Synopsis

Molecular Modeling and Atomistic Simulations of the Structural and Optical Properties of Polycarbonates

Introduction

Molecular modeling techniques have proven to be a useful tool in the investigation of the physical properties of polymers. To judiciously and efficiently design materials, which have particular properties for specific applications, there is a need to understand the structural and dynamic behavior of polymer chains at the molecular level. Computer simulations assist in gaining an insight into the molecular and mesoscale structures and properties of polymers. Some of the physical properties of polymers at the macroscopic scale are also dictated by the structural aspects of single polymer chains and condensed polymer phases at the molecular length scales. Various computational modeling approaches such as molecular mechanics, molecular dynamics and Monte-Carlo simulations, have been applied to the study of polymers in order to determine their structure, conformations and physical properties. Quantum chemical calculations at different levels of accuracy have also been widely applied for determining the accurate geometry, conformation and energetics of relatively small fragments of polymer chains such as repeat units or monomers.

Optical properties of materials, especially polymers, are of importance in a variety of application areas including information storage systems and media. Polymers are used as substrate material as well as memory layer in compact discs. As a material for magneto optical (MO) disc substrate, bisphenol A polycarbonate (BPAPC) is thought to be most suitable currently, because of its excellent thermal, mechanical and low hygroscopic properties. However, the large birefringence due to optical refractive index anisotropy of the phenyl rings in BPAPC renders the exact focus of the optical beam unsuitable for the purpose of reading and writing due to the anisotropic changes in the state of polarization of light in going through this material. The property “optical anisotropy” of polymer chains is, therefore, of considerable fundamental and practical relevance in providing an understanding of material behaviour and for the molecular design of materials with suitable properties. The chemical structure of the polymer chain repeat unit, conformations of the chain and the flow conditions which orient the chains during the processing of these materials, dictate their optical properties. Several experimental reports exist in literature where attempts have been made to lower the birefringence by structural modification of the bisphenol unit by various strategies.

Conformational features of Bisphenol A Polycarbonate (BPAPC) have been the focus of considerable research since the pioneering work by Williams and Fiory. Various calculation methods have been utilized to investigate the conformational characteristics of BPAPC and the significant results have also been summarized. The calculated chain dimensions of BPAPC from Rotational Isomeric State (RIS) models were in close agreement with the experimental values from light scattering and SANS measurements. RIS models for various structural modifications of BPAPC were formulated from conformational energy calculations of the corresponding bisphenyl fragments neglecting torsional and coulombic interactions. The calculated
characteristic ratio of these polycarbonates (PC's) were insensitive to substitution of one or both of the methyl groups by either hydrogen atoms, phenyl rings or to substitution of the isopropylidene group by cyclohexyl group.\textsuperscript{12,13}

The optical anisotropies ($\gamma^2$) of structural analogues as well as for BPAPC chains have been determined from Depolarized Rayleigh Scattering and electric birefringence experiments by Flory and co-workers.\textsuperscript{14,15} The polarizability tensors of carbonate group and phenyl groups in BPAPC were deduced from the model compounds utilizing the Valence Optical Scheme (VOS). $\gamma^2$ calculated for BPAPC via the Rotational Isomeric State method using the derived polarizability tensors were in excellent agreement with the experimental values. Low-frequency DRS measurements by Floudas et al.\textsuperscript{16} give results similar to those obtained from the earlier reports for BPAPC dilute solutions as well as for the bulk amorphous state, indicating only slight differences in this optical property between the single chain and the amorphous states. There are no reports in literature on theoretical as well as experimental studies on mean-squared optical anisotropy, $\langle \gamma^2 \rangle$, of structurally modified polycarbonates.

Previous studies in literature on model compounds containing carbonate groups include ab initio calculations using a variety of basis sets such as STO-3G, HF-631G*, HF-631G**, 6-311G** and hybrid density functional theory (B3LYP, 6-31G** basis set) calculations in the gas phase.\textsuperscript{17a-d} Polarizability anisotropies of a group of organic molecules dimethyl carbonate (DMC), methyl phenyl carbonate (MPC) and diphenyl carbonate (DPC) in solution in carbon tetrachloride were calculated by Sun and Mumby.\textsuperscript{18} A direct approach that takes into consideration the solute molecular structure, liquid structure of the solvent and DFT techniques have been proposed to compute the apparent polarizabilities for molecules in dilute solution in non-polar solvents. Except for MPC and DPC, the results were in favorable agreement with the experimental data.

Simulations of structural properties of bulk amorphous BPAPC in the glassy as well as melt states have been reported.\textsuperscript{19} The chain conformations in the bulk, radial distribution functions, static structure factor derived from simulations were compared with the experimental values. Bulk amorphous models have also been reported for BPCPC using atomistic simulations and for TMPC via coarse-graining Monte-Carlo methods.\textsuperscript{20-24} The scattering functions obtained from experiments were compared with those calculated from the generated bulk structures.

Although numerous experimental reports on birefringence of BPAPC and various structurally modified polycarbonates exists in literature,\textsuperscript{25a-c} there have been no attempts till date on theoretical approaches for the estimation of this important property of polycarbonates. Stress optical coefficient of polyethylene melts have been determined via molecular dynamics and monte-carlo techniques.\textsuperscript{26,27} The model used in both cases was relatively simple and reasonable agreement with the experimental data was obtained.

**Objectives of the present work**

1. To determine the conformational states and energetic information of model compounds of various structurally modified polycarbonates using force-field based energy minimization. To formulate the RIS models of these polycarbonates, by using the conformation and geometry derived from
conformational energy calculations and to calculate the unperturbed chain dimensions as a function of temperature and chain length.

2. To formulate a new methodology for the calculation of mean-squared optical anisotropy of structurally modified polycarbonates having two different types of substitution (a) cyclohexylidene group at the C₆ carbon (b) methyl groups on the backbone phenyl rings. The parameters required for the calculation of the optical anisotropy of model analogues, monomer units as well as chains, will include the polarizability tensors of the constituent groups derived from experimental data and their geometry as obtained from force-field based conformational energy calculations, in each of these polycarbonates.

3. To determine the accurate geometry of the structural analogues of substituted polycarbonates by quantum chemical calculations. Polarizability tensors and optical anisotropies of the bisphenol and carbonate fragments will be calculated from their corresponding energy optimized geometries.

4. To derive bulk amorphous models of structurally modified polycarbonates in the glassy state via detailed atomistic simulations. Structural properties of these amorphous models will be calculated and compared with available experimental data. Comparison between the different polycarbonates will be made in order to present the influence of chemical structure on the bulk properties.

5. To calculate the orientational optical birefringence of polycarbonates in the glassy state via atomistic simulations under a tensile load.

The thesis is organized into eight chapters as follows:

Chapter 1: Introduction
This chapter describes the application of various molecular modeling techniques for determining the conformationally dependent structural and optical properties of single chains and condensed amorphous phase of polymers. The literature status on the conformationally derived chain properties of polymers, studied using RIS theory will be presented. The detailed emphasis will be on the molecular modeling studies on polycarbonates till date.

Chapter 2: Scope and Objectives of the Present Work
The scope and objectives of the present thesis will be described in this chapter.

Chapter 3: Conformational Analysis, RIS models and Single Chain Properties of Structurally Modified Polycarbonates
This chapter describes the conformational features of BPAPC and structurally modified bisphenol polycarbonates studied using the PCFF force field by taking into consideration all possible intra and interatomic potential energy interactions. The polycarbonates with different chemical modifications include (1) cyclohexyl group at the C₆ carbon, BPCPC (2) trimethylcyclohexylidene group at C₆, TMPCPC, (3) cyclohexyl group at C₆ and methyl groups on backbone phenyl rings, DMBPC (4) methyl groups on backbone phenyl rings, DMPC. The RIS models for these polycarbonates, formulated from the geometry, conformation and statistical weights will be developed. The conformational properties like the mean-squared end-to-end distance, radius of gyration, persistence length and characteristic ratio of polycarbonates will be presented. A comparison of the average
chain dimensions of these polycarbonates with respect to BPAPC will be given. The chapter will also present results on molecular dynamics calculations performed for a few of the structural moieties, to rationalize the some interesting unusual observations on the variation of chain dimensions for one of the polycarbonates. The influence of chemical structure on conformational properties is brought forth in this chapter.

Chapter 4: Optical Anisotropy of Structurally Modified Polycarbonates Having Cyclohexylidene and Methyl Substituents Using the Rotational Isomeric State Method

In this chapter, a new methodology for formulation of the polarizability tensors of polycarbonate molecular fragments will be described, which is applicable to substituted bisphenyl fragments, diphenyl carbonates and repeat units of various structurally modified polycarbonates having cyclohexylidene group at the Cα carbon and methyl groups on backbone phenyl rings. This theoretical approach utilizes polarizability tensors of constituent groups that have been derived from DRS measurements and the geometry from conformational energy calculations. The method is an extension of Flory's work on BPAPC. The optical anisotropy of bisphenyl and carbonate fragments, repeat units and single chains of structurally modified polycarbonates studied will be presented. The contribution of the various conformers towards the optical anisotropy is analyzed in detail. A critical evaluation of the various structural and conformational features responsible for lowering the optical anisotropy in structurally modified polycarbonates will be presented. A comparison of the calculated single chain optical anisotropy with the optical properties in the bulk state, for e.g. the stress optical coefficient in the glassy and melt states will be presented.

Chapter 5: Ab initio Calculations on Small Molecule Fragments of Structurally Modified Polycarbonates

This chapter will describe the results of quantum chemical calculations of model analogues of structurally modified polycarbonates using ab initio method. The optimized geometries of various bisphenyl and carbonate fragments of various structurally modified polycarbonates having cyclohexylidene group at the Cα carbon and methyl groups on backbone phenyl rings, calculated using HF/6-31G and HF/6-31G** basis sets will be presented. The polarizability tensors and optical anisotropy calculated from the optimized geometries of these fragments will be given. A comparison will be made between the optical anisotropies of bisphenyl and carbonate fragments calculated using the ab initio method and those calculated using the experimental group polarizability tensors via the VOS scheme.

Chapter 6: Detailed Atomistic Simulations of Structurally Modified Polycarbonates in the Glassy State

This chapter describes the generation of bulk amorphous structures of structurally modified polycarbonates in the glassy state via atomistic Monte-Carlo and molecular dynamics simulations in the NVT ensemble at 300 K. The polycarbonates studied here include BPAPC, BPCPC, TMPC, DMBPC and DMPC. The conformations of polycarbonate chains in the bulk obtained from these simulations will be compared with the single chain conformational statistics derived using the RIS method, the results of which are presented in chapter 3. The
calculated cohesive energy densities and solubility parameters of these amorphous polycarbonates will also be presented. Also the radial distribution functions and the static structure factors will be given. Free volume distributions and ring plane orientations of these polycarbonates will be presented. The detailed interplay between the chemical structure of the polycarbonate, its packing in the bulk state, and the interatomic energy potentials will be brought forth.

Chapter 7: Atomistic Simulations of the Orientational Birefringence of Polycarbonates in the Glassy State

This chapter will describe a new theoretical approach based on fully atomistic molecular simulations, for the calculation of the orientation dependent birefringence of amorphous polycarbonates in their glassy state. The methodology uses an unstretched (unstressed or unstrained) starting sample of the polymer and performs repeated sequences of uniaxial extension in the tensile mode followed by molecular mechanics relaxation. The strain is applied till the inception of the plastic deformation. The birefringence and the instantaneous sample engineering stress at every strain step during the computer simulated creep experiment would be the outcomes of this simulation procedure. Results of the birefringence as a function of stress and strain and the stress optical coefficient will be presented and compared with available experimental data from literature. The accompanying molecular scale structural changes and their influence on the average orientation of the polymer chain segments will be discussed in relation to the birefringence. The effect of the fundamental optical properties of the molecular groups in the polymer chain, on the birefringence properties, in conjunction with the orientational effects of the polymer chain segments, will be understood and presented in detail.

Chapter 8: Summary and Conclusions

This chapter summarizes the results of the present thesis. The most important and significant conclusions from this work will be highlighted.

Appendix

Appendix – I: Formulation of the polarizability tensor and calculation of optical anisotropy of substituted bisphenyl fragment will be described in detail. A sample calculation will be given.

Appendix – II: Optical anisotropy per repeat unit in polycarbonate chain considering lower number of rotational states per bond in the repeat unit will be presented.

Appendix – III: Optical anisotropy per repeat unit, which is averaged over the symmetric conformers in each polycarbonate, will be presented.

Appendix – IV: Mean potential energies, individual energy components for each of the 10 amorphous cells in the case of all five polycarbonate will be given. This section will also present information on solubility parameter and chain dimensions of the all the equilibrated amorphous structures of the polycarbonates.
References


10. de Chirico, A. Chim. Ind. 1960, 42, 248


