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Note

Molecular dynamics study of polygalacturonic acid chains in aqueous solution

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Abstract

Molecular dynamics (MD) simulations were performed on a system consisting of polygalacturonic acid (PGA) chains. MD experiments were conducted both in vacuo and in the presence of water. The PGA chains were formed by 12 GalA units and each chain had a molecular weight of 2132. Three chains were enclosed in the simulation cells. NPT runs, carried out either in the absence and in the presence of water molecules, evidenced the collapse of the chains which aggregate due to the formation of hydrogen bonds. NVT trajectories performed in the presence of water molecules show that the solvent moves in channels which separate the PGA aggregates. These findings well agree with experimental results about gel formation by PGA and other pectins in strong acid media. © 1997 Elsevier Science Ltd.

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1. Introduction

Acid sugars play an important role in the biochemical processes involved in the plant nutrition. They are found both in monomeric and polymeric forms, on the root surfaces and cell walls. The polymers are the main constituents of the mucilaginous soil–root interface (mucigel): they behave as an accumulator for the nutrients and are involved in the diffusion process of the ions towards the absorbing cells [1–3]. These properties may be due to the polygalacturonic acid (PGA) chains which are the main constituents of the root mucilage [4–6]. Electron microscopy studies evidenced that these polymers are organized in a fibrillar structure [7–9]. The PGA is abundant in the primary cell walls of dicots [10] and is an important constituent of the apoplastic transport system of the plants. These structures act as selective filters for the nutritive elements and regulate the movement of ions through and out the cells [11]. In recent years Gessa and Deiana [12,13] synthesized a network of Ca-polygalacturonate suitable as a model of the soil root interface, which exhibits a fibrillar structure similar to that of natural root mucilages. In a previous work [14], we applied the molecular dynamics to the study of the movement of Ca^{2+} ions around PGA chains each formed by four units and evidenced the existence of channels where the Ca^{2+} ions move. Computational chemistry methods may greatly help to

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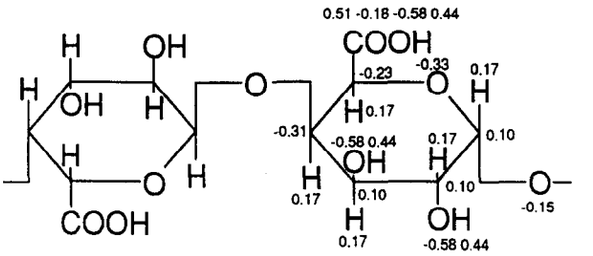
understand and explain the gel formation by PGA chains and the diffusion of ions inside it. This study reports the results of a molecular dynamics survey about the aggregation process between PGA chains in aqueous solution. The forces driving the aggregation processes are individuated in the formation of hydrogen bonds which lead to the chain collapse.



Scheme 1. The PGA chain.

2. Materials and methods

The DLPOLY2 program was used to carry out the molecular dynamics (MD) experiments. [1] We used the AMBER plus GLYCAM force field [15] while atomic charges were calculated by ab initio calculation at the 6-31G * accuracy level. Periodic boundary conditions were adopted and the Ewald summation method was employed. All calculation were performed on the CRAY-C90 and CRAY-T3D at CINECA, Italy and on an IBM RS6000 located at the Department. The PGA structure on which computations were done and the computed partial atomic charges are shown in Scheme 1.

Preliminary MD runs were done, in the absence of the solvent, on a system composed by three PGA chains each counting eight units. Three independent trajectories each of the duration of 50 ps were generated after allowing the system to equilibrate for 10 ps. The results, which are not presented here, indicated that the PGA chains assemble to form close aggregates.

Successively we extended the PGA chains length up to 12 units, with an overall molecular weight of 2132 per chain, and started an in vacuum experiment involving three chains. Three independent trajectories were generated from different initial configurations of the PGA chains. The initial cell was chosen as a cubic box with 50 Å side and one of the starting configuration is shown in Fig. 1.

Three trajectories were calculated as follows: the system was first allowed to vary its volume by performing a NPT (Number of molecules, Pressure and Temperature constant) run at 298 K and 1.0 atm for a duration of 100 ps; the cell edge at this point had reduced to about 22 Å. A 100 ps NVT (Number of molecules, Volume and Temperature constant) run at 700 K was then performed and the system was finally equilibrated for 50 ps at 298 K in the NPT ensemble. All these points were then discarded and a final run of 200 ps was performed recording the trajectory. The runs were stopped at 200 ps as no significant variation was observed in the average total energy over the last 100 ps.

The MD runs in the presence of water were performed surrounding the above equilibrated system with a shell of 200 water molecules. The *wateradd* DLPOLY utility was used to add the water molecules. A dielectric constant value of 1.0 was employed in all the experiments.

3. Results and discussion

The side length of the simulation cell after the NPT simulations, averaged over the three runs, was 20.0 Å for the system in vacuo and 21.6 Å for the system in water. Snapshots along the x, y and z axes of the 200 ps final configuration of the PGA-water

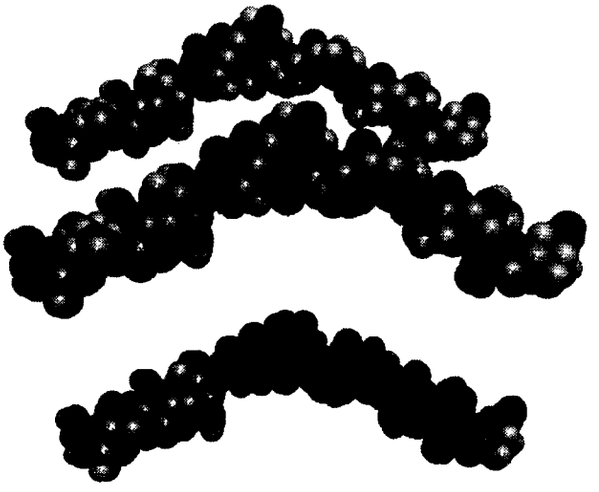


Fig. 1. One of the starting configurations of the PGA chains.

[1] DLPOLY2 is a package of molecular simulation routines written by W. Smith and T. R. Forester, copyright the Council for the Central Laboratory of the Research Councils, Daresbury Laboratory, Nr Warringron (1994–1996).

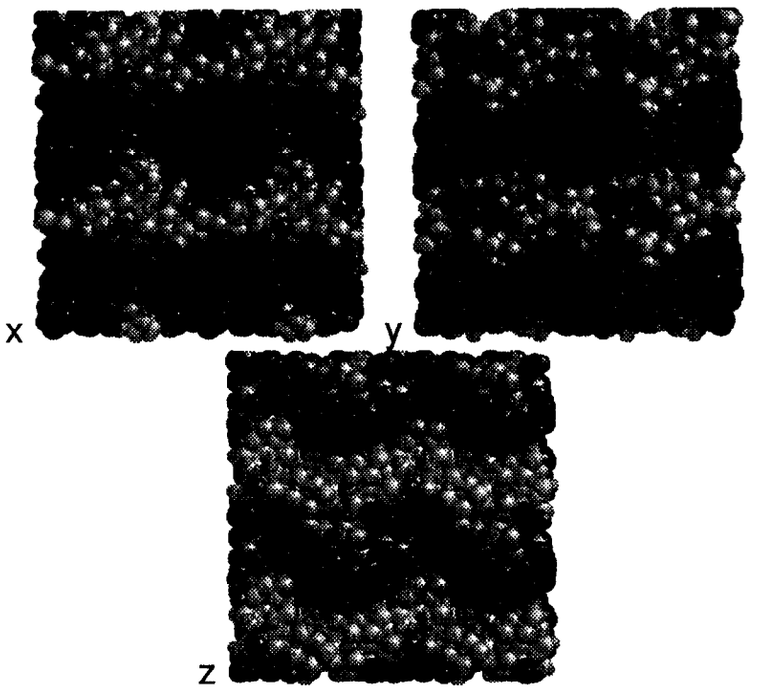


Fig. 2. Snapshots along the x, y and z axes of the final configuration of the PGA-water system. Solvent molecules appear to be restricted in channels among the PGA network.

system are shown in Fig. 2. A cubic box with 43.2 Å side length is illustrated. We observe a considerable aggregation of the PGA chains which collapse forming a sort of precipitate and reducing considerably the volume of the cell. These findings agree with the direct observation of aggregate formation among PGA chains in the absence of calcium ions [16].

The water molecules appear to move inside channels between the PGA aggregates and only a few diffuse inside the collapsed PGA structure. The computed diffusion coefficient of the water molecules is 7.9×10^{-10} m^2/s

The calculated radial distribution functions ($g(r)$) for the hydrogen and the oxygen atoms are shown in Fig. 3a. We remind that the $g(r$X–Y) function gives the probability to find a pair of the atoms X and Y at

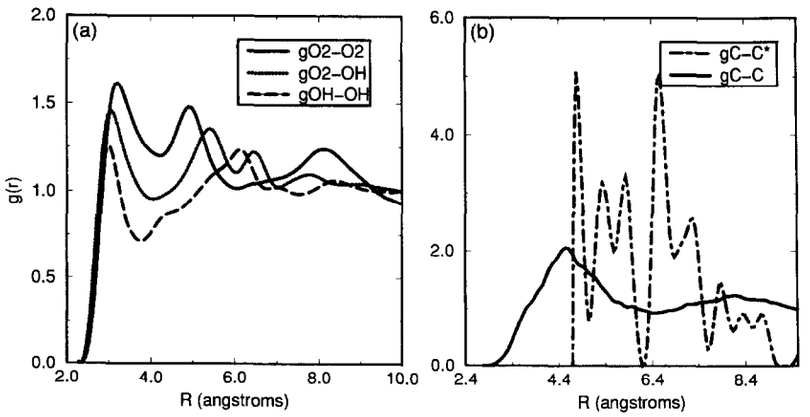


Fig. 3. (a) Radial distribution functions for the hydrogen and oxygen atoms. (b) Radial distribution functions for the carboxylic carbon atoms. * Single chain case.

a distance r, relative to the probability expected for a completely random distributed sample at the same density.

The $g(r\text{H–O})$ exhibit a peak at an r value of about 1.9 Å for both the hydroxylic and the carboxylic oxygens. This indicate the formation of hydrogen bonds between the hydrogen and the oxygen atoms of both the alcoholic and the carboxylic functions. The second shoulder at $r = 4$ Å is probably due to the order of the OH distribution along the polymer chain. Water also, even in a lesser extent, exhibits hydrogen bonding with the border OH groups of the PGA chains. The carbon–carbon $g(r)$ for the carboxylic (C) carbon atoms are reported in Fig. 3b and compared with the $g(r)$ computed from a run with a single 24 units PGA chain. The plots give evidence of the interchain interactions which keep together the chains. The single-chain $g(r)^*$ shows a series of sharp peaks starting at $r = 5$ Å which are attributable to the chain period, the broadened peak at about 4.7 Å by the $g(r)$ the three-chain system accounts for the carboxylic groups involved in interchain hydrogen bonding.

These results show a good qualitative agreement with the reports about gel formation and precipitation of PGA chains. The analysis of the MD trajectories, moreover, allows confirmation of the collapse of PGA chains in strong acidic media is mainly due to the formation of interchain hydrogen bonds. Both the hydroxylic and the carboxylic groups seems to be involved in such a mechanism. Once the chains collapsed, the solvent molecules are mainly confined to the free space among the aggregated chains and only a few can diffuse through the PGA network. We retain that these findings justify a more intensive calculation effort devoted to describe the interactions and the conformation of the PGA chains involved in the metal chelation processes. The knowledge and the understanding of such phenomena have a basic importance in the study of the soil–root interface ionic transfer which is the first stage of the plant nutrition mechanism, but must consider the presence of Na^+, and/or Ca^{2+} ions, and an increment in the chain length.

Acknowledgements

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