect of temperature on potentiometric irreversibility in PMAAI does not seem to be large. A titration carried out at 40°C in 1 M NaCl (c.f. Figure 4) gave a degree of irreversibility intermediate between those for the 10°C and 25°C data shown in Figure 1. A more critical factor in determining the degree of irreversibility is the extent to which the PMAAI was deionized by acid addition on the lower plot before alkali titration was commenced. This is illustrated for 1 M electrolyte in Figure 1 (□) and for 3 M electrolyte in Figure 2 (●) where only a small degree of irreversibility is observed when the direction of titration is reversed at  $i \sim 0.35$ . Significant potentiometric irreversibility is associated with reversal of titration at  $i \leq ca. 0.25$ .

The phase separation which is commonly observed<sup>5</sup> in PMAAI solutions at  $i < ca. 0.25$  is not considered to be the cause of the observed potentiometric hysteresis. The precipitated or coacervated polyacid is readily titrated reversibly over this region if a short period (approx. one minute) is allowed for diffusion of titrant. The redissolution of the phase separated material also proceeds readily without noticeable effect on the continuity of the titration plots. The irreversible behaviour is most apparent at higher pH when the polymer is completely dissolved according to both visual and spectroscopic criteria (see below).

The effect of time on the pH of solutions was small when compared with the pH differences between upper and lower titrations. The most unstable region within the titration plots is the region  $i > 0.5$  on the lower (acid titration) pathway, where a tendency for the pH to drift upwards was observed. For example, in 1 M electrolyte the pH on the lower plot increased from 7.05 to 7.32 at  $i = 0.9$  over 80 min while on the upper plot the pH remained sensibly constant over the same length of time. At lower degrees of ionization no instability in pH was detected within these time scales. In 3 M electrolyte the observed time dependence of the pH was negligible throughout the titration range.

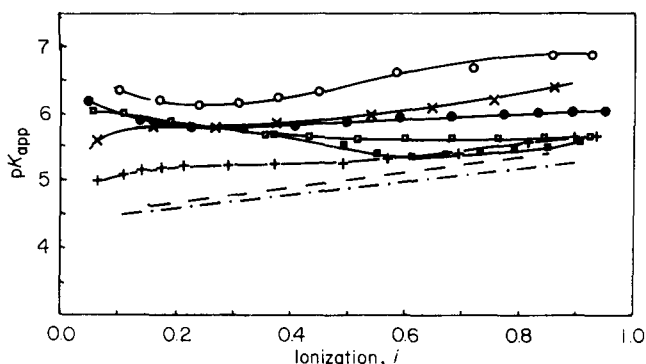
Potentiometric hysteresis of the kind described above in 1:1 electrolyte, solutions, has not been observed in

either atactic or isotactic poly(acrylic acid)s. Data for potentiometric titrations of the polyacrylic acids together with the poly(methacrylic acid) in various concentrations of 1:1 electrolyte are presented as the apparent  $pK$  ( $pK_{app} = pH + \log[(1-i)/i]$  in Figure 3. The data for the PMAAI are for lower (acid titration) pathways only.

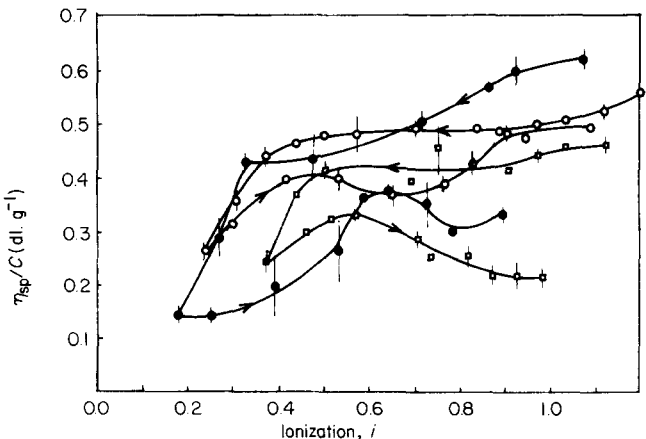
#### Viscometric titrations

Viscometric titrations are confined to the region of complete solubility and in experiments in 1 M electrolyte, deionization down to  $i=0.2$  was achieved without apparent phase separation. The results of viscometric titrations in 1 M and 3 M electrolyte are shown in Figures 4 and 5. The viscometric data for 10°C in 1 M electrolyte given in Figure 4 and the corresponding potentiometric data in Figure 1 were obtained simultaneously; the data for 3 M electrolyte in Figures 2 and 5 were also obtained simultaneously.

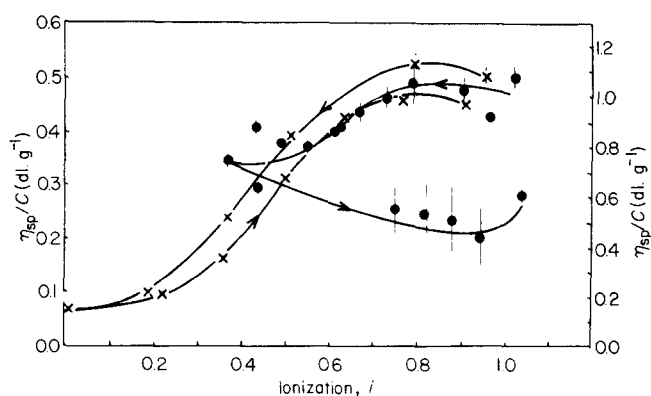
The reduced viscosities in 1 M and 3 M electrolyte solutions are of similar magnitude suggesting that long range electrostatic interactions have been suppressed and effects observed are the consequence of electrostatic and van der Waals interactions between near-neighbouring units. The results show that on the lower (acid titration) pathway of the potentiometric titration the molecular dimensions remain extended until approximately half ionization below which the dimensions decrease. On subsequent reionization with alkali, the dimensions



**Figure 3** Apparent  $pK$  versus degree of ionization,  $i$ , for various poly(carboxylic acids) at 20°C. PMAAI in 0.1 M  $\text{NaClO}_4$ ,  $\circ$ ; PMAAI in 1 M  $\text{NaClO}_4$ ,  $\bullet$ ; PMAAI in 3 M NaCl,  $\square$ ,  $\blacksquare$  (c.f. Figure 2); PMAAS in 0.1 M  $\text{NaClO}_4$ ,  $\times$ ; PMAAS in 1 M  $\text{NaClO}_4$ ,  $+$ ; Isotactic poly(acrylic acid), dashed line; atactic poly(acrylic acid), dash-dot line (1 M NaCl). Data for PMAAI are for acid titrations. Carboxyl concentration  $\sim 2 \times 10^{-3}$  M



**Figure 4** Reduced viscosities versus degree of ionization,  $i$ , for PMAAI in 1 M NaCl at 10°C (c.f. Figure 1),  $\square$ ; at 25°C,  $\bullet$ ; and 40°C,  $\circ$ ; carboxyl concentration  $\sim 2 \times 10^{-3}$  M. Bars indicate the scatter of experimental data



**Figure 5** Reduced viscosities versus degree of ionization,  $i$ , at 25°C for PMAAI in 3 M NaCl (c.f. Figure 2),  $\bullet$ ; PMAAS in 1 M NaCl,  $\times$ ; carboxyl concentration  $\sim 2 \times 10^{-3}$  M. Bars indicate the scatter of experimental data

initially increase but then pass through a maximum in the region of half ionization. The contraction of the molecular dimensions on titration with alkali for  $i > ca. 0.5$  is apparently arrested at  $i \sim 0.7$  when the experiment is conducted at 40°C; the thermal energy clearly assists in surmounting the conformational free energy barrier between the respective states on acid and alkali titration for  $i > 0.7$ . However, the potentiometric data at 10°C in 1 M electrolyte in Figure 1 and the simultaneous viscometric data in Figure 4 show that irreversibility in viscometric data is not of necessity accompanied by potentiometric irreversibility. The same conclusion is to be drawn from the simultaneous potentiometric and viscometric data for 3 M electrolyte given in Figures 2 and 5. On the other hand, potentiometric irreversibility is apparently associated with the extent of deionization which is achieved in the region  $i < ca. 0.5$  and the conformational changes which accompany this process introduce a 'proton trapping' mechanism.

Viscometric data for PMAAS are also given in Figure 5. The differences between acid and alkali titrations are hardly outside of experimental error. They may reflect a small degree of isotactic placements along the polyacid chain. However, we conclude that PMAAS is essentially potentiometrically and viscometrically reversible on the time scale of these experiments. In a similar investigation of the atactic poly(acrylic acids) in 1:1 electrolytes, the potentiometric and viscometric titrations were found to be reversible also.

#### U.v. spectrophotometric titrations

Ultraviolet spectra of PMAAI and PMAAS at several degrees of ionization in 0.1 M  $\text{NaClO}_4$  and 1 M  $\text{NaClO}_4$  are shown in Figures 6 and 7. The shoulder of the  $\pi \rightarrow \pi^*$  absorption band ( $\lambda_{max}$  in the vacuum u.v.) and the much more weakly absorbing  $n \rightarrow \pi^*$  band ( $\lambda_{max} \approx 210$  nm) are best separated for PMAAS in 0.1 M electrolyte.

The effects of ionization and electrolyte concentration on the  $n \rightarrow \pi^*$  band both appear to be small factors apparently giving rise to small hyperchromic shifts. Thus the increases in absorbance for  $\lambda = 190-210$  nm with ionization and electrolyte concentration are presumably the consequence of bathochromic shifts of the  $\pi \rightarrow \pi^*$  band. (A relative increase of the  $\pi$  energy level with ionization and/or a decrease of the  $\pi^*$  level with increase in electrolyte concentration would each reduce the energy of the transition relative to the energy gap for unionized states in a less polar environment<sup>8</sup>).

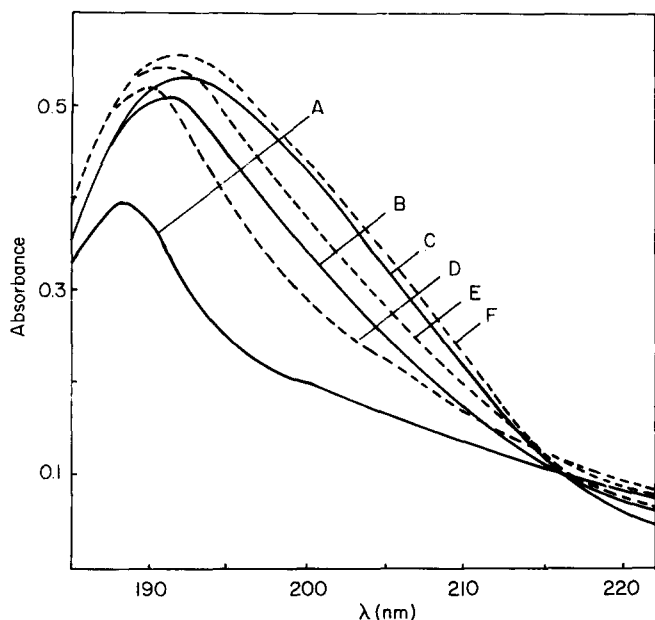


Figure 6 U.v. spectra for PMAAI in 0.1 M NaClO<sub>4</sub>: *i*=0.11, A; *i*=0.59, B; *i*=0.99, C; in 1 M NaClO<sub>4</sub>, *i*=0.14, D; *i*=0.50, E; *i*=0.99, F. Carboxyl concentration  $\sim 2 \times 10^{-3}$  M

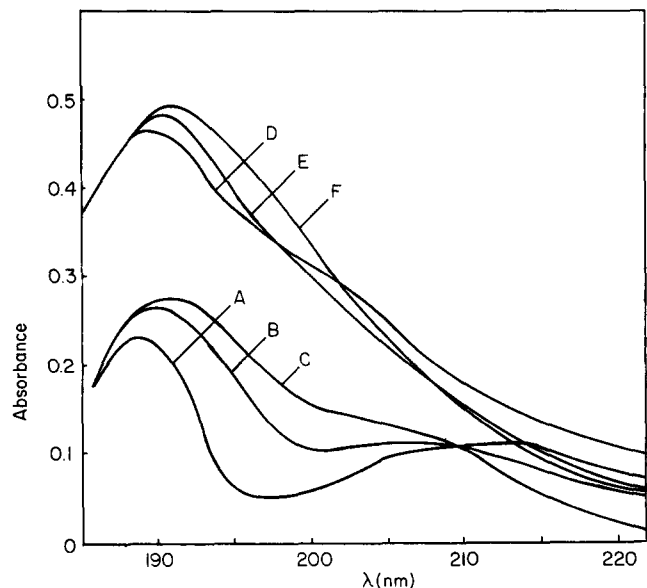
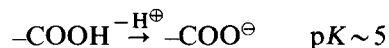


Figure 7 U.v. spectra for PMAAS in 0.1 M NaClO<sub>4</sub>: *i*=0.07, A; *i*=0.54, B; *i*=0.97, C; in 1 M NaClO<sub>4</sub>, *i*=0.12, D; *i*=0.49, E; *i*=0.98, F. Carboxyl concentration  $\sim 2 \times 10^{-3}$  M

Low molecular model acids show greater sensitivity to the environment than do the polyacids. This is possibly due to easier accessibility of the chromophore to the solvent environment. In hexane, the  $\pi \rightarrow \pi^*$  band does not feature in the spectrum of acetic acid<sup>3</sup> for  $\lambda > 185$  nm but very strong absorbance of simple carboxylic acids is observed in 1 M electrolyte at low degrees of ionization (see Figure 8). Thus the low profile of the  $\pi \rightarrow \pi^*$  band for PMAAS in 0.1 M NaClO<sub>4</sub> at *i*  $\sim 0$  may reflect a more paraffinic environment of the carboxyl groups in this polyacid than in the case of PMAAI. Such a situation might be expected when each polyacid is in largely all-*trans* conformations and the carboxyls in PMAAS are flanked by methyl groups whereas those in PMAAI are flanked by others of their own kind at close range.

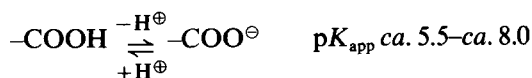
The spectrophotometric titrations (Figure 8)  $\epsilon_{200}$  versus *i* for acetic acid and 1,6-hexanedioic acid in pure water

give linear plots over the range  $0 < i < 1.0$  corresponding to the process



However, the conformationally hindered 2,2-diethylpropanedioic acid has a distinct change in gradient of  $\epsilon_{200}$  vs. *i* at *i*=0.5. This steep rise in extinction coefficient for *i*>0.5 is presumably associated with the repulsive interaction between the charged groups which are constrained to remain at close range (2–3 Å) following breakdown of the ionic hydrogen bond at *i*=0.5. (A disproportionate increase in the  $\pi$  energy level relative to the more expanded  $\pi^*$  state may account for the observed red shift.)

Thus at least three factors require consideration in accounting for the changes in the polyacid spectrophotometric titrations in Figure 8. It is not clear whether the mutual orientations of adjacent carboxyls are also significant. However, if the spectrophotometric titrations are considered in terms of the three factors discussed above the processes occurring over each pathway of the PMAAI titrations are consistent with the simple exchange.



Nevertheless, the irreversibility in the potentiometric data is reflected in the different gradients of the acid and alkali spectrophotometric titrations. (The data for PMAAI in 0.1 M and 1 M electrolyte in Figure 1 was obtained simultaneously with that in Figure 8.) Thus according to the above discussion, the steeper gradients of  $\epsilon_{200}$  vs. *i* for the alkaline titrations reflect closer interactions between adjacent carboxyls. A conformational transformation which placed neighbouring functional groups at closer range would also account for the less facile proton release on the alkaline titration pathway.

#### Conformational changes

A more detailed account of the conformational analysis is given in the following paper<sup>9</sup>. However, the scheme

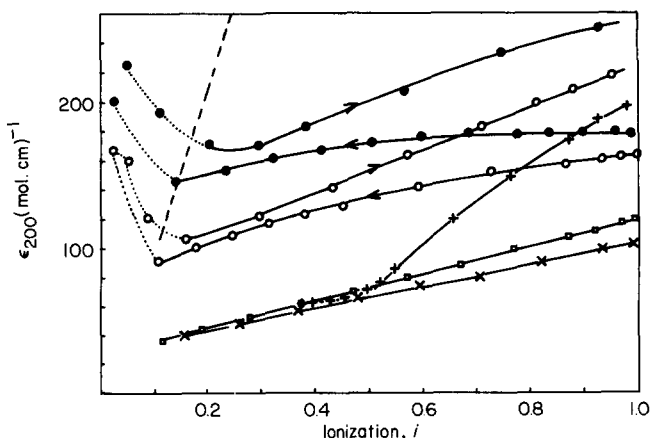


Figure 8 U.v. spectrophotometric titrations for PMAAI and low molecular weight carboxylic acids. Extinction coefficient at 200 nm  $\epsilon_{200}$  versus degree of ionization *i* at 20°C for PMAAI in 0.1 M NaClO<sub>4</sub>, ○; PMAAI in 1 M NaClO<sub>4</sub>, ●; ethanoic acid, ×; hexanedioic acid, □; 2,2-diethylpropanedioic acid, +; hexanedioic acid in 1 M NaClO<sub>4</sub>, broken line. Carboxyl concentration  $\sim 2 \times 10^{-3}$  M

outlined differs from previous speculation<sup>1</sup> involving intramolecular hydrogen-bonding for which no strong evidence is provided by the experimental data. Rather, an attempt is made to explain the results in terms of irreversible conformational behaviour with the ability of neighbouring carboxyls to ionize depending on their separation.

A scheme of the principal conformational changes which account for the observed potentiometric and conformational irreversibility is proposed as follows:

*Acid titration.*  $1.0 > i > 0.5$  extended  $|tg|$  helices;  $i \sim 0.5$  extended  $|tt|$  sequences of same displaced state;  $0.5 > i > 0$  reduced dimensions by proliferation of random sequences of each displaced  $|tt|$  state.

*Alkali titration.*  $0 < i < 0.5$  extension of dimensions by increase in sequences of the same  $|tt|$  displacement. Introduction of  $|gg|$  causes molecular coiling giving rise to a maximum in molecular dimensions without further ionization. Re-conversion to  $|tg|$  states is very slow.

In the strong electrolyte solutions used in this work the conformational behaviour should be dominated by the influence of near neighbour interactions. In the present conformational analysis<sup>9</sup>, the disposition of the individual hydrogen atoms incorporated in the methyl and methylene groups is considered. A significant conclusion of the analysis is the importance of interdigitation of these hydrogens whenever methyl and/or methylene groups interact in low energy conformations. The ability of the methyls and/or methylenes to 'mesh' together like gear wheels is found to be sensitive to their rotational states. For unionized PMAAI, the lowest energy dyad states are found to be the  $|tt|$  and the  $|tg|$  states with energy minima which are computed to be at approximately the same value (ca. 6 kcal mol<sup>-1</sup>). Here, a vertical line denotes the C<sub>α</sub> atom.

The *gauche* states are defined according to the stereochemical convention for the assignment of bond rotational states<sup>10</sup> whereby a *g* state is obtained by an approximate 120° clockwise rotation of a *d* bond or anticlockwise rotation of an *l* bond from the *trans*(*t*) state at zero degrees. A *d* bond has the carboxyl group to which it is attached on the right when viewing from C<sub>α</sub> to CH<sub>2</sub> and an *l* bond has the carboxyl on the left.

In PMAAI the  $|tg|$  and  $|tt|$  states each have two displaced minimum energy locations. One of the  $|tg|$  states (-20, 135) should be of greater probability than the other (5, 100) particularly in fully ionized chains whereas each displaced  $|tt|$  state (10°, -25°) and (-25°, 10°) is of equal probability. Thus  $|tg|$  or  $|tt|$  sequences of the same displaced state will have extended dimensions. Regular sequences of the same displaced  $|tt|$  should be favoured in the region  $i = 0.5$  as such sequences give greater separation of alternate carboxyls. However, random sequences of each displaced  $|tt|$  state, which become more prevalent as the chain is deionized at  $i < 0.5$ , give rise to reduced molecular dimensions. This is a consequence of the dissimilarity of the skeletal bond angles at the C<sub>α</sub> atoms (ca. 110°) and the methylene groups which, according to the present work, are strained to ca. 129°.

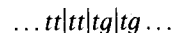
The alternative *gauche* state is the  $\bar{g}$  state but these are likely to have high energy interactions with neighbours in 1:1 electrolytes. Thus although they may occur in specific conformational sequences in complexes with multivalent ions (see below)  $\bar{g}$  states are ignored in 1:1 electrolyte

solutions. The  $|gg|$  state has an accessible energy giving wide separation of carboxyls (6–6.5 Å) permitting both groups to ionize simultaneously. However,  $|gg|$  must be flanked by  $|tt|$  sequences and will thus occur at intervals along the chain where they are effective in reducing the dimensions of the molecular coil by introducing 'kinks' into the extended  $|tt|$  sequences without increasing the degree of ionization<sup>9</sup>.

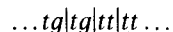
However, a significant conclusion of the hydrogen interdigitation requirement is that an isolated *g* state within an otherwise all *trans* sequence



is of high energy (ca. 12 kcal mol<sup>-1</sup>) owing to mismatch of the interacting methyl and methylene rotations. Thus for PMAAI the mixed sequences



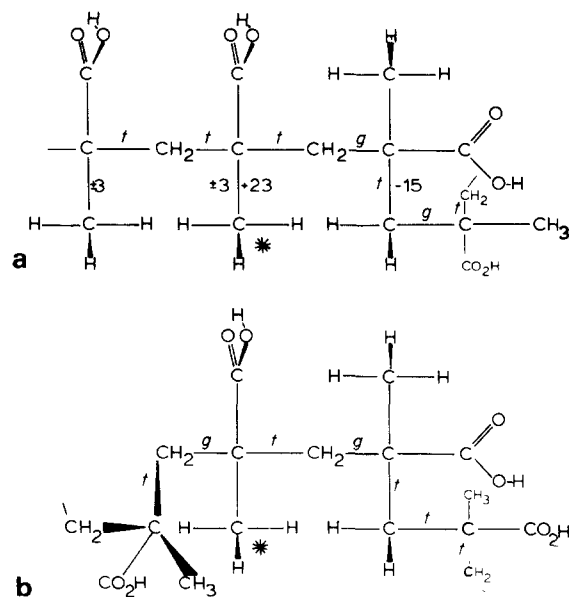
is similarly of high energy but



is of low energy because the methyl group has become free to conform to the methylene at the  $|tg|tt|$  junction (see Figure 9). This suggests that the interconversion of  $|tt|$  and  $|tg|$  states may tend to occur sequentially (cooperatively) from a terminus and not randomly along the chain. According to Manning's theory<sup>11</sup> of polyelectrolyte solutions counterion condensation will occur when the charge density parameter

$$\zeta = e^2/DkTb \geq 1$$

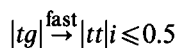
where  $e$  is the electronic charge,  $D$  is the dielectric constant,  $k$  is the Boltzmann constant and  $b$  the interchange spacing. In water at 25°C ( $D=78$ ) an interchange spacing of less than 7.14 Å should bring



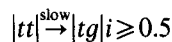
**Figure 9** Projections of sections of PMAAI chain viewed in the plane of the skeletal backbone: (a) showing conflicting rotational requirements for  $-\text{CH}_3^*$  in the  $|tt|$  dyad ( $+3^\circ$ ) and the  $|tg|$  dyad ( $+23^\circ$ ) in a  $\dots |tt|tt|tg|tg \dots$  sequence; (b) showing  $-\text{CH}_3^*$  flanked by  $-\text{CO}_2\text{H}$  and  $-\text{CH}_2-$  and thus free to interdigitate with the latter in a  $\dots |tg|tg|tt|tt \dots$  sequence

about counterion condensation so as to restore  $\zeta$  to unity. In PMAAI the adjacent carboxyl separations in  $|tg|$  states (5–6 Å) are sufficient to allow monovalent electrolyte (cationic) condensation and the simultaneous ionization of neighbouring carboxylates. However, in  $|tt|$  the atoms of the carboxyls lie in approximately parallel planes with a separation (*ca.* 3 Å) which is within the sum of their van der Waals radii; they are thus too close for effective screening by solvent or counterion condensation. The interaction of charged groups would be repulsive in the extreme even in the presence of the strongest 1:1 electrolyte. Thus in all-*trans* conformations only *ca.* 50% ionization is expected.

However, the observed irreversible phenomena require that the sequential deionization process



proceeds much faster than the sequential ionization process



Several factors can be identified which may provide the basis of an explanation for the irreversibility. Following deionization in  $|tg|$  sequences the conversion to either of the  $|tt|$  states can proceed one dyad at a time and interdigitation requirements in this state involve only methyl groups with short relaxation times. On the other hand a carboxylic acid group intermediate between two charged groups in  $|tt|$  will ionize only by a simultaneous cooperative manoeuvre of both dyads and the interdigitation of methyl and methylene in  $|tg|$  involves relaxation of the inflexible skeletal backbone.

The absence of irreversible behaviour in PMAAS is consistent with a low expectation of methyl–methylene interactions in this chain. In the racemic displaced  $|tt|$  state the neighbouring carboxyls are widely separated (*ca.* 5 Å) and in  $|tg|$  the methylene interacts with a carboxyl group which, being planar, is readily accommodated by the hydrogen atoms of the methylene group.

#### Interactions of PMAAI with multivalent cations

The ‘binding’ of multivalent ions to poly(carboxylic acids) is known to facilitate proton release by effectively reducing the local electrostatic field in the neighbourhood of adjacent carboxylates to a greater degree than is achievable by monovalent cations<sup>12</sup>. Depending on the chemical nature of the multivalent ion the binding may be purely electrostatic in nature or a more specific chelation by the carboxylates may be involved. Depending on its chelation requirements, a strongly binding multivalent cation is likely to stabilize preferentially certain conformational states, thus modifying the potentiometric behaviour which is observed in the presence of 1:1 electrolyte alone.

#### Diamino alkanes

Potentiometric and spectrophotometric titration data for PMAAI and conventional (largely syndiotactic) PMAA in 0.1 M NaClO<sub>4</sub> in the presence of 1,6-diamino hexane and 1,2-diamino ethane are shown in Figures 10 and 11. The ratio  $\frac{[\text{H}_3^+\text{NR}^+\text{NH}_2]}{[\text{H}_3^+\text{NR}^+\text{NH}_3]}$  for the

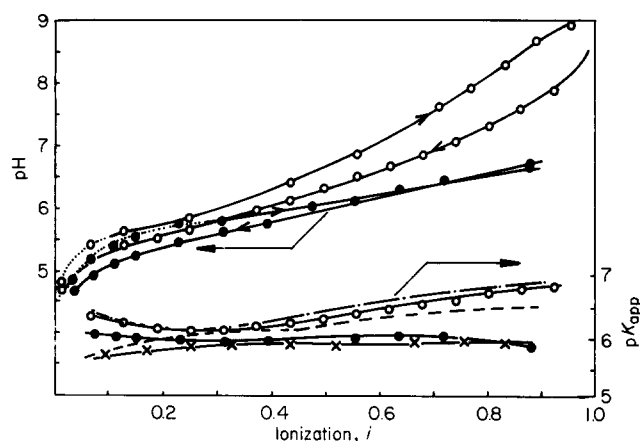


Figure 10 pH and apparent pK versus degree of ionization, *i*, in the presence of diamines in 0.1 M NaClO<sub>4</sub>. PMAAI with 1,6-diaminohexane ([carboxyl]:[–NH<sub>2</sub>]=1:2.03), ○; PMAAI with 1,2-diaminoethane ([carboxyl]:[–NH<sub>2</sub>]=1:1.04), ●; ‘Conventional’ PMAA (*ca.* 80% syndiotactic triads, 10<sup>–2</sup> M) titrated with 1,2-diaminoethane, ×; ‘Conventional’ PMAA (10<sup>–2</sup> M carboxyl concentration in 0.1 M NaClO<sub>4</sub>, alone, dashed line; PMAAI in presence of 0.1 M NaClO<sub>4</sub> alone, dash-dot line. Carboxyl concentration for PMAAI experiments ~2 × 10<sup>–3</sup> M

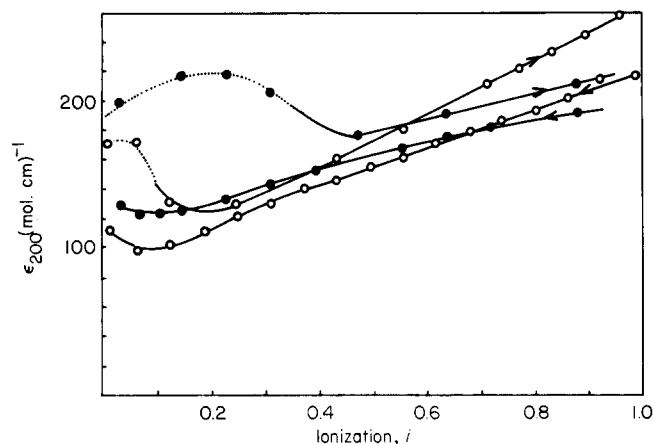


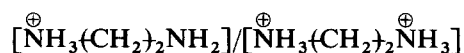
Figure 11 U.v. spectrophotometric titrations of PMAAI in the presence of 1,6-diaminohexane, ○; and 1,2-diaminoethane, ●; conditions as in Figure 10

diamines in polyacid-free water is readily obtained from

$$\log_{10} \left\{ \frac{[\text{H}_3^+\text{NR}^+\text{NH}_2]}{[\text{H}_3^+\text{NR}^+\text{NH}_3]} \right\} = \log_{10} K_{a1} + \text{pH}$$

where  $K_{a1}$  is the greater of the acid dissociation constants for the diamines. Thus for diamino hexane ( $K_{a1} = 1.73 \times 10^{-11}$ ;  $K_{a2} = 1.39 \times 10^{-12}$  (ref. 13)) at pH9 more than 98% of diamine is doubly charged. However, the experimental data shows that 1,6-diamino hexane has only a moderate influence on the potentiometric and spectrophotometric titrations of either PMAAI or conventional PMMA. The behaviour is apparently that to be expected for 1:1 electrolyte solutions intermediate in concentration between 0.1 M and 1 M. The length (*ca.* 9.0 Å) and flexibility of 1,6-diamino hexane clearly gives rise to a rather weak, non-specific interaction with PMAA.

On the other hand diamino ethane ( $K_{a1} = 2.73 \times 10^{-8}$ ;  $K_{a2} = 1.94 \times 10^{-11}$ ) has had a marked effect on the potentiometric behaviour. In pure water the ratio



is 0.85 at pH 6.7, the upper pH limit of the data. However, the experiments suggest that the ionization of both polyacid and diamine has been considerably enhanced over that in simple electrolyte solutions. Thus the potentiometric irreversibility has virtually disappeared and the  $pK_a$  of the polyacid is considerably reduced particularly at higher degrees of ionization. Thus for  $i > ca. 0.2$  there is no distinction between the potentiometric behaviour of PMAAI and 'conventional' PMAA.

In terms of the conformational model of PMAAI described above, these results are consistent with the preferential stabilization of  $|tg|$  states by the 1,2-diammoniummethane ion. The quaternary nitrogen atoms are spaced at approximately 4 Å and the molecule is *ca.* 6.5 Å in overall length. These dimensions are easily accommodated by an oxygen from each carboxylate when the intervening dyad is in a  $|tg|$  conformation. This specific interaction has thus increased the rate of ionization by alkaline titrant. Furthermore, the reduction in the repulsive interaction between neighbouring carboxylates has given rise to less steep gradients of u.v. spectrophotometric titrations in accord with observations of PMAAI in 1:1 electrolytes.

#### Magnesium and calcium

Potentiometric titrations for PMAAI in the presence of  $Mg^{2+}$  and  $Ca^{2+}$  ions are shown in Figure 12. The data show only a minimal influence of  $Mg^{2+}$  on the potentiometric behaviour. This conclusion is reflected in the spectrophotometric titration (not shown) which is essentially indistinguishable from that for the solution with 0.1 M electrolyte alone<sup>3</sup> (Figure 8). These observations are consistent with the low value of the binding constant  $K_b$  ( $= [M^{2+}_{bound}]/[M^{2+}_{free}][COO^-]$ ) for  $Mg^{2+}$  as found by O'Neill and coworkers<sup>14</sup> using equilibrium-dialysis. These workers reported values of 14 decreasing to 9 for  $K_b$  over the range  $0.25 < i < 0.75$ .

However, the noticeable reduction in the potentiometric irreversibility in the presence of  $Ca^{2+}$  ion suggests a stronger interaction with PMAAI than in the case of the smaller ion. This presumably reflects, at least in part, the greater diameter and the lower enthalpy of hydration<sup>14</sup> of  $Ca^{2+}$  (366 kcal mol<sup>-1</sup>) compared with that for  $Mg^{2+}$  (459 kcal mol<sup>-1</sup>) and according to the scheme described above, promotion of the stability of ionized neighbouring

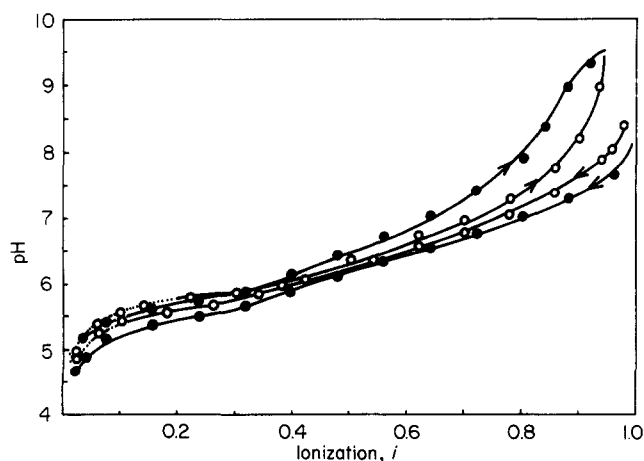


Figure 12 pH versus degree of ionization,  $i$ , for PMAAI in 0.1 M  $NaClO_4$  in the presence of  $CaCl_2$  ( $[carboxyl]:[Ca^{2+}] = 3.06:1$ ),  $\circ$ ; in presence of  $Mg(ClO_4)_2$  ( $[carboxyl]:[Mg^{2+}] = 2.02:1$ ),  $\bullet$ ; carboxyl concentration  $\sim 2 \times 10^{-3}$  M

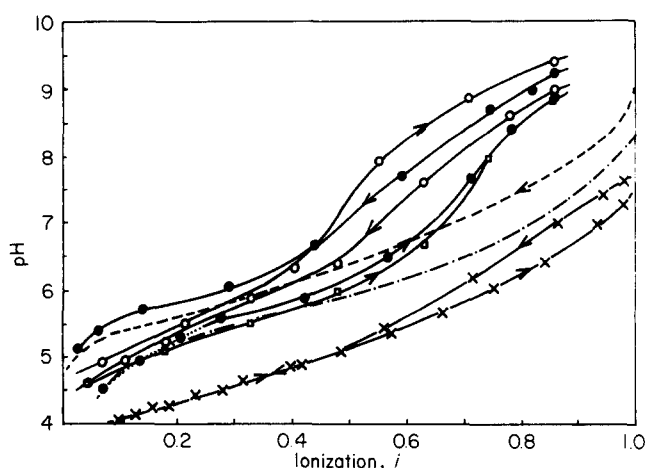


Figure 13 pH versus degree of ionization,  $i$ , in 0.1 M  $NaClO_4$  in the presence of  $Cu(ClO_4)_2$ . For PMAAI, successive aliquots of  $Cu(ClO_4)_2$  were added at the low pH limit of each titration cycle to give the following  $[carboxyl]:[Cu^{2+}]$  molar ratios 9.4:1,  $\bullet$ ; 4.7:1,  $\circ$ ; 2.3:1,  $\square$ . PMAAS,  $[carboxyl]:[Cu^{2+}] = 4.0:1$ ,  $\times$ . Carboxyl concentration 1 to  $3 \times 10^{-3}$  M according to dilution by titrants. PMAAI, (---); PMAAS, (-.-.-)

carboxyls in  $|tg|$  states. Simultaneous measurements of  $Ca^{2+}$  activity using a specific ion electrode suggest that the binding constant  $K_b$  (defined above) decreases from *ca.* 2700 to *ca.* 700 over the range  $0.1 < i < 0.9$  on the lower (acid titration) pathway<sup>3</sup>. However, less calcium is bound on the upper (alkaline titration) pathway for  $i > ca. 0.5$ , the discrepancy being *ca.* 20% at  $i = 0.9$ .

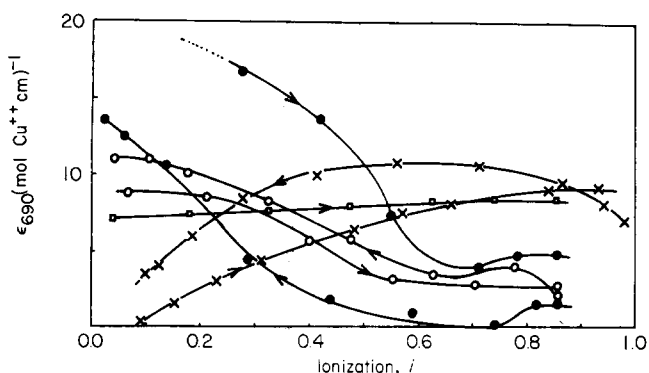
#### Cupric ion

The cupric ion is known to interact strongly with PMAAI. O'Neill and coworkers<sup>14</sup> found that the binding constant for  $Cu^{2+}$  increased from 13 400 to 18 000 over the range  $0.5 < i < 0.9$ . For PMAAS  $K_b$  increased from 180 to 6100 over the range  $0.1 < i < 0.9$ . These authors and Kolawole and Bello<sup>16</sup> proposed complex stoichiometries of 4:1 (4 moles of carboxyl per mole of  $Cu^{2+}$ ) at low degrees of ionization and 2:1 at higher degrees of ionization or in the presence of excess  $Cu^{2+}$ .

Potentiometric titration data for PMAAI in 0.1 M  $NaClO_4$  and various concentrations of  $Cu^{2+}$  are given in Figure 13. The data were obtained in a single experiment. Successive aliquots of  $Cu(ClO_4)_2$  were added at the low pH limit of each titration cycle. Potentiometric data for PMAAS: $Cu^{2+}$  with a 4:1 molar ratio of  $[carboxyl]:[Cu^{2+}]$  is also shown.

The potentiometric data show that in marked contrast to the effects of diammoniummethane and  $Ca^{2+}$  ions the interaction of  $Cu^{2+}$  with PMAAI has not promoted ionization of the polyacid in the region  $i > 0.5$ . Although there is evidence of strong counterion binding for  $i < 0.5$  the structures which are stabilized in this region suppress the ionization of the remaining groups to a greater degree than in the presence of 0.1 M  $NaClO_4$  alone. This is particularly true for the lower concentrations of  $Cu^{2+}$ . However, the binding of  $Cu^{2+}$  to PMAAS has facilitated proton release over the full titration range. The complexes between PMAA and  $Cu^{2+}$  were observed both visually and spectroscopically to remain in solution at both acidic and alkaline limits of the titrations following the initial addition of  $Cu^{2+}$ .

The carboxyl spectra in the u.v. range are complicated by the changes in absorption due to the  $Cu^{2+}$  ion. However, a discernible feature of the PMAAS spectra is a

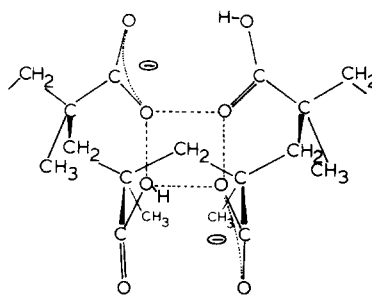


**Figure 14** Visible spectrophotometric titrations for PMAAI and PMAAS in 0.1 M NaClO<sub>4</sub> in presence of Cu(ClO<sub>4</sub>)<sub>2</sub>. Conditions and symbols as in Figure 13

pronounced blue shift of the  $n \rightarrow \pi^*$  band for  $0 < i < 0.5$  suggesting association of the  $n$  electrons of two adjacent carboxylates with the available Cu<sup>2+</sup> ions.

However, the broad band in the visible range with  $\lambda_{\max} \sim 700$  nm which gives rise to the blue-green colouration is readily monitored (Figure 14) and indicates a quite different pattern of absorption for PMAAI and PMAAS. For 9.4:1 and 4.7:1 molar ratios, PMAAI forms a strongly coloured complex in the region  $i < 0.5$  with the changes in the apparent extinction coefficient (per mol Cu<sup>2+</sup>) reflecting the closeness of binding as suggested by the potentiometric data. A different kind of interaction is indicated for PMAAI with an equivalent concentration of Cu<sup>2+</sup> and for PMAAS. While the latter is very effective in releasing protons the correlation with the visible spectrum is less clear.

Cupric ion complexes with oxygen containing ligands commonly adopt distorted octahedral coordination in both neutral and negatively charged complexes<sup>17</sup>. In complexes with bidentate ligands four chelate oxygens are in a square planar arrangement having sides of ca. 2.8 Å, with water oxygens approximately normal to the plane at longer range (ca. 3.5 Å). In PMAAI, symmetrical sequences centred on  $[tt]$  and involving  $\bar{g}$  states such as  $[t\bar{g}]tt[\bar{g}t]$  give four chelate oxygens in an approximately square planar arrangements as shown in Figure 15. The higher energy  $\bar{g}$  states would be stabilized by a strong interaction with the Cu<sup>2+</sup> (note Cu–O bond strength in the acetylacetonate complex is estimated to be ca. 49 kcal mol<sup>-1</sup>). Alternatively, a low energy but longer sequence giving square planar carboxyls is obtained from  $[\bar{g}\bar{g}]\bar{g}t|tt|t\bar{g}[\bar{g}\bar{g}]$ . These arrangements of carboxyls are not available in PMAAS and any similar arrangement involves at least one ‘along chain’ methyl–methylene interaction in the central  $[t\bar{g}]$  dyad. The results indicate that the intensely coloured complex may be a half-ionized form of such an arrangement which breaks down at higher degrees of ionization. While the 2:1 molar complex in PMAAS is plausibly a chelation by adjacent approximately coplanar carboxyls in  $[tt]$  states where a close approach to accommodate the small Cu<sup>2+</sup> is



**Figure 15**  $[t\bar{g}]tt[\bar{g}t]$  sequence in PMAAI ( $i=0.5$ ) giving a plausible arrangement of carboxyls for octahedral coordination of Cu<sup>2+</sup>

possible, the corresponding arrangement in PMAAI is not so readily postulated. A strong affinity for the  $[tg]$  arrangement might be expected to result in full ionization of the chain. However, the *trans*–*cis* structure with coplanar carboxyls, which is discussed in a following paper<sup>9</sup>, could chelate a small strongly bound ion and further discussion on this point is reserved until there.

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