Chapter 8

Summary and Conclusions
Polymers play an indispensable role in our everyday life, ranging from the simplest organic conjugated polymer—polyethylene, to a variety of materials such as, unbreakable utensils, LCD TV sets, aerospace machinery, electrical sockets, or biopolymers such as DNA, proteins and polypeptides that are essential for life.

Organic conjugated polymers based on the carbon backbone chain are basically insulators in their virgin state. Though the low electrical conductivity of polymers has found its immense use in the manufacture of insulators and dielectric substances, researchers have always been interested in producing polymers which exhibit conductivity similar to that of metals. The key characters of a potential electrically conducting polymer include, low band gap, high electronic delocalization, ability to exhibit large electronic conductivity, reversibility with respect to doping and undoping cycles along with excellent stability in electrochemical environment and processes. Today, the study of these materials has become one of the foremost areas of research and their enormous applications have revolutionized the electronics industry, providing alternatives to silicon and germanium. The biggest application of electrically conducting polymers lies in their future use as sensors, actuators, as well as in rechargeable batteries and microelectronic devices. Credit goes to the vast technological development in the electronics industry which has initiated extensive research in developing application specific devices. The advantages of electrically conducting polymers include—ease of fabrication, possibility of handling under ambient conditions, relatively large scale and inexpensive production, electronic tunability, possibility of making composites and blends with other polymers and inorganic materials, tunable mechanical and chemical characteristics such as, solubility, strain, stress and cross-linking properties.
During the last two decades, researchers have succeeded in preparing several conjugated polymers with high electrical conductivity. By bringing about subtle changes in the chemical structure of the molecules, the bulk electrical and optical properties of the material can be modified and regulated. One of the fundamental challenges in the field of conducting polymers is to design low band gap intrinsically conducting polymers so that there is no need to dope them. This is because; the process of doping of electrically conducting polymers is often the source of chemical instability in them. Another problem often associated with doped polymers is their poor process-ability which is because of the insolubility and infusibility of these polymers. Thus, for successful designing it is necessary to have a complete understanding of the relationship between the chemical structure of polymer and its electronic and conduction properties such as, ionization potential ($IP$), electron affinity ($EA$) and band gap ($E_g$). The band structure can be tuned by altering either or both the electronic structure and stearics of the backbone. Once an understanding of the vital structure-activity-property relationship is achieved, desired electronic properties may be “tailored” by specific synthesis after molecular designing. Through modifications in the chemical structure of conjugated polymers, band gaps as small as 0.5 eV have been achieved.

To make ends meet, several strategies are being put to use, namely, substitution polymerization, ladder-growth polymerization, topological growth and copolymerization including donor-acceptor moieties. Though several such routes are being followed for designing novel electrically conducting polymers, a widely used approach is the donor-acceptor (D-A) polymerization technique which was suggested
by Havinga et al. The basic idea followed in this strategy is that a regular alternation of donor (electron rich) and acceptor (electron deficient) moieties along a conjugated chain is expected to lower the band gap. It has been generally observed that higher is the electro negativity difference between the donor and acceptor moieties, lower would be the band gap of the resulting polymer. Moreover, D-A polymers possess higher stability because of π-conjugation in the chain.

The basic aim of our study is the investigation of electronic structure and conduction properties of novel binary (two-component) and ternary (three-component) copolymers. When it comes to designing a polymer, there can be enormous ways in which the homopolymer units may be arranged to form a polymeric chain. As a result, the task of synthesizing a polymeric chain with desired properties becomes very cumbersome and expensive. Therefore, theoretical studies on polymers have a great worth and can serve as important guidelines in the designing and manufacturing process. The ambit of “theoretical designing of electrically conducting polymers” has been extended in the recent years with scientists venturing into the use of several optimization and search techniques available. Problem specific algorithms and simulation techniques such as genetic algorithm, ant-colony optimization and traveling salesman problem are increasingly being used along with the conventional methods, in order to evolve automatic solutions with the help of fast computing software available. In the present work, we have endeavoured to the use of one such computational method of optimization for designing of low band gap polymers, known as the genetic algorithm (or GA). GA has proved to be a very versatile technique for theoretical designing of low band gap polymers which possess high level of delocalization.
Genetic algorithm belongs to the broader family of optimization algorithms known as *evolutionary algorithms*, that use techniques inspired by evolutionary biology such as inheritance, mutation, selection, and cross-over (also known as recombination). It is one of the biology inspired computing techniques that emulate the basic *Darwinian concept of natural selection*. The GA starts with a group of initial, randomly generated solutions. Each solution is represented in the form of bit-strings (sequences of zeros and ones) of specified length. Once the first population is generated, the fitness (how good is the proposed solution) of each individual (or *chromosome*) of the population is calculated through an evaluation function, also known as the **fitness function**. The next populations (or *off-springs* arising from parents) are then generated by repeatedly using the operators like selection and cross-over among the individuals of a population, until the desired and pre-set criterion of convergence is achieved. To achieve the optimum solution from GA, i.e., the copolymer possessing minimum band gap along with maximum delocalization in the chain, we have combined it with two numerical methods namely, NFC (negative factor counting) and IIM (inverse iteration method).

Copolymerization is a very efficient strategy for designing polymers having properties intermediate between those of the constituent homopolymers. We have combined the strategy of copolymerization with that of D-A polymerization to investigate the electronic and conduction properties of novel binary copolymers, with the help of GA. We have considered four novel copolymers of dicyanomethylene based D-A polymers in which PCNTh is a common component, while the other component has been varied by replacing hetero atom S of the aromatic ring with groups like CF₂, O, SiH₂ and CH₂. The trends in electronic properties suggest that the IP value is found to be the
lowest for the CH\textsubscript{2} containing copolymer (IP=8.478 eV). As a result the copolymer containing PCNTh along with CH\textsubscript{2} groups is expected to be the best possible candidate for p-doping. On the other hand, the copolymer made of PCNTh along with CF\textsubscript{2} groups has maximum IP value (9.192 eV); therefore it is the most unsuitable for the p-doping process. The copolymer comprising PCNTh along with SiH\textsubscript{2} groups has maximum EA value of 8.303 eV and is hence expected to be a better candidate for n-type or reductive doping. Hence the replacement of S atoms from the homopolymer units with the less electron donating groups like CF\textsubscript{2}, O, SiH\textsubscript{2} and CH\textsubscript{2} not only makes the polymers better intrinsic conductors but also better candidates for forming conducting materials through doping (both p- and n-doping).

In another set of investigations on novel binary copolymers, we have examined copolymers of furan and silole based D-A polymers. The first copolymer comprising of PFuCO (O atom as electron donor and >C=O group as acceptor moiety) and PSIFCO (SiF\textsubscript{2} group as electron donor and >C=O group as acceptor moiety) belongs to Type-II staggered class, while the second copolymer comprising of PFuCO and PSIFCH (SiF\textsubscript{2} group as electron donor and >C=CH\textsubscript{2} group as acceptor moiety) belongs to Type-I class. The effect of variation in block sizes (of the D-A homopolymer units) on the electronic properties of the resulting copolymer has also been investigated in both the cases. The GA optimized solution is found to contain a higher percentage of PFuCO (than PSIFCH) because of its low IP value (8.558 eV). This implies that the introduction of >C=O as bridging groups in the polymeric chain proves to be more effective in designing a low band gap copolymer as compared to >C=CH\textsubscript{2} groups. This is because of the strong electron withdrawing nature of the >C=O group which enhances intrinsic conductivity and extends the π-conjugation in
the polymer chain. Oxygen being highly electronegative withdraws $\pi$-charge towards itself. Moreover, the Type-II copolymer has a higher EA than the Type-I copolymer, hence it is expected to be a better candidate for n-doping (or reductive doping). The electronic properties of the resultant copolymer are found to be intermediate between those of the corresponding homopolymers.

Further, we have extended our investigations to novel ternary copolymers of D-A polymers based on polypyrrole (PPy), polythiophene (PTh) and polyfuran (PFu) as repeat units. In order to investigate the effect of substitution on the behaviour and properties of the copolymers, we have introduced $>\text{C}=\text{O}$ and then $>\text{C}=\text{CF}_2$ groups in PPy, PTh and PFu. Again GA helps us find out the optimum ternary copolymer with minimum band gap. We arrive to the conclusion that in all the three copolymers, the optimized solution is found to contain the maximum percentage of pyrrole based units. The introduction of electron withdrawing carbonyl group in the backbone chain of the copolymer increases its intrinsic conductivity as well as dopant-philicity because of extended $\pi$-conjugation in the chain, which in turn, is due to charge transfer within the backbone.

Hence we conclude that copolymers of donor-acceptor polymers offer several advantages as compared to their carbon analogues. The extensive $\pi$-conjugation in the backbone adds to the stability of the copolymer. Substituents can be easily introduced in such systems via electrophilic substitution reactions. Therefore, chemical engineering at the molecular level of the polymer can be used along with theoretical designing in order to fine-tune the properties of the polymer and serve as important aids in designing novel materials.
Another category of polymers which we have intensively investigated for the electronic structure and conduction mechanism is biopolymers. Biopolymers such as proteins, polypeptides and nucleic acids are the foundation of the living cell. They catalyze a number of vital biochemical processes. The possibility of electron delocalization over large regions and the ability of biomolecules to sustain electrical conductivity were first suggested by Szent-Gyorgyi. The study of the phenomena of electronic conduction in proteins and polypeptides is absolutely necessary since energy transfer is inherent in almost all biological processes. In addition, there is much interest at the moment in the possibility of using these biological molecules to develop bio-medical devices such as, transducers, bio-sensors, actuators, and state-of-the-art molecular-electronic devices. As a result, the investigation of the electronic structure and conduction properties of these biopolymers offers immense potential. But owing to the structural complexity of these biomolecules, the quantum mechanical investigation of the electronic structure of proteins is a very challenging task. This is because, in addition to various bonding and non-bonding interactions present between the α-helical and β-pleated chains, the ions and water molecules surrounding these biomolecules make the determination of electronic structure even more difficult.

We have used the GA to design model binary polypeptide chains with minimum band gap and maximum electronic delocalization, as well as, to investigate their electronic properties. For our calculations, we have considered polypeptide chains comprising of glycine and alanine units. All the calculations have been performed using Clementi’s basis sets and the effects of both MB (minimal basis) as well as DZ (double zeta) basis sets on the band gap values have been studied. We have also investigated the
effect of change in secondary structure of the polypeptide chains, viz., the α-helix and β-pleated sheet structures along with the effects of electron correlation and hydration on the electronic properties. It was observed that the band gap value decreased on changing the chain conformation from the anti-parallel β-pleated to α-helical form and also when a DZ basis set was employed in the calculations. The band gap was also found to decrease in presence of a solvation shell. The DOS curves further lend a qualitative perspective to the results obtained from GA. All the above mentioned investigations on binary polypeptide chains were simultaneously performed using systematic search. The results were found to be in very good agreement to those obtained from GA. As a result, the GA technique proves its accuracy and vigour.

Further, the calculations have been extended to model ternary polypeptides comprising of glycine, alanine and serine as amino acid residues. The effect of use of a DZ basis set on the electronic structure and conduction properties of the model aperiodic polypeptide chains has been investigated along with studies including, effect of change in secondary structure and effect of hydration. We have also performed calculations to study the effect of H\(^+\) and Li\(^+\) ion-binding to the peptide group. Further, we have also investigated the change brought about in electronic properties of the polypeptide, if one of the amino acids, alanine, is replaced by leucine. Similar to the observation in binary polypeptides, it was found that the band gap decreased on changing the chain conformation from the anti-parallel β-pleated to α-helical form and also when a DZ basis set was employed in the calculations. The band gap was also found to decrease in presence of a solvation shell and in presence of cations in the vicinity of the polypeptide chain. Moreover, remarkable lowering in band gap was seen when we replaced alanine with leucine in the polypeptide.
Although, a drawback of the *ab initio* Hartree-Fock crystal orbital method is the neglect of correlation between motions of electrons with opposite spins; with the result, this method slightly overestimates the band gap values.

The results presented here contain useful theoretical predictions. We conclude that theoretical studies using artificial intelligence methods can provide an insight into the relationship between the structure and electronic properties of conjugated polymers, thereby contributing to a better understanding of the various structural aspects of these materials which contribute to their favourable electronic properties and hence conductivity. GA technique drastically cuts down the time required for computation purpose and gives the optimized composition of the copolymer/polypeptide which possesses minimum band gap along with maximum electronic delocalization.