Chapter 2: Scope and Objectives of the Present Work

2.1. Introduction

Comprehension of the relation between macroscopic properties of a polymer and its chemical structure is a formidable and intricate subject in the field of polymer science. This is usually dealt with by systematic experimental studies of a class (or family) of polymers having different chemical structures and relating the effect of the structure to associated physical properties. The same goal can also be achieved in a different way i.e. by the application of various molecular modeling methods to study a series of polymers. Prime objective of the work presented in this thesis is to study the relation between the chemical structure and optical properties of a series of structurally modified polycarbonates using various molecular and atomistic simulation methods. In defining and achieving this purpose, a very detailed level of structural and geometric information is additionally brought out connecting various responses, origins and events at the molecular level and physical properties at the larger scale which provide new and fundamental understanding into the relationships that we seek. Currently there is lack of fundamental insights on the influence of different structural groups towards the conformation at the level of the repeat unit, single chain and condensed polymeric phase and its effect on polymer properties like polarizability, optical anisotropy and birefringence. Therefore molecular simulation studies, which can provide fundamental understanding of the effect of monomer structure towards these properties at various levels, constitute the prime objective of the present work.

Anisotropy in the optical polarizability of polymer chains is manifested in the birefringence of their condensed phase and is of considerable importance with potential technological applications in the area of information storage.\(^{1-13}\) 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 properties tailored towards specific applications. The chemical structure of the repeat unit and the conformations of the chain molecule, and the flow conditions which orient the chains during the processing of these materials, dictate their optical
properties.\textsuperscript{4-9} An understanding of the effect of chemical structure of the polymer repeat unit or small molecular fragments, on their optical anisotropy, therefore becomes an important step towards providing qualitative as well as quantitative understanding of the optical property at the macroscopic scale. In order to design new polymeric materials that have useful optical properties, such as low optical anisotropy, $\langle \gamma^2 \rangle$ and low birefringence, a thorough understanding of various structural and conformational features that control these properties is required.

Polymers are virtually indispensable as materials for a variety of optical applications. In the area of optical data storage technology bisphenol A polycarbonate (BPAPC) is widely used as a substrate material due to its combination of favourable properties such as transparency, heat resistance, toughness, stiffness, dimensional stability and economical processing. The disadvantage posed by BPAPC is its high intrinsic birefringence.\textsuperscript{4-9} Polarizable phenylene rings along the backbone of this polycarbonate are known to provide positive birefringence. High birefringence and refractive index anisotropy renders exact focus of optical beam unsuitable for the purpose of reading and writing.\textsuperscript{4} Birefringence in polymers occurs mainly due to the intrinsic chemical structure, which results in different polarizabilities and hence different refractive indices in different directions.\textsuperscript{10-13} In amorphous samples in their glassy state, a part of the birefringence occurs due to the residual stresses prevailing as a result of molding conditions, which orient the chains in the direction of the stress. Although processing conditions can minimize stress and orientational birefringence, a further reduction of the intrinsic birefringence of polycarbonate is desirable. Thus, although audio compact disks (CDs) are manufactured exclusively of BPAPC, birefringence issue still precludes its use in larger form factor disks.\textsuperscript{4-6} Increasingly stringent requirement to be met in terms of lower birefringence means that development and molecular design of suitable chemically modified or substituted polycarbonate is required. Polarizability of the monomer unit and the degree of polymer chain orientation determine the level of birefringence in the plastic substrate. Therefore polycarbonates with low anisotropy of their molecular polarizability are preferred. Researchers have attempted structural modification of the bisphenol unit to derive potential polymers having low birefringence
than BPAPC by various strategies: 

(i) replacement of aromatic phenylene rings by less polarizable symmetric cyclic fused rings; (ii) polycarbonate variants produced by replacing the isopropylidene group by a cyclohexyl; (iii) modified polycarbonates with lateral methyl groups or with lateral groups based on bis-(3-phenyl-4-hydroxyphenyl)-derivatives, and by incorporation of aliphatic substituents. Although a vast amount of literature do exist on various aspects of synthesis and optical property characterization of polycarbonates, a fundamental understanding on the relationship between the chemical structure and the polarizability, optical anisotropy and birefringence and systematic theoretical studies of the polymer is currently lacking.

The main objective of the present work is to study a series of polycarbonates with different chemical structures by various molecular simulation techniques for determining polymer conformations and optical properties. The property of interest in this study is the optical properties of polycarbonates, specifically, the polarizability, optical anisotropy and birefringence. In this work, conformations of BPAPC and different substituted polycarbonates will be studied in detail, i.e., at the monomer, repeat unit, single chain and also in the amorphous condensed phase using different atomistic simulation methods. The focus is on (i) the averaged chain dimensions; (ii) polarizability and single chain optical anisotropy; (iii) packing and structure of the amorphous glassy condensed state; (iv) changes in orientation and packing in the glassy state as a result of deformation, and (v) birefringence in the glassy state. The various structural modifications to BPAPC of interest in the present work include substitutions at the C_6 atom by cyclohexylidene ring, substitutions on the phenylene rings by methyl groups and both types of substitutions simultaneously. Optical properties of these substituted polycarbonates in terms of the stress-optical coefficients in the glassy and melt states have been quantified by experimental measurements in the literature. Relatively, little advancement has been made in the area of molecular simulation studies of structurally modified polycarbonates and, specifically, with regard to optical properties of these polymers.
2.2. Objectives

2.2.1. Conformational analysis, RIS models and single chain properties of structurally modified polycarbonates

Conformational properties of polymer chains are of significant importance in various areas of polymer science.\textsuperscript{21} The influence of conformational properties on the behavior of chains in solution and in the condensed bulk phase is related to and controlled to various extents by intrachain properties and local segment level structure. A fundamental understanding of conformational aspects and conformationally averaged statistical properties of polymer chains forms an intrinsic part of the overall relationship between chemical structure and macroscopic polymer properties.

Theoretical studies on the various single chain conformational aspects of BPAPC have been the subject of numerous investigations.\textsuperscript{22-24} Except for the studies on conformations of a series of polycarbonates using a force-field that neglected a variety of interactions,\textsuperscript{25,26} there are no theoretical studies in the literature concerning the conformational aspects and single chain properties of substituted polycarbonates. The focus of the present work is to bring out the effect of structural modifications on the conformational characteristics of small molecular segments constituting substituted polycarbonates as well as those of the single chains using a well defined force-field which satisfactorily takes into account all the interactions. The information derived from conformational analysis will be then used to formulate explicit RIS models for these structurally modified PC's and these will in turn be used to calculate the averaged chain dimensions as a function of temperature and molecular weight. Another objective in this work is to understand the local conformational behavior and properties of such fragments constituting the polycarbonate chain, and to obtain detailed information on the effect of substituent chemical structure on the chain dimensions. Another important purpose of this simulation study is to understand the role of intramolecular rigidity in a qualitative way among the various polycarbonates as dictated by their chemical structure. Theoretical study of conformational properties and chain dimensions in such polycarbonates has not been presented prior to the present work and would provide important fundamental insights into the local and long-range behavior of polymers composed of such complicated structural repeating units.
2.2.2. Optical anisotropy of structurally modified polycarbonates having cyclohexylidene and methyl substituents using the rotational isomeric state method

Optical properties of BPAPC with respect to its polarizability, optical anisotropy and birefringence have been investigated in detail by various experimental methods. The theoretical estimation of the mean-squared optical anisotropy ($\langle \gamma^2 \rangle$) of BPAPC have been reported by Erman et al.\textsuperscript{30,31} using the RIS/VOS approach and found to be in excellent agreement with the experimental value from scattering experiments. Polarizability tensors of the phenyl and carbonate groups have been derived from experiments on model compounds and these satisfactorily take into account the mutual inductive effects and the condensed phase. The motivation for the present work here is the lack of theoretical studies on $\langle \gamma^2 \rangle$, of structurally modified polycarbonates and a lack of experimental studies with systematic structural variation concentrating on the polarizability and optical anisotropy of these polycarbonates. The present work addresses new understanding of the relationship of atomic level structure, monomer conformations, chain conformational structure, and intrinsic group polarizabilities, to the single chain optical anisotropy of BPAPC and four structurally modified polycarbonates.

One of the objectives of the present work is to derive and implement a new methodology for formulation of the polarizability tensors of polycarbonate molecular fragments, which is applicable to substituted bisphenyl fragments, diphenyl carbonates and repeat units of various structurally modified polycarbonates having cyclohexylidene group at the C$_\alpha$ carbon and methyl groups on backbone phenylene rings. This theoretical approach will utilize polarizability tensors of constituent groups that have been derived from DRS measurements and the geometry from conformational energy calculations. Another objective is the application of RIS/VOS for the calculation of single chain optical anisotropy of structurally modified polycarbonates. Polarizabilities and conformational averaged optical anisotropies of different bisphenyl and carbonate fragments along with the results on substituted polycarbonate chains will be presented. Another objective is to analyze in detail the contribution of the various conformers to the optical anisotropy in these polycarbonates. 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.

2.2.3.  Ab initio calculations on small molecule fragments of structurally modified polycarbonates

Geometry and conformations of the BPAPC repeat unit have been accurately derived using different quantum chemical methods.\(^{36-40}\) One of the objective of the present work is to perform ab initio calculations on bisphenyl fragments corresponding to the four structurally modified polycarbonates being studied here. Calculations will be performed using the ab initio method and the optimized geometries of various bisphenyl and carbonate fragments of various structurally modified polycarbonates having cyclohexylidene group at the C\(_n\) carbon and methyl groups on backbone phenyl rings. Another objective of the present work is to derive the polarizability tensors and calculate the optical anisotropy of the various conformers corresponding to these bisphenyl and carbonate fragments using the ab initio method. The optical anisotropies of these bisphenyl fragments will then be compared with those calculated using the experimental group polarizability tensors via the VOS scheme.

2.2.4.  Detailed atomistic simulations of structurally modified polycarbonates in the glassy state

BPAPC is one of the most widely studied polycarbonate by experimental and theoretical methods with the prime objective of understanding the local structure and molecular motions in the glassy state.\(^{41-44}\) There are a few reports in the literature concerning the atomistic simulation and coarse-grained molecular simulations of bulk amorphous state of substituted polycarbonates.\(^{45-49}\) One of the objective of the present work is to investigate the local structure of BPAPC and four substituted polycarbonates in their amorphous glassy state using atomistic simulations with full chemical details and to understand the effect of these structural modifications on the short-range order. The results presented in this work will include amorphous models for these polycarbonates with full atomistic description, the conformational features and packing of chains in the
bulk, their torsion distributions, structure factors, radial distribution functions, the geometric packing correlation between phenylene rings and the bulk phase free volume distributions. One of the important objectives of this work is to understand the effect (influence) of chemical structure of the polycarbonate on the detailed amorphous structure of its glassy state and the cohesive energies, via the complex relationship link provided by the intermolecular energetics and packing effects. Simulation studies of this kind, through which interrelationships between the amorphous structures, bulk properties and the chemical structure of the polymer will be brought forth for a set of chemically different polymers having systematic structural differences within the same class, are important in providing valuable understanding in the area of polymer science. These types of simulation studies are scarce in the literature.

2.2.5. Atomistic simulations of the orientational birefringence of polycarbonates in the glassy state

Polycarbonates as a class of structures have been extensively investigated experimentally for their optical birefringence both in glassy as well as the melt state. There are very few theoretical and modeling reports in literature which deal with optical birefringence of amorphous thermoplastic polymers as a function of stress or strain (deformation), and these reports have looked at very simple model alkane based polymers such as polyethylene in the melt state. Although numerous experimental reports on birefringence of BPAPC and various structurally modified polycarbonates exists in literature, there have been no attempts till date on computer simulation studies for the estimation of this important property of polycarbonates. One of the objectives of the present work is to perform atomistic simulations of the uniaxial tensile deformation of BPAPC and two substituted polycarbonates, in the glassy state. The polycarbonate chains will be treated explicitly with full chemical description of the individual structures. An extensive analysis of the orientation behaviour of the specific chemical groups as a function of deformation will be presented. In the case of BPAPC, analysis will also be provided on the packing and orientations of phenyl rings and carbonate groups in the bulk and how it varies as a result of deformation. Another objective of this work is to calculate the birefringence of these oriented polycarbonates as a function of deformation. A
methodology will be presented for the calculation of birefringence of glassy amorphous polymers by atomistic simulations, which takes into account the individual group polarizability tensors in the repeat unit along with the chain geometry and conformation. The effect of various substitutions on the orientation and optical birefringence of polycarbonates will also be brought forth in this work. There are no reports till date on atomistic simulations of deformation of any substituted polycarbonate.

2.3. References


Chapter 3: Conformational Analysis, RIS models and Single Chain Properties of Structurally Modified Polycarbonates

3.1. Introduction

Rotational Isomeric State (RIS) method presents a very efficient way of providing quantification of the conformational properties of macromolecules which typically assume a large number of conformations. Conformational characteristics of bisphenol A polycarbonate (BPAPC) have received considerable attention since the pioneering work by Williams and Flory who formulated the RIS model for BPAPC. Various calculation methods have been utilized for investigations on the conformational characteristics of BPAPC and significant results have been summarized. Laskowski et al. proposed a RIS model for BPAPC based on the energetic and geometrical information from ab inito calculations on model compounds. Hutnik et al. formulated the RIS model for BPAPC using a force-field developed based on the results of molecular mechanics and available ab inito calculations on molecular analogues of BPAPC. In this RIS model rotations about all bonds in the repeat unit were explicitly considered and the cis, trans conformation (c-t) of the carbonate group was also included which was neglected in previous studies. A variety of experimental methods have also been applied to investigate the chain conformational characteristics of BPAPC in solution and in the amorphous bulk glassy state. The chain dimensions derived from these above mentioned RIS models were in favourable agreement with available experimental data in the case of BPAPC.

Conformational characteristics of structurally modified polycarbonates (PC's) have received little attention except for the RIS models derived for a series of Cα (isopropylidene carbon) substituted polycarbonates, and also the studies on the effect of articulated side groups at the Cα atom on the main chain flexibility of PC's. The existing RIS models for structurally modified PC's were derived by neglecting a variety of interactions including those based on electrostatics and short-range dispersion forces. In these investigations,