

Scientific paper

Molecular Dynamics Simulation of Poly(methacrylic Acid) Chains in Water[†]

Boštjan Jerman,* Črtomir Podlipnik and Ksenija Kogej

Department of Chemistry and Biochemistry, Faculty of Chemistry and Chemical Technology,
University of Ljubljana, Aškerčeva 5, P. O. Box 537, SI-1000 Ljubljana, Slovenia

* Corresponding author: E-mail: bostjan.jerman@fkk.uni-lj.si

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[†]Dedicated to Prof. Dr. Jože Škerjanc on the occasion of his 70th birthday

Abstract

Molecular dynamics simulation studies were performed on the isotactic and syndiotactic poly(methacrylic acid), i-PMA and s-PMA, respectively, in water at 25 °C in dependence on degree of neutralization, α , of carboxyl groups. The simulations were performed with a single chain built of 64 monomer units. For both polyacids results have shown that the compact coil conformation of i-PMA is stabilized by hydrogen bonds at low α values. Conformation of the i-PMA appears to be stiffer because of a large number of neighboring hydrogen bonds, whereas the s-PMA conformation has fewer neighboring hydrogen bonds and adopts a more curve-like conformation. Average polyion dimensions increase with increasing ionization. However, shorter distance between charges and shorter counterion contact distance for isotactic stereoisomer have been calculated using modified radial distribution function. This leads to a greater charge density and stronger counterion binding in the i-PMA case. In addition, tendency for local helix-like conformation of i-PMA, especially at low α values, has been recognized. We have shown that s-PMA is more extensively stabilized by hydration at $\alpha = 0$ than i-PMA. This demonstrates a larger hydrophobic character of i-PMA compared to s-PMA.

Keywords: Stereoregular poly(methacrylic acid), isotactic, syndiotactic, molecular dynamics, conformation.

1. Introduction

pH induced conformational transition of polyelectrolytes has for a long time been a subject of extensive investigations because of its important role in biological systems.¹ Among synthetic polyelectrolytes that undergo pH induced conformational transition poly(methacrylic acid) (PMA) is the simplest and one of the most studied representatives. PMA can be prepared in various isomer forms: as an atactic or heterotactic poly(methacrylic acid), a-PMA, and also as a highly regular syndiotactic or isotactic polyacid, s- or i-PMA, respectively. They differ in the placement of charged groups along the backbone chain. Two neighboring monomer units can be in *meso* (*m*) or *racemo* (*r*) placement. Three neighboring monomer units are forming a triad and i-PMA consists of *meso-meso* triads (*mm*), s-PMA of *racemo-racemo* triads (*rr*) and a-PMA consists of *rm* or *mr* triads.²

Solution properties such as charge density and hydrophobicity of PMA are strongly influenced by chain mi-

crostructure and are different for i- and a-PMA.^{1–11} This has an influence on solution behavior of PMAs. i-PMA is, in contrast to a- or s-PMA, insoluble in water below a certain critical degree of neutralization of carboxyl groups,^{4,5,10} and it behaves as a weaker acid over the whole range of degrees of neutralization, α .^{3,6,8–11} On the other hand, a- and s-PMA display similar solution behaviour,^{3,6,11} which may be a consequence of the fact that so called conventional PMA (or a-PMA) is usually predominantly syndiotactic.³

It has been demonstrated that stereoregular polymers often have characteristic local conformations in solution, although their overall conformation can well be approximated by random coils.^{12,13} For example, syndiotactic poly(methyl methacrylate), s-PMMA, in benzene has a locally preferred curvature¹² and appears to be more strongly coiled than isotactic PMMA, i-PMMA.¹³ However, i-PMMA has a rather random overall conformation with local helical sequences.^{5,14,15} Furthermore, Muroga et al. showed that local conformations are not much affected by the presence of the charges: i.e. they are similar for the

corresponding stereoregular poly(sodium methacrylates) in aqueous solution.

The majority of studies on polyelectrolyte conformations until now have been restricted to the so-called conventional polymers with no control of tacticity using various experimental techniques.^{3,12,16,17} These polymers are usually the atactic variety. Less effort was generally devoted to the precise determination of the composition of polymers with respect to triad content and to systematic experimental and theoretical studies of the influence of chain stereoregularity on solution properties of these polyacids.^{3,11,17,18} In the past, several conformational analyses of the ester forms of PMA, that is of PMMA chains, have been carried out using various molecular mechanics potentials.^{13,19,20}

A limited number of molecular dynamics simulations of synthetic polyelectrolytes are described in recent literature. On the other hand, nucleic acids have been widely studied by MD and other simulations in detail.^{21–24} Since the PMA chains display similar solution behavior as nucleic acids due to their polyelectrolyte nature, they can be treated in similar way in theoretical studies.

Theoretical studies using advanced theories and techniques on PMA are rare. Nishio for example has studied structurally related poly(acrylic acid) with Monte Carlo simulation.²⁵ As far as we could ascertain, there is only one comparative theoretical study on stereoisomers of PMA that aimed at determining the local conformation of these polyacids in water.¹⁸ The computational method applied there was quantum mechanical semiempirical molecular orbital calculations (MO calculations) applied to an oligomer containing 15 monomer units. Longer polymer chain could give some more information about the microstructure and with the use of appropriate tools, possible intramolecular interactions and average chain structure properties can be determined.

In this paper we report a comparative molecular dynamics study on two stereoisomers of PMA, namely *s*- and *i*-PMA, in terms of average chain parameters. The change of these parameters upon ionization of the polyacid will be monitored. These parameters will be obtained by using a modified radial distribution function on the resulting snapshots of molecular dynamics (MD) simulation. Our main goal is to check if there exists an indication of hydrogen bond formation, what are the differences between *s*-PMA and *i*-PMA in this respect, to explain higher charge density of the *i*-PMA and finally, to explain the insolubility of *i*-PMA in water in the un-ionized state.

2. Experimental

It has been mentioned that PMA and various nucleic acids behave similarly in solution and that mainly explicit solvent are used in theoretical calculations with the latter ones,^{21–23} although there are studies of nucleic acids in

continuum solvent as well.²⁴ Due to the limited computational ability, a number of simulations of ten and to avoid the influence of the chain tail on the structure of smaller polymer, an implicit solvent was chosen as a compromise.

From the computational point of view MO calculations are very time-consuming and MD simulation is a faster option for the study of longer polymers, e.g. such with up to 100 monomer units. This is the main reason to use the MD simulation. Initial models of *i*- and *s*-PMA were built within the Maestro interface.²⁶ The degree of polymerization of polyacids was 64. This is a compromise between physical relevance of the system and computational cost. Our previous work in this system showed that the 64-mer chain is long enough to explore local structural properties.¹¹ We selected five different α values to investigate the influence of degree of neutralization, α , on the structure of PMA: $\alpha = 0, 0.25, 0.50, 0.75,$ and 1.00 . The ionized molecules were created with random replacement of hydrogen that is bound to carboxylic oxygen with sodium ion and subsequent change of carboxylic oxygen atom type from covalently bonded one to a charged one.

The calculations were performed using the MacroModel.²⁷ An enhanced version of OPLS 2005 force field was used.²⁸ Bulk water solvation was simulated using MacroModel's generalized Born GB/SA continuum solvent model.²⁹ Within this model solvent is treated as an analytical continuum starting near the van der Waals surface of the solute, and has a dielectric constant of 78 for the bulk water and a dielectric constant of 1 for the molecule. The extended non-bonded cutoff distances were 10 Å, 50 Å and 4 Å for van der Waals, electrostatic and hydrogen bond interactions, respectively.²⁷ The initial structures were first minimized using Polack-Ribiere Conjugate Gradient algorithm.³⁰ The minimization was stopped either after 5000 steps or after the energy gradient converged below $0.05 \text{ kJ mol}^{-1} \text{ \AA}^{-1}$. The minimized conformations were used as a starting point for stochastic molecular dynamics (SD).³¹ SD includes random forces that simulate the buffeting of a system by solvent molecules. Time step in SD simulations was 1.5 fs, bond lengths were constrained to their equilibrium using SHAKE algorithm³² with a tolerance of 0.00005 \AA . The equilibration of the system was achieved by gradually increasing the temperature from 0 K to the target temperature of 298.2 K by coupling it with a thermal bath. This procedure lasted 200 ps.³³ After equilibration we performed 2.0 ns SD simulation and atomic coordinates for subsequent analysis were collected every 2 ps.

A modified Radial Distribution Function (RDF) was used for structural analysis of both PMA isomers. This formulation of RDF was proposed by Gasteiger et al.³⁴

The definition of RDF that was used in this work is the following:

$$RDF(r) = \sum_{i \in N} \sum_{j \in M} p_i p_j \exp\left(-B(r - d_{ij})^2\right) / 4\pi r^2 \quad (1)$$

where d_{ij} is the distance between atoms i and j , that are members of two different subsets N and M respectively and B is a smoothing parameter. p_i and p_j are properties of corresponding atoms. In our case p_i (p_j) = 1 if an atom i (j) is a member of the subset N (M) and 0 if not. RDF is calculated in equally distributed points (20 points/Å) from 1 to 10 Å. For all calculations the smoothing parameter B is set to 100 Å⁻². The subsets N and M are formed according to MacroModel atom type or by the ASL definitions (Atomic Scripting Language implemented in Maestro).

Backbone torsion angles, end-to-end distances, hydrogen bonds and distances between charges were also measured and averaged through the final configurations using Schrodinger Maestro and its measurement tools.

3. Results and Discussion

The calculations were carried out for two isomers of PMA; one chain consisted only of isotactic triads and the other one was purely syndiotactic. Because syndiotactic and atactic (often called conventional) PMA display very similar solution behavior, we have built a syndiotactic polymer also as an approximation for the atactic one.

The results of molecular dynamics simulations are sampled conformations. Figure 1 presents the final result-

ing snapshot of the MD simulation for the un-ionized i- and s-PMA and also for the fully ionized, i- and s-PMA. It can be qualitatively seen, that the calculated conformation for both acids at $\alpha = 0$ is much more compact than the extended one at $\alpha = 1$. This has already been recognized experimentally by many authors.^{3,6,7,11,12} The compact form at $\alpha = 0$ starts to expand upon neutralization, becomes more rigid and distances within the polymer chain become larger. More detailed pictures of the conformation of i- and s-PMA are presented in Figure 1.

For $\alpha \leq 0.25$ the linear charge density is low and distances between charged monomers are large. In such a situation, the electrostatic interactions acting along the chain are weak and do not influence the local conformation appreciably. Conformation of the polymer is stabilized in this range by short range interactions, such as hydrogen bonds, van der Waals and hydrophobic interactions.^{3,10} Above $\alpha > 0.5$, chain is practically completely expanded and dimensions do not change much. Pleštil noted that the expansion of polyions is attributable exclusively to the presence of charges.¹⁶

At very low α values polyelectrolyte chain is stabilized by short range interactions as previously stated. Syndiotactic PMA has so-called »zig-zag« conformation with carboxyl groups alternating on the both sides of the backbone (for more detail see Figure 1). In such a confor-

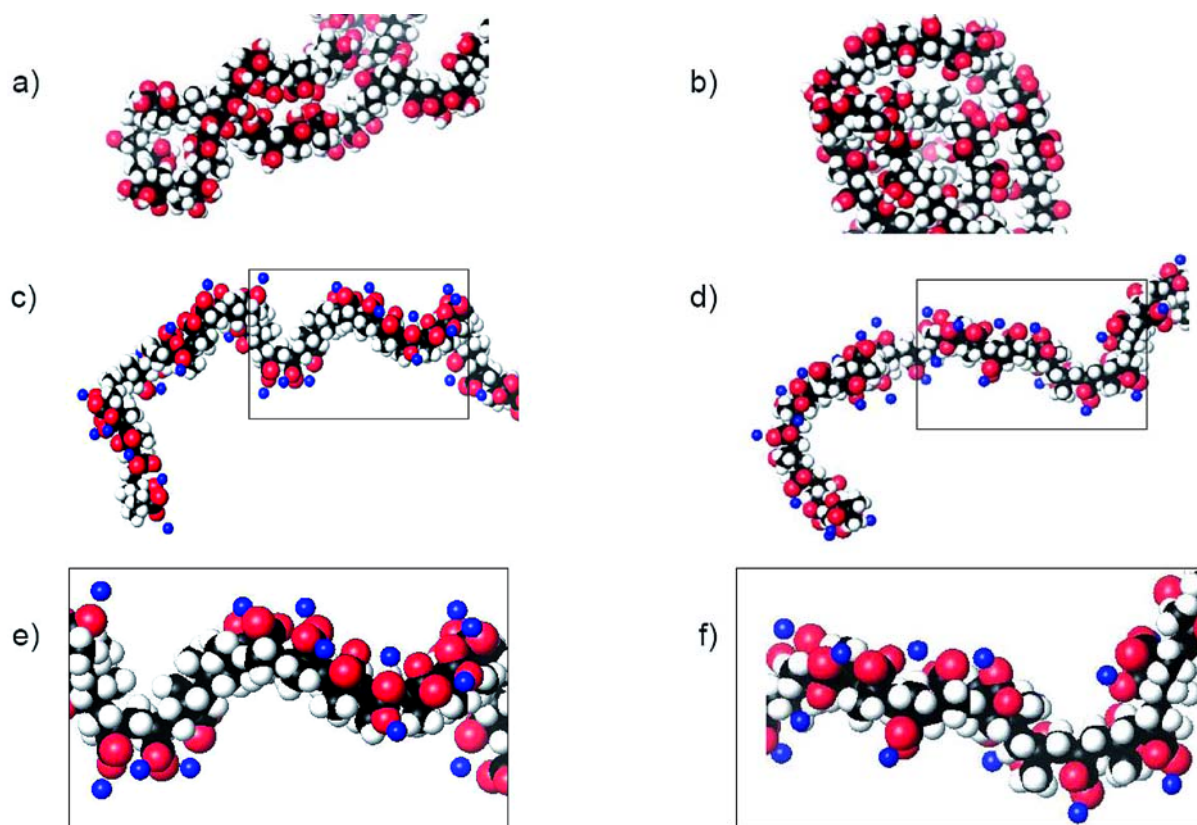


Figure 1: Snapshots of i- and s-PMA chains: a) i-PMA: $\alpha = 0$, b) s-PMA: $\alpha = 0$, c) i-PMA: $\alpha = 1.0$, d) s-PMA: $\alpha = 1.0$, e) detailed i-PMA structure at $\alpha = 1$, and f) detailed s-PMA structure at $\alpha = 1$.

mation, most of carboxyl groups are pointing out of the compact coil and can be hydrated by water molecules. Such compact conformation leads to the solubility of *a*- and *s*-PMA at low α . On the other hand, the conformation of *i*-PMA at low α values is less compact. A larger portion of COOH groups in this form point into the coil and thus a larger portion of hydrophobic methyl groups is exposed to the solvent. This may be the reason for the insolubility of *i*-PMA chains at $\alpha = 0$.

Parameters for determining hydrogen bonds were the following: maximum distance between donor and acceptor was chosen to be 2.50 Å, minimum donor angle was 120° and minimum acceptor angle was 90°. It has been found that both isomers are extensively stabilized by hydrogen bonds (H-bonds) in the range of $\alpha < 0.25$ (Figure 2). This behavior was actually expected because of the very compact conformation of both polyacids in this range. Two kinds of H-bonds were identified in the process of neutralization, i.e. those participating between neighboring and those participating between non-neighboring groups. Neighboring H-bonds were mostly observed with *i*-PMA because the orientation of carboxyl groups in isotactic triads is such that atoms find themselves often within the contact distance recognized for a hydrogen bond. Some neighboring hydrogen bonds were also determined with *s*-PMA, but to a much lesser extent.

Very compact conformation for both isomers at $\alpha = 0$ is stabilized due to a large abundance of non-neighboring H-bonds. With introduction of charges, the compact form starts to expand and the number of non-neighboring

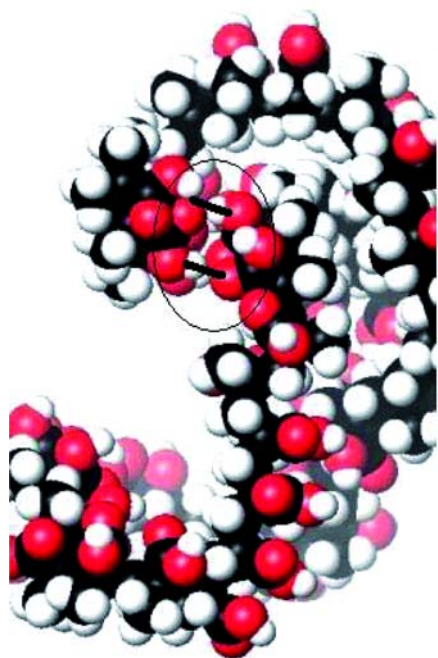


Figure 2: Detail of a compact structure of *i*-PMA at $\alpha = 0$. H-bonds are marked with straight black line.

hydrogen bonds starts to decrease. In fact, with *s*-PMA they already disappear at $\alpha = 0.25$, both neighboring and non-neighboring ones. With *i*-PMA, the situation is different. The number of non-neighboring H-bonds starts to decrease upon charging, but at the same time the number of neighboring H-bonds starts to increase until α reaches 0.5 and then falls back to zero at $\alpha = 1$. Clearly result at $\alpha = 1$ stems from the fact that there are no more hydrogen atoms on the chain. The fact that *i*-PMA is strongly stabilized by hydrogen bonds leads to a greater rigidity of the *i*-PMA chain.¹⁸ Increasing number of hydrogen bonds in the region $\alpha < 0.5$ can be connected with the irreversible conformational transition of *i*-PMA in aqueous solution,^{3,4,8,10} the mechanism of which is not known yet. H-bonds could play an important role in this peculiar phenomenon.

As counting of hydrogen bonds has shown, there is a pronounced rigidity of the chain for the *i*-PMA as compared to *s*-PMA. By measuring the end-to-end distances for *i*- and *s*-PMA in the whole range of α , information on stiffness or rigidity of the chain can be obtained. In the region $\alpha < 0.5$, the end-to-end distances for *i*-PMA are larger than those for *s*-PMA. This is repeatedly an indication of the greater stiffness of the *i*-PMA chain. The reasons for this may be two: an increasing number of neighboring H-bonds for *i*-PMA and sterical hindrance of carboxyl groups that are situated close to each other. In the region $\alpha > 0.5$ the repulsion between charges becomes strong and end-to-end distances become independent of α and also independent of the stereoregular type of the polyelectrolyte chain.

Calculated equilibrium structures of *i*- and *s*-PMA at low α values are stabilized by short range interactions. These are more than one order of magnitude smaller than long range electrostatic interactions. The latter ones are clearly predominant at higher α and make the main contribution to the potential energy of the system. In the range $0.25 < \alpha < 1$ equilibrium potential energies are approximately (see Table 1) the same for both stereoisomers of PMA. However, the energy values of -694 kJ/mol and -511 kJ/mol for 64-mer *s*-PMA and *i*-PMA at $\alpha = 0$, respectively, show that the non-charged *s*-PMA is more stable than the non-charged *i*-PMA.

Table 1: Average potential energies of the last ten snapshots in equilibrium of *i*-PMA and *s*-PMA in water for different values of α . All energies are in kJ/mol.

	$\alpha = 0$	$\alpha = 0.25$	$\alpha = 0.5$	$\alpha = 0.75$	$\alpha = 1$
<i>i</i> -PMA	-511.4	-11940	-23393	-34800	-46215
<i>s</i> -PMA	-694	-11987	-23346	-34702	-46136

Stabilization of the conformation at $\alpha = 0$ due to the solvent is more pronounced in the case of *s*-PMA. This finding is in agreement with previous findings^{7,10,11,18} and

suggests that s-PMA chain may be more extensively hydrated in an aqueous environment than i-PMA chain; i.e. i-PMA has a larger hydrophobic character. We assume that the reason for the greater stability of s-PMA may be mainly due to lower steric hindrance between COOH groups that are in s-PMA further apart than in i-PMA. This conformation of i-PMA has, as many authors have reported, locally helical structure, which is supposed to affect solution properties of i-PMA especially its insolubility in water at low α values.^{5,6,34}

Vlachy et al. reported using MO calculations that i-PMA forms a 10/1 helix having a pitch of 20.93 Å.¹⁸ This points to the reduced size of the polyion compared to the extended oligomer with 10 monomer units, which would have the size of 25.2 Å. MD calculations have not shown such an ideal helix-like conformation of i-PMA, but local helical distribution of charges can be identified and measured. It can be seen, however, that this is far from ideal geometry (Figure 3). The pitch was measured and its value is in the range between 20 and 21 Å. It is becoming slightly larger upon neutralization due to electrostatic forces. Helical conformation is also more pronounced at lower α values (at $\alpha = 0$ and 0.25). On the other hand Kusanagi reported that i-PMMA double stranded helix dimer is more stable than separate helices.³⁵ It has also been discovered that thermoreversible gelation of i-PMA at low α values proceeds in two steps: a change in conformation from coil to helix, followed by a side by side association of these helices. This intermolecular association of i-PMA is ascribed to strong intermolecular cooperative hydrogen bonding, which can only be disturbed by solvents capable of forming strong hydrogen bonds like DMF or DMSO.⁵

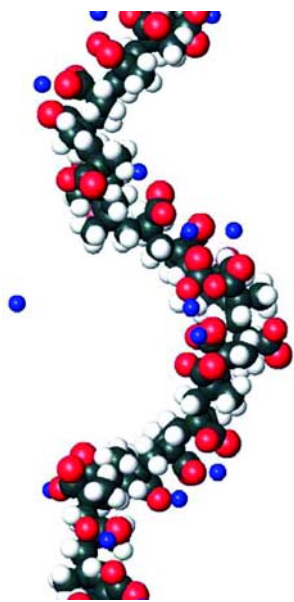


Figure 3: i-PMA in local helical conformation at $\alpha = 0.25$.

It may be concluded that short range interactions stabilize i-PMA chain if the chain is in helical conformation. This results in a more rigid chain, in reduction of dimensions of the polyion and in significantly different backbone torsion angles for i- and s-PMA.

Previous theoretical studies (MO calculations)¹⁸ have shown that i-PMA can be stable in a bent- and in a helix-like conformation, whereas s-PMA exists only in regular, that is bent-like conformation. Helical and regular extended conformations differ in the backbone torsion angle τ , which is measured as an angle between two planes in $C^\alpha - CH_2 - C^\alpha - C(OOH)$ sequence. Vlachy et al. have calculated a torsion angle of 34° for helical microstructure of i-PMA. For the bent conformation of i-PMA, the average backbone torsion angle regularly alternates between -73.1 and -31.6° and in the case of s-PMA, the assignment of the backbone torsion angle is unambiguous, leading to the bent conformation of the chain. The average backbone torsion angle in s-PMA alternates between $71^\circ \pm 4^\circ$ and $-73^\circ \pm 4^\circ$. When measuring backbone torsion angles on our resulting snapshots of MD simulation, we discovered that backbone torsion angles vary as the local microstructure changes in the polyion but there are also some angles that are more probable than others. We derived a distribution of all possible torsion angles that displayed the probability for certain angles. The most probable backbone torsion angles for i-PMA were around -42° and -75° . Almost all the measured angles for i-PMA were negative, indicating that angle was traced anticlockwise along the bonds. Although this result is more in favor of bent conformation of i-PMA, there exist helical microstructures in the i-PMA chain (Figure 3), but they are not the most probable ones. At low α values ($0 < \alpha < 0.25$) the probability for the helix-like torsion angles is greater than at other α values. Backbone torsion angles become more distributed over all angles with charging. Regarding measured backbone torsion angles for s-PMA, they alternate between $(68-73)^\circ$ and $-(70-86)^\circ$. This result is in good agreement with Vlachy et al. Larger deviations in the magnitude of the torsion angle indicate higher flexibility of s-PMA chain as compared to i-PMA.

The structural parameters that were of a special interest for us were the distance between the charges, the distance of a closest approach of the counterion to the polyion and some other parameters. The first two parameters are especially important for the behavior of various thermodynamic properties.^{3,11,18}

Distances between charges were measured within the Maestro suite and they showed us that the average distance between neighbouring charges on the chain is in the range of 3 – 3,4 Å for both PMAs and is smaller in the i-PMA case. Sodium ions seem to be very tightly bound to the polyion (in the range 3.5 Å – 5 Å from the backbone) so the local distribution of charges should be very important. In i-PMA charges are helically distributed on the surface of the polyion (10/1 pitch) so the bound counterion

should be in the local field of high charge density. In s-PMA charges regularly alternate on the both side of the chains and thus the bound counterion is expected to be in the weaker electrostatic field (Figure 1,3).

In previous paper,¹¹ $C^\alpha - Na^+$ distances were measured using RDF for PMA isomers and results have shown that this distances are smaller for i-PMA than for s-PMA (a-PMA).

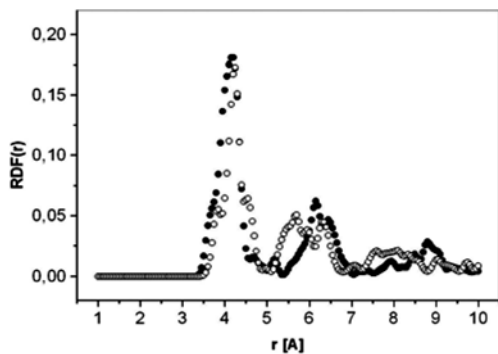


Figure 4: RDF for $C^\alpha - Na^+$ distance at $\alpha = 1$ for i-PMA (●) and s-PMA (○).

In this study we also performed similar calculations that were averaged through a great number of equilibrium conformations (Figure 4). From the first peak we determined the $C^\alpha - Na^+$ distances, which were 4.15 Å and 4.25 Å for i-PMA and s-PMA, respectively. The smaller contact distance with the i-PMA case may be a consequence of stronger binding of sodium ion to the polyion. Images of i-PMA have also shown that the position of a counterion is always in the middle between two charged carboxyl groups. This is a consequence of the isotactic conformation of the chain, where all charged groups are on the same side of the chain and close together. This is not the case with s-PMA, where counterion has just one charged group in its vicinity. This is clearly seen from the Figure 5. Primary peak in this figure shows us two things, (i) smaller contact distance of a counterion for i-PMA and (ii) the height of this peak, which is double the size of the peak for s-PMA, indicates that the position of a counterion is between two charged groups.

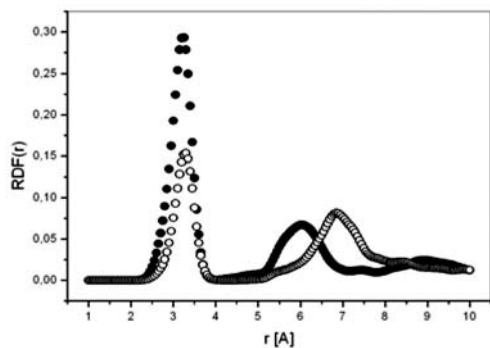


Figure 5: RDF for $Na^+ - sp^2 C$ distance at $\alpha = 1$ for i-PMA (●) and s-PMA (○).

From the secondary peak in this figure one can clearly see that the counterion is locally in the field of higher charge density in the i-PMA case since the neighboring charged group is closer in the i-PMA case. Counterions are therefore more strongly bound to the i-PMA chain than to s-PMA chain. Difference in conformation between two isomers can also be confirmed by secondary peak in the Figure 4, where the position of dual secondary peak for s-PMA indicates greater local flexibility of s-PMA chain. This is in agreement with the previous finding that i-PMA chain is stiffer and more rigid than s-PMA chain. Here we have to point out that flexibility itself does not contribute to the binding. Binding is determined by free energy differences.³⁶ However, when taking a larger portion of a chain into account, one can conclude that because of helical distribution of charges and because of specific position of counterions between the charged groups in the i-PMA case, the charge density is greater for i-PMA and this can be an explanation of higher activity and osmotic coefficients in the i-PMA case.^{11,18}

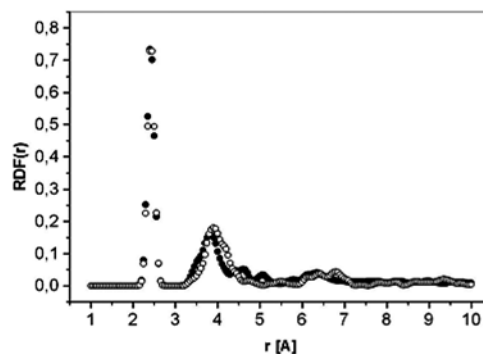


Figure 6: RDF for $C^\alpha - O(H)$ distances in i-PMA at $\alpha = 0$ (●) and $\alpha = 1$ (○).

Other structural parameters of the polyelectrolyte chain using RDF have also been measured. They pointed to some small but noticeable differences in i- and s-PMA chains. It was noted that the size of the polyion grows a bit upon charging (Figure 6). If the first peak is just slightly further in the $\alpha = 1$ case the secondary peak shows no doubt that distances between C^α and oxygen become larger upon charging. The same is also true for s-PMA. Obviously repulsive forces between charges make the chain not just more rigid but also little more stretched.

4. Conclusions

In this paper we present the results of molecular dynamics simulation for two stereoisomers of PMA in dependence on α . They show noticeable differences between i-PMA and s-PMA in terms of chain parameters. Through the whole range of α i-PMA appears to be stiffer than s-PMA. Both forms of PMA are stabilized by

H-bonds at very low α values. In this region i-PMA has a stiffer whereas s-PMA adopts a more curve-like conformation. i-PMA is stabilized by neighboring H-bonds to a much greater extent than s-PMA. The stiffness of the i-PMA chain is attributed to the presence of helix-like segments. However, at $\alpha = 0$ s-PMA appears to be more energetically stabilized by hydration than i-PMA. This result agrees with the fact that i-PMA has a more hydrophobic character than s-PMA at low α values. With the addition of charges (increasing α) PMA chain starts to expand to an extended rod-like conformation for both isomers, although i-PMA remains to be stiffer than s-PMA. This was confirmed by the end-to-end distance measurements. Average dimensions of polyions become larger upon charging. Using modified radial distribution function we measured various mean parameters of PMA chains and they appear to be in good agreement with previous findings. We measured distance between charges on the chain and contact distance of the counterion to the polyion. The results indicate a greater charge density and a smaller contact distance for i-PMA, which is in good agreement with previous findings.

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Povzetek

Izvedli smo simulacije izotaktične in sindiotaktične polimetakrilne kisline, i-PMA in s-PMA, z molekulske dinamiko v vodi pri 25 °C in v odvisnosti od stopnje nevtralizacije, α . Dolžina polimera je bila 64 monomernih enot. Rezultati so pokazali, da sta obe stereoizomeri polimetakrilne kisline stabilizirani z vodikovimi vezmi pri nizkih vrednostih α . Konformacija i-PMA je bolj toga od s-PMA zaradi velikega števila vodikovih vezi med sosednjimi skupinami. s-PMA, ki ima manj teh vezi, v vodi zavzame bolj vijugasto konformacijo. Opazili smo, da zavzame i-PMA pri nizkih α konformacijo vijačnice. Povprečne dimenzije poliona naraščajo za obe polikislini z naraščajočo stopnjo nevtralizacije, vendar pa smo pri i-PMA z uporabo modificirane radialne porazdelitvene funkcije ugotovili, da so razdalje med naboji in kontaktne razdalje približanja protiionov manjše kot pri s-PMA. Ugotovili smo, da je pri $\alpha = 0$ s-PMA energijsko bolj stabilizirana zaradi hidratacije kot i-PMA, kar kaže na bolj izrazit hidrofoben značaj i-PMA v primerjavi z s-PMA.