POLYMER SCIENCE

ENGINEERING AND SPECIALITY POLYMERS

Fundamentals of Electrically Conducting Polymers

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Keywords
Molecular design, copolymerization, transistor,sensor

Introduction

1. What are electrically conducting polymers? One fundamental property which normally distinguishes polymers from metals is electrical conductivity. The value of electrical conductivity for metals is very high and is generally of the order of **$10^4 – 10^6$ S cm^{-1}** (good conductors such as copper and silver have conductivities close to 10^6 S cm^{-1}) while for polymers which are generally insulators this value does not exceed **10^{-14} S cm^{-1}(**good insulators such as teflon and polystyrene have conductivity value close to 10^{-18} S cm^{-1}). Though the low electrical conductivity of polymers has found its immense use in the manufacture of insulators and dielectric substances, the question of producing polymers which exhibit a conductivity similar to that of metals, has always engaged researchers. During the last two decades, the researchers, through the simple modification of ordinary organic conjugated polymers, have succeeded in preparing polymers with high electrical conductivity. Called electrically conducting polymers or synthetic metals, these materials which combine the electrical properties of the metals with the advantages of polymers such as lighter weight, greater workability, resistance to corrosion and chemical attack and the lower cost have become extremely attractive and have infiltrated our day to day life with a wide range of products extending from most common consumer goods to highly specialized applications in space, aeronautics and electronics. It is, therefore, no wonder that these polymers are being called as the ***Materials of the 21st Century*.**

2. Discovery of electrically conducting polymers: A. J. Heeger, A.G. Mac Diarmid and H. Shirakawa (Nobel Prize winners in Chemistry of 2000) at the University of Pennsylvania in 1977, for the first time demonstrated that polyacetylene (PA), an intrinsically insulating polymer, becomes highly conducting on treatment with oxidizing (electron-accepting) or reducing (electron-donating) agents. This process is often referred to as **doping**. Oxidation is referred to as p-doping and reduction as n-doping. The behaviour of PA is thus comparable to that of classical semiconductors e.g. silicon, which too upon doping with donors or acceptors can be transformed into a conducting state.

When free standing films of PA (obtained by the polymerization of acetylene on the surface of suitable catalysts in an inert solvent) were p- or n- doped, their conductivity increased from an initial value of 10^{-9} Scm^{-1} to 10^2 Scm^{-1}. PA films, indicated by the general formula $(CH)_x$, form in cis or trans structures depending upon the temperature of polymerisation. Both cis and trans PA can be doped.

The room temperature conductivity of pure PA films varies from **10^{-5} Scm^{-1} for trans form to 10^{-9} Scm^{-1} for cis form.** Cis form can be converted to trans form by heating at ~200° C for ~1 hr. It is observed that doping ^{the} cis isomer is generally preferred since it is mechanically stronger, flexible and dopes to give higher conductivities.

In 1987, the BASF A.G. in Germany came out with doped PA having a conductivity of about 1.47×10^5 Scm^{-14}, which is comparable to the conductivity of copper (6×10^5 Scm^{-1}). Tsukamoto et al. in 1990 reported a conductivity of $9x10^5$ Scm^{-1} for doped PA. The

discovery of highly conducting PA led to a sudden spurt in research activity directed towards the study of new conducting polymeric systems.

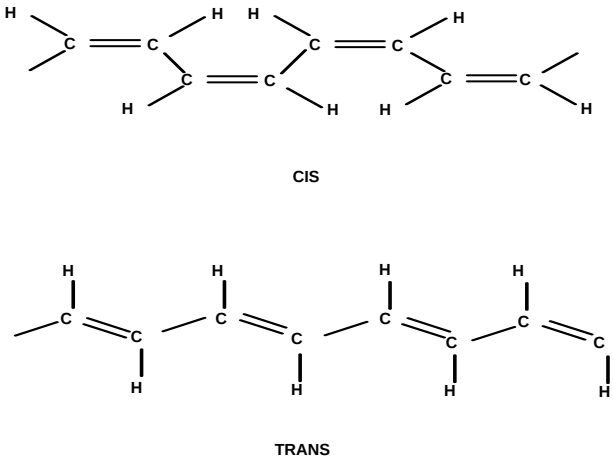


Fig.1:Cis and trans forms of polyacetylene

One of the drawbacks of doped PA is that it is unstable in air. Covalent bonds are formed between oxygen and carbon atoms (of PA) and the conjugation in PA gets interrupted and hence the conductivity of PA gets lowered.

3. Other Conducting Polymers: The instability of PA in air remains a limiting factor in its applications. This spawned efforts to discover other polymers that exhibit similar properties. A sudden spurt in this context came in 1980, when poly (p-phenylene) (PPP) was doped to conductivity level quite comparable to that in PA. This polymer is the first example of the non-acetylenic hydrocarbon polymer that can be doped with an electron-acceptor or an electron-donor to give polymers with conducting properties .This discovery was also important in the sense that it demonstrated the non-uniqueness of PA system and paved the way for the discovery of a number of new conducting polymers. These polymers, though they share many structural similarities, have a wide range of conductivity depending upon:

(i) The Doping Percent
(ii) The Alignment Of Polymer Chain and
(iii) The Purity Of The Sample.

At present many such systems are known and they include poly (p–phenylene sulphide) (PPS), polypyrrole (PPy), Polythiophene (PTP), polyfuran (PFU) and their derivatives. None of these polymers has however reached the high conductivity level of doped PA.

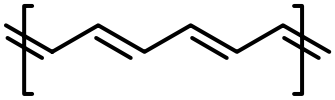
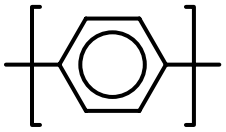
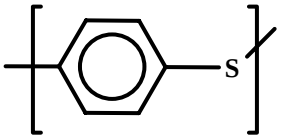
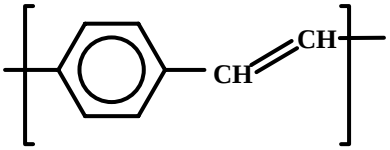
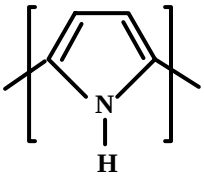
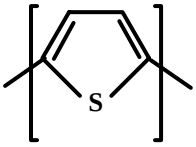
Polymers	Structures
Polyacetylene	
Polyparaphenylene (PPP)	
Polyparaphenylene sulphide (PPS)	
Polyparaphenylene vinylene (PPV)	
Polypyrrole (PPY)	
Polythiophene (PTP)	

Fig.2**:** Some important conducting polymers

4. Synthesis and Doping of Polymers: Electrically conducting polymers, in their doped form, are generally obtained by three different methods:

(1) Chemical synthesis of the polymer followed by doping with oxidizing or reducing agents.

(2) Chemical synthesis of the polymer and its subsequent doping by an electrochemical method.

(3) Electrochemical polymerization and simultaneous doping with desired dopant in a single operation.

The method used depends upon the nature of monomer required for polymerization. For example, PA and PPP are obtained by the chemical method employing different kinds of catalysts and coupling reactions. Although, doping of organic conjugated polymers by chemical methods has often been used, electrochemical doping is emerging as the preferred technique in many applications. This technique provides a potentially highly controllable and reproducible method for investigation of the doping process, in which the transfer of charge can be accurately monitored and regulated, giving a degree of control which is beyond the scope of gas or solution phase chemical doping.

Electrochemical Polymerization: Conducting heterocyclic polymers such as polypyrrole, polythiophene, polyfuran and their derivatives can be obtained in a single step from their monomers by electrochemical polymerization and simultaneous doping with the dopant and polymers thus obtained are purer and homogeneous. The mechanism of electrochemical polymerization involves various steps which are as follows:

(1) Oxidation of monomer to a radical cation.
(2) Dimerisation of radical cations followed by a proton loss to yield a neutral dimer.
(3) Oxidation of dimer to its radical cation.
(4) Reaction of dimer radical cation with another radical cation.

5. Common Structural Features of Conducting Polymers: The common structural features of these polymers include.

1) Conjugated system along the polymer backbone.
2) Generally planar structure
3) Intra-chain conductivity ($\rho_{||}$) is much larger, than the inter–chain conductivity ($\rho_{\perp}$).

The anisotropy ratio $\frac{\rho_{||}}{\rho_{\perp}} \approx 10^3 - 10^4$

is a parameter used to estimate the one-dimensionality of a particular system. In view of their large anisotropy ratio, these systems are also called quasi-one-dimensional systems.

Baughman et al. in 1982 have considered the various factors related to structure which lead to enhanced electrical conductivities in conducting polymers. It has been observed that polymers which have the most homogeneous chain structures appear to be the best conductors. Heterogeneity, on the other hand, can yield carrier localization on the chain unit, which provides the lowest potential for holes (or electrons in the case of donor doping). Bredas et al have shown that there exists a link between the homogeneous character of the polymer backbone and the width of the highest occupied π-band. The width of the π-bands can be correlated to the degree of delocalization of the π-systems along the polymer backbone and also to the mobility of the carriers in these bands. It was shown that as the ionization potential deceases and the width of the highest occupied π-band increases, the band gap decrease thus creating a better conductor. These results show why polymer research is primarily centered on π-bonded unsaturated systems since

these materials have low ionization potentials and large electron affinities. The π-electrons can be easily removed or added to these systems and little effect is noted on the σ-bonds which are necessary to hold the basic backbone of the polymer intact.

6. Nature of Processes Inducing High Conductivity in Conducting Polymers: Electrically conducting polymers are different form inorganic crystalline semi–conductors in two important structural features.

i) Polymers are molecular in character and lack long-range order: The combined influence of molecularity and disorder leads to profound differences between the fundamental physics phenomenon that occur in traditional covalent network semiconductors and those that characteristic of these polymers.

ii) Doping in polymers is a charge transfer reaction: The nature of processes which induce conductivity in both of them are different. In the doping of inorganic semiconductors; the dopant species occupies positions within the lattice of the host material and give rise to electron rich or electron deficient sites with no charge transfer occurring between the two sites, whereas the doping reaction of polymer gives rise to partial oxidation or reduction of polymer. It is now well established that the exposure of PA to an oxidizing agent X (or reducing agent M) leads to the formation of a positively (or negatively) charged polymeric complex and a counter ion which is the reduced X (or the oxidized M^+) form of the oxidant or reductant. The 'doping process' in the case of conducting polymers may therefore, more correctly be classified as a redox process of the following general scheme:

(i) Oxidation process (p–doping) :

$$Polymer + X \rightleftharpoons (Polymer)^{n+} + X^{n-} \qquad X = I_2, Br_2, AsF_5, \ldots.$$

(ii) Reduction process (n-doping) :

$$Polymer + M \rightleftharpoons (Polymer)^{n-} + M^{n+} \qquad M = Na, Li \ldots\ldots$$

The above reactions are most likely to occur in the case of unsaturated polymers with π-electrons, as they can be very easily removed from the polymeric chains to form polyion therefore, these are the types of polymers, which assume high conductivity on doping**.**

7. Nature of Charge Carriers in Conducting Polymers: The interaction of a polymer unit cell with all its neighbours in a polymer chain leads to the formation of electronic bands. The highest occupied electronic levels constitute the valence band (VB) and the lowest unoccupied levels, the conduction band (CB). The energy difference between the top of the valence band (VB) and the bottom of the conduction band (CB) is known as **band-gap (Eg)** and this band-gap determines the intrinsic electrical properties of the polymers.

Initially, the increase in conductivity observed upon doping organic conjugated polymers was thought to result from the formation of unfilled electronic bands. This assumption was, however, quickly challenged by the discovery that polyacetylene (PA), poly-paraphenylene (PPP) and polypyrrole (PPy) which display conductivity that does not seem to be associated with unpaired electrons but rather with **spinless charge carriers**. It has been found that high conductivities obtained upon doping in these polymers are associated with formation of self-localized excitations such as **solitons, polarons and bipolarons**. These quasi-particles which arise from a strong interaction between the charge on the chain (electron or hole) acquired as a result of doping and the molecular structure are the direct consequence of the strong electron-phonon interaction present in these quasi-one-dimensional polymers. Thus, charge-carrying species in doped organic conjugated polymers are not free electrons or holes as in the case with inorganic semiconductors but quasi-particles such as solitons, polarons and bipolarons which may move relatively freely through the material.

In order to have a detailed understanding of the nature of charge carriers and the mechanisms of their conduction, the conducting polymers may be divided into two categories :

(i) Polymers with degenerate ground state
(ii) Polymers with non-degenerate ground state

i) Polymers with degenerate ground state: The degeneracy of the ground state of trans-PA gives rise to the possibility of structural defects (kinks) in chains where there is a change in the sense of bond alternation.

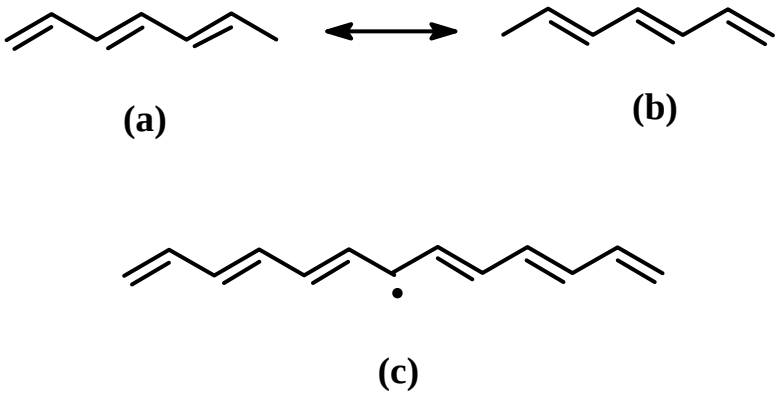


Fig.3:- (a) and (b) Degenerate ground states of trans – PA.

(c) PA chain with a defect (neutral soliton).

Associated with the structural kink is a localized electronic state with energy at mid-gap. The two alternative structures of PA have the same ground state energies. A single unpaired electron exists where the defect occurs and this produces an energy level at the centre of the energy gap. Therefore, PA can support solitonic defects. Optical absorption occurs for transitions across the band gap and to the mid-gap state (i.e. the unpaired electron resides in non-bonding orbital) (Fig. (a)). It is singly occupied for a neutral soliton (S^0) which has spin ½.

The soliton energy level can accommodate either 0, 1 or 2 electrons and thus the soliton may also be positively or negatively charged. (Fig.(b) and (c)) giving the unusual property of separating spin and charge. If the electron is removed, i.e. zero occupancy, a positively charged soliton (S^+) of zero spin results. Double occupancy gives a negative soliton (S^-) with zero spin. Thus, charged solitons are non-magnetic. Soliton (S) – antisoliton (S^-) pairs occur when a short segment of a PA chain has reversed bond-alternation. Thus, charged solitons are formed by electron transfer on to or off the polymer chain on doping with electron donors or acceptors.

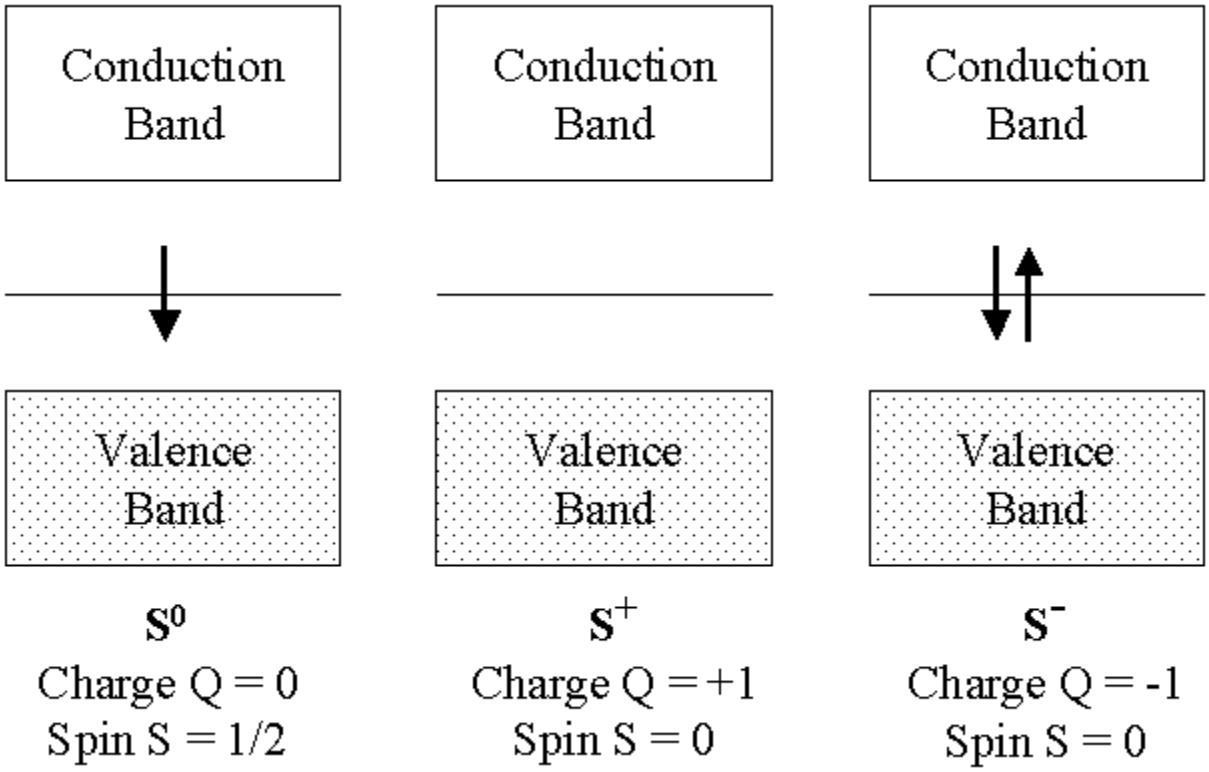


Fig.4: Charge and spin seperation in the case of (a) neutral soliton (S°),

(b) positive soliton (s^+) and (c) negative soliton (s^-).

The mid-gap optical absoption provides direct evidence for charged soliton states in doped polyacetylene. It was observed that as the doping proceeds, the mid-gap absorption appears, with an intensity that increases monotonically in proportion to the dopant concentration.These spectroscopic features are independent of dopant species and independent of whether the doping is p-type (oxidation) or n-type (reduction).

In pure undoped trans-PA, there are only neutral solitons on an average of ~1/3000 chain atoms as indicated by the ESR experiments and thus account for the observed para-magnetism in trans-PA

- . When trans – PA is doped (either n-or p-), a number of neutral solitons is used at an already very low doping level leading to the formation of charged solitons.
- On the other hand, in the case of defect free trans – PA chain, a charge transfer directly between doping agent and valence and conduction band, respectively will produce an ion radical in the chain, i.e. a defect pair instead of an isolated defect.

The following figure shows the mechanism of p-doping of trans-PA.

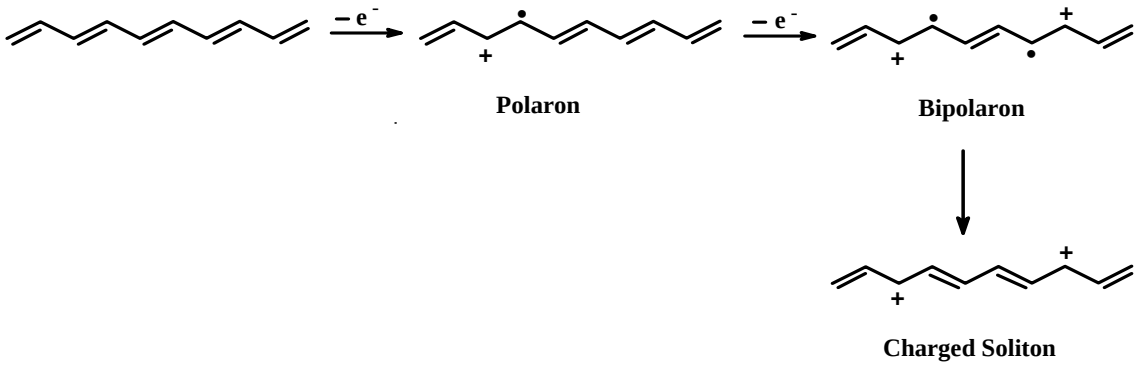


Fig.5: p- doping of defect free trans-PA

In this mechanism, trans – PA looses one e^- (p-doping) and stable ion-radical pair is formed, which is called **polaron** and its formation is accompanied by two energy levels obtained symmetrically above and below the middle level of the band-gap. With increased doping, increased concentration of polarons interact with each other and thus two polarons may couple to form **bipolarons,** which are spinless and further give rise to two charged solitons which produce a band half way between valence band and conduction band.

It can be shown theoretically that the formation of polarons is energetically more stable than the separation of ion-radical components along the chain into one charged and one neutral solition. Recently, theoretical investigations on soliton and polaron in trans – PA were done and interesting results were obtained. Theoretical studies of polarons and bipolarons were also done in the case of poly (triheterocycles) based on furan and thiophene. The results thus obtained provide a coherent interpretation of the experimental spectra of doped polyfuran and polythiophene.

ii) Polymers with non-degenerate ground state: In contrast to trans – PA, all other conducting polymers, including cis – PA cannot support solitons since they have energetically non-degenerate ground state and therefore the structures on either side of the charged defect would be of different energy. In these types of conjugated polymers, the nature of charge carriers is different. Since isolated solitons are unstable in polymers with structures that do not have equal ground-state energies e.g. Cis – PA, PPY, PTP and PPP, therefore for such polymers, charge exchange will lead to formation of S^0-S^+(S^-)

pairs, which will be strongly localized to form a polaron, well known in inorganic semiconductors.

At the polaron site, the polymer structure locally deviates towards the higher – energy structure but never achieves it. A polaron gives rise to two levels in the band-gap and several optical – absorption bands occur. In such polymers, it has been found that the formation of single solitons, whether as a result of doping or from inherent defects, is energetically unfavourable and the energetically preferred configurations involve paired sites.

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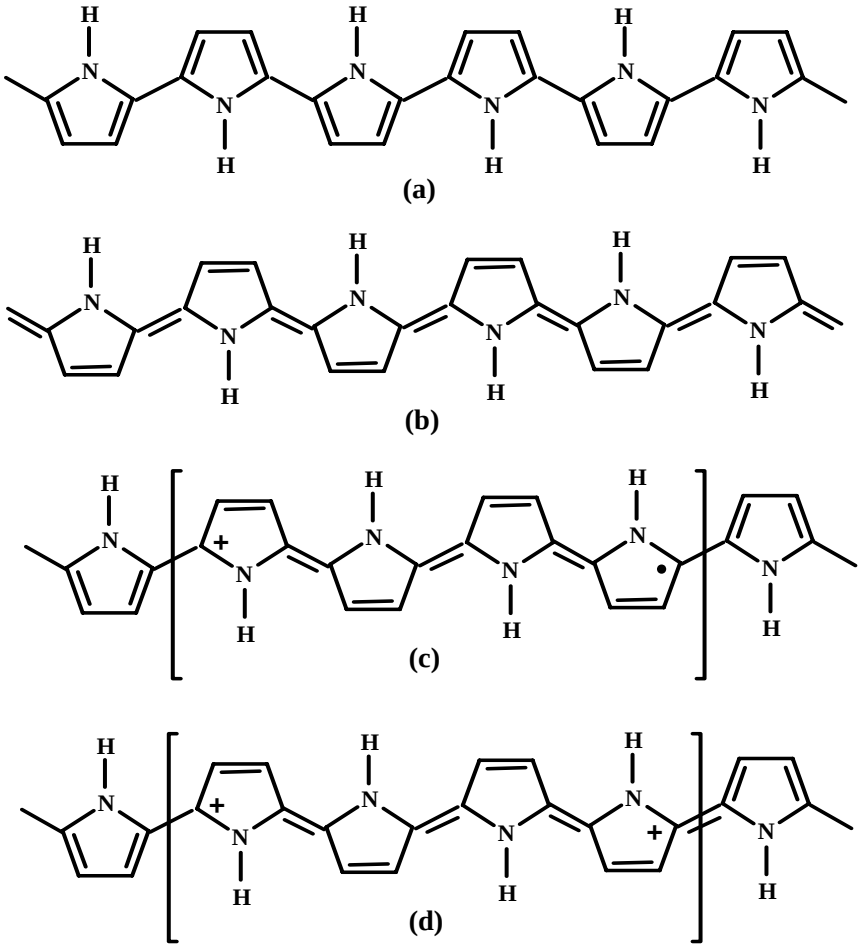


Fig.6: (a) and (b) Non-degenerate ground states of polypyrrole (PPY); (c) formation of polaron and (d) formation of bipolaron in PPY as a result of p-doping.

PPY is a poorly conducting material with a band-gap of 3.2 eV. The removal of an electron during p-doping-process (oxidation) leads to the formation of a polaron with a relaxation of the structural geometry of the polymers towards a quinoid form which has a larger affinity for charges extending over 4-pyrolitic rings (Fig (c)above). When a second electron is removed from the polymer chain, a bipolaron is formed (Fig.(d) above) which may be defined as a pair of like charges associated with a strong local lattice distortion, which again extends over four pyrolitic rings. This bipolaron lacks spin in contrast to polarons and neutral solitons. The formation of bipolaron implies that the energy gained

by the interaction with the lattice is larger than the Coulomb repulsion between the two charges of same sign confined in the same location. Thus, the formation of bipolaron is also supported by calculations which show that the formation of one bipolaron is thermodynamically more stable than that of two separated polarons, despite the Coulomb repulsion between two similar charges. This is due to the fact that

- The distortion energy E_{dis} for the bipolaron is larger than E_{dis} for the polaron.
- The electronic states appearing in the gap for a bipolaron are further away from the band edges than for a polaron.
- The decrease in ionization energy is much more in the bipolaron case than for two polarons.

The bipolaron binding energy has been found to be larger than that of two polarons by about 0.4 eV in PPY and 0.034 eV in PPP.

8. Factors Affecting the Conductivity of Conducting Polymers: Various factors that affect the conductivity of conducting polymers include:

(i)Conjugation length: Presence of conjugation is one of the structural features common to all the conducting polymers. It has been found that it is the conjugation length of the polymer chain, and not its chain length that is important for its high electrical conductivity. The conjugation length of a polymer chain is the average distance between two defects that interrupt the conjugation Experimentally, it has been found that **conductivity decreases rapidly with decreasing conjugation length.**

(ii)Temperature: Temperature dependence of conductivity can be understood by defining two conductivity regimes:

- The high conductivity regime with conductivity >**1000 S cm^{-1} ,** and
- The moderate and low conductivity regime with conductivity <**100 S cm^{-1}.**

Conductivity of polymers generally decreases with decrease of temperature. This temperature dependence of conductivity varies according to two factors:

1) Type of Conductivity System:
   - Moderate & low conductivity systems: Conductivity vanishes as T → 0.
   - High conductivity systems: Conductivity remains finite

2) Level of Doping:
   -Low Doped Sample: Temperature dependence of conductivity is very drastic.
   - High Doped Sample**:** Conductivity is nearly temperature independent.

(iii)Doping level: The conductivity of conjugated polymers is found to increase with increase in the doping level of the polymers. The doping level of the polymer is determined by the dopant concentration expressed in mol %.

(iv) Frequency Dependence: The electrical conductivity of conducting polymers can be decomposed into a d.c. part and an a.c. contribution. The d.c. contribution is frequency independent because in this case, current path involves several long distance hops

resulting in low d.c. conductivity. The a.c. contribution, on the other hand, increases linearly with frequency because electric field reverses sign while electron is waiting to hop.

Molecular Designing of Low Band-Gap Electrically Conducting Polymers

Band-gap control is one of the most important ways to improve the performance of conducting polymers in terms of conduction properties. Low band-gap conducting polymers have received increased attention due to their intrinsic physical properties. Intensive research has been dedicated to exploring novel conjugated polymers with small band-gaps, a property that is essential for high conductivity upon doping, for high non-linear optical response and for the possible transparency in the visible region of the absorption spectrum. 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 processibility which is restricted to a great extent because of the insolubility and infusibility of these polymers. The possible elimination of doping in preparing conducting polymers while still achieving high conductivity is one of the original motivations for need of small band-gap polymers. It is thought that low band-gap polymers would not only show high intrinsic conductivity (i.e. without doping) but possibly also a good transparency in the visible spectrum with many applications. Also, that may pave a way for real intrinsically metallic organic polymers. Therefore, at the present moment, the development of stable, processable polymeric materials with a low band-gap is an important issue for further advancements in these fields. Thus, substantial efforts have been devoted to the design of conjugated organic polymers with a small band-gap. These efforts go under the name of **Band Structure Engineering of novel polymers with low band-gaps**. To be successful in designing low band-gap polymers, it is necessary to have a complete understanding of the relationship between the chemical structure of the polymer and its electronic properties (such as ionization potential (IP), electron affinity (EA) and band-gap (Eg)) which determines its conduction properties. Once such an understanding is achieved, the desired electronic properties can be obtained by molecular design followed by specific synthesis.

Band-gap of a polymer is a measure of its ability to show intrinsic conductivity, while IP and EA values of a polymer determine its ability to form conducting polymers through oxidative and reductive doping respectively. The band structure can be tuned by altering either or both the electronic structure and stearics of the backbone. Of particular interest is the preparation of stable, low band-gap conductive polymers. These materials have attracted much attention due to their high visible transmissivity in the conductive form. Synthesis of low band-gap conjugated polymers is one of the major focusses in the field of organic conductors. The first low band-gap (Eg) polymer reported was **poly (isothianaphthene) (PITN) (Eg = 1.0-1.2 eV)**. This has been attributed to the ability of the fused benzene ring to stabilize the quinoidal form of the polymer in the conductive state. Despite this, the practical use of poly (isothianaphthene) became limited due to its environmental instability. All these efforts have been motivated by the desire to achieve reduction of Eg and the development of soluble polymers. Despite all these efforts, it has not yet been possible to synthesize many very low band-gap polymers, though many low band-gap polymers have recently been predicted on the basis of theoretical calculations

and they offer a challenge to the experimentalists to synthesize them.

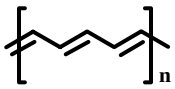
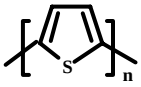
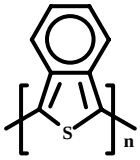
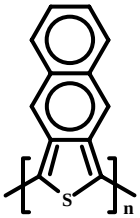
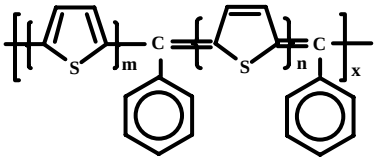
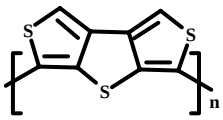
Name	Structure	Band gap (eV)
1. Trans-PA		**1.5**
2. Polythiophene		**2.1**
3. Polyisothian-aphthene		**1.0**
4. Polyisonapht-hothiophene		**1.4**
5. Poly[α-(5,5'-tetrathiophenediyl) benzylidene		**0.75-1.1**
6. Poly(dithieno-(3,4-b:3',4'-d)-Thiophene		**1.0**

Fig.7: Some low band gap conjugated polymers

Different Strategies used for Molecular Designing of Polymers: Various routes are followed to design conjugated polymers with tailor-made electronic properties using the existing knowledge of structure–property relationship of conducting polymers. These include:

i. Substitution/Fusion
ii. Ladder polymerization
iii. Topological methods
iv. Donor-acceptor polymerization
v. Copolymerization

i) Substitution / Fusion: In this route, one starts with low band-gap polymers and tries to modify their electronic properties by substitution provided their chemical nature and experimental conditions allow these reactions. The ideal starting materials for substitution include trans-PA with a band-gap of 1.5 eV and polythiophene (PTP) with a band-gap of 2.1 eV and that is why most of the studies using this route have been on the substituted derivatives of PA and PTP.

Steric effects of substituents play an important role during substitution process because bulky groups may introduce large non-bonded interactions between these groups and thus twist the polymer backbone which may lead to non-coplanarity and thus a decrease in orbital overlap and effective conjugation length which result in lower conductivities. The following two guidelines are of great help in the strategy of substitution:

(a) In polymers with degenerate ground state such as trans PA[50], band- gap is defined as :

$$Eg = 2 (Ee + Ei)$$

where, Ee = fixed external contribution to the Eg due to σ skeleton.
Ei = internal contribution from π-electron framework.

It is now well established that in the PA, internal contribution to the gap increases as a function of increasing bond length alternation along the chain.

(b) On the other hand, in polymers with non-degenerate ground state such as poly (p-phenylene) (PPP), polypyrrole (PPY), polythiophene (PTP) and polyfuran (PFU), theoretical calculations show that the band-gap does not decrease as a function of decreasing bond length alternation rather it is a function of increasing quinoid character of the polymer backbone. The greater is the quinoid contribution, the more stable is the ground state.

Using the above guidelines, some derivatives of PA and aromatic polymers have recently been studied. The effect of substituents on the band structure of PA have been investigated in few cases like fluorinated polyacetylene, polymono-fluoroacetylene (PMFA) and polydifluoroacetylene (PDFA); nitrogen containing analogues like polyazoethene (PAE), polyazine (PAZ), polymethineimine (PMI)[53] ; silicon containing analogues of PA such as polysilane (PS), polysemisiline (PSS), polysilacene (PSA)[54] and alkoxy-substituted poly(p-phenylenevinylene)s[55]. Polymers having azobenzene substituents in the main chain have been studied by A. Izumi et al. The azobenzene units in the conjugated polymer backbone make it a thermally stable polymer. Highly conductive new aniline copolymers containing butylthio substituent have also been successfully prepared with conductivity of the order of 1 S cm^{-1}. All these new butylthioaniline copolymers are highly soluble in common organic solvents despite the presence of large amount of bulky butythio substituent. Although in some cases,

substitution may decrease the conductivity of the polymer but the resulting polymer has higher EA and can, therefore, be used in LEDs.

A series of cyano-substituted distyryl benzenes have also been synthesized. It has been observed that by properly adjusting copolymer compositions, a combined high electron affinity and transport was achieved in a statistic copolymer namely poly (fluorenebenzothiadiazsole-cyanophenylenevinylene) (PFB-CNPV).A variety of novel soluble, conjugated PPP– and PPV– related polymers have also been synthesized using a synthetic approach that allows for the tailoring of the chemical structure of the polymer backbone.

Thus, all these various kinds of substituents are in use for improving solubility, decreasing band-gaps, increasing polarizabilities and conductivity and finally optimizing luminescence efficiencies.

ii) Ladder polymerization: One exciting possibility in the search for novel conducting polymers is provided by the ladder structures. Among ladder polymers, hydrocarbon polymers with fused aromatic rings have been the focus of enormous interest. Ladder structures are formed by joining simple polymers into symmetrical polymeric rings. The small energy-gap in ladder polymers is a consequence of the direct interplay of electron-lattice and electron-lattice interactions in them. This new class of polymers, frequently referred to as **one-dimensional graphite family**, includes polyacene (PAc), polyacenacene (PAcA), polyphenanthrene (PPh), polyphenanthro-phenanthrene (PPhP) and polyperinaphthalene (PPN) (Fig:-8). PAc and PAcA can be considered to be the laddered versions of two and three chains of trans-PA respectively while PPh and PPhP those of the corresponding cis-PA chains. One may continue building these series further---every higher member in a series has a larger carbon content ultimately leading to 1-D graphite. PPN can be considered to be a fused version of planar poly (p-phenylene) and cis-PA skeletons (Fig.8). The electronic structures and conduction properties of the members of I-D graphite family have been the subject of many theoretical investigations. PAc is the most studied polymer followed by PPN, PPh and PPhP of this family.

It has been observed that the coupling of trans – PA chains to form ladder polymers is accompanied by a decrease in the band-gap values. The decrease in the band-gap is accompanied by a corresponding increase in the electron affinity values implying thereby that PAcA is not only a better intrinsic conductor but also a very promising candidate for forming highly conducting n–doped materials. The ladder-type poly-p-phenylenes (LPPP) offer the opportunity to study large, rod-like chains of planarised phenylene units. The ground-state properties and excited states of ladder-type paraphenylene oligomers are calculated applying semi-empirical methods for upto eleven-phenylene rings.A scheme to interpret the excited states is developed which reveals the excitonic nature of the excited state. Ladder thiophene polymers have also been synthesized with decreased band-gap values. Unique new ladder polymers from dihydroxy-aromatic compounds and dialdehydes have also been prepared. It has been observed that ladder polymers with higher molecular weight showed better thermal resistance. Ladder polymers with band-gaps as small as 0.2 eV have already been synthesized.

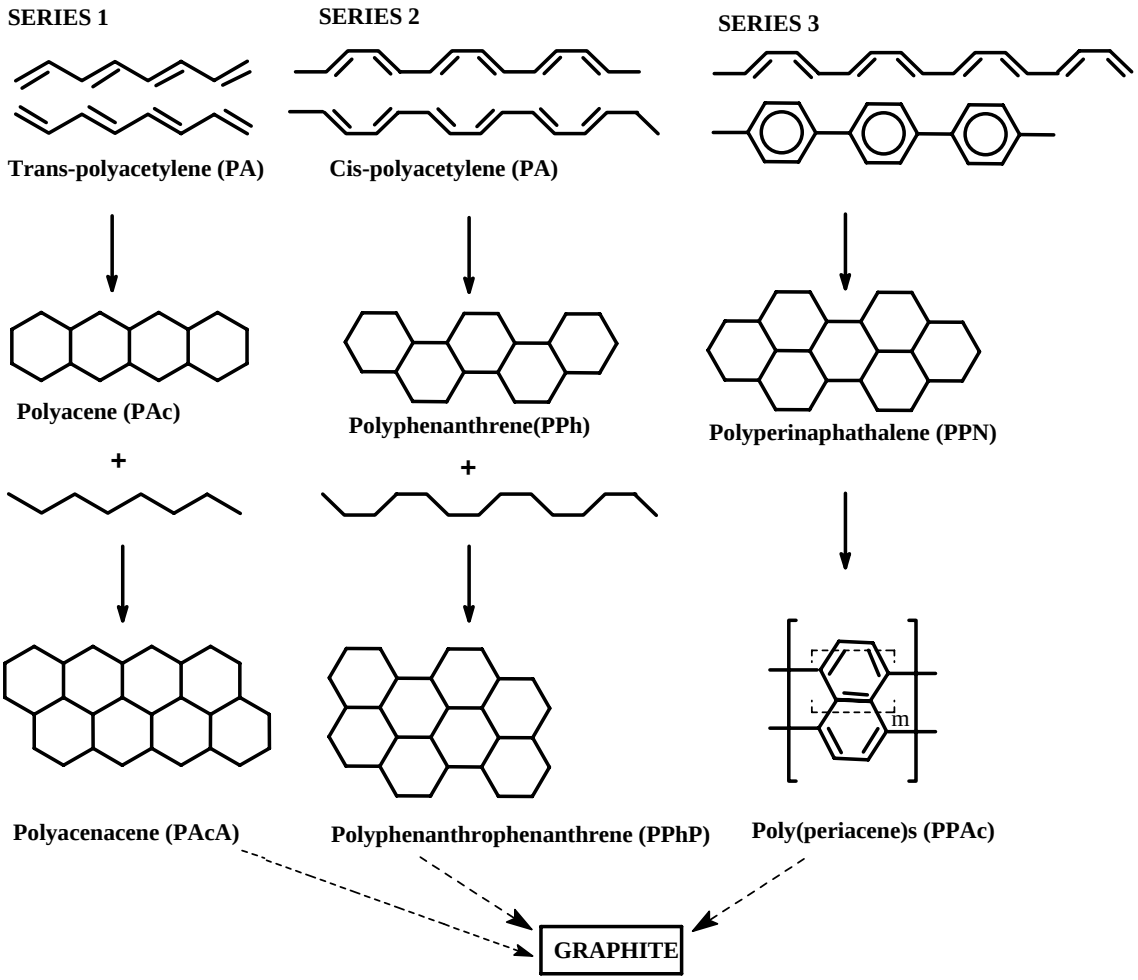


Fig 8:-Various members of the one-dimensional graphite family

Silicon containing ladder polymers have recently been synthesized by Hayashi et al. These are thermally stable and soluble polymers with small band-gaps and can be used for engineering the electronic properties. Various other ladder polymers with improved properties have also been synthesized *viz*. poly (aroylene benzimidazoles), polyepoxy-siloxanes and ladder polymers with thienylene units. Recently photoconduction study on a ladder type poly (paraphenylene) has also been done.

iii) Topological methods: In the case of fused ring polymers, the electronic properties are found to depend strongly on the particular way the rings are fused and the recognition of this has led to the employment of topological methods based on the concept of topomers. It means that one has to construct the corresponding oligomers of a pair of topomers as S- and T- topomers (Fig:-9). These are defined by building them from two indentical subunits connected by two bonds. In the S-topomer, the two bonds connect pairwise topologically equivalent atoms. While in the T-topomer, the end points of the two bonds are interchanged in one subunit. If, for example, A is the T- and B the S-topomer of the same subunit, then the following relations which are the consequences of

the interlacing theorem are valid for these pairs:

(i) The ionization potential (IP) of A is smaller than the IP of B.
(ii) The electron affinity (EA) of A is smaller than the EA of B.
(iii) The fundamental band-gap (Eg) of A is smaller than the gap of B.

Point (iii) follows immediately from (i) and (ii) because Eg = IP - EA. The gap of A is, therefore, located inside the gap of B on energy scale.

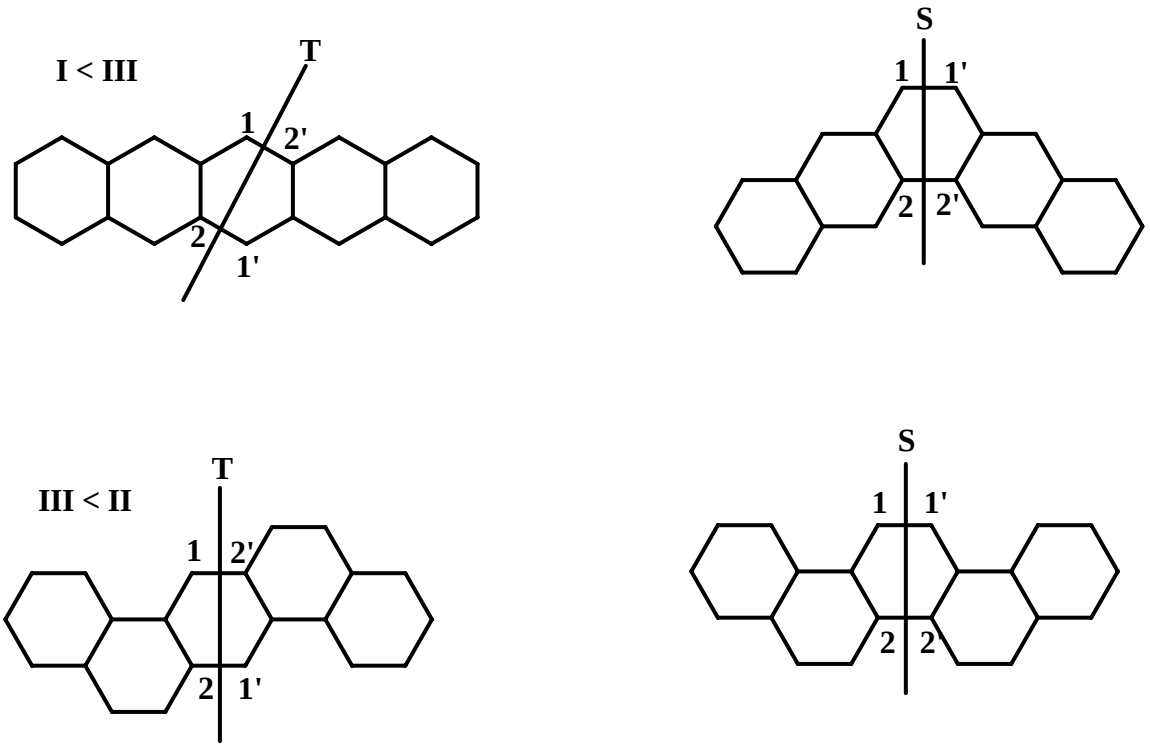


Fig.9: Representation of the oligomers of the polymers ; I (polyacene); II (polyphenantherene) and III (polybenzanthacene) as S- or T- topomers of the corresponding subunits. The pairs of equivalent points are denoted as (1,1') and (2,2') where the prime is used to distinguish between the subunits.

The above topological arguments have been used to rationalize the large differences in the electronic properties of fused ring polymers such as polyacene, polyphenanthrene and polybenzanthracene and in search for novel low band-gap conjugated polymers. Polyisophenanthrene, a new hypothetical polymer is predicted to have a band-gap between polyacene and polybenzanthracene.

Unique new ladder polymer (polyindenoindenes) consisting of condensed succession of six and five membered conjugated carbon rings have been synthesized. Seven topological isomers of these polyindenoindenes are considered theoretically. The results are analysed in terms of topological band-gaps and geometrical relaxation. Three isomers are expected to have a band-gap smaller than 0.2 Ev.

iv) Donor–acceptor polymerization: Another exciting possibility and successful route in designing of low band-gap electrically conducting polymers is provided by the donor-acceptor polymers. The synthesis of conjugated organic polymers with alternate donor-acceptor architectures are currently of interest because the built-in intramolecular charge transfer can facilitate ready manipulation of the electronic structure (HOMO/LUMO levels), leading to small band-gap polymers. That is how the donor-acceptor polymers have now become the subject of a large and growing interest. The principal idea behind donor-acceptor polymers is that a regular alternation of donor and acceptor like moieties in a conjugated chain will induce a low band-gap **(Fig:-11).**

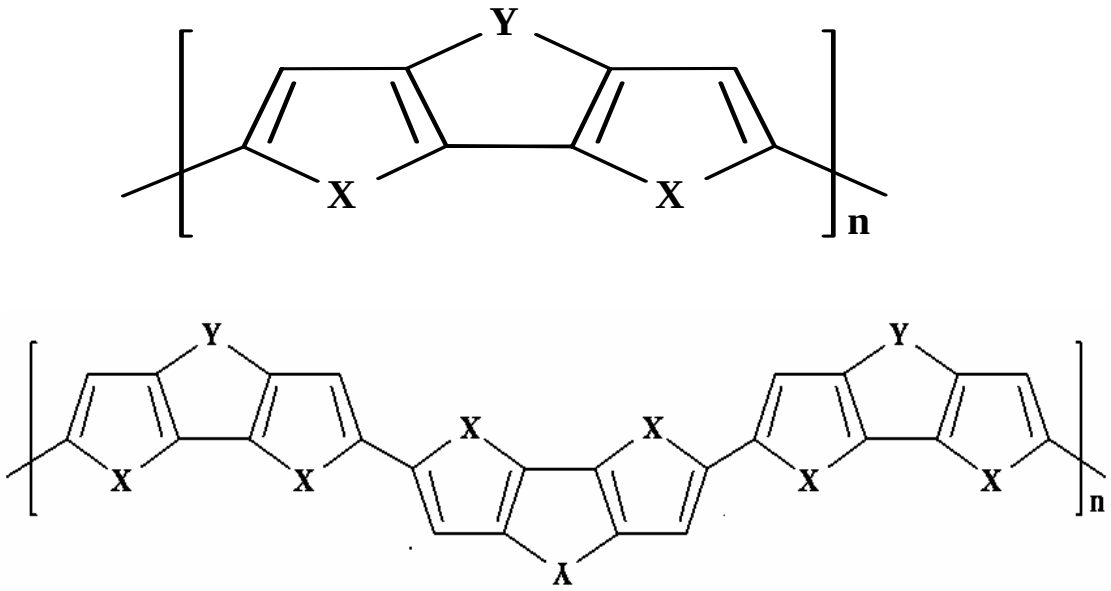


Fig.10: (a) Donor-acceptor polymers with alternate donor (X) and acceptor (Y) moieties
(b) Evolution of chemical structure of the polymer

The band-gap is expected to be the lowest for a combination in which the electronegativity difference between donor and acceptor moieties is the highest. Various novel donor-acceptor polymers differing in their electron donating and electron accepting moieties have been theoretically designed and investigated on the basis of one dimensional (SCF-CO) method at the (MNDO-AM1) level of approximation.

Using the above approach, novel thermally stable polymers polysquaraines and polycroconaines with band-gap values as low as 0.5 eV have been synthesized. These new materials show conductivities around 10^{-5} S cm^{-1} and are stable in air upto 250 ^{o}C or higher. Using a somewhat similar approach, Lambert and Ferraris have independently synthesized poly-4H-cyclopenta-dithiophene-4-one (PCDT) and polydicyano-methylene-cyclopenta-dithiophene (PCNTh), the two polymers with experimental band-gap values of 1.2 and 0.8 eV, respectively. Both PCDT and PCNTh consist of the same electron-donating bithiophene units as the repeating units bridged by an electron-accepting carbonyl group in PCDT and a dicyanomethylene group in PCNTh. The electronic and

geometric structures of PCNTh and its nitrogen analogue polydicyanomethylene-cyclopenta-dipyrrole (PCNPy) and also of polydicyanomethylene-cyclopenta-dicyclopentadiene (PPDCN) have been the focus of study by Toussaint and Bredas.

Polyamino squaraine (PAmSq) which consists of squaraine ring connected by simple amine units has also been studied. Prediction of small band-gap of ~ 0.5 eV is based on calculations of geometrical and the electronic structure using the Car-Parrinello technique of simultaneous optimization. Quantum chemical studies of the electronic structures of PCDT and PCNTh and donor-acceptor polymers based on polycyclopentadienylene (having electron-donating moiety CH_2) have already been studied by ***ab-initio* Hartree-Fock crystal orbital method.** The effect of donor-acceptor substitution on band-gap and conductivity has recently been investigated. The strategy of donor-acceptor polymerization was also adopted to reduce the energy-gap in substituted polythiophenes. It was observed that the band-gap goes down to 1.2 eV, which is a very low value in the class of polythiophenes. Meng and F. Wudl have recently synthesized and designed poly(benzothiophene-N-2-ethylhexy-4,5dicarboxylicimide) (EHI-PITN) and band-gap value was found to be 1.24 eV. Thus, the concept of donor-acceptor polymerization efficiently works for Band-Gap Engineering.

v) Copolymerization: Among the various routes presently followed for molecular designing of novel polymers with tailor-made conduction properties, the strategy of growing copolymers is highly exciting and promising. The copolymers can have tailor-made properties depending upon the choice of two semiconducting components, their relative amounts and their arrangement in the polymer chain. The electronic properties of a copolymer $(A_mB_n)_x$, though generally intermediate between those of its components $(A)_x$ and $(B)_x$, can be tuned by varying the molecular composition of the copolymer and by varying the arrangement of components (periodic or aperiodic) in the copolymer chain.

Depending upon the band alignments of the two constituent polymers, copolymers like the inorganic superlattices may be divided into four types *viz*. Type-I, Type-II staggered, Type-II misaligned and Type-III.

- Type- I: It applies to such systems where the energy gap of one component lies within the band-gap of the other component.
- Type-II: Staggered:- Systems in which the top of the valence band of one component lies within the band-gap of the other and the bottom of the conduction band of the second lies in the band-gap of the first belong to this category.
- Type–II: Misaligned**:-** In this type of copolymers, the band match up is such that the conduction band minimum of one is below the valence band maximum of the second component.
- Type–III**:** In this type one component is semi-metallic while the other is a normal semiconductor.

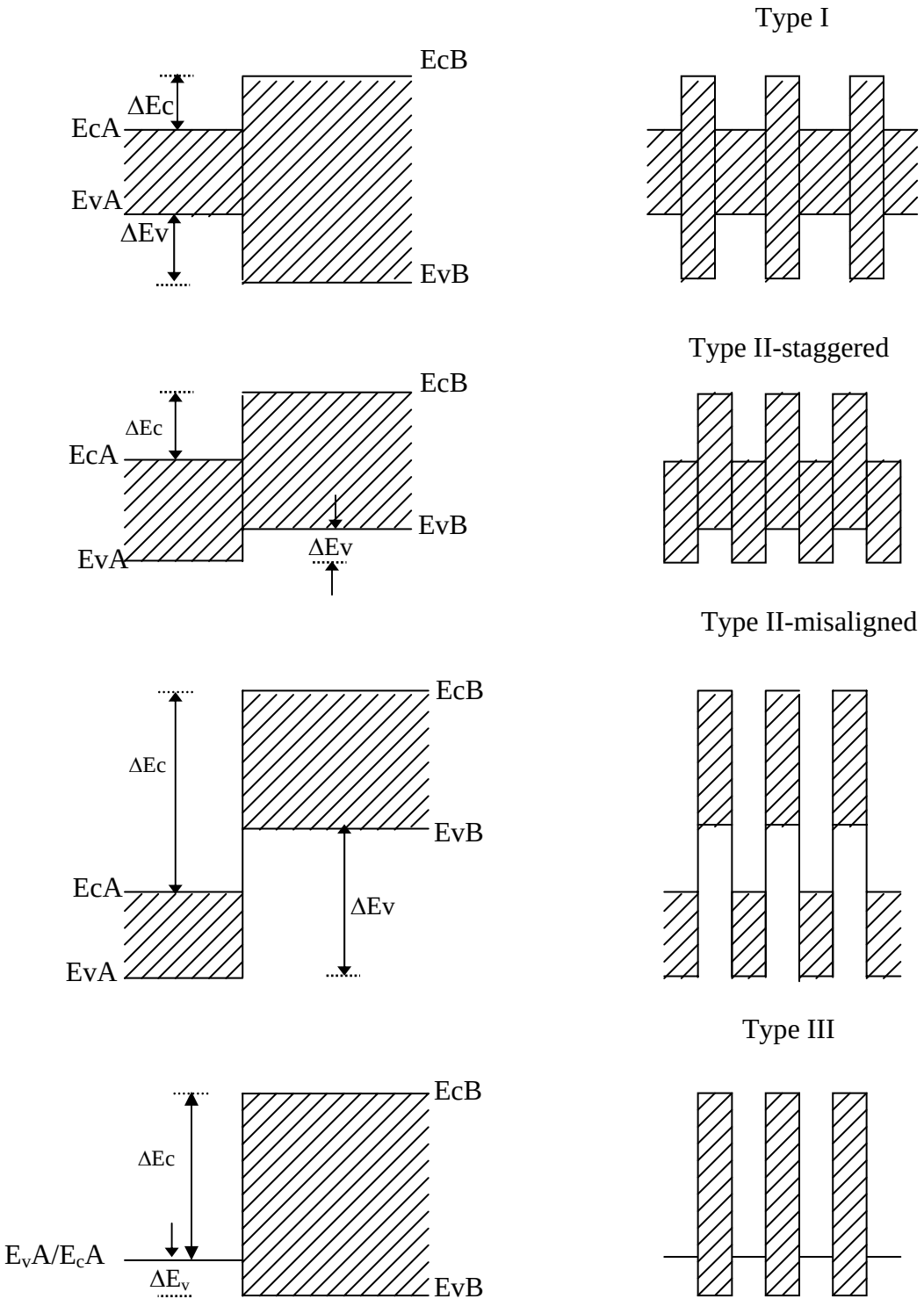


Fig 11: Band alignments of two components $(A)_x$ and $(B)_x$ in copolymers $(A_mB_n)_x$ in four different classes of copolymers; Type-I, Type-II staggered, Type-II misaligned and Type-III.

The electronic DOS of some model periodic and aperiodic copolymers belonging to the class of Type–I and Type–II staggered have been calculated by Bakhshi. There have also been quite interesting investigations of the various types of copolymers recently.These include systems such as cyclodiborazane – dithiafulvene copolymers, copolymers of fluorine – and alkoxy – substituted poly (p-phenylenevinylene), diol-type copolymers, carbazole-quinoline and phenothiazine-quinoline copolymers and (pyrrole-g-caprolactone) copolymers. Highly conductive new aniline copolymers containing butylthio subsituent have also been studied. Copolymers of aniline with o- or m- toluidine and o-ethyl aniline have also been reporte. It has been found that these copolymers of aniline with substituted anilines show fairly good conductivity. The electronic properties of the hypothetical thiophene copolymers : poly(thienylenecyclopentadienylene) (PThS), poly(thienylene-oxocyclopentadienylene) (PthOPD) and poly(thienylenethiocyclypenta-dienylene) (PThTPD) have also been investigated theoretically.The calculated electronic properties of the copolymers are found to be about the average of the properties of the two corresponding homopolymers. Many other copolymers including (thienylene) – (1,6-dithienyl hexa-1,3,5–trienylene) copolymers, polypyrrole (PPy) and polyiso-naphthpyrrole (PINPy) copolymers,copolymers of pyridine with thiophene, N-methyl-pyrole and selenophene have also been the subject of study.

Applications of Conducting Polymers

The conducting polymers have a wide range of applications in electronic and opto-electronic devices such as sensors, plastic batteries, solar cells, field effect transistors, optical data storage, organic electro-luminescent devices, switching devices, frequency doubles and many more. Some of these important applications of conducting polymers are discussed here:

1. Light Weight and Rechargeable Batteries: This is one of the most publicized and promising application. In polymers where both p- and n- doping processes are feasible, the possibility exists of their use as both positive and negative electrodes in the same battery system. Some prototype cells are comparable to, or better than nickel-cadmium cells now in the market. The polymer battery, such as polypyrrole-lithium cell operates by the oxidation and reduction of the polymer backbone. During charging the polymer oxidizes anions in the electrolyte that enter the porous polymer to balance the charge created. Simultaneously, lithium ions in electrolyte are electrodeposited at the lithium surface. During discharging electrons are removed from the lithium, causing lithium ions to reenter the electrolyte. The positive sites on the polymer are reduced, releasing the charge-balancing anions back to the electrolyte. This process can be repeated about as often as in a typical secondary cell.

The above mentioned principle has also been used to make PA batteries with the following configuration in its fully discharged state .

$$(CH)_x / LiClO_4 – PC/(CH)_x$$

PA battery has higher energy and power densities as compared to ordinary batteries. The polymer electrode batteries have a longer shelf life than the metal electrodes of the ordinary batteries because the ions involved in the delivery and storage of charge come

from the solution rather than from the electrodes themselves and therefore these electrodes are saved from mechanical wear brought about by the dissolution and the redeposition of electrode materials that takes place during charge discharge cycles in ordinary batteries. The targets for a high energy density battery have been described as : spesific energy – 180 W h kg $^{-1}$, energy density – 360 W h dm^{-3} and cycle life - >500. Another advantage of polymer electrode batteries is the absence of toxic materials in them and therefore disposal problems are minimized. These batteries could be a potential breakthrough in the making of an electric car since these light weight batteries would not weigh a car down to the extent as the heavy lead acid batteries would do.

The Bridgestone Corporation of Japan have developed coin type rechargeable polymer lithium batteries with a conducting polymer polyaniline and the higher capacity lithium aluminium alloy as the two electrodes. One of the unique features of this rechargeable polymer lithium battery is that it can be used as a power source in combination with solar cells.

2. Solid State Batteries : The application of intrinsically conducting polymers in solid-state lithium ion polymer batteries has generated a lot of interest during the past few years. Batteries with high energy density and with full solid state configuration for both electrodes and electrolyte (crystalline, glassy and polymeric) using electrically conducting polymers have been studied both experimentally and theoretically. An iodine-doped PA film is placed in direct contact with a lithium disk in a Li/I_2-PA solid state battery . Contact between lithium and iodine doped PA brings about immediately a reaction with the formation of lithium iodide.

$$\mathbf{2x\ Li + CH\ (I_2)_{yx} \rightarrow 2x\ (1–n)\ Li + CH\ (I_2)_{y–nx} + 2xn\ LiI.}$$

These types of batteries have high durability and reliability. Using thin films of conducting polymers, these solid state batteries may provide plasticity – a feature which would be highly welcome in various applications. Study of polypyrrole (PPy) / polyimides (PI) composite has also shown its promising properties and potential for use in polymer lithium ion batteries and in supercapacitors. PPy film was found to be switchable between the anion – and cation-exchange states and PI was chosen as a matrix for polymer filled conducting composites because it possesses electroactivity and excellent mechanical properties. Thus, PPy/PI conducting composite is studied for application as a solid polymer electrolyte for lithium ion batteries. Lithium manganate / manganese composite oxides and lithium ion secondary batteries have also been synthesized.

3. Electroluminescent Devices: Electroluminescence – the generation of light, other than blackbody radiation, by electrical excitation – is a phenomenon that has been seen in a wide range of semiconductors, and for organic semiconductors was first reported for anthracene single crystals in the 1960s.These early studies established that the process responsible for electroluminescence requires injection of electrons from one electrode and holes from the other, the capture of oppositely charged carriers (so-called recombination), and the radiative decay of the excited electron-hole state (exciton) produced by this recombination process**.**

Since the first report of metallic conductivities in ‘doped’ polyacetylene, the science of

electrically conducting polymers has advanced very rapidly. More recently, much of a interest is shown in LEDs containing conducting polymers. Polymer LEDs now show attractive device characteristics, including efficient light generation, and there are several development programmes now set up to establish procedures for manufacture. The principal interest in the use of polymers lies in the scope for low-cost manufacturing, using solution-processing of film-forming polymers.

i)Polymer LED structures: Conjugated polymers derive their semiconducting properties by having delocalized π-electron bonding along the polymer chain. The π (bonding) and π*(antibonding) orbitals form delocalized valence and conduction wavefunctions, which support mobile charge carriers. Electroluminescence from conjugated polymers was first reported in 1990, using poly (p-phenylene vinylene), PPV was used as a single semiconductor layer between metallic electrodes. In this structure, the ITO layer functions as a transparent electrode, and allows the light generated within the diode to leave the device. The top electrode is conveniently formed by thermal evaporation of a metal. LED operation is achieved when the diode is biased sufficiently to achieve injection of positive and negative charge carries from opposite electrodes. Capture of oppositely charged carriers within the region of the polymer layer can then result in photon emission.

Diodes of this type can be readily fabricated by solution-processing the semi-conducting polymer onto the ITO-coated glass, even though the film thickness is no more than typically 100 nm. Spin-coating from solution has been demonstrated to be capable of producing highly uniform layer thickness, with a thickness variation of no more than a few angstroms spread over several cm^2. Electrodes are chosen to facilitate charge injection; ITO has a relatively high work function and is, therefore, suitable for use as a hole-injecting electrode; low-work function metals such as Al, Mg or Ca are suitable for injection of electrons.

PPV has an energy gap between π and π* states of about 2.5 eV, and produces yellow-green luminescence in a band below this energy, with the same spectrum as that produced by photoexcitation. We note that it shows broadening due to vibronic coupling, as is characteristic for optical transitions in molecular semiconductors where the excited state is confined to the semiconductors where the excited state is confined to the molecular unit, and is described as an exciton.

The levels of efficiency of the first, simple LEDs based on PPV, which were fabricated with aluminium negative electrodes, were relatively low, of the order of 10^{-4} photons generated within the device per electron injected (an internal quantum efficiency of 0.01%). These values have risen rapidly over the past 5 years as improved understanding of the operation of these devices, aided in considerable measure by parallel developments made with sublimed molecular film devices, has allowed considerable optimization of the device characteristics. The use of negative electrodes with lower work functions was shown to improve efficiency, and for single-layer diodes,an external efficiency of about 2 lumens per watt (2 lm W^{-1}) has been reported in devices made with ITO/MEH-PPV /Ca. Other early approaches used to increase efficiency include the use of copy polymers

based on PPV with higher luminescence efficiencies, and the use of hetero structure devices. More recently, very much higher efficiencies have been reported for diodes with single layer structures, but with a layer of poly(dioxyethylene thienylene) doped with polystyrene sulphonic acid between the ITO and the emissive polymer layers. Efficiencies in the green part of the spectrum of up to 16 lm W^{-1} are reported for diodes using copolymer 4 with composition x = y = 47%, z = 2% , and up to 22 lm W^{-1} for emissive polymers based on polyfluorene.

ii) Device operation: As described above, polymer LEDs operate by the injection of electrons and holes from negative and positive electrodes, respectively. Electrons and holes capture one another within the polymer film, and form neutral bound excited states (termed excitons). Excitons in conjugated polymers are generally considered to be more strongly localized than excitons in three-dimensional semiconductors, not least because the exciton is substantially confined to a single polymer chain. The spin wavefunction of the exciton, formed from the two spin-½ electronic charges, can be either singlet (S = 0) or triplet (S = 1), and a consequence of the confinement of the excitation is that the energy difference between singlet and triplet (the exchange energy) may also be large. Spin-allowed radiative emission (fluorescence) is from the singlet only, and when the exchange energy is large, cross-over from triplet to singlet is unlikely, so that triplet excitons do not produce light emission, other than by indirect processes such as triplet-triplet annihilation, or by phosphorescence.

The **internal quantum efficiency** η_{int}**,** defined as the ratio of the number of photons produced within the device to the number of photons produced within the device to the number of electrons flowing in the external circuit, is given by:

$$\eta_{\text{int}} = \gamma r_{st} q$$

where $\boldsymbol{\gamma}$ is the ratio of the number of exciton formation events within the device to the number of electrons flowing in the external circuit, $\mathbf{r_{st}}$ is the fraction of excitons which are formed as singlets, and **q** is the efficiency of radiative decay of these singlet excitons.

As we discuss below, the efficiency of radiative decay depends on the device structure, being strongly affected by the photonic structure of the device (for example, the proximity of metallic mirrors).In order to achieve efficient luminescence, it is, therefore, necessary to have good balancing of electron and hole currents, efficient capture of electrons and holes within the emissive layer, strong radiative transitions for singlet excitons, and efficient coupling of these excitons to photon states allowed in the device structure.

iii) Efficiency and stability: The model for device operation of polymer LEDs sets some limits to the efficiency of operation. From the above equation, we see that three factors are involved:

(1) Charge balancing, covered by γ, is in principle capable of reaching high values, particularly for hetero-junction devices.

(2) Recombination, covered by r_{st} is limited to 25 per cent if the creation of excitons is in the ratio 3:1 triplet:singlet.
(3) Radioactive emission from excitons, covered by $r_{st}q$ has now been measured in realistic conditions (the presence of electrodes), and there is rapid progress in obtaining high efficiencies.

iv) Towards applications: The performance of organic LEDs meets many of the targets necessary for applications in displays. Backlighting and segmented displays have been identified for early products by Philips, and this company has announced the setting up of a pilot line at Heerlen. Passive matrix-addressed displays are attractive, as the device construction is relatively simple. However, this does require that pixels are driven, row by row, under puled conditions, and both resistive losses in the conductive tracks and efficiency reductions for the diodes at high current densities limit the pixel number. Such displays have been developed with the sublimed molecular film devices of alphanumeric displays (64 x 256), where average luminances of around 100 cd m^{-2} are required (this is a typical computer monitor level), and as far as a ¼-sized VGA display (320 x 240). Extension to a full colour graphic display (for computer monitors and for video display) is very attractive, not least because organic LEDs provide full viewing angle and video-rate response times (in contrast to current liquid-crystal display technology). However, this required red, green and blue colours with appropriate chromaticity, methods for colour patterening, and also new addressing schemes. Rapid progress is being made with these three problems. Development of full colour has been reported, both for sublimed films and for polymer. Solution-processing of polymers offers new methods for colour patterning, among which there is particular interest in ink-jet printing, to place separated pixels of red, green, and blue-emitting polymers onto the prepared substrate. This is being developed by **Seiko-Epson and Cambridge Display Technology,** and the use of ink-jet printing has also been reported by other groups. Active-matrix transistor arrays, modified from those at present used for liquid-crystal displays, can now provide sufficient current-driving capability to meet the requirements of organic LEDs. This is made possible by the improved properties of polycrystalline silicon compared to those of amorphous silicon, and demonstrator active-matrix polymer displays have been made.

4. Transistors: Some doped polymers and oligomers show excellent semiconductor properties such as electron/hole mobility. With the additional advantage in terms of easier processability that these systems possess over conventional semiconductor materials, organic materials are promising candidates for the fabrication of electronic devices such as field effect transistors. One of the widely investigated applications of organic semiconductors is as thin film transistors (TFT's).

The basic function of a field effect transistor consists of controlling a current across two terminals called the source and the drain, in response to a voltage applied (gate voltage) at a third terminal (gate). The transistor could thus function as a switching device or as an amplifier. The utilization of a molecular material in a TFT can be illustrated by the following example, which also highlights the crucial control of device characteristics using molecular properties. Doped polythiophenes have been extensively studied as conducting polymers. It has been found that oligothiophenes like a-sexithienyl are

excellent semiconductors and can be used to make thin film transistors. An SiO_2 film is grown on an n-type silicon wafer and the oligomer film is deposited on the organic film to serve as the source and the drain. A contact deposited on the n-Si wafer serves as the gate of the TFT. When a variety of oligothiophenes were studied, it was found that the field effect mobility of this transistor peaked for the α-6T oligomer. **α-6T has a room temperature conductivity of ~10^{-6} Scm^{-1} and field effect mobility of 5 x 10^{-4} cm^2 $V^{-1}s^{-1}$**. For shorter oligomers the limited π-conjugation leads to high resistivities typical of insulators. Interestingly, in a longer oligomer like α -8T, even though the conductivity remains comparable to that of α -6T, the field effect mobility decreases. This is attributed to the possibility of formation of larger number of disorders as the oligomer length increases. One possible source of disorder is the formation of α, β'-type linkages. The probability of formation of such disorders increases with increasing length of the oligomer. For this reason, it is argued that TFT's based on oligomeric semiconductors are superior to those based on polymeric ones. Molecular design can thus be effectively used to control the device characteristics of these thin film transistors.

Since oxidation or reduction using hole or electron doping respectively can regulate the conductivity of these organic semiconductors, it is possible to devise transistors whose characteristics are controlled by the chemical medium by which they are surrounded with. This opens up possibilities for applications such as sensors.

Most conventional techniques for fabrication of such sidewalls are based on photolithographic patterning reactive ion etching or anisotropic wet chemical etching. Application of these techniques to polymer multilayer structures is difficult because of plasma-induced degradation of electroactive polymers and the lack of anisotropic etching techniques for polymers.

Different patterning techniques for low-cost fabrication of solution-processible polymer field-effect transistors (FETs) have been demonstrated, including photolithographic patterning, screen printing, soft lithographic stamping, micromolding in capillaries, and high-resolution inkjet printing. These techniques allow accurate definition of polymer patterns with micrometer resolution, but they do not permit the formation of vertical sidewalls and, with some exceptions such as near-field photolithography, their extension to submicron resolution patterning is complex and becomes more expensive the higher the required resolution.

Architecture: The transistor, in its various forms, is a three-terminal amplifying electronic device. The organic transistors fabricated to date have used a conventional 'field-effect' architecture; unfortunately, such devices involve relatively long conduction pathways which, owing to the low carrier mobilities of the organic materials, render them inherently slow. In an attempt to circumvent this problem, Yang and Heeger have developed different device geometry, more closely related to that of the vacuum-tube triode. The structure consists of a thin film of a semiconducting polymer sandwiched between two electrodes, with the third electrode – a layer of a porous metallic polymer – embedded within the semiconductor. The third electrode plays a role similar to that of the grid in a vacuum electrode. This thin-film architecture reduces the length of the conduction pathway, resulting in a relatively fast response time and, in contrast to

conventional field-effect transistors, does not require lateral patterning.

5. Conjugated Polymer Actuators: Conjugated polymer actuators which are based on conjugated polymers are studied here. These devices undergo volume changes during oxidation and reduction and are primarily used in biomedicine and biotechnology. The use of conjugated polymers as volume-changing materials began in the 1980s, primarily in bilayer device. One layer of the bilayer was typically a passive substrate onto which the active conjugated polymer layer was applied.

Bilayers were initially used to determine the amount of volume change mechanisms. Bilayers provided a simple way to study classical conjugated polymers, such as polypyrole, polyaniline and polythiophenes. The active polymer layer was deposited onto a substrate, usually by electrochemical synthesis.Under electrochemical oxidation and reduction, volume change in the active layer forced the assembly to bend, and the direction and magnitude of volume change could be deduced from the direction and degree of bending. Such bilayer structures were typically a few centimeters long and a few millimeters wide. These studies showed that the volume change in the conjugated polymer is dominated by ionic movement into and out of the polymer.

As mentioned above, the volume change of conjugated polymers is controlled by electrochemical processes, which cause ion insertion and de-insertion. There are two possibilities for ion flow.

- For a polymer (P) doped with a large immobile anion A^- in contact with an electrolyte containing a small mobile cation M^+

$$P^+(A^-) + M^+(aq) + e^- \leftrightarrow P^0(A^-M^+) \quad (1)$$

  i.e., cations are inserted and de-inserted.

- For a polymer doped with a small mobile anion in contact with an electrolyte containing both mobile cations and anions

$$P^+(A^-) + e^- \leftrightarrow P^0 + A^-(aq) \quad (2)$$

  i.e., anions are inserted and de-inserted.

In the former case, the volume expands in the reduced state of the polymer (a negative potential) and in the latter case, the volume typically expands in the oxidized state (a positive potential). In the latter case, there may be two moving species because not only reaction 2 occurs but reaction 1 can also occur, which can lead to a **"twitching" behaviour**. For monotonic motion, it is preferred to have only one moving species. Another detrimental effect that can occur with mobile cations and anions is **salt draining** over extended times in the reduced state. Both types of ions leave the polymer

$$P^0(A^-M^+) \leftrightarrow P^0 + A^-(aq) + M^+(aq) \quad (3)$$

For our microactuators, we normally use polypyrole (PPy) doped with the large immobile anion dodecylbenzene sulfonate (DBS) and an aqueous electrolyte of 0.1 M NaDBS.

The volume change is induced by changing the potential and thus altering the oxidation or reduction state of the conjugated polymer. Not only can we switch from completely oxidized or reduced states but we can also use intermediate states and thus achieve intermediate bending angles, both statically and dynamically.

To drive the actuators electrochemically, an ion source/sink is needed. Aqueous electrolytes have been demonstrated in macroactuator. In these devices, the polymer electrolyte is sandwiched between two conjugated polymer layers, which generate the bending force. The use of polymer electrolytes enables operation in a normal laboratory environment instead of in a liquid electrolyte. Another way to achieve operation of electroactive polymer actuators in air is to encapsulate the complete device: the electroactive polymer layer, a hydrogel electrolyte, and the counter electrode.

Because ion transport is controlled by diffusion, we thought that the classical conjugated polymers would be unsuitable for macroscale actuators; thick layers would require too much time for operation. It may be possible to engineer the materials so that they contain pathways for ionic transport, but this approach would require novel materials. We attempted to use cross-linked conjugated polymer gel electroelastomers as actuators; however, volume change in those materials was too large for use in bilayer structures,and their elastic modulus was too low. If thin layers of classic conjugated polymers were to be used, the speeds would be acceptable, but the forces would be small on the macroscopic scale.

On the microscopic scale however, the forces would be large, so microactuators would be practical. We started with devices with millimeter dimensions and made Au/PPy bilayers on a silicon wafer that curled under electrochemical control.This work demonstrated that standard methods of photolithography could be used to prepare mini-actuators. It was possible to actuate the polymer and Au bilayers even if the polymer thickness was < 1 μ m, which is much thinner than previous actuators (150 to 200 um). The road to microstructures was thus open.

6. Electromagnetic shielding: The dissipative abilities of polymers also make them ideal for electromagnetic shielding. By coating the inside of the plastic casing with a conductive surface, this radiation can be absorbed. This can best be achieved by using conducting plastics, which have good adhesion and thus give a good coverage and good thickness. Incorporated into computer cases, conducting polymers can block out electromagnetic interference in the megahertz range.

7. Printed circuit boards: Many electrical appliances use printed circuit boards. These are copper coated epoxy-resins. The copper plating is not very selective and adhesion is generally poor. This process is being replaced by polymerization of a conducting plastic. If the board is etched with potassium permanganate solution, a thin layer of manganese dioxide is produced only on the surface of the resin. This will then initiate polymerization of a suitable monomer to produce a layer of conducting polymer. This method is much cheaper, easy and quick to do and the adhesion achieved is also quite good.

8. Molecular electronics: Molecular electronics concerns itself with the electronic structures assembled atom by atom. One proposal for this method involves conducting polymers. A possible example is a modified PA with an electron-accepting group at one end and an electron-withdrawing group at the other. A short section of the chain is saturated in order to decouple the functional groups. This section is known as a spacer or a modulator barrier. This can be used to create a logic device. There are two inputs, one light pulse which excites one end and another which excites the modulator barrier. There is one output, a light pulse to see if the other end has become excited. To use this, there must be a great deal of redundancy to compensate for switching errors. Depending on the conducting polymer chosen, the doped and undoped states can be either colorless or intensely coloured.

9. Artificial nerves: Due to biocompatibility of some conducting polymers, they may be used to transport small electrical signals through the body, i.e. they act as artificial nerves.

10. Chemical, biochemical and thermal sensors: The chemical properties of conducting polymers make them very useful in sensors. This utilizes the ability of such materials to change their electrical properties during reaction with various redox agents (dopants) or via their instability to moisture and heat. An example of this is the development of gas sensors.It has been shown that polypyrrole behaves as a quasi 'p' type material. Its resistance increases in the presence of a reducing gas such as ammonia and decreases in the presence of an oxidizing gas such as NO_2. The gases cause a change in the near surface charge carrier (here electrons or holes) density by reacting with surface absorbed oxygen ions. An ideal chemical sensor should exhibit high sensitivity, selectivity, high operation speed, reversibility and stability under operating conditions and conducting polymers meet the above requirements.Conducting polymers such as polyfulvenes (PFV) and polythiophene (PTP) are expected to have profound uses in humidity sensors and radiation detectors. Another type of sensor developed is biosensors. This utilizes the ability of tri iodide to oxidize PA as a means to measure glucose concentration. Glucose is oxidized with oxygen with the help of glucose oxidase. This produces hydrogen peroxide which oxidizes iodide ions to form tri iodide ions. Hence, conductivity is proportional to the peroxide concentration which is proportional to the glucose concentration.

Suggested Reading:

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