Configurational Statistics of Poly(acrylic acid)

Milenko B. Plavšić

Belgrade University, Faculty of Technology and Metallurgy, P.O. Box 494,

YU-11001 Belgrade, Yugoslavia

Space-configurational features of atactic poly(acrylic acid) in unperturbed and expanded states were analyzed in terms of the extending and coiling tendency of the backbone bond rotational states. Conformational energy calculations were performed for dyads using semi-empirical relations and the statistical analyses using statistical weight matrices U' and U'' for respective dyad skeletal bond pairs reduced to the 2×2 order. Agreement with the experimental values of the characteristic ratio $C = (\langle r^2 \rangle_0 / nl^2) = 6.7$ was obtained for $\eta = 0.3 \pm 0.1$ and $\omega'' = (0.8—2.2)$, η expressing the preference for t over the g state and ω'' being a second order parameter for interactions of pendant groups.

INTRODUCTION

Conformational analysis is today an unavoidable factor for understanding the relations between structure and properties of long, flexible chain molecules. In a series of investigations over the last twelve years, the conformational analysis of vynil polymers has proved remarkably successful in the interpretation of configurational characteristics of vynil polymers. Such studies have been carried out especially on poly(methyl metacrilate)[1-5], poly(styrene) and its derivates (versatility of the analized properties should be emphasized; unperturbed dimensions, dipole moments, optical anisotropy, Kerr constant *etc.*)[6-10], poly(alkyl vynil ether's)[11]; poly(vynil acetate)[12], and polymers of higher complexity, but analyzed on the base of the experience accumulated on vyinl polymers.[13,14]

Derivates of poly(acrylic acid) (PAA) have also been studied[15-17] but, surprisingly, not PAA. One of the reasons is the significance of electrical repulsions and attractions, changing tremendously the configurations of such electrolytes as PAA.[18-20] In spite of that, a significant amount of information on the configurational features of PAA can be obtained from the investigations of a unionized PAA. This was already shown by Newman, Krigbaum, Laugier and Flory[21] who studied dilute solutions of (unionized) PAA in dioxane. In this respect, the general conformational model for vynil polymers, developed by Flory in 1974[22] can also be applied. Also Goran and Valeur[23] published in 1971 conformational energy calculations for oligomers of PAA. In this work conformational energy calculations and statistical analysis of rotational isomeric states, based on some new structural data and the dyad as a representative model, are performed.

STRUCTURAL INFORMATION

Bond lengths and most of the bond angles used in this study are listed in Table I.[24,37] The meso dyad of PAA is represented in Figure 1 with notation correspondent to Table I. The carboxyl group is assumed to be planar (with the bond O—H trans to C—C* bond) according to experimental evidence of many authors.[24-26]

TABLE I

Geometrical Parameters Used for PAA

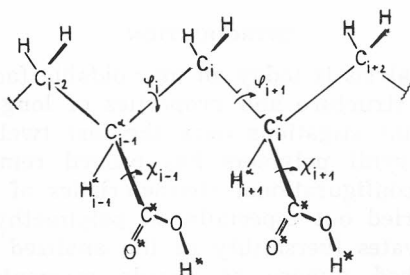| Bond	Length 10^8 (cm)	Bond angle (deg)	
C—C	1.53	C—C^α—C	112.0
C—C*	1.50	C^α—C—C^α	114.0
C—H	1.10	C—C^α—C*	112.0
C*—O	1.34	C*—C^α—H	107.0
C*=O*	1.20	C^α—C—H	109.5
O—H	1.04	H—C—H	109.5
		C^α—C*—O	111.0
		C^α—C*=O*	125.0
		C*—O—H	115.0

Figure 1.

On the base of the corresponding esters and model compounds[15,17] the plane of the carboxyl group can be taken to be so oriented as to bisect the skeletal bond angle at the C^α atom, the carbonyl bond being either cis ($\chi = 0°$) or trans ($\chi = 180°$) to the C—H^α bond. Due to the planarity of the carboxyl group and small dimensions of the acid hydrogen, it can be assumed that the difference between these two conformations does not significantly influence the unperturbed dimensions.[15]

It stands to reason that χ-rotations can significantly influence some other properties (e. g. dipole moments) and must be taken into account in such cases.

CONFORMATIONAL ENERGIES

Conformational energy was calculated as the sum of two terms: (1) intrinsic torsional energy and (2) interaction energies between pairs of

non-bonded atoms — of the van der Waals and coulombic type. Bond lengths and bond angles were taken as constants. A threefold intrinsic torsional energy function with a barrier of 11.7 kJ/mol (2.8 kcal/mol) was assigned to each C—C bond.[27] Nonbonded interactions between atoms separated by more than two bonds were estimated using the Lennard-Jones function $E_{ij} = (\alpha_{ij}/r_{ij}^{12}) - (b_{ij}/r_{ij}^{6})$ for each pair of interacting atoms. No substitution of characteristics of several atoms by group parameters was employed: each atom was treated separately. The constants b_{ij} from the Lennard--Jones function were evaluated according to the Slater-Kirkwood formula from atom polarizabilities α_i and effective numbers of electron N_i.[28,29] Values used for the calculations are given in Table II, together with the adjusted[30] van der Waals radii. The constants a_{ij} were selected to minimize the energy E_{ij} when r_{ij} is set equal to the sum of these van der Waals radii for the given pair. The partial charges are assigned to the atoms of carboxyl groups (Table II), for calculations of coulombic interactions.[23]

TABLE II

Parameters Used in Energy Calculations

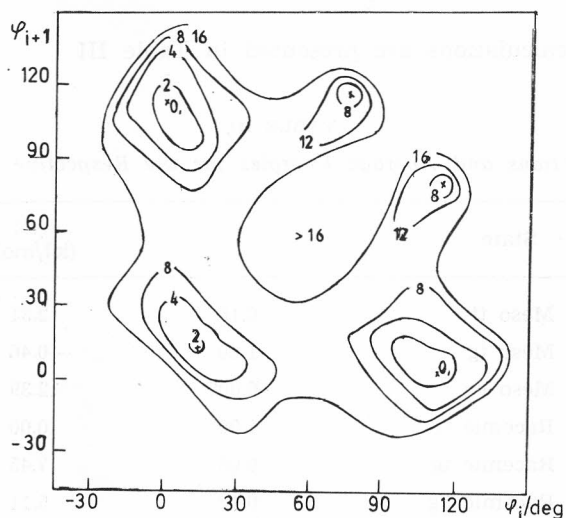| Atom	electrons-N Effective no. of	Polarizability- $\alpha^3 \cdot 10^{34}$ (cm³)	van der Waals radius $r \cdot 10^8$ (cm)	Partial charges — $q \cdot 10^9$ (C)
H	0.9	0.42	1.3	—
C	5.0	0.93	1.8	—
C*	5.0	1.23	1.8	0.855
O	7.0	0.70	1.6	—1.374
O*	7.0	0.84	1.6	—0.384
H*	0.9	0.42	1.3	0.903

Figure 2.

Conformational energies calculated for meso dyad are shown in Figure 2, as the function of rotation angles φ_i and φ_{i+1} (Figure 1). Countures are shown at intervals of energy quoted in kJ/ mole relative to minimum energy of the dyad. The adjoining carboxyl groups are in their preferred orientations, e. g. $\chi_{i-1} = \chi_{i+1} = 0°$ (Figure 1). In both cases, the diagrams present areas of the lowest energy and not complete ranges of rotation angles. The analyses of poly(methyl acrilate) and poly(methyl metacrilate) show the same energy map patterns. This is an obvious consequence of the similar geometry. The energy surface is symmetric in the tt and unsymmetric in the gt and tg domains. There is no splitting of meso tt and meso and racemic tg and gt states, but meso gg is split due to the strong repulsions between H^α atoms »face to face« in gg. The coordinated adjustment in φ_i and/or φ_{i+1} rotation (of the opposite sign for the respective rotation angles) changes the energy surface steeply, bringing it to the two minima, but still of high energy relative to tt or tg/gt states. Also the racemic gg state shows a slight tendency of forming two gg minima to alleviate CH_2—H^α second order interactions.

The $\bar{g}$ conformations[22] impose severe interactions between atoms of the ester group and the groups (atoms) bonded to the adjacent C^α atom, as it was already established for PMA and PMMA.[15] States of the lowest energy (highest probability) are racemic tt, meso tg/gt and meso tt. Partition functions for all combinations of t and g states of dyads were calculated by taking the sums of Boltzmann factors of the conformational energy at 10° intervals over the respective domains. Energies were averaged over the corresponding domains, and normalized relative to the minima for tt state of the racemic dyad:

$$z_\zeta = \int \int_\zeta \exp(-E/RT)\, d\varphi_i\, d\varphi_{i+1} \tag{1}$$

$$\langle E \rangle_\zeta = z^{-1} \int \int_\zeta E \exp(-E/RT)\, d\varphi_i\, d\varphi_{i+1} \tag{2}$$

The results of calculations are presented in Table III

TABLE III

Partition Functions and Average Energies for the Respective Conformations

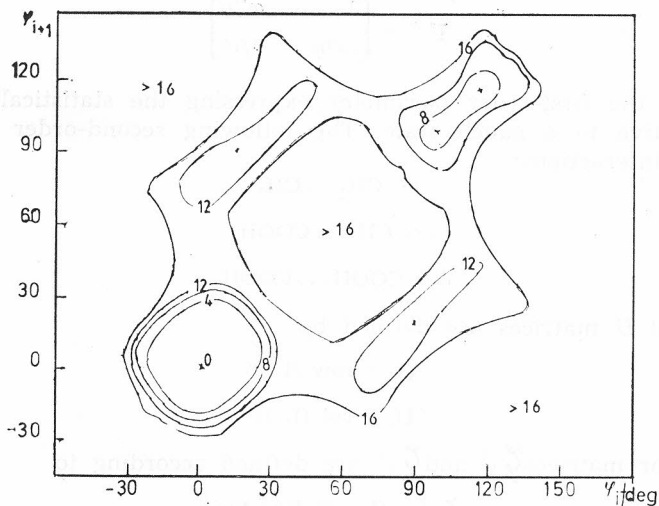| State	z_ζ	$\langle E \rangle$ (kJ/mol)
Meso tt	0.10	2.31
Meso tg	1.20	—0.46
Meso gg	0.007	12.39
Racemic tt	1.00	0.00
Racemic tg	0.05	7.45
Racemic gg	0.12	5.11

Figure 3.

CHARACTERISTIC RATIO

The characteristic ratio defined by[27]

$$C_n = \frac{\langle r \rangle_o^2}{nl^2} \tag{3}$$

$\langle r \rangle_o^2$ — the square of the magnitude of the end-to-end vector averaged over all configurations of the unperturbed chain

n — the number of skeletal bonds

l — length of a skeletal bond

was calculated for the atactic chain, according to the matrix generation method which takes the following form when applied to a vynil chain[31]

$$\langle r^2 \rangle_o = Z^{-1} \, \mathcal{G}_o \, (\prod_{k=1}^{x-1} \mathcal{G}_k{}' \, \mathcal{G}_k{}'') \, \mathcal{G}_x \tag{4}$$

where Z is the configuration partition function given by

$$Z = U_o \, (\prod_{k=1}^{x-1} U_k{}' \, U_k{}'') \, U_x \tag{5}$$

According to the results of energy calculations, statistical weight matrices for the pair of bonds with meso (m) and racemic (r) dyads may be expressed as follows

$$U' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \tag{6}$$

$$U_m{}'' = \begin{bmatrix} \omega'' & 1/\eta \\ 1/\eta & \omega/\eta^2 \end{bmatrix} \tag{7}$$

$$\mathbf{U}_r'' = \begin{bmatrix} 1 & \omega'/\eta \\ \omega'/\eta & 1/\eta^2 \end{bmatrix} \tag{8}$$

η — denotes the first-order parameter expressing the statistical weight of a trans relative to a gauch state. The following second-order parameters characterize interactions:

$$\omega: CH_2 \dots CH_2$$

$$\omega': CH_2 \dots COOH$$

$$\omega'': COOH \dots COOH$$
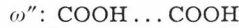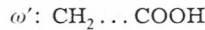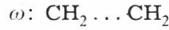
The terminal U matrices are defined by

$$\mathbf{U}_o = \text{row } (1, 0) \tag{9}$$

$$\mathbf{U}_x = \text{col } (1, 1) \tag{10}$$

The generator matrices $\mathcal{G}_k'$ and $\mathcal{G}_k''$ are defined according to

$$\mathcal{G}_k' = (\mathbf{U}_k' \otimes \mathbf{E}_5) \| \mathbf{G}_k' \| \tag{11}$$

$$\mathcal{G}_k'' = (\mathbf{U}_k'' \otimes \mathbf{E}_5) \| \mathbf{G}_k' \| \tag{12}$$

and terminal $\mathcal{G}$ matrices

$$\mathcal{G}_o = \mathbf{U}_o \otimes \mathbf{G}_1 \tag{13}$$

$$\mathcal{G}_x = \mathbf{U}_x \otimes \mathbf{G}_x \tag{14}$$

Here $\mathbf{E}_5$ is the identity of order five and $\mathbf{G}$ is the generator matrix for bond i defined by

$$\mathbf{G}_i = \begin{bmatrix} 1 & 2l^T & l^2 \\ O & \mathbf{T} & \mathbf{l} \\ 0 & O & 1 \end{bmatrix}_i \tag{15}$$

l_i and l_i^T are the column and row forms of the bond vector, $\mathbf{T}_i$ is the transformation relating the Cartesian coordinate system for bond i + 1 to that for bond i[27], $\| \mathbf{G}_k \|$ is the diagonal array of the generator matrices $\mathbf{G}_k$ for each of the two rotational states t and g. $\mathbf{G}_1$ is the first row of $\mathbf{G}$ for the first bond, and $\mathbf{G}_x$ is the last column of $\mathbf{G}$ for the final bond of the chain of x units.

On the base of energies estimated in the previous section and equations (1), (7) and (8), accepting the 2×2 scheme as reliable, e. g.

$$\mathbf{U}'' = \begin{bmatrix} z_{tt}'' & z_{tg}'' \\ z_{gt}'' & z_{gg}'' \end{bmatrix} \tag{16}$$

where statistical parameters estimated in the following range: $\eta = (0.83 - 2.86)$ $\omega'' = 0.10$ $\omega' = (0.10-0.14)$ $\omega = 0.014$.
    The calculations of

$$\mathbf{C}_\infty = \lim_{n \to \infty} C_n \tag{17}$$

were carried out for the atactic chain, the temperature being 300 K. A set of ten Monte Carlo chains consisting of 200 dyads were generated with Bernullian distributions of meso and racemic dyads. The expectation w_m for meso dyads was 0.5. Figure 4 presents the results of calculations of the characterristic ratio for different values of η and ω'', in comparison with the experimental values from the literature.[21,32-36]
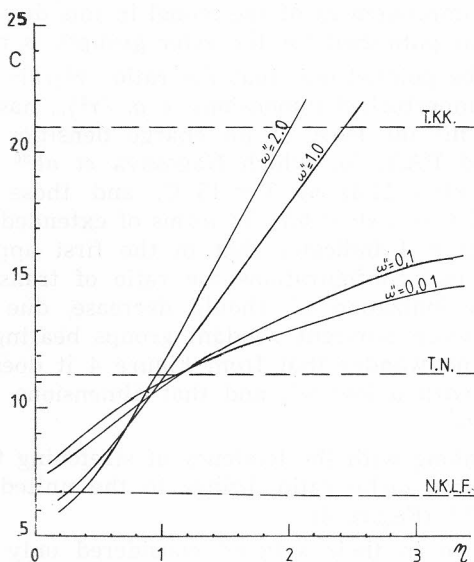

Figure 4.

DISCUSSION

The results of conformational energy calculations point to only a few rotational states of significantly lower energies: racemic tt, meso tt, tg, gt, and to some extent racemic gg. Thus, it seems reliable to apply a simple 2×2 scheme, already used for the PMMA and PMA analysis.[1,15] Besides, in PMA and PMMA the asymmetry of -COOR group interactions is significantly increased due to the voluminous $R = CH_3$ in comparison with $R = H$ in PAA.

From the application of the 2×2 scheme it follows that the system is strongly sensitive to only two parameters: η and ω''. Simultaneous varying of both of them reproduces the experimental characteristics ratio in dioxane[21] in the range of $\eta = (0.2 - 0.4)$ for $\omega'' = (0.8 - 2.2)$. The increase in both parameters leads to the dominance of extended conformations: more trans states relative to gauche, and more meso tt states, which steeply increase the characteristic ratio, as it can be seen in Figure 4. The values of η corresponding to the experimental results are to some extent lower than predicted by the conformational energy calculations based on the semi-empirical formula. In terms of energy this means a difference of only (approximately) 1.75 kJ/mol (417 cal/mol) (for η estimated from meso tg/gt state). It means that PAA is in unperturbed state even more coiled than this model predicts, but by adjustment of η an acceptable representation can

be achieved (hoping to be useful, as already demonstrated for the adjusted 2×2 scheme for PMMA).

The system is less sensitive, in the range of interest, to the ω'' values, but its behaviour is much more complex. It is intelligible, because in such a simplified scheme as 2×2, ω'' includes the effects of different kind of forces, possibilities of adjustment of pendant groups by rotation, (chain —) curvature effect due to the shifting of meso minimum from $\varphi_i = 0$, $\varphi_{i+1} = 0$ position etc. For an improvement of the model in this direction, more detailed information, like that published for the ester group[37], is necessary.

Here it should be pointed out, that the ratio $\langle r^2 \rangle / nl^2$ commonly analyzed in the function of unperturbed dimensions, e. g. $\langle r^2 \rangle_o$, has also other aspects. The values of $\langle r^2 \rangle / nl^2$ for PAA at all charge densities are between those of the fully charged PAA, for which Nagosava et al.[36] claim the value of $\sigma = 2.38$ (e. g. $\langle r^2 \rangle / nl^2 = 11.3$) at $T = 15\,°C$, and those of the acid form in dioxane[21] $\sigma = 1.83$ ($\langle r^2 \rangle_o / nl^2 = 6.7$). In terms of extendedtrans configurations of chain bonds, Figure 4 indicates that in the first approximation for the full range of PAA coil configurations the ratio of trans/gauche states goes from 0.2 to 1.2. By ionization ω'' chould decrease, due to the increase of repulsion forces between adjacent pendant groups bearing the charge of the same sign, so it is no wonder that from Figure 4 it does not seem possible to achieve $C = 6.7$ with a low ω'', and that dimensions of the coil increase with a decrease of ω''.

This tendency, along with the tendency of stretching the chain, expressed in terms of the trans/gauche ratio, brings to the united, effect just in the proximity of $C = 11.3$ (Figure 4).

Valeur and Gorin in their article[23] considered only the conformational energy and not the characteristic ratios and related properties. In general, their conclusions are in agreement with this work : they also found meso tt, g^+t, tg^- and racemic tt and g^+g^+ states significant. In addition, they found racemic tg^+/g^+t states of low energy. However, their results are not based on the integrated energy over conformational-space areas, but on the single-optimal-point analysis.

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SAŽETAK

Konfiguracijska statistika poli(akrilne) kiseline

Milenko B. Plavšić

Analizirane su prostorno-konfiguracijske karakteristike ataktne poli(akrilne kiseline) u neporemećenom i raširenom stanju s obzirom na težnju rotacionih stanja osnovnog lanca opružanju ili sklupčavanju lanca. Proračuni konformacijske energije izvedeni su za diadu, korišćenjem semi-empirijskih relacija, a statistička analiza korišćenjem matrica statističkih težina U' i U'' za odgovarajuće parove veza u diadi. Matrice su svedene na red 2×2. Saglasnost sa eksperimentalnim vrednostima za karakteristični odnos $C = (\langle r^2 \rangle_o / nl^2) = 6{,}7$ je dobijena za $\eta = 0{,}3 \pm 0{,}1$ i $\omega'' = (0{,}8{-}2{,}2)$, gde η izražava preferenciju za rotacijsko stanje t s obzirom na stanje g osnovnog lanca, a ω'' je statistički parametar drugog reda za interakcije bočnih grupa.