CHAPTER 1

LOW BAND GAP $\pi$-CONJUGATED POLYMERS

1.1. Introduction

Importance of the optoelectronic properties of low band gap $\pi$-conjugated polymers have been recognized and built up with the spectacular developments in the area of advanced organic material research. At the molecular level, $\pi$-conjugated systems represent the simplest models of molecular wires,\textsuperscript{1} which together with their ability to respond to external stimuli such as light, current and pH have contributed to the emergence of the concept of molecular electronics and logic functions.\textsuperscript{2,3} Conjugated polymers form the integral part of several molecular electronic devices, that have given rise to considerable research efforts in basic as well as applied aspects of organic material science with the view to developing new materials for information and communication technologies.\textsuperscript{4} From the practical viewpoint, conjugated polymers are being explored for numerous exciting applications such as large-area flexible polymer Light Emitting Diodes (LEDs) that can emit light virtually in any part of the visible spectrum, all-polymeric Field Effect Transistors (FETs) that give access to high-tech, but low-cost plastic electronics and polymers with metallic conductivity for the simple fabrication of conductive films, for electromagnetic shielding or antistatic applications. Advantage of using polymers to the electrical/electronic industries include the ease and low cost of their preparation and fabrication as compared to inorganic semiconductors and metals, and their mechanical properties, particularly flexibility and impact resistance.\textsuperscript{4-11} Besides, conjugated polymers are amenable for structural modifications, which facilitate the tuning of their electronic and mechanical properties.
The first major breakthrough in the area of conducting polymers or 'synthetic metals' was achieved in 1977 when MacDiarmid, Heeger and Shirakawa showed that polyacetylene, which is an insulator could become highly conducting on treatment with oxidizing or reducing agents.\textsuperscript{12-14} Subsequently, several classes of conjugated polymers based on aromatic precursors such as pyrrole,\textsuperscript{15,16} benzene,\textsuperscript{17} aniline or thiophene\textsuperscript{18,19} have been developed. In addition to their improved environmental stability, these polymers differ from polyacetylene by (i) their nondegenerate ground state, which has important role in the mechanism of charge transport\textsuperscript{20} and (ii) their ability to afford doped conducting polymers in a single step via electrochemical polymerizations. However, application of these polymers has been hampered to a large extent due to the doping, which renders the polymer difficult to process. In this context, it has become extremely important to design conjugated polymers that show intrinsic conductivity without compensating their solubility and processability. The band gap energy ($E_g$), which is the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is the key factor, which determines the electronic and conducting properties of conjugated polymers. Therefore, control of the HOMO-LUMO gap by structural modification is of great significance in the designing of low band gap polymers. Several molecular engineering strategies have been developed in recent years towards the designing of low band gap polymers \textit{via} modification of the molecular structures and molecular ordering (self-assemblies). Before coming to details of these aspects, it would be appropriate to have a brief mention regarding the band theory of conjugated polymers.

1.2. Electrical Conductivity and Band Theory of Conjugated Polymers

Conjugated polymers are organic semiconductors with electronic energy levels hardly differ from inorganic semiconductors. In both the cases, their
electrons are organized in bands rather than in discrete levels and also their ground state energy bands are either completely filled or empty.\textsuperscript{21, 22} Since semiconducting polymers are conjugated molecules, these states are usually $\pi$-states. The electronic and optical properties of these polymers result from a limited number of states around the highest occupied and the lowest unoccupied levels. Figure 1.1 shows the frontier energy levels of oligothiophenes with $n = \text{1-4}$ and of a polythiophene as a function of oligomeric chain length.\textsuperscript{23} At each stage, the addition of a thiophene unit causes more and more hybridization of the energy levels that results in the formation of bands instead of discrete levels. Since the geometry of $\pi$-orbitals is three dimensionally organized, these $\pi$-orbital interactions lead to a three-dimensional band structure.

\begin{center}
\textbf{Figure 1.1.} Calculated (frontier) energy levels of oligothiophenes with $n = \text{1-4}$ and of polythiophene, where $E_g$ corresponds to the band gap.
\end{center}

According to the band theory, the highest occupied band, which originates from the HOMO of each single thiophene unit, is called the valance band and the corresponding lowest unoccupied band originating from the LUMO of each single thiophene unit is called the conduction band. The band
gap \((E_g)\) of the polymer depends on the separation \(\Delta E\) between the HOMO and LUMO energy levels of the monomers and the bandwidth \(W(\beta)\), which is a function of hybridization \((\beta)\) of monomer levels in the polymer.\(^{24}\) In search of small band gap polymers, so far the main focus has been on the increase of bandwidth \(W(\beta)\), by going from aromatic to quinoid structures.\(^{25}\) However, the most widely used fragments, such as thiophene, pyrrole, phenylene or vinylene, have too large HOMO/LUMO gap \((\Delta E)\), which can only be partially closed by band formation. Hence in order to achieve a polymer with a smaller band gap, it would be appropriate to start from monomers with a small \(\Delta E\), such as in organic dye molecules.\(^{26}\)

1.3. Importance of Low Band Gap Polymers

The limited industrial scale utilization of conjugated polymers is mainly associated with their poor performance in terms of conductivity, charge storage capacity and environmental stability. Despite these limitations, during the last few years enormous work has been devoted to the design and applications of conjugated polymers in the field of electronic and photonic devices. Electroluminescent diodes (LEDs) are probably the most successful example.\(^{27,28}\) While high band gap conjugated polymers are important for LED applications, low band gap polymers are required for intrinsically conducting materials. Reduction of \(E_g\) will increase the thermal population of the conduction band and thus increase the number of intrinsic charge carriers. This will lead to true “organic metals” showing intrinsic electrical conductivity without resorting to oxidative or reductive doping. The lower oxidation potential associated with narrow band gap implies more stabilization to the doped state. The low \(E_g\) of conjugated polymers results in a red shift in the absorption and emission spectra, which make them available in the visible spectral range and potentially useful for the fabrication of LEDs operating in the IR region.\(^{29}\) Furthermore, the increased electron affinity associated with a low-
lying LUMO level allows the fabrication of LEDs with stable metal electrodes. Besides, the decrease of $E_g$ implies the optimization of the electron transmission properties of the conjugated polymers which have important implication in the designing of materials with quadratic or cubic nonlinear optical properties.

The $E_g$ of a conjugated molecule is usually determined from the low energy absorption edge of the electronic absorption spectrum or from the solution oxidation ($E_{ox}$) and reduction ($E_{red}$) potentials. For a molecular material, the $E_g$ can be estimated from $E_{ox}$ and $E_{red}$ using the following equation (1.1) by neglecting the intermolecular interactions.

$$E_g \sim (E_{ox} - E_{red}) + (S^+ + S^-) \left[1 - \frac{1}{1/(\varepsilon_1) + 1/(\varepsilon_2)}\right]$$

...eqn. (1.1)

where $S$ is the solvation energy of the ionized molecules minus the solvation energy of the neutral molecule and $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constants of the solution and the solid, respectively.

For conjugated polymers, many factors are contributing to the existence of a finite $E_g$ value of the system. One of the major contributions is from Peierls instability, which depends on the degree of bond length alternation in the conjugated segment. This "bond length alternation" is due to a gain in electronic energy that overcompensates the loss of "elastic" energy and is called the Peierls effect. This contribution of bond length alternation ($E^{\delta}$) to $E_g$ is related to the difference between the length of the single and double bonds. Another important factor, which influences the $E_g$, is the occurrence of interannular rotations. Since the orbital overlap varies approximately with the cosine of the twist angle ($\theta$), any departure from coplanarity will result in an increase in $E_g$ and the corresponding distortion $E^0$ contributes to an increase of the $E_g$. Also, in certain poly(aromatic) systems, aromatic resonance energy of the cycle ($E^{\text{Res}}$) gives some contributions to the final value of $E_g$. 
The most common way to modify the HOMO and LUMO levels of a π-electron system involves the introduction of electron-releasing or withdrawing substituents that will increase the HOMO or decrease the LUMO levels. Hence a contribution from the nature of substituents \( E^{\text{Sub}} \) is also involved in the \( E_g \) of a polymer. In addition to the above factors, the intermolecular interactions are accountable for the determination of \( E_g \). The interaction between individual molecules that are responsible for their organization into a condensed phase \( (E^{\text{Int}}) \) can represent an important contribution to the \( E_g \). To a certain extent, this interaction can minimize the Peierls instability.\(^{33}\) Thus, the band gap energy is a combined contribution of all these parameters and is represented by the following equation.

\[
E_g = E^{\delta r} + E^\Theta + E^{\text{Res}} + E^{\text{Sub}} + E^{\text{Int}} \quad \ldots \ldots \text{eqn. (1.2)}
\]

Among these energetic factors, the major contribution to the \( E_g \) comes from \( E^{\delta r} \) and \( E^{\text{Sub}} \) which correspond to the minimization of bond length alternation along the main chain and the alternation of electron donor-acceptor substituents of the polymer chain. These aspects, particularly the minimization of bond length alternation via fused ring aromatic systems\(^{18,29,30}\) and ladder polymers\(^{34,35}\) and the use of donor-acceptor monomers will be discussed in the following sections.

1.4. Minimization of Bond-Length Alternation

In polyacetylene, when the double bonds are completely delocalized along the polymer chain, all the carbon atoms become identical and thus polyacetylene acts as a pure metallic conductor. This is depicted in Figure 1.2, where the band gap energy difference between a ‘bonding’ ground state and an ‘anti-bonding’ excited state is zero due to the equivalence or degeneracy of the energy states in an infinite chain which results a metal-like half-filled band.\(^{36,37}\) Thus, the minimization of bond length alternation along the polymer backbone
is an important guideline in band gap reduction. Some of the approaches to minimize the bond length alternations are discussed below.

Figure 1.2. Band gap formation by localization of double bonds in \textit{trans}-polyacetylene.

1.4.1. Fused Ring Systems

The quinoid form (2) of polythiophene has enhanced double bond character over its aromatic form (1), which results a reduction in band gap. However, the quinoid form (2) is energetically unfavourable to the ground state of the polymer and hence its contribution is very less to the observed band gap of polythiophenes, which is very high (~2 eV). In order to expect a large band gap reduction in this class of polymers, it is essential to make the quinoid form energetically feasible. In this context, Wudl \textit{et al.} have introduced polyisothianaphthene (PITN) (3) polymers, the quinoid form (4) of which is more stable leading to low band gap polymers (Chart 1.1).\textsuperscript{38}
The energetically favoured quinoid structure of PITN can be intuitively concluded by considering the resonance stabilization energy of individual benzene (1.5 eV) and thiophene (1.26 eV) rings.\textsuperscript{39} The fusion of aromatic benzene (5) and thiophene (6) rings is depicted in Scheme 1.1. The higher aromatic stabilization energy of the fused benzene ring over thiophene facilitates the existence of a stable quinoid structure in the thiophene unit. Hence, the quinoid form is more favourable in PITN, whereas it is energetically unfavourable in polythiophenes.

\textbf{Scheme 1.1.} The aromatic stabilization during the ring fusion between benzene and thiophene.

Subsequent to this report, considerable theoretical interests have been focussed on this area, which led to the synthesis of a variety of other new low band
gap polymer such as poly(alkylisothianaphthene)s \(^7\), poly(dialkythienopyrazine)s \(^8\), poly(dialkoxysothianaphthene)s \(^9\) and various fused poly(thienothiophene)s \(^10-13\) (Chart 1.2).\(^{43-47}\)

\[
\begin{array}{c}
\text{7} \\
\text{8} \\
\text{9} \\
\text{10} \\
\text{11} \\
\text{12} \\
\text{13}
\end{array}
\]

**Chart 1.2**

A number of thiophene and pyrrole based monomers has been reported as precursors of the corresponding low band gap polymers. The main advantage of these monomers are their low potential, which facilitates their electropolymerization. Since, the oxidation potential of the precursor decreases with increase in conjugation length,\(^{48}\) electropolymerization occurs at lower positive potentials with a minimum side reaction of the cation radical.\(^{49,50}\) A few representative examples for the precursors of low \(E_g\) polymers are bithienyls \(^14\) and \(^15\),\(^{51-53}\) terthienyls \(^16\) and \(^17\),\(^{54,55}\) dithienylethylene \(^18\),\(^{56,57}\) difurylethylene \(^19\)\(^{58}\) and diheteroarylene methine \(^20\) (Chart 1.3).\(^{59-63}\)
An important development in the area of low band gap polymers is the report by Jenekhe in 1986 on the synthesis of poly(arylenemethine)s 21a-c. By varying the length and ratio of the quinoid and aromatic blocks in 21a-c, the band gap could be tuned in between the limiting values for all-quinoid and all-aromatic conjugated chains. Thus, polymers containing variable ‘x’ and ‘y’ blocks have been prepared which showed band gaps as low as 0.75 eV.\(^{64-67}\) Later, Aota et al. reported a water-soluble polymer (22) prepared from the addition-condensation polymerization of pyrrole and sodium o-benzaldehydesulfonate. Adopting similar synthetic procedures, they also reported a porphyrin linked \(\pi\)-conjugated polymer (23). In these cases, the reported band gaps are less than 0.5 eV (Chart 1.4).\(^{68,69}\)
1.4.2. Ladder Polymers

Another approach in band gap reduction via minimization of bond length alternation is by minimizing the structural deformations that lead to the localization of alternating double and single bonds along the conjugated main chain. This has been achieved by the construction of ladder polymers\textsuperscript{70-73} of which the best-known example is polyacene \textsuperscript{24}. This polymer can be viewed as a fusion of two \textit{trans}-polyacetylene chains as shown in Scheme 1.2.
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Kivelson and Chapman proposed that 24 should be metallic and could possibly exhibit superconducting properties.\textsuperscript{74} A band gap of 0.5 eV was calculated for 24 by Yamabe \textit{et al.}\textsuperscript{75} while a zero band gap was predicted by Brédas \textit{et al.}\textsuperscript{76} However, it is not necessary to have such a low band gap to all ladder polymers. For example, polyphenanthrene 25, which can be considered as two fused \textit{cis}-polyacetylene chains, has a calculated band gap of 4-5 eV. This high energy value could be due to the large difference in energy between the aromatic and quinoid structures (Scheme 1.3).\textsuperscript{77,78}

\begin{center}
\includegraphics[width=\textwidth]{Scheme1.3.png}
\end{center}

\textbf{Scheme 1.3}

A variety of ladder polymers such as polyperinaphthalene (26), polyquinoxaline (27) and polyphenylene (28) have been reported, that can be viewed as partially rigidified poly(\textit{p}-phenylene)s where the bridging unit is responsible for the improved planarity of the system.\textsuperscript{79-82} In a different approach, Tour \textit{et al.} have synthesized a ladder polymer (29) in which consecutive phenyl rings are bridged by an imine group.\textsuperscript{83} Due to the extreme insolubility of ladder polymers, synthesis of many of these are achieved by a polymer precursor route where the noncyclized precursor, which is soluble in solvents, can be cyclized to form the ladder polymer as and when it is required for studies or applications.
Analysis of the evolution of the optical properties of oligomers as a function of chain length has shown that for an equal number of benzene rings, the fully bridged oligomers absorb at a considerably longer wavelength, thus confirming that planarization significantly increases the effective conjugation.\textsuperscript{84}

This rigid and regioregular structure, imparts minimum energy loss by non-radiative decay and thus exhibits a high quantum efficiency of photoluminescence (>60%) which is useful for the fabrication of light-emitting diodes.\textsuperscript{85-87}

As illustrated with several of the above examples, low band gap in \(\pi\)-conjugated polymers can be achieved to a certain extent by the rigidification of the polymer backbone, by enhancing the coplanarity of the repeat units or by enhancing the quinoid character of the aromatic moieties. Even though rigidification of the polymer backbone into ladder systems represents an efficient strategy in reducing the band gap, this approach is restricted mainly to phenylene based structures. Owing to the high resonance energy of the benzene ring, and due to the insolubility, phenylene based ladder polymers are not the
best candidates for the designing of extremely low band gap polymers. These limitations have led further developments in this area, in search of other alternate approaches.

1.5. Donor-Acceptor Systems

A strategy to induce minimum twisted arrangements in conjugated polymers involves construction of A-B type systems where the A-unit has strong electron-donating moieties and the B-unit has strong electron-withdrawing moieties. Strong interaction of the donor-acceptor moieties enhances double bond character between the repeat units, which stabilizes the low band gap quinoid-like forms within the polymer backbones.\(^4,88\) Hence, a conjugated polymer with an alternating sequence of the appropriate donor and acceptor units in the main chain can induce a reduction in its band gap energy.

The recent molecular orbital calculations have shown that the hybridization of the energy levels of the donor and the acceptor moieties yield an unusually low HOMO-LUMO separation to D-A monomers.\(^89,90\) This is depicted in Figure 1.3. Further hybridization upon chain extension enhances the band gap reduction as shown in Figure 1.4. During the progress of polymerization, the HOMO and LUMO levels of the repeating unit disperse into the valance and conduction bands. At each stage of monomer addition, the magnitude of \(W_L\) and \(W_H\) increase, which strongly depend upon the degree of overlap between the aromatic orbitals in the coupling position of the monomer units. Thus, \(W_L\) and \(W_H\) get maximum values at an unobstructed overlap and in such a condition the molecule can exist in its lowest band gap level. However, deviations from this ideal situation may happen when the steric hindrance forces the consecutive aryl units out of plane or when the size of the atomic orbitals (AOs) at the coupling position is diminished.
Figure 1.3. Hybridization of the energy levels of donor (D) and acceptor (A) fragment leads to a D-A monomer with an unusually low HOMO-LUMO energy separation.

Further reduction in band gap is possible by enhancing the strength of donor and acceptor moieties via strong orbital interactions. In donor-acceptor systems, the introduction of electron withdrawing groups reduces $E_g$ by lowering the LUMO levels whereas, the introduction of electron donating groups reduces $E_g$ by raising the HOMO levels. Commonly employed electron-donating moieties are thiophene or pyrrole with various substitution patterns, which often represent the best choice since these are electron rich subunits that
allow numerous chemical transformations. The most widely used electron withdrawing groups are cyano and nitro groups. Using the combinations of these donor and acceptor groups, a variety of monomers have been synthesized which undergo facile electrochemical or chemical polymerizations leading to the formation of a variety of low band gap polymers.\textsuperscript{91-98}

Polymers 30a-c that are prepared by electrochemical methods showed band gaps of 0.6, 1.5 and 1.4 eV, respectively.\textsuperscript{91} Analogously synthesized polymers 31a-b showed band gap values of 1.3 and 1.0 eV for 31a and 31b, respectively (Chart 1.6).\textsuperscript{92} Comparison of the band gap of 30c with structurally analogous polymers 31a-b having unchanged acceptor unit revealed a drastic reduction in band gap of 30c. This anomalous reduction in $E_g$ can be explained in terms of the residual doping associated with the electrochemical polymerization. The electronic absorption spectrum of polymer 30c showed a shoulder band at higher wavelength, which may indicate the residual doping and therefore, prevents the accurate determination of the band gap energy.

Conjugated polymers (32-35) containing pyrrole and/or thiophene as electron donating and cyano-substituted aryl unit as electron accepting groups have been prepared by the electrochemical oxidation methods (Chart 1.7).\textsuperscript{93-95} The band gaps estimated for these polymers are much lower when compared to
the identical polymers without a cyano-group. Exceptionally, polymer 34 exhibits much higher $E_g$ value because of the enhanced steric hindrance along the pyrrole-phenyl bond. Apart from cyano substituted electron accepting groups, conjugated polymers containing other electron accepting groups are also known, an example of which is shown in Scheme 1.4.\textsuperscript{96-98} Solution and solid-state optical band gaps of 36 are 1.4 and 1.1 eV, respectively. This low $E_g$ observed in the solid state, suggests a rigidification in the conjugated backbone due to the occurrence of mesomeric structures, which may presumably be weak in the solution state.

\begin{center}
\includegraphics[width=\textwidth]{chart}
\end{center}

\textbf{Chart 1.7}

\begin{center}
\includegraphics[width=\textwidth]{scheme}
\end{center}

\textbf{Scheme 1.4}
The observed $E_g$ in many cyano and nitro substituted conjugated polymers are much higher than their expected values. One possible explanation for this observation is available from the frontier orbital calculations of bithiophene and its cyano substituted derivatives as reported by Brédas and Ferraris et al. Figure 1.5 displays the frontier orbitals for the bithiophene (37) and the cyano substituted fused bithiophene (38).

![Frontier orbitals of bithiophene and cyano substituted fused bithiophene](image)

**Figure 1.5.** Calculated frontier orbitals of bithiophene 37 and (dicyanomethy-lidenecyclopenta)dithiophene 38.

In bithiophene (37), substitution of electron withdrawing groups in 3 and 3'-positions stabilize both HOMO and LUMO, whereas in the fused system (38), substitution at 3 and 3'-positions will not stabilize or affect the HOMO energy level. This is due to the antisymmetry of the HOMO, which creates a node at the 4-position. The symmetric LUMO of the fused system is stabilized by the substitution of electron withdrawing groups. Besides the lowering of LUMO energy, the size of the atomic orbitals (AOs) on the coupling positions
(2,2'-positions of bithiophene) is considerably reduced. This results in a weak orbital overlapping in the bridging position and thereby decreasing the magnitude of \( W_L \). Hence the observed band gap is much higher than the expected level in these polymers. An approach for minimizing this problem is selection of an aryl unit, which bears one or more electronegative atoms in the ring, close to the coupling positions. This will increase the AO coefficients at coupling positions as in the case of pyridine based polymers 39-41 containing strong electron deficient imine nitrogen (Chart 1.8).^{100-102}

![Chart 1.8](image)

The optical band gap values observed were higher for all these polymers, which are attributed to a poor electron accepting strength of the pyridine unit. To a certain extent, the electronegativity of acceptor unit can be increased by replacing the pyridine unit with pyrazine. Due to the inherent difficulty of functionalization and polymerization of pyrazines, several pyrazine fused systems such as quinoxaline and 2,1,3-benzothiadiazole, were proposed (Chart 1.9).^{100,102-104} However, the copolymers derived from quinoxaline or 2,1,3-benzothiadiazole as the acceptor and thiophene as the donor showed band gap energy values greater than 1.0 eV. This may be due to the fact that in quinoxaline and 2,1,3-benzothiadiazole, the electron accepting part is outside the conjugated backbone that may adversely affect the AO coefficient of the LUMO level.
Further improvement in reduction of band gap energy was achieved by acceptor units in which the pyrazine or thiadiazole unit is fused onto a thiophene unit instead of phenyl ring. Since the coupling positions are part of a 5-membered thiophene ring, the electron donating sulfur atom will contribute more to the orbital coefficients. Chart 1.10 shows a few examples of polymers belonging to this class. Yamashita et al. have synthesized a series of trimeric thiophene derivatives in which the middle thiophene unit is fused with pyrazine or thiadiazole moieties which can subsequently be electropolymerized to the corresponding low band gap polymers 45 and 46, respectively. The optical absorption and redox properties of 45 can be appreciably controlled by putting appropriate substituents on the pyrazine and thiophene rings. Compared to isothianaphthalene derivatives, the thienothiadiazole moiety of the polymer 46 has lower HOMO-LUMO gap. Excellent results were obtained by the electropolymerization of pyrrole-based monomers containing thienothiadiazole or pyrazine as the acceptor and pyrrole as the donor leading to polymers 47 and 48, respectively.
Electropolymerization of a bithiophene monomer containing alternate pyrazine and dioxoethylene moieties results a donor-acceptor polymer 50 with a band gap of 0.36 eV (Scheme 1.5). However, this lowest value is not reliable because of the difficulties in the adequate dedoping process in electropolymerized conjugated polymers.

Scheme 1.5

Electron withdrawing power of quinoxaline or 2,1,3-benzothiadiazole can be further increased by fusion of another pyrazine or thiadiazole ring onto the vacant sites of the phenyl ring to yield pyrazinoquinoxaline, thiadiazoloquinoxaline and benzobis(thiadiazole). The corresponding polymers 51-53, were prepared electrochemically from their thiophene linked
monomers. The reported band gaps of these polymers are 0.5, 0.7 and 0.9 eV, respectively (Chart 1.11). In a subsequent paper, Tanaka and Yamashita have reported the synthesis of a series of mixed trimers composed of aromatic heterocycles and a novel non classical thiophene with pyrazine-dihydropyrazine redox system (Scheme 1.6). The oxidized forms of these compounds have much lower optical and electrochemical energy gaps when compared to many of the above reported systems. Especially the pyrrole derivative 55c showed a 1000 nm red shift of the absorption band when compared to the corresponding terthiophene 55b. The reported band gap of 55c is around 0.6 eV.

![Chart 1.11](image-url)
The various examples cited above reveal that the trimeric precursor, containing electron accepting and donating groups, offer several possibilities to the designing of conjugated polymers whose electronic properties and band gaps can be tuned by varying the electron donor-acceptor strength of the monomers. This approach has been successfully used for the synthesis of several copolymers, containing hybrid ring systems, leading to polymers with lowest band gaps reported so far. However, the scope of this approach has some serious limitations. For example, the high lying HOMO levels of some of the precursors limit the efficiency of electropolymerization. In addition, ambiguity exists in many cases whether the reported band gaps correspond to the neutral polymer. In this context, designing of alternate approaches towards low band gap polymers has become extremely important.

1.6. Donor-Acceptor Copolymers Based on Squaraine Dyes

A class of polymers, which comes under the category of donor-acceptor conjugated polymers, is polysquaraines, which are derived from squaraine dyes. Since, organic dye molecules in general have inherently low HOMO-LUMO
energy gap, extension of their conjugation length is expected to generate polymers with low band gap energy. With this idea, many research groups have attempted the synthesis of conjugated polymers based on squaraine dyes.

3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid) undergoes condensation reaction with a variety of electron rich aromatic and heterocyclic molecules such as N,N-dialkylamines, benzothiazoles, phenols, azulenes and pyrroles to form highly colored polar zwitterionic dyes which possess intense absorption in the visible and near-infrared region. A representative example is shown in Scheme 1.7.

![Scheme 1.7](image)

Schmidt has proposed the widely accepted name “squaraine” for this class of dyes. In the solid state, due to strong intermolecular donor-acceptor interactions, the absorption of these dyes becomes very broad and red-shifted to near IR region. These properties have made squaraines ideally suited for applications in xerographic photoreceptors, solar cells and optical recording media. The technological importance of these dyes led to several studies pertaining to the excited state and related photophysical properties which have considerably contributed in the synthesis of a variety of squaraine dyes with improved properties.

The report on a squaraine based polymer can be traced back to 1965, when Triebs and Jacobs reported the formation of an insoluble material upon reaction of pyrrole with squaric acid (Scheme 1.8). The intractable nature prevented any further studies with this material. Later, Chen and Hall have
reported the polycondensation of squaric acid with $N$-alkylcarbazoles, which resulted in the formation of the insoluble polymer 61 having 36-43% of 1,2-oriented squarate units based on IR spectral analysis.\(^{137}\)

Havinga \textit{et al.} have made significant contributions to the synthesis and studies of several polysquaraines and polycroconaines.\(^{138,139}\) Condensation of benzobisthiazoles with squaric acid and croconic acid, resulted in several polysquaraines (63) and polycroconaines (65), respectively, some of which showed absorption close to the near infrared region (Scheme 1.9 and 1.10). The band gap of these polymers were in the range of 1.0-0.5 eV. Due to the better donor-acceptor interactions, polycroconaines showed lower band gaps when compared to the polysquaraines. Subsequently, Havinga \textit{et al.} have reported the synthesis of the water soluble polysquaraines 66 and 67 and the polycroconaine 68 in order to evaluate their photoconductivity (Chart 1.12).\(^{140}\)
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Condensation of squaric acid with aromatic primary diamines such as \( p \)-phenylene diamine is known to form polyamides of squaric acid.\textsuperscript{141-146} Neuse and Green have carried out extensive studies on the synthesis of polyamides of squaryl esters and dianilines, which are composed of both the 1,2- and 1,3-oriented cyclobutenone repeat units (69) (Chart 1.13).\textsuperscript{147-149} However, these condensation reactions differ from the usual squaraine dye formation and hence the products do not have any properties of the squaraine dyes. Certain nonconjugated squaraine polymers containing repeat units of squaraine and long alkyl chains are also known in the literature.\textsuperscript{150} The reaction of diethyl squarate with a quinolidine bis-quaternary salt yielded polysquaraine (70) with a nonconjugated structure (Chart 1.13).
Recently, our group has reported the synthesis and properties of a series of oligo- and polysquaraines 71-74 derived from pyrrole derivatives that are
soluble in organic solvents (Chart 1.14). Polymers 71 and 72 showed interesting properties such as pH and solvent dependent changes in the optical properties. The oligosquaraine 73 was water soluble and showed higher conductivity when compared to 71 and 72. The polysquaraine 74 containing the oxyethylene side chain showed enhanced specificity and selectivity towards the detection of Li$^+$ over Na$^+$ and K$^+$. The sensing property of polysquaraines was studied using the change in fluorescence emission before and after the metal binding events. The enhancement of fluorescence after metal binding suggests a planar rigid structure to the polymer backbone as shown in Scheme 1.11. Similar studies were performed with model squaraine dyes, however the binding response was very weak. This suggests the importance of a macromolecular structure in the signal amplification during metal binding.

![Chart 1.14](image-url)
Lynch and coworkers have reported the synthesis and properties of several pyrrole and carbazole based polysquaraines.\textsuperscript{155-157} However, none of these polymers showed the expected low band gaps despite the theoretical prediction that extension of conjugation in squaraine dyes can lead the formation of low band gap polymers.\textsuperscript{89} This could be due to the fact that in polysquaraines the low band gaps are originating from a narrow HOMO-LUMO energy separation, typical of donor-acceptor (D-A) fragments. However, on chain extension through polymerization of each D-A fragment, the hybridization not only raises the energy of HOMO but also the LUMO energy level by similar amount. Therefore, in polysquaraines, both HOMO and LUMO levels are shifted up equally and hence no considerable reduction in band gap is observed. Under this condition, the construction of extremely low band gap polysquaraine is possible only by allowing the HOMO level to participate in hybridization and the LUMO level is ‘pinned’ at the originally low value of the fragment. The exclusion of LUMO level from hybridization unalters its energy levels during chain extension whereas, the HOMO energy increases during hybridization, which eventually leads to a narrow band gap. This ‘pinning’ of the LUMO level may be annihilating the overlap of these orbitals throughout the polymer chain, by making this interaction symmetry forbidden. This is may be the case of the hypothetical polymers 75-76 as illustrated in Figure 1.6.
Figure 1.6. “Pinning” of the LUMO level at its originally low value by introducing nitrogen atoms in the main chain of polysquaraine copolymers.

The interaction between the HOMO of squaraine and the $p_z$ orbital of nitrogen results in a hybridization upon chain extension. Since the interaction between the nitrogen $p_z$ orbital and the LUMO of squaraine is forbidden for symmetry reasons, the LUMO energy level is unaffected. However, the symmetry allowed interactions of HOMO with $p_z$ orbital, shift the energy of HOMO and consequently the band gap energy decreases. The calculated band gap of the polymer 76 is as low as 0.2 eV. The decrease in band gap energy of 76 over 75 is probably due to the effect of increased conjugation in 76. Hence the extension of conjugation by choosing symmetrically allowed interaction between HOMO level of squaraine and $p_z$ orbital of nitrogen containing heterocycles, one can ideally design extremely low $E_g$ polysquaraines. However, there were no systematic efforts to design low band gap polysquaraines until recently we reported the synthesis of several low band gap polysquaraines which form the center theme of the present thesis.\textsuperscript{158}
1.7. Control of Optical and Electronic Properties of \( \pi \)-Conjugated Polymers via Molecular Assembly

In the earlier discussed sections, we have seen the importance of the structural modifications of \( \pi \)-conjugated systems to control the HOMO-LUMO energy gap and thereby their optical and electronic properties. It is now well understood that the functional properties of \( \pi \)-conjugated polymers are not only influenced by the structural characteristics but also by the interplay between the intrinsic features of the polymer chains and the interchain interactions. Therefore, molecular assembly of \( \pi \)-conjugated polymers are rapidly becoming a method to optimize the performance of devices based on organic materials, by directing the formation of ordered supramolecular structures.\(^{159-163}\) The solid-state molecular packing and the interchain distance emerging out of such molecular self-assembly has strong impact on the performance of electrooptical and molecular electronic devices based on conjugated polymers. In order to have a better understanding, it is important to generate such self-assembly and aggregates in solution, which will provide more freedom to evaluate their structure-property relationship. With this objective, solution self-assembly of several \( \pi \)-conjugated polymers and their model systems were investigated in recent years. In this context, polythiophenes and poly(phenyleneethynylene)s have attracted considerable attention of organic material scientists.\(^{164-172}\)

Generally, the microscopic molecular ordering process can be controlled by a range of specific molecular level interactions such as \( \pi \)-stacking, hydrogen bonding, hydrophobic and polar associations and van der Waals interactions. Several studies have been carried out to understand the role of these interactions, which lead to a macroscopic change in the properties by external stimuli such as temperature, pressure, solvent, and light. In the case of \( \pi \)-conjugated polymers, the \( \pi-\pi \) interaction is the major driving force for the formation of stacked assemblies. In most of the cases, these molecules form a
stacked structure with plane-to-plane distance of 3.4-3.8 Å, which is somewhat longer than the plane-to-plane distance of graphite (3.35 Å).\textsuperscript{165}

Aggregation of conjugated polymers \textit{via} self-stacking is extensively studied in the case of alkyl substituted thiophenes and thiazoles. The recent developments in the synthesis of regio and sterio regular polythiophenes have provided better polymers for the study of \(\pi\)-stacking in solution state. Yamamoto \textit{et al.}\textsuperscript{165} have synthesized a series of regioregular poly(3-alkylthiophene)s and studied the \(\pi\)-stacking of these polymers both in solution as well as in solid states. Figure 1.7 shows a view of the \(\pi\)-stacking in poly(3-alkylthiophene)s induced by the addition of methanol into a polymer solution in dichloromethane. The nature of stacked aggregates such as size, mode of packing etc. are tremendously influenced by the regularity of the polymer repeating units, length of alkyl chain substituents and the solvent medium.\textsuperscript{173-179} McCullough \textit{et al.} have reported the molecular assembly of regioregular polythiophenes with improved electrical and optical properties.\textsuperscript{180,181} Their studies have revealed that the regularity and ordering in the polymeric structure lead to a remarkable enhancement in the electrical properties.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure17.png}
\caption{The \(\pi\)-\(\pi\) interaction of regioregular 3-hexyl polythiophenes}
\end{figure}

Numerous studies have been focussed on the effect of different side groups in the optoelectronic properties of conjugated polymers.\textsuperscript{173,180-182} In many cases, it was demonstrated that side groups such as alkyl chains, that bring only minor changes to the intrachain electronic properties, are capable of inducing
significant changes to the optical and electronic properties in the aggregated form of the polymer. Depending on the nature of substituting side groups, many interchain interactions are possible, which will lead to different kinds of aggregates. Apart from these interactions, the conformational changes associated with the molecular ordering can also influence the property of the polymeric assemblies.

Poly(phenyleneethynylene)s are a class of conjugated polymers that has received considerable attention from the viewpoint of self-assembly and aggregate formation. Moore et al. have synthesized various phenyleneethynylene macrocycles, 77-79 with different side-chain linking groups and m-phenyleneethynylene oligomers, 80 (n = 8, 9, 10, 12, 14, 16, 18) bearing ester-linked triethylene glycol side chains to investigate their tendency to undergo solvent induced π-stacking and aggregation (Chart 1.15). Their studies using various spectroscopic techniques proposed the existence of two types of π-stacked supramolecular organizations. The first is the intramolecular conformational ordering of the oligomers and the second is the intermolecular aggregation of the macrocycles (Figure 1.8). Among the various macrocycles 77-79, 77 showed an intermolecular association involving π-stacking. This substituent effect could be attributed either due to electrostatic reasons (e.g. electron-rich rings) or due to steric effects (e.g. conformational differences at the ring/side-chain juncture). In linear oligomers, the helix formation via intramolecular conformational ordering causes an abrupt change in the intensity of π-π* bands. In dilute solutions of “poor” solvents, chains long enough to fold back on themselves adopt helical conformations. This intramolecular structure is presumably stabilized by π-stacking interactions of a similar nature to those that drive the macrocycles to aggregates in solution. At higher concentrations, long chain oligomers undergo intermolecular aggregation. The possible mode of intermolecular association of the helical conformation is in the form of stacked
aggregates, analogous to the stacking of macrocycles (Figure 1.8). The major conclusion from these studies is that solvent can play a dramatic role in modulating the strength of the interactions that drive the association of \( \pi \)-stacked structures. For a given solvent, the nature of the side chain-linking group strongly influences the \( \pi \)-stacking propensities. The helical stacking of these synthetic oligomers can be considered analogous to the folding of biological macromolecules such as protein.

**Chart 1.15**
Bunz et al.\textsuperscript{166,183} have reported the aggregation behaviour of substituted linear poly(\(p\)-phenyleneethynylene)s (PPEs) (81 and 82) in solvent mixtures and in thin films (Chart 1.16). Their studies on the absorption and emission behaviour of polymers 81 and 82 in chloroform, chloroform/methanol solutions, and in the solid state, unambiguously proved the presence of aggregates in the mixed chloroform/methanol solvent and in thin films. Both, absorption and emission studies showed a red-shifted absorption band upon addition of methanol. Since the UV-vis spectra of PPEs are highly independent of the conformations of the phenyleneethynylene units, the observed bathochromic shift in absorption spectra is concretely attributed to the formation of aggregates in PPEs. Accounting the rigidity and planarity of these systems, the probable aggregation is via \(\pi-\pi\) stacking of the polymeric backbone. The nature of substituents and solvents induces the \(\pi-\pi\) stacking via planarization of conjugated segments.
Another important property of π-conjugated polymers is their chromic behavior with solvents and temperature. The intriguing chromic phenomena of conjugated polymers have been reported both in solution and in the solid state.\(^{184}\) For conjugated polymers, these chromic behaviors are particularly promising for sensor applications. Even though major studies have done with polythiophenes, chromic properties are not excluded for many other conjugated polymers such as polydiacetylenes,\(^{185-187}\) polysilanes,\(^{188}\) polygermanes\(^{189}\) and poly(alkylbithiazoles).\(^{165,190,191}\) In most of the cases, these optical features have been related to a planar/non-planar conformational transition of the backbone. Any twisting of the backbone conformation via molecular interactions modify the effective conjugation length, which will result a shift in absorption spectrum in the UV-vis range.\(^{32}\) Recent theoretical and experimental studies on various polythiophene derivatives and oligomeric model compounds indicated that these chromic properties are driven by a delicate balance between repulsive intrachain steric hindrance and attractive interchain (or intrachain, through chain folding) interactions.\(^{192-194}\) In regioregular head-to-tail polythiophene derivatives, the linear side chains maintain the planar conformation of the polymer backbone at low temperature. Disordering of the side chains lead to less planar conformations and the concomitant backbone twisting can be due to temperature
(thermochromism), solvent (solvatochromism), light (photochromism) or to a range of specific molecular interactions with the side chains.

At low temperature, many of the regioregular polythiophenes such as poly(3-alkoxy-4-methylthiophene)s (83), poly(3-alkylthiophene)s (84) and poly(3-(alkylthio)thiophene)s (85) can form coplanar or nearly coplanar assemblies that are disrupted upon heating due to a disordering of the side chains (Chart 1.17). These structural changes with temperature can be easily viewed in the UV-vis absorption spectra. The planar conformations always afford a low energy transition because of the stronger effective conjugations. In regioregular polythiophenes, the cooperative twisting of the backbone was revealed by the presence of an isosbestic point in the temperature-dependent optical measurements whereas, in non-regioregular polythiophenes, only localized conformational defects can be created along the backbone, leading to a monotonic blue shift in the absorption maximum upon heating.194

Recent report on polythiophene (86) with oligo(oxyethylene) side chain showed a strong chromic response in the presence of selective alkali-metal ions (Chart 1.18).195 Metal ion interactions can modify the side chain organizations and subsequently the conformation of the backbone, which eventually gives a drastic change in the absorption spectra.
The thermochromic and solvatochromic effects are not exclusive to polythiophenes. Several reports can be found in many other related aromatic polymers. In this regard, recently Leclerc et al. have reported the thermochromic and solvatochromic behaviour of certain conjugated polymers such as poly (1,4-(2,5-dialkoxyphenylene)-2,5-thiophene)s (87), poly(1,4-(2,5-dialkylphenylene)-2,5-thiophene)s (88), poly(1,4-(2,5-dialkylphenylene)-2,5-furan)s (89) and poly(1,4-(2,5-dialkylphenylene)-2,5-furan)s (90) (Chart 1.19). The UV-vis absorption studies of these polymers in mixed solvents and at lower temperatures revealed the formation of red shifted aggregates. The X-ray diffraction measurements of the polymer films have revealed a lamellar structure for these semi-crystalline polymers with an interlamellar spacing of 20.1 Å, at room temperature. Upon heating, the interchain distance increases slightly to 22.1 Å. In addition, significant structural modifications associated with either backbone or side-chain stacking take place. All these chromic effects are associated with the main-chain and side-chain disordering upon heating due to intrachain interactions, which are in principle different from the interchain interactions as in the case of π-stacking and aggregations.
In order to differentiate the intrachain vs interchain interactions and to gain more insight into the aggregation behaviour of conjugated polymers, Apperloo et al. have recently synthesized several oligothiophenes (91) functionalized with poly(benzyl ether) dendrimers (Chart 1.20). The concentration dependence of the molecular organization in these systems confirms that the changes observed in the absorption spectra are due to interchain interactions while the intrachain preorganization results in a marginal concentration dependent change. The driving force for the aggregation is attributed to the strong π-π interaction of the oligothiophene units and is more exothermic for longer thiophene.

The brief survey of the recent literature on low band gap polymers presented in this chapter illustrates the importance of structural modifications in tuning the optical and electronic properties of π-conjugated polymers. Equally important is the molecular assembly and aggregation, which play a key role in controlling some of the intrinsic electronic properties of conjugated systems. This area continues to be challenging to the organic material chemists due to the ever-increasing importance of π-conjugated polymers in advanced technological applications.
1.8. Origin and Objectives of the Present Investigation

Narrowing of the HOMO-LUMO energy gap in \( \pi \)-conjugated systems towards metallic conductivity in synthetic polymers is a challenging topic. Since, long wavelength absorption is a signature of the low band gap, it is extremely important to synthesize conjugated polymers that absorb in the near infrared (NIR) region. Even though structural modifications and extension of conjugation can improve the absorption of polymers to longer wavelength, it is difficult to improve the absorption beyond a certain conjugation length due to conformational reasons. Since, conventional synthetic strategies have several limitations, a new approach towards NIR absorbing, low band gap polymers has become demanding.

Due to the inherently low HOMO-LUMO separation of organic dyes, they are potential building blocks for the designing of NIR absorbing polymers. In this context, squaraine dyes are ideal candidates due to their interesting optical properties. However, most of the earlier attempts to synthesize squaraine
dye based low $E_g$ polymers, were not very successful. This is contrary to the theoretical prediction that extension of conjugation in squaraine dyes may provide low band gap polymers. This has prompted us to further investigate on the possibility of designing low $E_g$ polymers based on squaraine dyes. In addition, since squaraine dyes are known to form different kinds of aggregates in solution and in solid-state, we speculated that squaraine polymers may have better tendency to form aggregates which may strongly influence their optical and electronic properties.

With the above views, we set out to design new strategies to synthesize low $E_g$ polymers based on squaraine dyes which absorb in the NIR region. Role of the solubility inducing alkyl side chains on controlling the optical and electronic properties was a major concern of the present studies. Another important objective of the present investigation was to gather informations on the aggregation phenomenon of polysquaraines in solution. To gain better insight on aggregation, we undertook studies on the synthesis and aggregation of several model squaraine dyes with extended conjugation. The present thesis is a systematic investigation centered on the above objectives.
1.9. References


24. Using Hückel terminology, there will be a set of $\beta$'s which describe the hybridization interaction between each pair of levels.


