Acknowledgment

Dr. K. Sreekumar- My Supervising Guide – For being most generous supervisor, suggesting a novel problem and the barrierless freedom offered during my research period.

Prof. M. R. Prathapachandra Kurup -Head of the Department for providing necessary facilities for carrying out this research.

Dr. K. K. Mohammed Yusuff - former Head of the Department - For the guidance and financial support during the early stage of my research.

Dr. S. Sugunan - former Head of the Department.

Dr. N. Sridevi - For the support given to me during the beginning of my research period.

All other faculty members and non-teaching staff of the department - For generating a research culture and ambience.

Dr. Swapan K. Pati, JNCASR, Bangalore - Our collaborator.

Prof. Sourav Pal, NCL, Pune –For offering me a summer research studentship.

Dr. Reji Philip, RRI, Bangalore - For NLO measurements.

Sandeep C. S – For his help in NLO measurement.

Ayan Datta - For helping me to do the ZINDO calculations.

Dr. Anas K – Great supporter- For taking NMR and IR spectra

Dr. Suja Haridas - My ever green friend-for a real support through my research period

Suni V- My roommate – For her support and encouragement.

Mini, Bessy and Roshini – My hostel mates-for making a friendly atmosphere during my dry hostel days.

All other friends - For their love, support and help.

Rajesh, Kannan, Suresh, Mangala and other lab mates- for their tolerance and support.

CDRI-Lucknow, SIF- IISc, Bangalore- For Spectral analysis

DRDO- For the financial support

My father, brother and family – For their love, patience, support and interest.

Neena Susan John- My great friend- For her pure love.

Sajeev- My husband- For being mine.

My mother- For being my mother. She is my real strength. She taught me how elaborate the definition of a mother is!

Daly

If everything were linear, nothing influences nothing.

Albert Einstein

PREFACE

Current research in nonlinear optics is focused on the design and synthesis of nonlinear optics active materials in view of their tremendous potential for application in telecommunication, optical computing and data storage. The *state of the art* in the field of NLO has been to construct smart polymeric materials with large second order optical response functions. Hence present-day polymer synthesis has the challenge of constructing smart polymeric materials with second-order nonlinear optical (NLO) properties. One can design macroscopic nonlinear materials by knowing their microscopic nonlinear coefficients (molecular hyperpolarizabilities) that are the molecular equivalents of bulk nonlinear optical susceptibilities.

The necessary and essential condition for the existence of second order hyperpolarizability is the attainment of charge and spatial asymmetry. The requirement for second-order (and other even–order) nonlinear materials is particularly stringent, because such processes are forbidden in centrosymmetric materials in the electric-dipole approximation of the matter-field interaction. The most common way to break centrosymmetry in polymers is through electrical poling. Alternatively, second-order NLO devices can be constructed by synthesizing nonlinear molecules as chromophores into a noncentrosymmetric supramolecular structure. When such structures extend to macroscopic dimensions, the poling of chromophores can be achieved through chemical synthesis, and there is no need for external poling. The permanent dipole moment of such structures can be very large because of the coherent addition of dipole moments achieved by a high degree of polar order.

A facile way to synthesize chiral main-chain NLO polymers involves the polycondensation of chiral units and donor–acceptor-conjugated chromophores. The use of chiral building blocks tends to crystallize the polymer into a chiral supramolecular organization. Additionally, cooperative chiral order plays a vital role in the self-

assembly of ordered supramolecular structures. Chiral order in a polymer material always exists in parallel with its optical activity.

The present work emphasizes the use of chirality as an efficient tool to synthesize new types of second order nonlinear materials. Second harmonic generation efficiency (SHG) is used as a measure of second order nonlinear response. Nonlinear optical properties of polymers have been studied theoretically and experimentally. Polymers were designed theoretically by *ab initio* and semiempirical calculations. All the polymeric systems have been synthesized by condensation polymerization. Second harmonic generation efficiency of the synthesized systems has been measured experimentally by Kurtz and Perry powder method.

Objective of the present study

- Theoretical optimization of linear and nonlinear coefficients in terms of substituent, spacer and chiral effects
- Design of polymeric structures with high second order NLO activity, based on the theoretical results.
- Theoretical evaluation of NLO activity of designed polymer systems
- Synthesis and experimental evaluation of the NLO efficiency of the polymers.

This thesis comprises of six chapters,

Chapter 1 - Nonlinear Optical Properties of Polymers: a Review

This chapter presents an introduction about the nonlinear optical properties of polymeric systems, especially based on the chiral aspects. This chapter will also give a general introduction on the different types of theoretical calculations used in the present work.

Chapter 2 - Optimization of Nonlinear Optical Properties by Substituent Position, Geometry and Symmetry of the Molecule: An A*b Initio* Study

Static polarizability and first and second order hyperpolarizability tensors are computed at the correlated level (MP2, using GAMESS-US, Quantum chemical code) for

a series of *para*-nitroaniline derivatives. The importance of including electron correlation effects in the determination of equilibrium structure and the molecular properties are investigated. Qualitative description of the substitution effects, planarity and symmetry effects of the molecule on the molecular susceptibility are studied. Effect of methyl/ ethyl substitution on amino nitrogen and ring carbons of *para*-nitroaniline on the electric properties is investigated.

Chapter 3 - Effect of Spacer Groups on the Non Linear Optical Properties

The odd-even oscillations of the effect of spacer methylene groups on the electric properties of organic molecules (of the type O_2N-Ph-N=N-Ph-$(CH_2)_n$-Ph-N=N-Ph-NO_2) are calculated using sum-over -states (SOS) method. The calculations are performed using a ZINDO code which uses CI and correction vector method. The molecules exhibited a very strong odd-even oscillation behavior for the first Hyperpolarizability. The effect of spacer methylene groups on *para*-nitroaniline (PNA) derivatives by varying the number of CH_2 groups is also studied. The polymeric systems incorporating PNA derivatives were synthesized by the condensation polymerization of PNA derivatives with azo chromophores. The SHG efficiency was calculated experimentally by Kurtz and Perry powder method. While substituting both the hydrogens of -NH_2 in *para*-nitroaniline, instead of showing odd even oscillation, the SHG efficiency increased with increase in the number of CH_2 groups. The calculations at the Hartree-Fock level (6-31++G** basis set, available in the Gaussian 03 quantum chemical package is used for the calculation.) and the ZINDO-SOS method have shown agreement with the experimental observations.

Chapter 4 - Chiral Polyesters Containing Azomesogens for Nonlinear Optics: Role of Stereochemistry of Chiral Molecules

A series of polymers are synthesized by incorporating the chiral monomers and azomesogens. The monomers and polymers are designed using tools of computational chemistry at the Hartree-Fock level and ZINDO calculations. The polymers were designed as condensation polymers of three repeating units (each repeating unit contains of *one* chiral molecule, *one* azo chromophore and *one* acid chloride). Since the chiral molecules are incorporated in the polymer chain, noncentrosymmetric

supramolecular structures are obtained. In the polymer, such structures extend to macroscopic dimensions and the poling of chromophores can be achieved through chemical synthesis (chemical poling). Hence there is no need of external poling. The permanent dipole moment of the polymeric systems is large because of the coherent addition of dipole moments achieved by a high degree of polar order. The chirality of the material is associated with the helical supramolecular configuration of the backbone, and strong coupling exists between the backbone and the chromophore. Thus the polymeric systems with chiral molecules showed enhanced SHG efficiency which was double as that of the reference molecule, 2-Methyl, 4-nitroaniline.

Chapter 5 - L-Tyrosine Based Chiral Poly (ester-amide) s Containing Main Chain and Side Chain Azo Group

This chapter includes the design of L-tyrosine based chromophore with high β values. It also includes the design of chiral and achiral diols for polycondensation with the designed chromophore for the purpose of studying the effect of incorporation of additional chiral molecules into an already chiral medium. The poly (ester-amide) s are synthesized using high temperature polycondensation method and SHG efficiencies are measured using Kurtz and Perry powder method. Thus, the concept of design and synthesize of highly active NLO materials is attempted in this work.

Chapter 6 - L-Tyrosine Based Chiral Poly (ester-amide) s Containing Azo Group in the Side Chain

This chapter discusses the effect of side chain azo group in the chiral framework of L-tyrosine. The comparison is made with the polymers containing both the main chain and side chain azo group incorporated with in the same L-tyrosine chiral framework. Poly (ester-amide) s with only side chain azo group have been designed and the properties are studied using *ab initio* and semiempirical methods. All the systems are synthesized in the laboratory and SHG efficiency is measured experimentally using Kurtz and Perry powder method.

References are given to the end of each chapter. A summery of the work done and conclusions drawn out of the study are given towards the end of the thesis.