

CONFORMATIONAL CHARACTERISTICS OF POLY(ACRYLIC ACID) AND POLY(METHACRYLIC ACID)*

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ABSTRACT

A full-relaxation optimization of molecule and the Dreiding force field are employed to obtain the geometry parameters and the conformational energy surfaces of meso or racemic dyad of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA). Three different carbonyl-bond orientations of side-groups resulted in the differences in depth of potential wells in their energetic contours for a meso or a racemic dyad. These discrepancies are interpreted as a result of various fine structures corresponding to grid search conformations as well as thereby different interactions. The analysis on the most stable conformations of PMAA confirmed that the ester groups are nearly perpendicular to the plane defined by the two adjacent skeletal bonds but may possibly change their relative orientations to meet the requirement of lower energy during the conformational state transition. For each polymer, two global energy maps of a meso and a racemic dyad were finally constructed from the superposition of energy data for the three kinds of side-group orientations by the Boltzmann factors. From an ensemble average, the proposed scheme with three rotational isomeric states (RIS) allowed us to access the experimentally unperturbed dimensions of PAA chain via the configurational statistical mechanics. Although the calculation was based on the short-range, local interactions, it was interested to note that the experimental characteristic ratios just fell within the range calculated for atactic chains.

INTRODUCTION

The configurational characteristics of polyelectrolytes in solution is still a thorny subject whether in theoretical or in experimental frameworks^[1,2]. Owing to the effect

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of strong electrostatic interactions between the macroions and mobile counterions, as well as repulsions between neighboring macroion and between similarly-charged ionic groups within a macroions, the local and global conformational changes of polyelectrolytes have not been extensively described by the most widely accepted theories^[3-5] which are developed from the classical two-parameter theories^[6] of neutral polymer solutions. Moreover, the physical properties of polyelectrolyte are influenced by various other conditions such as temperature, ionic strength and solvent. For an isolated neutral macromolecule, its configuration may be possibly predicted by the rotational isomeric state (RIS) model^[7] using knowledge of geometrical parameters and torsional potentials. However, for a single polyelectrolyte chain even in vacuum, the situation becomes much more complex since we wonder how to evaluate the effect of long-range electrostatic interactions within a macroions on the energetic contours of bond pair. Nevertheless, some attempts^[8-9] have been given in understanding of structure and dynamics of polyelectrolytes by the combination of molecular mechanics or molecular dynamics with the RIS approximation.

The conformational profiles of diad structures of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) have been determined as a function of tacticity, extent of ionization and presence of counterion^[8]. Low ionization PAA as well as high ionization and counterion-complexed PMAA showed a strong preference for tt backbone torsional-states either for meso or racemic diad structures. Although the calculation was on the basis of short-range, local interactions, the dyad model provided a selfconsistent explanation of the rod-to-coil and coil-to-rod transitions respectively, observed in PAA and PMAA with increasing counterion concentration. Such two inversely conformational transitions with respect to increasing counterion concentration are consistent with many experimental observations^[10-20]. Molecular dynamics^[9] of chain segments of 32 monomers based on the minimum-energy conformations^[8] of PAA and PMAA diads also indicated that stabilization of the tt conformer states by long-range interactions constitutes a secondary mechanism favoring the same transition behaviors^[8]. However for PAA, the rod-to-coil transition behaves contrary to the other studies^[2,21]. By using the polarized Raman spectroscopy and a simplified RIS model, it was reported that the persistence length changes from 1.46 nm when the molecule is un-ionized to 1.76 nm when it is ionized^[21]. To understand the conformational transitions with increasing salt concentrations, one should first clearly characterize the structure and interactions of neutral polymers. For a vinyl polymer with ester groups, our previous work^[22,23] showed that different dyad models with carbonyl-bond orientations lead to different geometries and energy contours. Obviously, PAA and PMAA have the same problems of carbonyl-

bond orientations. Therefore, it is not the purpose to see a change in dimension with increasing ionization, instead, we here report some initial results of conformational characteristics of PAA and PMAA using the molecular mechanics and the configuration statistics^[7]. The study presents approaches to average the contributions from all kinds of carbonyl-bond orientations and to calculate reasonable energy maps of dyads.

METHOD

Three dyad models (**A**, **B** and **C**) of PAA and PMAA are defined as in the case of PMA^[22] and polyacrylamide^[23] according to the carbonyl-bond orientations. χ is defined as the dihedral angle between the carbonyl and C $^{\alpha}$ -R (here R is H or CH₃). A full-relaxation optimization of molecule and the Dreiding^[24] force field in POLYGRAFTM were employed to obtain the geometric parameters and the conformational energy surfaces. The energy contours were calculated as functions of two skeletal bond rotational angles Φ_i and Φ_{i+1} . The data points in the energetic maps computed were at intervals of 10° in Φ_i and Φ_{i+1} . The effective cut-off value of a distance between two arbitrary non-bonded atoms is defaulted as 0.85 nm. The statistical pre-average^[22,23] and the matrix generator technique^[7] were used to estimate the weight of state and unperturbed chain dimensions. It is very difficult to determine exactly the statistical weight matrix U'_i for the pair of bonds flanking a side-group. Simplifying approximately the third-order interaction into the second-order for PAA chain, we simply have^[25,22]

$$U'_i = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix}.$$

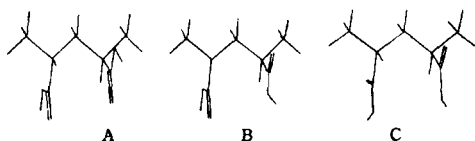


Fig.1. Different combinations of the two side-groups of a meso PAA dyad. **A**, two carbonyls are *cis* to C $^{\alpha}$ -H; **B**, one carbonyl is *cis* while the other is *trans* to C $^{\alpha}$ -H; **C**, two carbonyls are *trans* to C $^{\alpha}$ -H.

RESULTS AND DISCUSSION

Conformational energy contours

(a) *Symmetry*: The calculation showed that the symmetry of energy contours is resulting from the symmetry of the models. The symmetric models **A** and **C** yield symmetric energy contours. The unsymmetry model **B** leads to unsymmetric

Table 1 Lists of the dihedral angles and the energies for nine conformers with the energy minima less than 6.0 kcal/mol for each meso or racemic dyad in the models **A**, **B** and **C** of PAA*

	Model	gg	gt	gg ⁻	tg	tt	tg ⁻	g ⁻ g	g ⁻ t	g ⁻ g ⁻
Meso	A	70°,	70°,		180°,	190°,	190°,	260°,	300°,	260°,
		100°,	170°,		60°,	170°,	290°,	60°,	180°,	290°,
		3.99	2.008		0.000	0.4585	2.008	3.447	0.000	3.990
		60°,						300°,		290°,
		70°,						100°,		300°,
	B	3.984						3.447		3.984
		60°,	70°,		180°,	190°,	190°,	270°,	300°,	300°,
		60°,	170°,		60°,	170°,	280°,	60°,	180°,	300°,
		5.023	2.967		1.020	1.392	2.369	4.499	1.053	3.078
								300°,		
	C							100°,		
								4.478		
		60°,	70°,		180°,	190°,	190°,	260°,	300°,	300°,
		60°,	170°,		60°,	170°,	290°,	60°,	180°,	300°,
		4.105	3.321		2.072	2.531	3.321	5.507	2.072	4.105
G Averaged from A, B, C							300°,			
							100°,			
							5.507			
	60°,	70°,		180°,	190°,	190°,	260°,	300°,	300°,	
	60°,	170°,		60°,	170°,	290°,	60°,	180°,	300°,	
Racemic	A	3.086	1.987		0.000	0.4621	1.987	3.447,	0.000	3.086
								300°,		
								100°,		
	B							3.447		
		60°,	70°,		160°,	170°,	170°,		300°,	
		60°,	160°,		70°,	170°,	300°,		170°,	
	C	2.893	2.450		2.445	0.000	4.584		4.586	
		60°,	70°,		160°,	170°,	180°,			
		60°,	160°,		70°,	170°,	300°,			
	G Averaged from A, B, C	3.676	3.125		3.169	0.9709	3.351			
		60°,	70°,		160°,	170°,	180°,		300°,	300°,
		60°,	160°,		70°,	170°,	300°,		180°,	300°,
	A	4.234	3.864		3.868	1.941	3.793		3.794	4.162
		60°,	70°,	60°,	160°,	170°,	180°,	270°,	300°,	300°,
		60°,	160°,	270°,	70°,	170°,	300°,	60°,	180°,	300°,
B	2.917	2.460	5.402	2.465	0.000	3.304	5.403	3.304	4.120	

* All energies have the same unit of kcal/mol. For the three specified models, the energies have been normalized by 7.94 for meso and 19.94 for racemic of the model **A**

Table 2 Lists of the dihedral angles and the energies for nine conformers with the energy minima less than 5.0 kcal/mol for each meso or racemic dyad in the models **A**, **B** and **C** of PMAA*

	Model	gg	gt	gg ⁻	tg	tt	tg ⁻	g ⁻ g	g ⁻ t	g ⁻ g ⁻
Meso	A		60°, 170°, 1.411			190°, 200°, 3.385	190°, 300°, 1.025		280°, 180°, 4.895	
						160°, 170°, 3.602				
		B	60°, 170°, 2.595	90°, 300°, 4.397		190°, 200°, 3.812	190°, 300°, 0.000			
				30°, 290°, 3.585						
		C	60°, 40°, 4.928	60°, 170°, 1.423	90°, 300°, 3.927		190°, 300°, 1.003			
					60°, 270°, 4.036					
	G Averaged from A, B, C	60°, 40°, 4.765	60°, 170°, 0.	60°, 270°, 3.729	180°, 80°, 4.764	160°, 170°, 3.227	190°, 300°, 0.000		280°, 180°, 4.764	320°, 300°, 4.765
				90°, 300°, 3.729		190°, 200°, 3.227				
Racemic	A					170°, 170°, 0.00				310°, 300°, 3.870
	B					170°, 170°, 0.9767				300°, 300°, 2.684
	C					170°, 170°, 1.957				300°, 300°, 1.493
	G Averaged from A, B, C					170°, 170°, 0.00				300°, 300°, 1.458

* All energies have the same unit of kcal/mol. For the three specified models, the energies have been normalized by 30.86 for meso and the model **B** and 21.90 for racemic of the model **A**

map for a meso or a racemic dyad. (b) *Energy difference between meso and racemic dyads*: It was found that there existed great energy difference between the dominant racemic dyad and the dominant meso dyad for such two polymers, respectively. The conformational energy of the dominant racemic dyad (19.94 kcal/mol) is larger than that of the dominant meso dyad (7.94 kcal/mol) about 12 kcal/mol for PAA. However, it is lower than that of meso dyad (21.91 to 30.86 kcal/mol) for PMAA around 9 kcal/mol. This means that the energy normalization by a common factor between meso and racemic maps appears impossible. (c) *Energy contours among the three models*: Except for the depth of potential wells, the shape and position of potential wells among the three models have no significant changes. It is shown from Tables 1 and 2 that the tt conformation of each racemic dyad model of the two polymers have an obvious preference over the other conformations in the maps of the three models, especially for PMAA. The sequence in which the models are ranked according to their lowest energies is from low to high by $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$ for the racemic dyad of the two polymers; however, for the meso dyads of PAA, the most stable conformation is tg g⁻t and the same energy sequence is still $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$; for the meso dyads of PMAA, the preferred conformation is tg⁻ or gt and the energy sequence is altered as $\mathbf{B} \rightarrow \mathbf{C} \rightarrow \mathbf{A}$. (d) *Superposition of conformational energy data*: With the similar

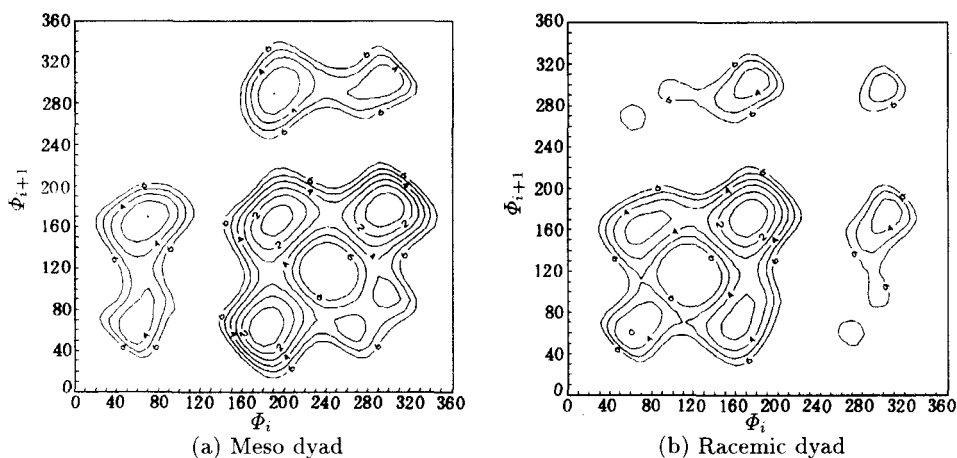


Fig.2. Finally global conformational energy contours for the meso and the racemic dyad of PAA chain calculated as a function of bond rotations Φ_i and Φ_{i+1} . The two maps were averaged from the three individual maps of the models $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ for the meso or the racemic dyad, respectively. The energy contours for the meso and the racemic dyad are labelled in kcal/mol and normalized by their own lowest energies. The cut-off energy is selected as 6 kcal/mol

ideas^[22,23], we performed the superposition of conformational energy data for the

three dyad models and then obtained four global contours as shown in Figs.2—3 for the two polymers. The proposed three models with the initial carbonyl-bond orientations provide each meso or racemic dyad more opportunities to undergo various thermodynamic equilibrium states. The molecular geometries and the energy components optimized from the force field are all significant. Thus, the global contour is more reasonable and realistic than the individual energy maps of the three models.

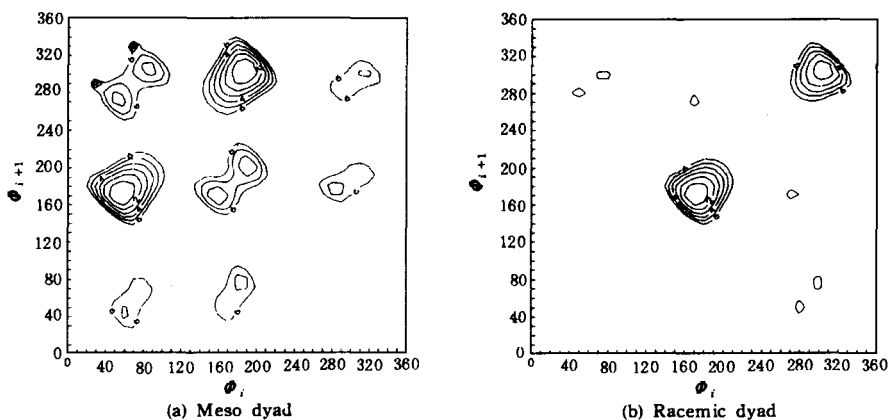


Fig.3. Finally global conformational energy contours for the meso and the racemic dyad of PMAA chain calculated as a function of bond rotations Φ_i and Φ_{i+1} . The two maps were averaged from the three individual maps of the models A, B and C for the meso or the racemic dyad, respectively. The energy contours for the meso and the racemic dyad are labelled in kcal/mol and normalized by their own lowest energies. The cut-off energy is selected as 6 kcal/mol

Analysis on conformations with the lowest energy

To analyse the re-orientation of carbonyl-bonds, the two dihedral angles^[22] (χ_1, χ_2) of the most stable conformations of the meso and the racemic PMAA dyad are summarized in Table 3. In order to compare with the results obtained by Smith and Boyd^[26], we also presented the values of dihedral angles between $C^\alpha-C^\#$ and $C^*=O$ in the brackets. Here, C is the skeletal carbon atom located between two carbon atoms flanking the ester group. Table 3 showed that: (1) The value of χ corresponding to the most stable state is about 0° or 180° . It should be noted that one of two carbonyl-bonds in each *tg*⁻ conformation of the three meso dyad models has significantly changed into the *trans* or *cis* orientations in order to meet the requirement of lower energy. While the other dihedral angle has only a small deviation from the initial value. No obvious variation occurred for the two dihedral angles of each most stable *tt* conformation of the three racemic dyad models. Two carbonyl-bonds still nearly adopt their initial orientations. (2) The total en-

ergy of the racemic dyad is considerably lower than that of the meso dyad. This discrepancy is mainly contributed from the lower electrostatic interaction potential in racemic dyad. (3) Two angles "60" and "120" are approximately designated from the numbers in the brackets. However, the angles of "90" and "150" are not found as reported in the early studies^[22,26]. This indicated that side-groups are nearly perpendicular to the plane defined by two adjoining backbone bonds during the conformational state transitions.

Table 3 Conformer with the lowest energy in each contour for different orientational dyad models of PMAA*

	Model 1	ϕ_1, ϕ_2	E_{total}	E_{bond}	E_{angle}	E_{tor}	E_{invsion}	E_{vdw}	E_{el}	$\chi_1(^{\circ})$	$\chi_2(^{\circ})$
Meso	A	190°, 300°	31.88	6.203	7.980	1.373	.002	20.745	-4.426	1.80 (-124.39)	-175.86 (58.23)
	B		30.86	6.175	8.017	0.377	.00004	20.676	-4.392	2.09 (-124.10)	3.03 (-123.04)
	C		31.86	6.199	7.968	6.363	.0001	20.700	-4.378	-177.66 (56.35)	2.77 (-123.31)
Racemic	A	170°, 170°	21.90	5.989	7.922	0.447	.005	21.066	-13.526	-1.30 (124.47)	-1.27 (124.49)
	B		22.88	6.006	7.848	1.434	.003	21.092	-13.502	-1.14 (124.62)	179.56 (-54.86)
	C		23.86	6.025	7.765	2.418	.0001	21.116	-13.463	179.77 (-54.67)	179.80 (-54.63)

* The total and component energies are labelled in kcal/mol. ϕ and χ are the dihedral angles along the main chain and the side-group, respectively. The subscripts "1" and "2" refer to the first and the second dihedral angles when we view the dyad molecule from the lower to higher atom number. The data in brackets represent the dihedral angles between $C^{\alpha}-C^{\#}$ and $C^* = O$. $C^{\#}$ is the skeletal carbon atom located between two carbon atoms flanking the ester group

Characteristic ratio

It is seen from Fig.4 that at least several hundreds of bonds are required to approach the equilibrium characteristic ratio C_n . The syndiotactic chain is much more rigid than the isotactic one for PAA under the unperturbed state. When the chains are very long, the values of C_n tend to 67.2 and 9.6 for syndiotactic and isotactic chains, respectively. The persistence lengths are correspondingly 5.22 and 0.81 nm for such two chains. This is attributed to different distributions of the conformational energies for the two stereoregular chains. The meso dyad has the dominant conformational states tg and g⁻t but the racemic has only the tt state. With the similar idea, the tt conformation of racemic PMAA has greater preference over the other conformations than that of racemic PAA, this means that PMAA is more rigid

than the PAA for the syndiotactic chain with the same chain length. To calculate the unperturbed dimensions of PMAA, one needs a reasonable evaluation of weight contribution of CH_3 groups flanking the skeletal chain and consideration of higher-order interactions. This remains a further investigation. In Fig.5 shown are the characteristic ratios C_n of stereochemical and atactic PAA chains. Each point for atactic chain results from an average among more than 10000 Monte Carlo chains with 1000 bonds at 300K. One can also see from Figs.4—5 that atactic chain becomes more

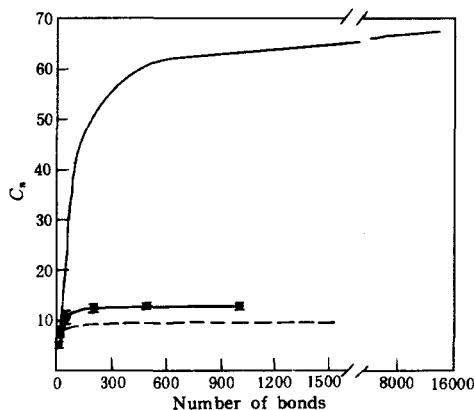


Fig.4. The dependence of unperturbed characteristic ratio on chain length for three kinds of stereochemical PAA chains at 300K, — syndiotactic; --- isotactic; ■ atactic with 50% meso

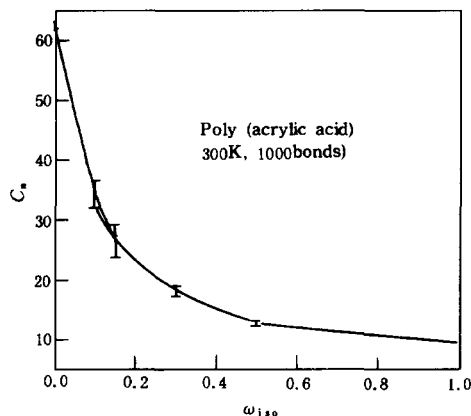


Fig.5. Characteristic ratios of PAA chain with 1000 bonds at 300K. The points in the range $0 < \omega_{\text{iso}} < 1$ represent averages for more than 10000 Monte Carlo chains

flexible, when the content of meso dyad reached 50%. For such an atactic chain, C_n and the persistence length are respectively 1.292 and 1.06 nm. Newman et al. reported $C_\infty = 6.3$ for un-ionized PAA in dioxane^[27], while Takahashi et al. reported $C_\infty = 11.3$ for fully ionized PAA in 1.5 M NaBr at the θ condition^[28], both

values were derived from intrinsic viscosity data. Using a light-scattered method, Takahashi et al. also reported $C_\infty = 21$ for PAA in 1.5 M NaBr at the θ condition^[29]. Allegra et al. performed a calculation of the unperturbed dimensions of ionized PAA as a function of tacticity and found $C_\infty \sim 10$ when the chain was atactic^[30]. The combination of polarized Raman spectroscopy and a simplified RIS model revealed that the persistence length changes from 1.46 nm when un-ionized to 1.76 nm when ionized^[21]. Although the present calculation is based upon the short-range, local interactions for un-ionized PAA, it is significant to note that the experimental dimensions just fell within the range calculated. Undoubtedly, the examination of U' matrix and the consideration of high-order interactions are needed to improve our calculating results.

Keywords:

Poly(acrylic acid); Poly(methacrylic acid); Configurational statistics; Conformational energy; Dyad structures

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