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Conformational properties of poly(diallyldimethyl ammonium chloride) (PDDA) determined by combination of molecular dynamics, rotational isomeric states and Monte Carlo procedures

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Abstract

A theoretical model describing the conformational properties of poly(diallyldimethyl ammonium chloride) (PDDA) is developed with the following strategy: molecular dynamics simulations are performed on model molecules representing dimers of PDDA. The results are employed to formulate a rotational isomeric state model for these molecules in terms of short-range interactions. Furthermore, the MD trajectories permit the evaluation of conformational energies and probabilities for the 27 conformations allowed to the three bonds sequence contained in the dimers. These probabilities are then employed to generate single chains of PDDA in vacuo according to standard Monte Carlo procedures and their main squared end to end distance $\langle r^2 \rangle$ are computed. The procedure (MD simulations, evaluation of energies and probabilities and MC calculations) is then repeated for two more realistic systems obtained by fitting into a cubic box, having side length L and periodic boundary conditions, a forty repeating units oligomer of PDDA together with 40 Cl^- as counterions and 500 water molecules (referred to as water system, $L = 2.95$ nm, $d \approx 1$ g cm^{-3}) or the oligomer with its counterions, 500 water molecules and 20 NaCl molecules (referred to as salt system, $L = 3.02$ nm, $d \approx 1$ g cm^{-3}). The behavior of the three systems is noticeably different and the value of unperturbed dimensions computed for the realistic systems are in good agreement with preliminary results of experimental measurements being carried out in our laboratory.

Keywords: Conformational properties; Unperturbed dimensions; Poly(diallyldimethyl ammonium chloride) (PDDA)

1. Introduction

During the last years, molecular dynamics simulations (MD) have become a very valuable tool for the theoretical analysis of a wide variety of systems, including polymer chains [1]. Indeed, the computational power provided by even very modest equipments permits quite realistic representations of relatively long chains, either isolated in vacuo or in condensed states such as bulk or solution. However, in many cases, MD by itself is unable of producing reasonable values for magnitudes that imply correlation among a relatively large number of skeletal bonds. A good example is the end to end distance r of a long polymeric chain. Thus, if we attempted to simulate a 100 repeat units chain of any polymer (for instance polyethylene) and tried to compute $\langle r^2 \rangle$ by averaging the square of the separation between first and last skeletal atoms along the MD trajectory, the results would be quite different from experimental values. The reason is very simple: MD simulations are quite slow sampling the conformational space available to rotations over single bonds because they have to surmount relatively high rotational barriers. Consequently it is impossible to perform a MD simulation that could statistically sample the practically infinite number of conformations accessible to a set of a few hundred skeletal bonds.

However, MD simulations could perform good statistical sampling for sequences of a few consecutive skeletal bonds even when they are contained within a long polymeric chain (with the added advantage that, in this case, several equivalent sequences could be defined and evaluated at the same time and their results averaged in order to increase the accuracy of the simulation). Such MD simulations produce excellent probability distributions for the rotational

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states allowed to the polymer backbone. These probabilities can be computed neglecting all kind of correlations (independent rotations approximation), taking into account correlations among first neighbors (i.e. allowing first and second order interactions), or even long range correlations up to ca. five or six consecutive skeletal bonds. The probability distributions thus obtained could then be used to formulate a statistical weight matrix model of the polymer (RIS) [2,3], which allows evaluation of conformational properties, unperturbed dimensions for instance, for the whole chain employing the matrix multiplication scheme [2–6]. Alternatively, the probability distributions obtained by MD with the desired degree of correlations among consecutive bonds, could be used to compute averages for the whole chain by standard Monte Carlo (MC) techniques, which are much more efficient than MD sampling large conformational spaces by generating only the most probable conformations.

Thus, it seems that the combination of MD simulations, RIS and MC provide an excellent technique for analyzing conformational properties of many polymeric systems. These procedures are applied in the present work to the conformational analysis of poly(diallyl, dimethyl ammonium chloride) (PDDA), whose structure is schematically represented in Fig. 1. This is a polyelectrolite (it contains a neat charge equivalent to a proton per repeating unit) which is currently investigated in our laboratory [7] employing Size Exclusion Chromatography (SEC) procedures with multiple detectors [8–13] that allows the experimental evaluation of many conformational properties such as coefficients for the scaling law, unperturbed dimensions, etc. PDDA is been used at industrial level as coagulant in treatment of water and in the paper production industry. Furthermore, some technological applications based on the formation of monolayers of PDDA, either alone or with some other polyelectrolites, are currently being investigated which might take advantage of a molecular characterization performed from both experimental and theoretical approaches. Commercial samples [14] of this polymer are water solutions containing Cl^- as counterions and polymeric chains with ca. 84% of *trans* units, 14% of *cis* units and about 2% of allicyclic units in which bond 2–3 is broken (see Fig. 1) while bond 1–2 becomes double. We have not taken into account this last kind of units in the present analysis since its inclusion would noticeably complicate the model, and therefore increase the uncertainty of the calculations, while their effect in the experimental results is probably negligible due to their low incidence.

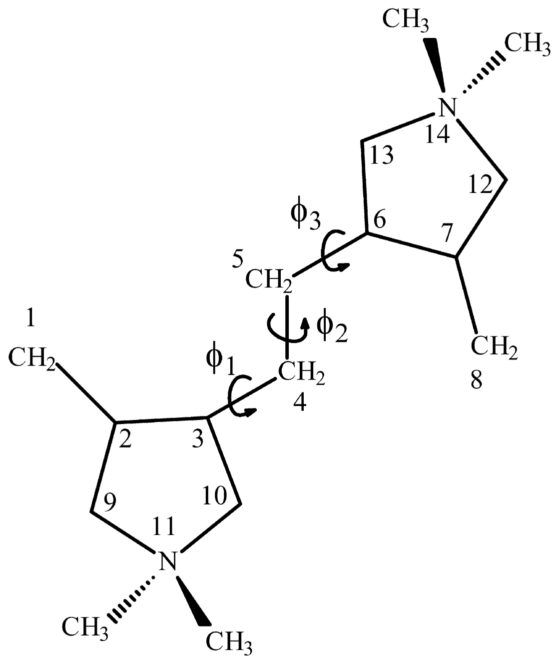

Fig. 1. Schematic representation of a dimer of PDDA showing its three rotational angles. Some of the groups on the molecule have been arbitrarily numbered in order to facilitate the assignment of conformational interactions. Two configurations (i.e. *cis* and *trans*) are allowed to each skeletal CH–CH bond within the cycles.

The strategy employed in the present work can be summarized as follows: MD simulations were performed for model compounds of dimers of PDDA, i.e. molecules as the one represented in Fig. 1 with H atoms replacing the continuation of the polymeric chain. All the allowed configurations for the pair of cycles were studied, i.e. *cis–cis*, *trans–trans*, *cis–trans* and *trans–cis*. Analysis of the MD trajectories allows the formulation of a statistical weight matrix model for the PDDA chain in terms of short-range interactions. Furthermore, probability distributions for the three rotatable bonds appearing on the dimer can be evaluated neglecting correlations among those bonds (i.e. independent bonds approximation), taking into account first neighbors correlations (which allows the evaluation of first and second order interactions), or including correlations for the three rotatatable bonds, thus producing a table with the probabilities assigned to all the three^3 conformations accessible to the dimer. This last table was then employed to generate polymeric chains with different number of repeat units and compute their averaged dimensions according to standard MC procedures.

However, a single model molecule of a dimer isolated in vacuo and with no counterions is not a realistic representation of the experimental situation in which polymeric chains, with their respective counterions, are dissolved in water and, in many cases, different ionic salts such as NaCl are added in order to improve the performance of the SEC equipment. Consequently, the analysis indicated above, although very useful for outlining a conformational model of the polymer, might produce values, which cannot be directly compared with experimental results. For this reason, the whole analysis (MD simulations, evaluation of probability distributions, and MC calculations of chain dimensions) is repeated for two more realistic systems obtained by fitting into a cubic box having Periodic Boundary Conditions (PBC) a relatively long oligomer, its

Cl^- counterions, water molecules and, in one of the systems, NaCl molecules. Chains dimensions obtained with these systems are noticeable different from those computed in the analysis of the dimer model compound and agree reasonably well with the experimental results obtained up to date [7].

2. Theoretical analysis

2.1. Molecular dynamics software and force field

The DL_POLY package [15] and the AMBER force field [16–20] were employed in all the MD simulations. A time step $\delta = 1$ fs (i.e. 10^{-15} s) was used for the integration of the equations of motion. The temperature of the system was kept constant by means of a Nose–Hoover thermostat [21] with a relaxation time of 500 fs. An equilibration time of 500 fs was allowed to the system to adapt to new conditions whenever the parameters were externally modified, for instance the temperature that was modified with increments of 50 K during thermostation or the side of the cubic box holding the system that was changed with increments of 0.1 nm (see below). A home made routine was incorporated to the package [22]. It acts at regular time intervals, i.e. every 1000 integration steps, randomly selecting one atom of the system and resetting its velocity to the thermal value but with random direction. The effect of this modification is unnoticeable for magnitudes that are averaged over the whole MD trajectory such as temperature, energies, probability distributions, etc. However, it helps the system to overcome potential energy barriers and therefore speeds up the transition from one minimum to another. Thus the long time intervals in which the system remains almost unchanged within a local energy minimum are noticeably decreased and the statistical sampling of the whole conformational space is improved. In fact, the slow rate of conformational changes and the consequent poor statistical sampling is one of the worst difficulties in MD simulations performed at relatively low temperatures, as it was indicated above.

Coulombic energies were computed as pairwise interactions among partial charges assigned to every atom of the system by means of the MOPAC-AM1 [23]. Fig. 2 shows the partial charges assigned to the *cis* configuration of one repeat unit. It is interesting to notice that the excess positive charge (i.e. one proton per repeat unit) is not placed at the N atom, instead it is delocalized mostly among the H atoms. A cut-off distance $r_c = 0.8$ nm was used for van der Waals interactions, i.e. interactions between atoms i and j were set to zero when their distance r_{ij} is larger than r_c.

2.2. Molecular systems

Fig. 1 shows a schematic representation of a dimer of the PDDA chain. It contains three rotatable bonds that are represented by ϕ_1, ϕ_2 and ϕ_3. The skeletal CH–CH bond within the cycle has a fixed orientation of ca. $\phi_{cy} \approx -170$, -50^0 respectively for *trans* and *cis* configurations. H-terminated molecules with this structure having each one of the four combinations of configurations for the two cycles (i.e. *trans–trans*, *cis–cis*, *trans–cis* and *cis–trans*) were investigated in the first place. They will be referred to as dimers. In each case, the geometry of the molecule was first optimized by minimizing the energy with respect to all internal coordinates. This optimized structure was employed as starting point for a MD simulation at $T = 50$ K and the temperature of the system was raised as explained above until 500 K in order to facilitate the transition among different conformational minima. After the system was equilibrated at the working temperature of 500 K the simulation was continued for 2×10^6 integration cycles and the values of the three rotational angles were recorded every 100 integration cycles for posterior analysis. Thus, the number of recorded conformations for the system was 20,000 with a time gap of 100 fs between consecutive conformations.

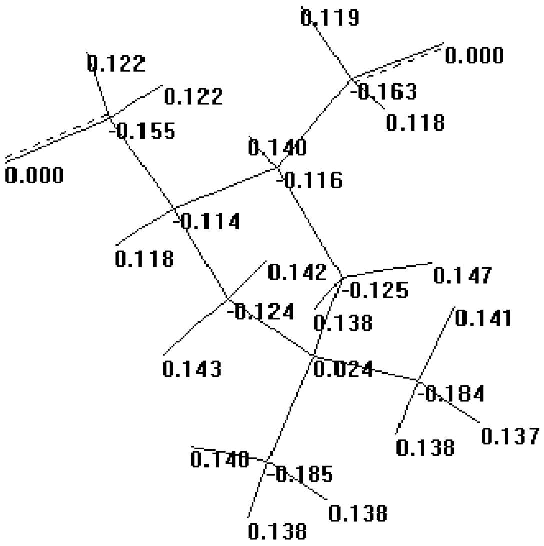

Fig. 2. Partial charges (in electron units) assigned to a repeating unit of the PDDA chain having the cycle in *cis* configuration. See text for details.

The second system was aimed to simulate a water solution of PDDA. It will be referred to as water system. It was formed by a forty repeat units oligomer, with their corresponding Cl^- as counterions and 500 molecules of water packed into a cubic box of side $L = 2.951$ nm with periodic boundary conditions that produces a macroscopic density of ca. 1 g cm^{-3}. The side of the box was initially set to 8 nm in order to be able of holding the oligomer without producing interpenetration of the chains that would raise unrealistically high values of energy, thus rendering very difficult and inaccurate any possible minimisation scheme. A MD simulation was then started under NVT conditions with $T = 500$ K in order to produce a high atomic mobility. The side of the box was decreased with increments of 0.1 nm, as explained above, until the desired value of L was reached. Then the system was submitted to a series of simulated annealing, under NVT conditions, in which the temperature was varied between 50 and 500 K in order to homogenise the atomic distribution. The last part of the MD trajectory was the data collecting stage and consisted in 10^6 integration steps performed under NVT conditions during which the values of ϕ_1, ϕ_2 and ϕ_3 for 20 pairs of units in the central part of the oligomer (i.e. disregarding 10 units at each extreme in order to avoid end effects) were recorder with intervals of 100 fs. Alike values for the twenty diads were averaged in order to improve the accuracy of the probability distributions. The whole procedure was repeated for three similar systems. One of them had all the cycles of the oligomer in the *trans* configuration, the second one had all the cycles in *cis* and in the third one the configuration followed a perfectly alternating sequence *trans–cis–trans–cis*….

The third system was intended to simulate the effect of addition of NaCl to a water solution of PDDA and will be named salt system hereafter. Thus, it was formed by a forty units oligomer of PDDA with its Cl^- counterions, 500 molecules of water and 20 molecules [24] of NaCl. The side of the cubic box containing this system was set to $L = 3.032$ nm in order to produce a macroscopic density of 1 g cm^{-3}. This system was treated with the same procedure explained above for the water system.

2.3. Rotational isomeric states model

Fig. 3 shows the evolution with time of the three rotational angles within a *trans–trans* dimer and indicates that the interconversion among the allowed rotational states is rather fast at the working temperature of 500 K. Analysis of the data represented in Fig. 3 allows the evaluation of the probability distribution for each one of the three rotatable bonds under the assumption of independent rotations. The results are shown in Fig. 4 which indicates that each bond has three allowed orientations which represent the staggered positions, i.e. $\phi \approx 180$, $\pm 60°$. These rotational isomers will be represented by negative *gauche* (g^-, $\phi \approx 60°$), *trans* (t, $\phi \approx 180°$) and *gauche* (g, $\phi \approx -60°$) and will be always written in the order g^-, t, g (i.e. in the order of increasing values of ϕ). The three bonds show a strong preference for *trans* while g^- and g present first order interactions that will be represented by σ_1 in the cases of ϕ_1 and ϕ_3 (these two bonds behave on the same way) and by σ_2 in the case of ϕ_2. Moreover, g orientations over ϕ_1 raises an interaction between groups 5 and 10 (see Fig. 1) or between 4 and 13 in the case of ϕ_3. This interaction will be represented [25] by ω. In the case of ϕ_2, g^- raises interactions among groups 7 and 13 on the second ring with 2, 3, and 10 on the first one depending on the values of ϕ_1 and ϕ_3. This interaction will be represented by ω'. All these characteristics could be incorporated into a very simple model for this dimer with

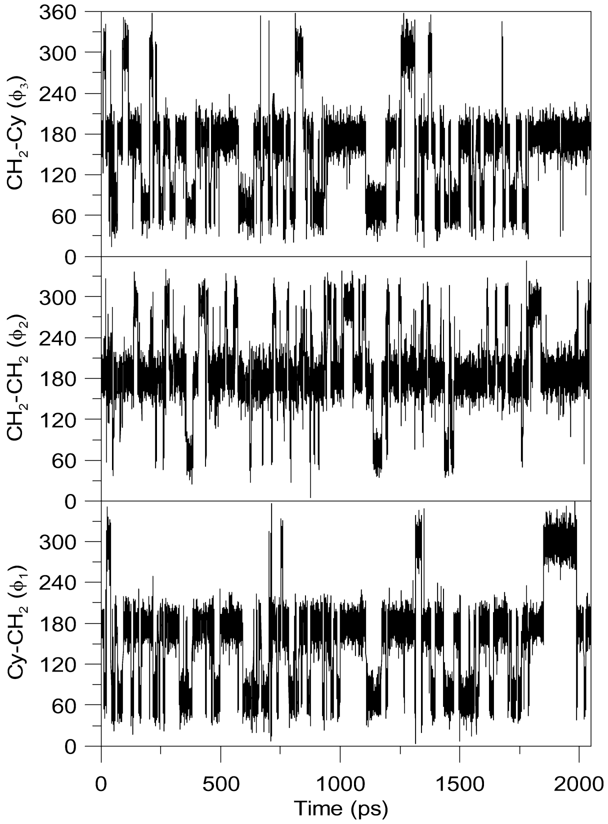

Fig. 3. Time evolution of the three rotational angles of a *trans–trans* dimer of PDDA during a 2000 ps MD trajectory performed at 500 K.

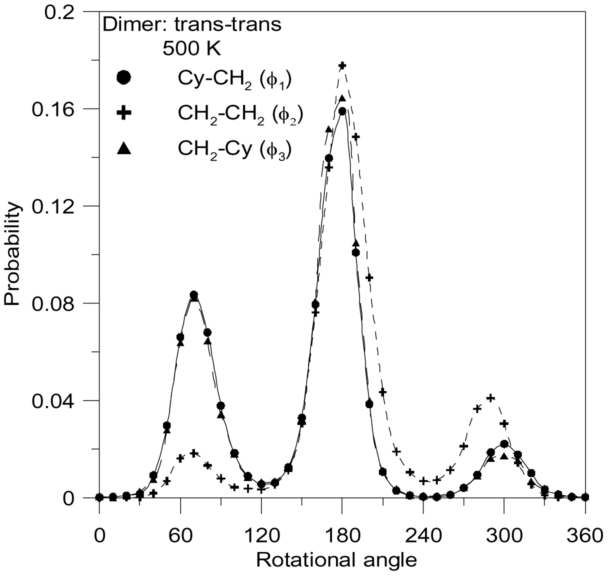

Fig. 4. Distribution probability for the three rotational angles of a *trans–trans* dimer of PDDA obtained from a 2000 ps MD trajectory performed at 500 K.

the following statistical weight matrices

$$\textit{trans}-\textit{trans}: \quad U_1 = \begin{bmatrix} \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \end{bmatrix}$$

$$U_2 = \begin{bmatrix} \sigma_2\omega' & 1 & \sigma_2 \\ \sigma_2\omega' & 1 & \sigma_2 \\ \sigma_2\omega' & 1 & \sigma_2 \end{bmatrix} \qquad U_3 = \begin{bmatrix} \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \end{bmatrix} \tag{1}$$

Comparison of the data shown in Fig. 4 with the statistical weight matrices indicated in Eq. (1) allows obtaining a rough estimate of the conformational energies as: $E_{\sigma 1} \approx 0.66$, $E_{\sigma 2} \approx 1.52$, $E_{\omega} \approx 1.32$, $E_{\omega'} \approx 0.83$, all in kcal mol^{-1}. The values of these energies can be refined through comparison among a priori probabilities for consecutive pairs of bonds computed from the statistical weight matrices indicated in Eq. (1) and those directly obtained from the MD trajectory.

Fig. 5 shows, as an example, the distribution of a priory probabilities obtained for the pair of bonds ϕ_1, ϕ_2 by analysis of the MD trajectory. Integration of those probabilities in the vicinities of the maxima provides the following probabilities for all the allowed orientations of both pairs of bonds, with the states written in the order g^-, t, g

$$\textit{trans}-\textit{trans}: \quad P_{12} = \begin{bmatrix} 0.062 & 0.249 & 0.004 \\ 0.007 & 0.437 & 0.160 \\ 0.001 & 0.077 & 0.003 \end{bmatrix},$$

$$P_{23} = \begin{bmatrix} 0.062 & 0.007 & 0.001 \\ 0.249 & 0.437 & 0.077 \\ 0.004 & 0.160 & 0.003 \end{bmatrix} \tag{2}$$

According to standard procedures of the matrix multiplication scheme [2–6], the probability for pair of bonds n, m being in rotational state i,j can be computed as

$$P_{12}(i,j) = \frac{1}{Z_{12}}(1 \quad 0 \quad 0)U_1^0(i)U_2^0(j)\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix},$$

$$P_{23}(i,j) = \frac{1}{Z_{23}}(1 \quad 0 \quad 0)U_2^0(i)U_3^0(j)\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \tag{3}$$

where the partition functions for the two pairs of bonds, Z_{12} and Z_{23}, are given by

$$Z_{12} = (1 \quad 0 \quad 0)U_1U_2\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix},$$

$$Z_{23} = (1 \quad 0 \quad 0)U_2U_3\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \tag{4}$$

with the U matrices indicated in Eq. (1) and $U_m^0(i)$ being obtained from U_m by replacing all its elements by zero except those of column i which are left unchanged.

A numerical routine was employed to minimize the standard deviation between probabilities obtained from MD (Eq. (2)) and those computed with Eqs. (1), (3) and (4) with different values of the conformational energies, taking as first guess the values indicated above. The results are summarized in the second column of Table 1.

The statistical weight matrices indicated in Eq. (1), and their equivalent expressions for the other configurations of the dimer given below, together with the numerical values of the conformational energies collected in Table 1 can be used to compute averages of any conformational property of the polymer chain according to standard procedures of the

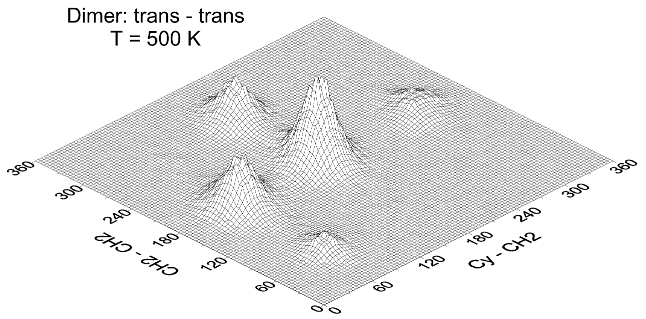

Fig. 5. Probability distribution for simultaneous orientations of ϕ_1, ϕ_2 rotational bonds on a *trans–trans* dimer of PDDA as obtained from a 2000 ps MD trajectory performed at 500 K.

Table 1
Conformational energies (in kcal mol^{-1}) obtained through comparison of a priori probabilities for adjacent pairs of bonds obtained from MD trajectories with those computed by matrix multiplication scheme. Statistical weights are taken to be single Boltzman's factors of their corresponding energies, i.e. for instance $\omega = \exp(-E_{\omega}/RT)$

Parameter	Conformational energy		
	Molecular system		
	Dimers	Water	Salt
σ_1	0.64	1.17	1.09
σ_2	1.28	1.24	1.14
σ_3	1.07	1.08	1.21
σ_4	2.61	1.81	1.62
σ_5	2.19	1.83	1.64
ω	1.19	0.29	0.21
ω'	1.46	1.26	0.99
ω''	2.55	2.26	1.68

matrix multiplication scheme [2–6]. However PDDA contains only three rotatable bonds in the repeat unit, which are separated from the next unit by a rigid bond belonging to a cycle. Consequently, a better representation of the polymer might be obtained by computing the a priory probabilities for the 27 states allowed to a full repeat unit and employing those results to generate different conformations of the chain according to MC procedures.

The probability distributions for the states allowed to simultaneous orientations of the three rotatable bonds may be obtained by analysis of the MD trajectory. The results thus obtained are shown in Table 2 for the more probable conformations. They can also be computed from the statistical weight matrices as

$$P_{123}(i,j,k) = \frac{1}{Z_{123}}(1\quad 0\quad 0)U_1^0(i)U_2^0(j)U_3^0(k)\begin{pmatrix}1\\1\\1\end{pmatrix},$$

$$Z_{123} = (1\quad 0\quad 0)U_1U_2U_3\begin{pmatrix}1\\1\\1\end{pmatrix} \tag{5}$$

Table 2
Averaged locations of rotational states and probabilities at 500 K for simultaneous orientations of the three rotatable bonds within a PDDA dimer obtained from MD trajectories. Only the most probable states are included in the table. The last column collects the probabilities calculated at 300 K from those of 500 K by assuming that the ratio between the probability of any state i, p_i, and that of the all *trans* state p_{ttt} is given by $p_i/p_{ttt} = \exp - E_i/RT)$ at any temperature

$\langle\phi_1\rangle$	$\langle\phi_2\rangle$	$\langle\phi_3\rangle$	Prob. (500 K)	Prob. (300 K)
trans–trans configuration				
176.4	181.3	176.5	0.2634	0.4623
70.5	181.3	176.5	0.1383	0.1580
176.4	181.3	70.4	0.1383	0.1580
176.4	289.0	176.5	0.0729	0.0543
70.5	181.3	70.4	0.0726	0.0540
176.4	181.3	298.9	0.0416	0.0213
300.0	181.3	176.5	0.0416	0.0213
cis–cis Configuration				
174.5	180.1	186.0	0.4682	0.7151
70.2	180.1	186.0	0.1593	0.1186
174.5	180.1	290.1	0.0542	0.0197
70.2	180.1	290.1	0.0542	0.0197
174.5	73.0	186.0	0.0337	0.0089
174.5	287.9	186.0	0.0337	0.0089
cis–trans Configuration				
174.7	182.3	176.0	0.3563	0.5884
174.7	182.3	70.5	0.1871	0.2010
70.2	182.3	176.0	0.1212	0.0976
70.2	182.3	70.5	0.0637	0.0333
174.7	182.3	299.7	0.0563	0.0271
174.7	72.4	176.0	0.0393	0.0149
174.7	288.8	176.0	0.0393	0.0149

The same analysis explained above for the *trans–trans* configuration may be applied to all the other configurations allowed to the dimer. Thus. Fig. 6 represents the probability distribution obtained for independent rotations in the case of *cis–cis* configuration. As in the previous case, *trans* is by far the preferred orientation. However, in the present case g^- and g orientations over ϕ_2 are equivalent while g^- for ϕ_1 paramount to g for ϕ_3 and vice versa. The appropriate statistical weight matrices are

$$cis-cis: \qquad U_1 = \begin{bmatrix}\sigma_3 & 1 & \sigma_3\omega'' \\ \sigma_3 & 1 & \sigma_3\omega'' \\ \sigma_3 & 1 & \sigma_3\omega''\end{bmatrix}$$

$$U_2 = \begin{bmatrix}\sigma_4 & 1 & \sigma_4 \\ \sigma_4 & 1 & \sigma_4 \\ \sigma_4 & 1 & \sigma_4\end{bmatrix} \qquad U_3 = \begin{bmatrix}\sigma_3\omega'' & 1 & \sigma_3 \\ \sigma_3\omega'' & 1 & \sigma_3 \\ \sigma_3\omega'' & 1 & \sigma_3\end{bmatrix} \tag{6}$$

with ω'' representing the interaction among groups 1 and 5, or 4 with 8 (see Fig. 1).

A priori probabilities obtained from the MD trajectory are in this case

$$cis-cis: \qquad P_{12} = \begin{bmatrix}0.059 & 0.213 & 0.000 \\ 0.008 & 0.638 & 0.067 \\ 0.000 & 0.014 & 0.001\end{bmatrix}$$

$$P_{23} = \begin{bmatrix}0.001 & 0.067 & 0.000 \\ 0.014 & 0.638 & 0.213 \\ 0.000 & 0.008 & 0.059\end{bmatrix} \tag{7}$$

and the optimized values of the conformational energies are also included in the second column of Table 1.

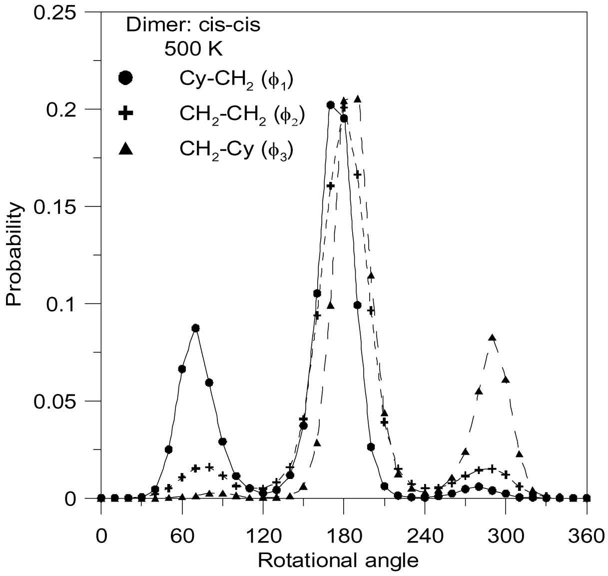

Fig. 6. Same as Fig. 4 for *cis–cis* configuration of the dimer.

Average location of rotational states and probabilities for the main conformations for the three rotatable bonds are summarized in Table 2.

The matrices for the *cis–trans* configuration may be formulated as

$$cis-trans: \quad U_1=\begin{bmatrix}\sigma_3 & 1 & \sigma_3\omega'' \\ \sigma_3 & 1 & \sigma_3\omega'' \\ \sigma_3 & 1 & \sigma_3\omega''\end{bmatrix}$$

$$U_2=\begin{bmatrix}\sigma_5 & 1 & \sigma_5 \\ \sigma_5 & 1 & \sigma_5 \\ \sigma_5 & 1 & \sigma_5\end{bmatrix} \quad U_3=\begin{bmatrix}\sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega\end{bmatrix} \tag{8}$$

i.e. U_1 and U_3 taken, respectively, from *cis–cis* and *trans–trans*, with the two *gauche* states for ϕ_2 being equivalent.

The probabilities for pairs of bonds, obtained from the MD simulation, are

$$cis-trans: \quad P_{12}=\begin{bmatrix}0.043 & 0.338 & 0.003 \\ 0.009 & 0.494 & 0.079 \\ 0.000 & 0.033 & 0.001\end{bmatrix}$$

$$P_{23}=\begin{bmatrix}0.038 & 0.012 & 0.000 \\ 0.282 & 0.507 & 0.075 \\ 0.005 & 0.080 & 0.001\end{bmatrix} \tag{9}$$

and the optimized value of the new conformational energy is also included in the second column of Table 1 while all the information concerning the location and probabilities for simultaneous orientations of the three rotations is in Table 2.

The *trans–cis* configuration is equivalent to *cis–trans* with reversal of angles, i.e. reading it from right to left.

The same analysis was performed for all the configurations of both the water and the salt systems. Thus, Fig. 7 shows, as an example, the probability distribution obtained for *cis–cis* configuration of the salt system under the independent rotations approximation. Analysis of the probability distributions obtained from the MD trajectories for simultaneous orientations of pairs of bonds provides the values of the conformational energies collected on columns three (water system) and four (salt system) of Table 1. Probability distributions for the more stable combinations of simultaneous orientations of the three rotatable bonds on each repeat units are summarized in Table 3 (water system) and Table 4 (salt system).

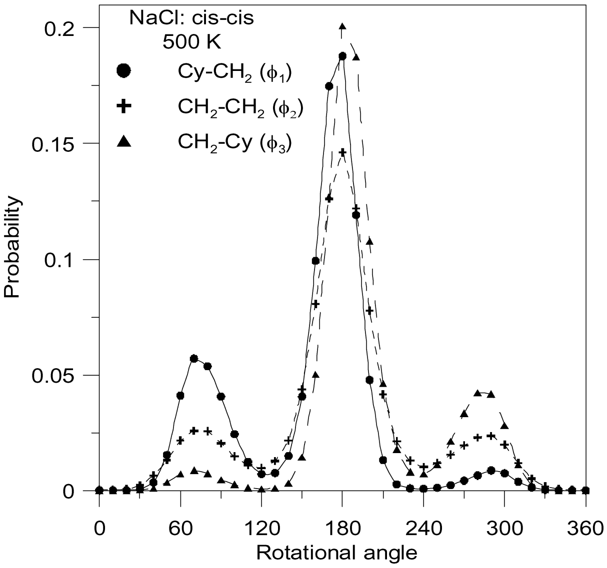

Fig. 7. Same as Fig. 4 for *cis–cis* configuration of the salt (NaCl) system.

2.4. Conformational averages for polymeric chains

Standard procedures of MC sampling were employed to generate chains containing up to 200 repeat units with a predetermined value for the fraction of *trans* units (p_t) and random placement of *cis* and *trans* cycles. The procedure was repeated 1,000 times. Once the configuration of the chain was determined, 1,000 different conformations were generated according to the probabilities for the three rotatable bonds summarized in Tables 2–4, so that all the results presented below are averages over 10^6 different geometries of the chain. Full tables containing the probabilities of all 27 different

Table 3

Averaged locations of rotational states and probabilities at 500 K for simultaneous orientations of the three rotatable bonds within a PDDA dimer obtained from MD trajectories computed for the water system. Only the most probable states are included in the table. The last column collects the probabilities calculated at 300 K from those of 500 K by assuming that the ratio between the probability of any state i, p_i, and that of the all *trans* state p_{ttt} is given by $p_i/p_{ttt} = \exp - E_i/RT)$ at any temperature

$\langle\phi_1\rangle$	$\langle\phi_2\rangle$	$\langle\phi_3\rangle$	Prob. (500 K)	Prob. (300 K)
trans–trans configuration				
177.6	184.9	177.7	0.2834	0.5461
181.6	294.4	180.4	0.1256	0.1408
298.9	182.3	176.9	0.0875	0.0770
175.6	173.1	73.7	0.0743	0.0586
74.5	174.1	175.6	0.0735	0.0576
175.9	182.0	297.7	0.0525	0.0329
71.6	166.6	71.4	0.0466	0.0270
cis–cis Configuration				
176.4	179.9	184.7	0.3826	0.6457
79.1	172.6	184.4	0.1580	0.1478
170.1	89.8	181.0	0.0831	0.0507
72.6	62.9	180.0	0.0772	0.0448
74.1	174.4	282.6	0.0675	0.0358
171.2	177.3	277.0	0.0611	0.0304
cis–trans Configuration				
177.1	181.7	180.6	0.3591	0.6954
77.9	175.6	183.3	0.0825	0.0599
177.7	183.9	287.2	0.0790	0.0558
179.6	290.6	184.5	0.0788	0.0556
177.4	179.4	76.0	0.0671	0.0425
292.3	180.3	180.8	0.0485	0.0247
73.1	71.0	175.4	0.0388	0.0170

Table 4
Averaged locations of rotational states and probabilities at 500 K for simultaneous orientations of the three rotatable bonds within a PDDA dimer obtained from MD trajectories computed for the salt system. Only the most probable states are included in the table. The last column collects the probabilities calculated at 300 K from those of 500 K by assuming that the ratio between the probability of any state i, p_i, and that of the all *trans* state p_{ttt} is given by $p_i/p_{ttt} = \exp - E_i/RT)$ at any temperature

$\langle\phi_1\rangle$	$\langle\phi_2\rangle$	$\langle\phi_3\rangle$	Prob. (500 K)	Prob. (300 K)
trans–trans configuration				
178.9	183.7	178.8	0.2670	0.5180
183.1	295.5	181.9	0.1358	0.1679
176.4	183.7	297.9	0.0749	0.0622
297.4	181.5	175.1	0.0692	0.0546
174.3	172.3	72.6	0.0643	0.0482
70.9	167.6	71.2	0.0521	0.0340
73.9	173.6	174.9	0.0459	0.0275
cis–cis Configuration				
175.3	179.7	183.8	0.3605	0.6456
79.2	173.5	184.5	0.1253	0.1110
175.6	186.2	280.5	0.0900	0.0639
179.2	285.1	197.0	0.0745	0.0466
167.8	84.2	180.5	0.0719	0.0439
74.8	70.1	180.6	0.0633	0.0355
cis–trans Configuration				
177.7	181.3	181.0	0.3313	0.6226
182.2	292.0	184.7	0.1215	0.1170
177.5	187.2	287.7	0.1028	0.0886
178.5	180.1	78.1	0.0664	0.0427
80.9	183.1	182.9	0.0663	0.0426
288.5	173.5	175.4	0.0530	0.0294
169.8	65.9	177.6	0.0296	0.0111

states allowed to each unit, not only the summaries collected in Tables 2–4, were employed in the calculation. These probabilities were, in principle, obtained at 500 K in order to increase the mobility of the atoms, thus improving the statistical sampling of MD. They were scaled to 300 K in order to facilitate the comparison with experimental results obtained [6] at 25 °C. The scaling was performed assuming that the probabilities were Boltman's factors of their corresponding energies. Thus, the ratio between the probability of any state i, p_i, and that of the all *trans* state p_{ttt} is given by $p_i/p_{ttt} = \exp(-E_i/RT)$ at any temperature.

Values of the mean squared end to end distances computed during MC sampling were transformed into dimensionless characteristic ratios $C_N = \langle r^2\rangle_0/Nl^2 = \langle r^2\rangle_0/4X(0.154)^2$, where X represents the number of units contained in the chain. Each unit was assumed to containing four C–C bonds of length 0.154 nm. Typical standard errors on the computed averages of p_t and $\langle r^2\rangle_0$ amounted to less than 1%.

Fig. 8 shows the values of C_N as function of the number of repeat units X for chains with $p_t = 0$ and 1 for the three systems studied in this work. The values computed with $p_t = 0$ (i.e. *cis* configuration) of water and salt systems are almost identical. As is apparent from Fig. 8, the asymptotic limit for $N \to \infty$ is reached in all the cases for chains containing ca. $X \approx 80$ repeat units. Consequently, values computed with $X = 200$ units seems to be a good approximation for high molecular weight polymers. Fig. 9 shows the values of C_N as function of p_t for the three systems.

3. Discussion

All the results presented above indicate that the three rotatable bonds on the repeat unit of PDDA exhibit a strong preference for *trans* conformation. Indeed, at 300 K and according to the probabilities summarized in Tables 2–4, more than half of the repeat units are in the all-*trans* conformation. It might seem surprising that, while the preference for *trans* conformations is stronger in the case of *cis* than in *trans* configurations, the former (i.e. $p_t = 0$) exhibit smaller molecular dimensions than the later one, as it is shown in Figs. 8 and 9. The reason is very simple, the two skeletal bonds that propagate the polymer chain emerge roughly in the same direction from a cycle having *cis* configuration while their directions are almost opposite in the case of *trans* configuration. Consequently, cycles in *cis* configuration produce U turns in the polymer backbone and therefore decrease noticeably the molecular dimensions. On the contrary, *trans* configurations on the cycles together

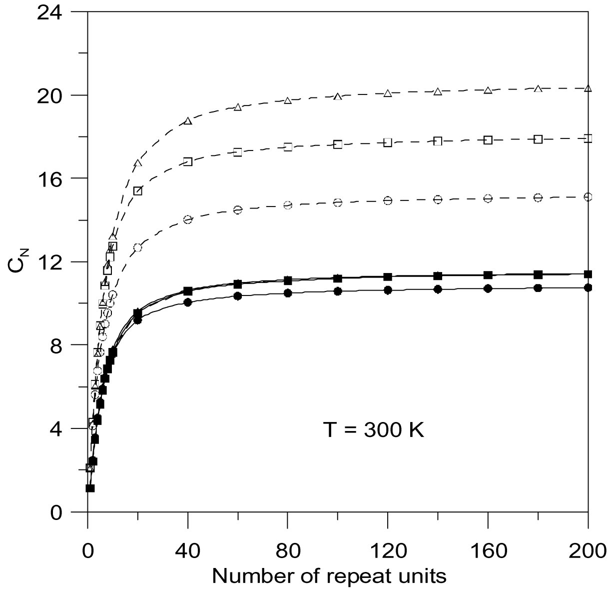

Fig. 8. Characteristic ratio of the molecular dimensions $C_N = \langle r^2\rangle_0/Nl^2$, as a function of the number of repeat units. Calculations were performed by MC sampling at $T = 300$ K as explained in the text. Filled symbols and solid lines represent values obtained for chains having $p_t = 0$ (i.e. all the cycles in the *cis* configuration) while open symbols and dot lines indicate $p_t = 1$ (all the cycles in *trans*). Circles were obtained with the probabilities computed for dimers (Table 2), squares correspond to probabilities of the water system (Table 3) and triangles indicate results for the salt system (Table 4). Values obtained for water and salt systems at $p_t = 0$ (i.e. solid squares and triangles) are almost identical.

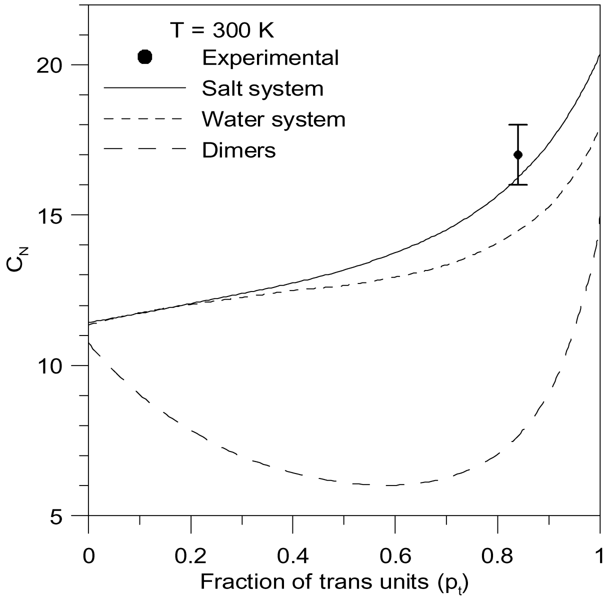

Fig. 9. Values of C_N for chains containing 200 repeat units computed at $T = 300$ K with the probabilities obtained with the three systems studied here as function of the fraction of *trans* units p_t. The circle represents the experimental value ($C_N = 17 \pm 1$) obtained at 25 °C in water solution containing a concentration 0.5 M of NaCl.

with *trans* conformations on the bond give raise to very extended chains.

The effect of including water molecules and ionic salt into the system could be analyzed through comparison among Eqs. (2), (7) and (9) with Eqs. (10) or (11), or among Tables, 2, 3 and 4. The small molecules of water and the ions increase the preference for *trans* conformations in diads containing at least one of the cycles in *trans* configuration (i.e. *trans–trans* or *cis–trans*) while they decrease the incidence of *trans* conformations in the case of *cis–cis* diads. A possible explanation of this effect would be that the solvation of the polymeric chain, with its corresponding decrease of intramolecular interactions, might be somehow hindered in the case of *cis–cis* configuration in which the two continuations of the chain are almost parallel and rather close to each other, so that it would be difficult for a small molecule or an ion to place itself between those two groups. Differences in probabilities among the three systems produce rather minor changes on the molecular dimensions of chains containing low fractions of *trans* configurations (i.e. when p_t is close to zero, see Figs. 8 and 9), because then, the effect of U turn indicated above is dominant in determining the length of the chain. However, the effect is much stronger in the case of high fractions of *trans* configuration (p_t close to unity) where there is a good correlation between *trans* conformations and molecular dimensions.

Probability distributions for the two condensed systems studied here (i.e. water and salt systems), are very similar. The largest discrepancies being observed in the conformational factors ω, ω' and ω'' penalizing one of the *gauche* orientations vs. the second one, see Table 1. These energies are smaller in the salt than in the water systems. Consequently, differences in population among the two *gauche* states are also smaller in the case of the salt system. This effect produces a more symmetric propagation of the chain, and consequently slightly higher molecular dimensions, in the case of the salt system, as could be seen in Fig. 9.

At this moment, we are performing a experimental study of PDDA in water solutions [7] employing SEC techniques with multiple detectors [8–13]. The results obtained so far indicate that employing pure water as solvent produces irregular and difficult to analyze chromatograms, which precludes obtaining accurate results of molecular properties. This kind of behavior has been observed in many other systems [7–13] and, in some cases, can be overcome by additions of ionic salts to the solvent. Thus, in the case of PDDA, addition of NaCl to a concentration of ca. 0.5 M produces a system which is very close to unperturbed conditions at 25 °C (i.e. the q exponent on the scaling law $\langle s^2 \rangle = QM^q$ amounts to ca. 0.51). The experimental value of C_N obtained in this systems is 17 ± 1 which is represented by the circle on Fig. 9. Agreement between experience and the theoretical value obtained through simulation of the actual experimental conditions (i.e. the salt system) is very good. We are carrying out measurements with different ionic salts in order to investigate the effect that the size and/ or charge of the ions might have on the conformational properties of the polymer. However, final results are not yet available.

4. Conclusions

The combination of MD simulations, RIS analysis and MC sampling seems to be a very powerful tool for the evaluation of conformational properties of polymer chains. The results are very sensitive to the kind of system simulated at the MD stage, i.e. isolated molecules or solutions with or without additives. Theoretical values of unperturbed dimensions of PDDA in water solution containing NaCl presented in this work are in good agreement with experimental values determined in the same conditions.

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[24] The number of added salt molecules should be large enough as to produce a noticeable effect in the calculation and yet low enough as to represent a reasonable macroscopic concentration. A number of ca. 20 molecules (producing a macroscopic concentration of 1.2 M) represents a good compromise.

[25] Strictly speaking, the interactions represented by ω, ω', etc. are not first order. However, due to the rigidity of the two cycles, the same or very similar interactions appear for a given position of one bond regardless of the orientations of the other two. For this reason, they are assigned to orientations over just one bond.