Conformations in partly ionized poly(methacrylic acid): 1. Ionic hydrogen bonds in syndiotactic chains

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Comparisons of u.v. spectrophotometric titrations of some dicarboxylic acids, 'conventional' poly(methacrylic acid) and poly(acrylic acid) suggest that ionic or acid-salt hydrogen bonds form between adjacent carboxyl groups in racemic dyads in partly ionized forms of poly(methacrylic acid). The ionic hydrogen bonds form in *tt* conformations of the dyads. The maximum concentration of ionic hydrogen bonds occurs at 50% ionization in pure syndiotactic chains in the presence of electrolyte to give a chain having four-bond repeating units. Bonds 1 and 2 are presumed to be fixed in *trans–trans* conformations while bonds 3 and 4 retain some conformational freedom although this is somewhat reduced as a consequence of side group rotations necessary for hydrogen bonding. While ionic hydrogen bonds may form across meso dyads in $t\bar{g}$ conformations, isotactic chains incorporating ionic hydrogen bonds are predicted to be less stable than the corresponding syndiotactic chains.

INTRODUCTION

There has been considerable interest for a number of years in the nature of the local interactions which stabilize the conformations of poly(methacrylic acid) and its ionized forms in aqueous solution[1–10]. This interest has largely been concerned with the nature of the so-called conformational transition in poly(methacrylic acid). Several experimental techniques including dilute solution viscometry[5], elastic neutron scattering[9] and potentiometry[2,4,5], may be applied to show that during progressive neutralization of the poly-acid with sodium hydroxide in aqueous solutions a 'coiled' form of the molecule persists up to a degree of ionization, α, in the range of 0.2 to 0.4. Further ionization brings about extension of the molecule following accumulation of electrostatic energy within the domain. This behaviour contrasts with the structurally related poly(acrylic acid) which shows no tendency to remain in a coiled form at low degrees of ionization[5].

Several workers have investigated the conformational transition in poly(methacrylic acid) using ultra-violet spectroscopy[5–7]. However, no interpretations of the experiments in terms of structural changes were discussed. In this paper, u.v. spectrophotometric titrations of some dicarboxylic acids, poly(methacrylic acid) and poly(acrylic acid) are compared. These results and those from other techniques which have been documented are considered in light of the local interactions in partly neutralized forms of poly(methacrylic acid).

EXPERIMENTAL

Preparation of conventional poly(methacrylic acid)

Methacrylic acid was supplied by Koch–Light Ltd and purified by distillation under vacuum. Poly(methacrylic acid) was prepared by polymerization of 50 ml of methacrylic acid in solution in 200 ml of 2-butanone with 0.01 g of benzoyl peroxide as initiator. After warming the mixture to 66°C with continual stirring, the polymerization proceeded rapidly and the product was collected as a fine suspension. Following prolonged dialysis to remove unconverted monomer a yield of 85% was obtained.

The tacticity of the product was determined first by methylating the poly(methacrylic acid) using diazomethane according to the method of Katchalsky and Eisenberg[1]. The n.m.r. spectrum of the poly(methyl methacrylate) product in solution in *o*-dichlorobenzene was obtained using a 220 MHz Perkin–Elmer spectrometer. The spectrum was analysed using the method of Bovey[11]. The polymer was found to consist of 80% racemic dyads; the triad tacticities are 64% syndiotactic, 32% heterotactic and 4% isotactic.

The dicarboxylic acids, pentanedioic acid, 2,2′-diethylpropanedioic acid and 3,3′dimethylpentanedioic acid, were obtained commercially and used as supplied. Sodium perchlorate solution was prepared by neutralization of 'Analar' perchloric acid with sodium hydroxide to pH7.

The spectrometer was a single beam instrument assembled around a Barr and Stroud monochromator. The source was a deuterium lamp operating at 300 mA from a stabilized power supply, and the detector was an Aminco photomultiplier which was connected to an amplifier. Transmittance and optical density could be read from a meter incorporated into the amplifier. The flow-through cell had a path length of about 8 mm and was constructed using silica windows with a PTFE spacer. The cell was connected to the titration vessel by 1 mm i.d. PVC tubing. The sample was circulated by means of a peristaltic pump. The total volume of the system was ~4 ml. The burette and a glass pH electrode with an in-built calomel reference electrode were sealed into the titration vessel and a slow stream of nitrogen was passed through the vessel to exclude carbon dioxide. The contents of the flask were mixed using a magnetic stirrer and all titrations were performed at ambient temperature. The degree

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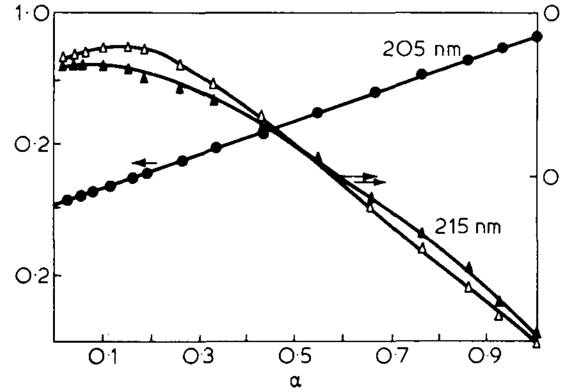


Figure 1 U.v. spectrophotometric titrations of pentanedioic acid (●), poly(acrylic acid) in the absence of electrolytes (△) and poly poly(acrylic acid) in 0.1 M NaClO$_4$ (▲); [–COOH] = 0.01 M

of ionization, α, is given by:

$$\alpha = (10^{-\mathrm{pH}} + b)/a \qquad (\mathrm{pH} < {\sim}10)$$

where a is the initial concentration of carboxylic acid groups and b is the concentration of added base.

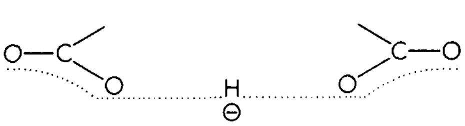
RESULTS AND DISCUSSION

The maximum in the ultra-violet absorption peak for the carboxylate anion occurs at about 180 nm and the maxima for various undissociated saturated carboxylic acids in aqueous solution range between about 204 nm for acetic acid to about 212 nm for poly(methacrylic acid). The region of overlap of the two absorption peaks between about 100 nm and 240 nm may be studied by spectrophotometric titrations over the range of the degree of neutralization, α, using conventional instruments which operate in the near u.v.[5–7]. The absorption curves for various degrees of neutralization for simple monofunctional carboxylic acids and for unsubstituted dicarboxylic acids such as pentanedioic and hexanedioic acids in aqueous solutions pass through a single isobestic point. As shown in the publications by Barone *et al.*[5] and Michaeli[7], the poly(acrylic acid) system also conforms fairly well to this type of behaviour. On the other hand, spectrophotometric titrations of substituted aliphatic dicarboxylic acids such as 2,2′-diethylpropanedioic acid and 3,3′-dimethylpentanedioic acid and also poly(methacrylic acid) do not conform to this simple behaviour. As shown for poly(methacrylic acid) in the publications by Barone *et al.*[5] and Michaeli, the absorption curves do not pass through a single isobestic point over the range in α.

Spectrophotometric titrations at fixed wavelengths which conform to the former type of behaviour are shown in *Figure 1*. The plot for pentanedioic acid is linear over the full range in α; the plot for poly(acrylic acid) is essentially linear for $\alpha > {\sim}0.2$ and is largely unaffected by addition of 0.1 M of non-absorbing electrolyte. The plots in *Figures 2* and *3* for the substituted dicarboxylic acids and poly(methacrylic acid) however, are characterized by definite changes in slope in the region $\alpha = 0.5$. The gradients of the plots depend on the choice of wavelength for each titration in relation to the positions of the isobestic points on the absorption curves which vary slightly between the different systems. The choice of wavelength represents a compromise between experimental limitations at the shorter wavelengths close to 200 nm and small differences in optical densities of the several states at wavelengths greater than about 230 nm.

The spectrophotometric titrations suggest that whereas only the unionized acid and carboxylate ion are involved in the pentanedioic acid system (*Figure 1*), the plots in *Figures 2* and *3* may be accounted for if a third intermediate state is also present. This state has a maximum concentration at α equal to 0.5 for 2,2′-diethylpropanedioic acid and 3,3′-dimethylpentanedioic acid and at α between 0.4 and 0.5 for conventional poly(methacrylic acid) in the presence of sufficient electrolyte. In the absence of electrolyte, the intermediate state in the poly(methacrylic acid) system has a maximum concentration in the range of α between 0.2 and 0.3.

The factors affecting the dissociation constants of dicarboxylic acids have been studied extensively[12]. While electrostatic effects account for the differences in the two dissociation constants in many cases, it is generally accepted that certain dicarboxylic acids from intramolecular ionic, or acid-salt hydrogen bonds both in aqueous solution and in the solid state. These structures may be represented with a single delocalized electronic charge as follows:



The formation of these 'very strong' hydrogen bonds following ionization of the first carboxylic acid group is a major factor contributing to abnormally large differences between the two dissociation constants K_1 and K_2 (or of K_1 and K_E, the latter being the dissociation constant for the monoesterified acid).

The work of McCoy[13] concerned with equilibria in aqueous solution and investigations on crystalline acid-salts reviewed by Speakman[14] demonstrated that both in solution and in the solid-state, the intramolecular hydrogen bonds are of the symmetrical type and that oxygen–oxygen distances should ideally be close to 0.245 nm. In addition, the atoms of the two carboxylate groups should be, as near as possible, coplanar. However, these requirements can be met by suitable rotations about covalent bonds in many dicarboxylic acids which are not of the 'high ratio' type. A further requirement of molecular rigidity or restricted conformational freedom about bonds connecting the carboxylic acid groups appears to be necessary. Thus, for pentanedioic

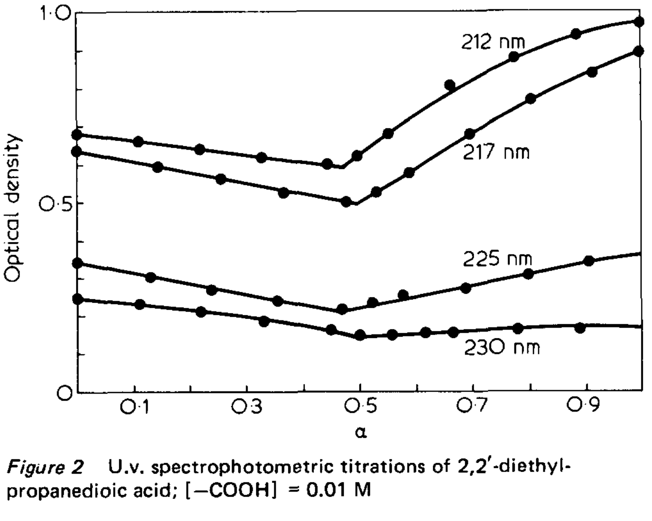


Figure 2 U.v. spectrophotometric titrations of 2,2′-diethylpropanedioic acid; [–COOH] = 0.01 M

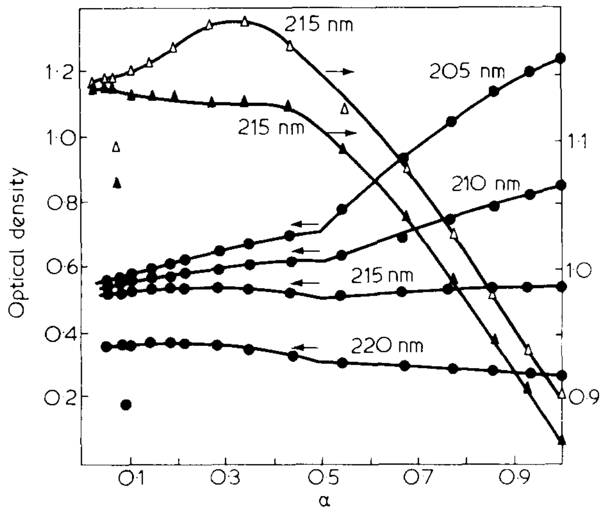


Figure 3 U.v. spectrophotometric titrations of 3,3′-dimethylpentanedioic acid (●), poly(methacrylic acid) in the absence of electrolytes (△) and poly(methacrylic acid) in 0.1 M $NaClO_4$ (▲); [–COOH] = 0.01 M

acid pK_1 and pK_2 are 4.34 and 5.27, respectively, whereas for 3,3′-dimethylpentanedioic acid, the corresponding values are 3.69 and 6.26, respectively. For 2,2′-diethylpropanedoic acid pK_1 and pK_2 are 2.21 and 7.29, respectively. In the latter case, the pK values can only be accounted for by the high stability of the acid-salt structure[12]. (Non-aqueous solvents apparently promote intramolecular acid-salt hydrogen bonding so that the unsubstituted acids propanedioic acid and pentanedioic acid have high K_2:K_1 ratios in solvents such as methanol and acrylonitrile[15]. Furthermore, Eberson has reported that substituted racemic butanedioic acids have 'normal' neutral intramolecular hydrogen bonds in methanol[16]).

If adjacent pairs of carboxyl groups in the polyacids are considered as structural units in their respective chains, these units are structurally analogous to substituted pentanedioic acids. In poly(acrylic acid) the analogous unit is a 2,4-disubstituted pentanedioic acid while in poly(methacrylic acid) it is a 2,2′, 4,4′-tetrasubstituted pentanedioic acid. The u.v. spectrophotometric titrations suggest that as in the 'high ratio' dicarboxylic acids intramolecular ionic hydrogen bonds are formed between adjacent pairs of carboxyl groups in 'conventional' poly(methacrylic acid) as the polyacid is neutralized over the range $\alpha = 0.0$ to ~0.45. The less sterically restricted poly(acrylic acid) system apparently does not form these structures in large concentrations, at least under the conditions of these experiments.

Ionic hydrogen bonds in syndiotactic poly(methacrylic acid)

'Conventional' poly(methacrylic acid) is generally found to be highly syndiotactic. Inspection of a molecular model at once shows that the carboxylate groups in racemic dyads may form intramolecular hydrogen bonds having the specific structural requirements outlined above only when the two intervening skeletal bonds of the polymer (i.e. those between the substituted carbon atoms C_α which are centred on the methylene group) have rotational states close to *trans–trans* conformations. The requirement of close approach to coplanarity of the half-ionized carboxylate groups also necessitates rotations about the C_α–C covalent bonds which connect the carboxyl side groups to the C_α atoms. If all carboxyl groups participate in ionic hydrogen bonding, the half-neutralized syndiotactic chain should have a repeat unit incorporating four skeletal bonds as shown in *Figure 4*. This repeat unit consists of two racemic dyads hereafter described as the 1,2-dyad and the 3,4-dyad.

Flory and coworkers have analysed the conformational states of several disubstituted vinyl chains including poly(methyl methacrylate)[17]. A major factor affecting the conformations adopted by such chains is the severe repulsive interactions between adjacent substituents in all conformational states of both meso and racemic dyads. In consequence, the skeletal bond angle at the methylene group is somewhat strained being increased to about 122° while the skeletal angle at C_α retains its approximate tetrahedral value. Replacement of the methyl group in the ester side chain by the hydrogen atom of the polyacid or the omission of a substituent in an ionized form should have little effect in relieving the strain. In the accessible conformations of poly(methyl methacrylate), the major contributions to the bond angle strain at the central methylene group arise from second order repulsive interactions involving the carboxyl carbon atoms and the methylene groups and methyl groups directly attached to the C_α atoms of the dyad. Consequently, in the undissociated polyacid and in the ionized forms, similar second order interactions should induce strain in the C_α–CH_2–C_α angles giving values similar to those in poly(methyl methacrylate).

Computations which are described more fully in a subsequent paper[18] show that clockwise side group rotations of between 25° and 30° together with rotations of between −8° and −10° for each skeletal bond give oxygen–oxygen distances of approximately 0.245 nm and approximately coplanar carboxylate groups. Furthermore, the hydrogen bond is approximately linear when judged by the criterion that linear 'very short' hydrogen bonds should have the angle C–O - - -O between 112° and 114° (ref 14). The skeletal backbone rotations are described according to the convention adopted by Flory and coworkers[19]. 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. Accordingly the racemic dyad comprises an enantiomeric bond pair |*dd*| (or |*ll*| where vertical lines indicate the locations of C_α atoms. A syndiotactic sequence is therefore written as . . . *l*|*dd*|*ll*|*dd*|*l* . . . Positive rotations are clockwise for *d* bonds and anticlockwise for *l* bonds.

Sundararajan and Flory[17] have shown that for both racemic and meso dyads of poly(methyl methacrylate), *trans–trans* conformations of bonds centred on methylene groups (i.e. |*tt*|) constitute the preferred sequence for the dyad. Our computations show that the conformational adjustments required for formation of the ionic hydrogen bond across the 1,2 dyad do not essentially change the preference for sequences in the region of *trans–trans* in either the 1,2 dyad or the 3,4 dyad[18]. This conclusion may be reached in the case of the 1,2 dyad by ignoring the hydrogen bond-

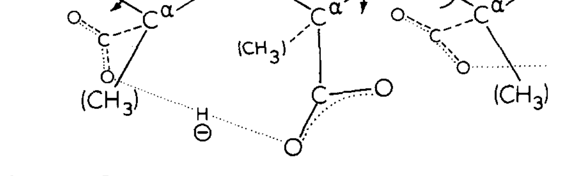


Figure 4 Proposed four bond unit in 50% ionized syndiotactic poly(methacrylic acid) in a |*tt*|t_3t_4| sequence

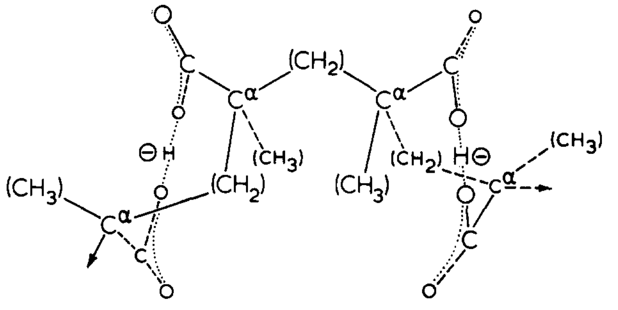


Figure 5 $|tt|g_3g_4|tt|$ sequence in 50% ionized syndiotactic poly(methacrylic acid)

ing energy and also, of course, the repulsive interaction between the oxygen atoms placed 2.45 Å apart which would be intolerable were the atoms not involved in hydrogen bonding.

With bonds 1 and 2 in the repeating unit fixed in conformations close to *trans–trans*, hindered rotations are still possible in the 3,4 dyad. Electrostatic repulsions between the neighbouring ionic hydrogen bonded dyads raise the overall energy of the 3,4 dyad and, as for poly(methyl methacrylate), $\bar{g}$ conformations are not accessible. However, the carboxylate side group rotations do not engender excessive repulsions. The effect of side group rotation is predicted to displace $|t_3t_4|$ and $|t_3g_4|$ energy minima away from their 'usual' positions at (0°, 0°) and (0°, 120°) as recommended for poly(methyl methacrylate)[17] to approximately (15°, 15°) and (15°, 135°), respectively, (rotational displacements of the opposite sign to the displacement of the *trans–trans* states in the 1,2 dyad). With the reassigned rotational state, $|t_3t_4|$ remains the preferred sequence but the size of its domain is reduced. The $|g_3g_4|$ sequence is relatively unaffected by side group rotations, however, as shown in *Figure 5*, and the conformational energy minimum may remain at (120°, 120°) in this case.

Ionic hydrogen bonds are in general regarded as 'very strong'; energies of 8–10 kcal mol^{-1} have been mentioned for acid–carboxylate hydrogen bonds[13]. However, the energy within the bond must be offset against the distortion energy within the structure which is required to bring about appropriate juxtaposition of the half-ionized carboxylate groups. According to the present analysis, this distortion energy includes the repulsive interactions engendered in the neighbouring 3,4 dyad by side group rotations. Furthermore, in salt-free solutions the hydrogen bonds apparently disintegrate beyond 20 or 30% neutralization. This may be in response to overwhelming constraints imposed on the specific bond conformations within the 1,2 dyads by the accumulation of electrostatic energy which precipitates chain expansion. In 0.1 M electrolyte, however, the electrostatic interactions are suppressed to a level which allows the ionic hydrogen bonds to survive to their maximum concentration.

Ionic hydrogen bonding in isotactic poly(methacrylic acid)

To the writers' knowledge, there is little experimental evidence reported in the literature which might be used in support of the occurrence of ionic hydrogen bonds in partly neutralized isotactic poly(methacrylic acid) systems. There are experimental difficulties in obtaining a sufficiently pure sample for u.v. spectrophotometric titrations[5]. However, comparisons of potentiometric titrations of syndiotactic, 'conventional' and isotactic polymers[5,20] confirm the similarity of syndiotactic and 'conventional' samples but show that isotactic poly(methacrylic acid) and its partly neutralized forms are weaker acids than the other systems throughout the full range of α both in pure water and in the presence of electrolytes (see *Figure 6*). Arguments based on stronger local electrostatic fields in the isotactic polymer may be considered to account for the difference of about 0.3 pK$_a$ units at degrees of neutralization in excess of 0.5 where adjacent carboxyl groups must be neutralized. However, the much larger discrepancy (~0.8 pK units) at only 10% neutralization in the presence of 0.1 N electrolyte is more difficult to account for in these terms. The potentiometric behaviour of polyelectrolytes is strongly influenced by electrostatic fields and the solvent structure around the macromolecules and the way it may change with ionization undoubtedly affects ion binding phenomena in general. Nevertheless, the formation of acid–carboxylate hydrogen bonds of greater stability in the syndiotactic polymer than in the isotactic polymer would account for the weaker acidity of the latter polyacid, at least in part, at degrees of ionization below 50%. The accumulation of electrostatic energy above 50% neutralization may result in 'premature' disintegration of acid-salt hydrogen bonds in the syndiotactic polyacid facilitating the release of the second proton within each dyad. This mechanism, which apparently occurs at ~30% neutralization in salt-free solutions, may contribute to the lower pK values of the syndiotactic polyacid above 50% neutralization.

Inspection of a model at once shows that $|t\bar{g}|$ or a $|\bar{g}t|$ sequence of rotational states should allow the formation of an ionic hydrogen bond within a meso dyad. With appropriate side group rotations and adjustments of the skeletal bond rotation angles, the disposition of atoms within the hydrogen-bonded meso dyad reproduces that within the racemic dyad except for the interchange of a single methylene group in the former for the methyl group in the latter. (NB $\bar{g}$ states become accessible in these systems if side group rotations are allowed) However, if by this device ionic hydrogen bonds form across alternate dyads (1,2 dyads) in a pure isotactic chain, the model shows that high energy conformations are engendered in the intervening 3,4 dyads.

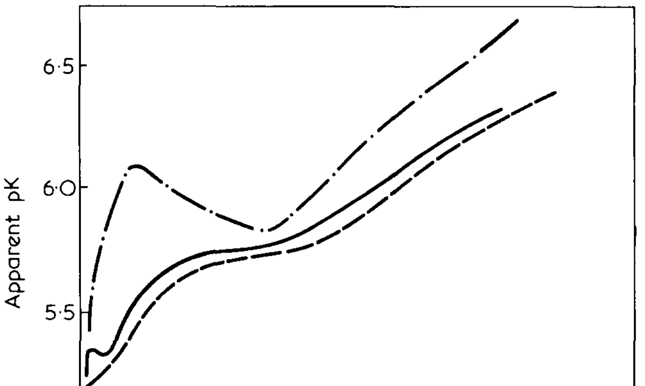


Figure 6 Potentiometric titrations of poly(methacrylic acid). — — — —, Syndiotactic; ———, conventional; — · — · — · —, isotactic polymer. (Data taken from ref 5)

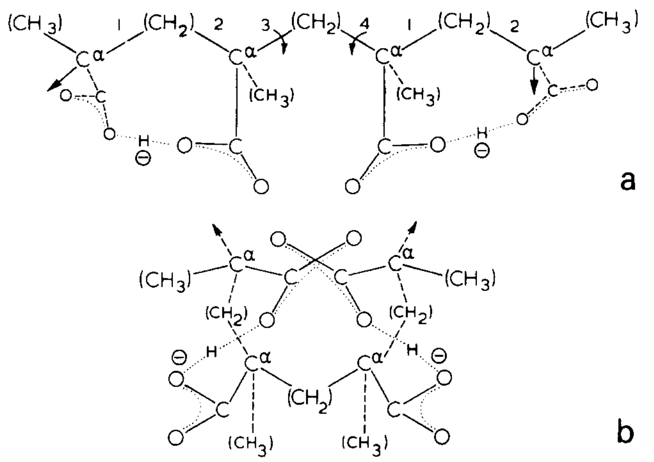


Figure 7 High energy conformations following ionic hydrogen bonding in the isotactic polymethacrylate system: (a) $|\bar{g}t|t_3t_4|t\bar{g}|$; (b) $|t\bar{g}|g_3g_4|\bar{g}t|$

The rotations of the half-ionized carboxylate groups of 3,4 dyads are in opposite directions so that in the meso case, excessive overlap of oxygen atoms occurs in the $|t_3t_4|$ state as shown in *Figure 7a.* Though this is the most favourable state for the racemic dyad it must become highly improbable for the meso dyad even when backbone rotational adjustments are considered. The other accessible conformations $|t_3g_4|$, $|g_3g_4|$ and $|g_3t_4|$ may occur when bonds 1 and 2 are exclusively $|\bar{g}t|$ or $|t\bar{g}|$. However, while $|\bar{g}t|g_3g_4|t\bar{g}|$ is accessible, $|t\bar{g}|g_3g_4|gt|$ is not (see *Figure 7b*).

From these considerations it is possible to conclude that if ionic hydrogen bonds do form in partly neutralized isotactic poly(methylic acid), the chains have less conformational freedom than the corresponding syndiotactic chain.

Ionic hydrogen bonding in 'conventional' poly(methacrylic acid)

As discussed above, coupling of carboxylate groups may occur across meso dyads in $|t\bar{g}|$ states, but the consequent increase in energy in $|tt|$ states of intervening meso dyads is expected to give rise to hydrogen bonds of lower stability in isotactic chains than are found in syndiotactic chains. However, it is apparent from a molecular model that if the meso dyad is isolated between racemic dyads, the latter may adopt $|tt|$ states having energies no greater than the $|t_3t_4|$ states in the half-neutralized syndiotactic chain, (a g state of the bond adjacent to the $\bar{g}$ state should be highly improbable, however). Thus, if both *dl* and *ld* meso dyads, separated by syndiotactic sequences of any length, regularly alternate along the chain as in *Figure 8a*, then it is possible to couple all carboxylate groups so that they are flanked by dyads having access to low energy $|tt|$ states. On the other hand, if the meso dyads are all of one type (e.g. *dl*) and it is assumed that in isotactic triads a 'terminal' uncoupled and unionized group is able to adjust so as to allow a low energy $|tt|$ state in the adjacent racemic dyad, then the fraction of uncoupled groups is equal to the fraction of meso dyads as shown in *Figure 8b*. Assuming that in 'conventional' PMA $|dl|$ and $|ld|$ meso dyads occur with equal frequency, randomly dispersed between the racemic dyads then the proportion of groups not partaking in ionic hydrogen bonding would be half of the fraction of meso dyads. For the polyacid sample used in the present work, this analysis predicts that 10% of carboxylate groups are not able to participate or that the maximum concentration of ionic hydrogen bonds occurs in the presence of electrolyte at $\alpha = 0.45$. The change in gradient in the u.v. spectrophotometric titrations of the polyacid shown in *Figure 2* occurs within the range α between 0.4 and 0.5, in agreement with this expectation. However, the accuracy of the experimental measurements does not allow for an unambiguous conclusion regarding the possibilities for ionic hydrogen bonding in meso dyads.

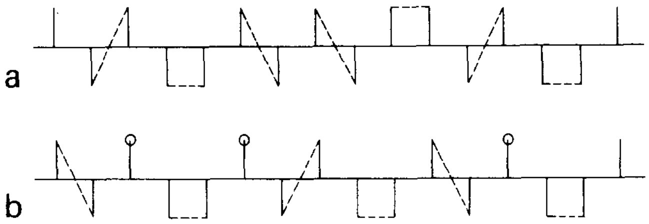


Figure 8 Illustrating the possible ways in which the maximum concentration of ionic hydrogen bonds may depend on the meso sequences in 'conventional' polymethacrylate systems: (a) all groups are coupled; (b) fraction of uncoupled groups equal to fraction of meso dyads

CONCLUSIONS

Ionic hydrogen bonds form between neighbouring carboxylic acid and carboxylate groups across racemic dyads having *trans–trans* conformations in poly(methacrylic acid). In the presence of electrolyte the maximum concentration of these hydrogen bonds should occur at 50% ionization for the perfectly syndiotactic polyacid as in the case of certain substituted dicarboxylic acids. At 50% ionization the syndiotactic chain should have a 4-bond repeating unit. Assuming that the disposition of atoms within dyads of the unionized polyacid is similar to that within dyads of poly(methyl methacrylate), the side group rotations which are necessary for hydrogen bonding in the *trans–trans* 1,2 dyads should still allow some conformational freedom within the 3,4-dyad. However, they are predicted to cause displacements ($\sim +15^\circ$) of the energy minima in the 3,4 dyad in the opposite sense to the displacements ($\sim -8^\circ$) of the *trans–trans* minima in the 1,2 dyad.

In the isotactic chain the geometrical requirements for ionic hydrogen bonding can be met by $t\bar{g}$ sequences in meso 1,2 dyads. However, high energy interactions engendered in the meso 3,4-dyads suggests that the 50% ionized isotactic chain has less conformational freedom than the corresponding syndiotactic chain. However, the possibility that ionic hydrogen bonding may occur by the cooperation of particular sequences in the isotactic chain is not ruled out and awaits further experimental investigation.

ACKNOWLEDGEMENTS

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REFERENCES

1 Katchalsky, A. and Eisenberg, H. *J. Polym. Sci.* 1951, **6**, 145
2 Oth, A. and Doty, P. *J. Phys. Chem.* 1952, **56**, 43

3 Morawetz, H. *J. Polym. Sci.* 1957, **23**, 247

4 Leyte, J. C. and Mandel, M. *J. Polym. Sci. (A-2)* 1964, 1879

5 Barone, G., Crescenzi, V. and Quadrifoglio, F. *Ric. Sci.* 1965, **35** (IIA), 393; *Ric. Sci.* 1965, **35** (IIA), 1069; *Ric. Sci.* 1966, **36**, 482

6 Mandel, M., Leyte, J. C. and Stadhouder, M. G. *J. Phys. Chem.* 1967, **71**, 603

7 Michaeli, I. *J. Polym. Sci. (C)* 1968, **16**, 4169

8 Lando, J. B., Koenig, J. L. and Semen, J. *J. Macromol. Sci. (B)* 1973, **7**, 319

9 Moan, M., Wolff, C. and Ober, R. *Polymer* 1975, **16**, 781

10 Schriever, J. and Leyte, J. C. *Polymer* 1977, **18**, 1185

11 Bovey, F. A. 'High Resolution NMR of Macromolecules', Acedemic Press, New York, 1972

12 Eberson, L. in 'The Chemistry of Carboxylic Acids and Esters' (Ed. Patai) Wiley–Interscience, New York, 1969, Ch6

13 McCoy, L. L. *J. Am. Chem. Soc.* 1967, **89**, 1673

14 Speakman, J. C. *Struct. Bonding* 1972, **12**, 141

15 Chantooni, M. K. and Kolthoff, I. M. *J. Phys. Chem.* 1975, **79**, 1176

16 Eberson, L. *Acta. Chem. Scand.* 1959, **13**, 224

17 Sundararajan, P. R. and Flory, P. J. *J. Am. Chem. Soc.* 1974, **96**, 5025

18 Davenport, J. N. and Wright, P. V. *Polymer* 1980, **21**, 293

19 Flory, P. J., Sundararajan, P. R. and DeBolt, L. C. *J. Am. Chem. Soc.* 1974, **96**, 5015

20 Nagasawa, M., Murase, T. and Kondo, K. *J. Phys. Chem.* 1965, **69**, 4005