Computational Approaches to the Calculation of Spectroscopic, Structural and Mechanical Properties of Polysaccharide Chains

by

Padmesh Anjukandi

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Declaration of Authorship

I, Padmesh Anjukandi, declare that this thesis titled, 'Computational Approaches to the Calculation of Spectroscopic, Structural and Mechanical Properties of Polysaccharide Chains' and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed: Padmesh Anjukandi

Date: 08/09/2010

"God Gave Me Nothing I Wanted, He Gave Me Everything I Needed."

Swami Vivekananda...

Abstract

In this thesis atomistic, statistical mechanical and coarse grained simulation techniques are used to study the properties of biopolymers and in particular the plant polysaccharide pectin. Spectroscopic aspects, structural and conformational behavior, and mechanical properties of the molecule in different physical states are addressed.

After an introduction to the area and the theoretical techniques utilised herein (chapter 1), chapter 2 deals with the spectroscopic characterisation of pectin. Spectra were obtained theoretically by undertaking complete energy minimisation and Hessien calculations using DFT techniques implemented in Gamess (PC & US) packages. The calculated IR absorptions of different pectinic species and oligomers coupled on different surfaces were compared with experimental results. Herein, it is confirmed that experimental FTIR studies coupled with DFT calculations can be used as an effective tool for the characterisation of pectin, and studying chemical coupling of the biopolymer to surfaces.

In chapter 3, the properties of single chain polymer systems in controlled solvent conditions were studied using Brownian dynamics simulations, motivated by the formation of secondary structure architectures in biopolymer systems. We focus on the conformational properties of the chain in the presence of an additional torsional potential. New, interesting, and biologically relevant structures were found at the single molecule scale when a torsional potential was considered in the calculations.

In chapter 4, results from DFT calculations carried out on single pectin sugar molecules (lengths and the free energies) are incorporated into a statistical mechanical model of polymer stretching, in order to obtain the force-extension behaviour of a single molecule pectin. This captures a good deal of the phenomenology of the single molecule stretching behavior of pectin.

Chapter 5 summarises the conclusions of the work and finally chapter 6 suggests direction for further work.

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Padmesh Anjukandi

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Contents

List of Figures

List of Tables

Abbreviations

FJC	**F**reely **J**ointed **C**hain
FRC	**F**reely **R**otating **C**hain
WLC	**W**orm **L**ike **C**hain
AFM	**A**tomic **F**orce **M**icroscopy
e-WLC	**e**xtensible **W**orm **L**ike **C**hain
DFT	**D**ensity **F**unctional **T**heory
HF	**H**artree **F**ock
MP	**M**Ø**ller** **P**lesset
CC	**C**oupled **C**luster
GVB	**G**eneralised **V**alence **B**ond
MCSCF	**M**ulti **C**onfigurations **S**elf **C**onsistant **F**ield
KS	**K**ohn **S**ham
MD	**M**olecular **D**ynamics
BD	**B**rownian **D**ynamics
LJ	**L**ennard **J**ones
FENE	**F**inite **E**xtensible **N**onlinear **E**longation
DP	**D**egree of **P**olymerisation
DM	**D**egree of **M**ethylesterification

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Dedicated to my beloved father . . .