

Polymeric phthalocyanines and other electrically conducting polymers for electronic and photonic applications—A review[†]

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Polymers are generally insulators and to exhibit electrical conductivity they must have ordered conjugation with extended pi electrons and large carrier concentrations. This review summarises the various methods of making conjugated polymers by either addition or condensation reactions of monomers by chemical or electrochemical routes. These reactions can follow either a direct route or an intermediate precursor route, followed by elimination, addition or isomerization reactions. Conjugated polymers are made conductive generally by doping or by thermal treatment. The doped polymers have limitations like poor stability, poor processibility and corrosivity. This review lists the various methods adopted for overcoming these drawbacks. The review also gives an account of various types of phthalocyanine polymers that have been prepared in our laboratory, and their electrical and magnetic properties. The conductivity of these polymers increases by seven orders of magnitude by thermal treatment. These polymers have suitable structures that facilitate solitonic, polaronic and bipolaronic conformations leading to large, ultra-fast nonlinear optical processes. The peripheral functional groups can be used for structural modifications to improve processibility and allow fabrication of various device structures such as films, channel wave guides, planar wave guides, fibres, etc. The presence of macrocyclic structures in these polymers imparts mechanical, thermal and environmental stabilities. Conjugated polymers, including phthalocyanine polymers, also exhibit nonlinear optical properties because of their response to high intensity radiations like laser. The requirements of organic molecules and polymers to have $\chi^{(2)}$ and $\chi^{(3)}$ properties, and the various methods used to study their behaviour as well as techniques employed to improve the nonlinear optical response are also discussed. The various methods that have been used to synthesize ladder polymers with solubilising groups for processibility have also been discussed.

Introduction

Organic and metallo organic polymers have attracted wide attention for their electrical, electronic, nonlinear optical, electrochemical and photochemical applications¹⁻¹¹. For polymers to exhibit electrical conductivity, ordered conjugated structures with extended pi electrons and large carrier concentration are prerequisites. The general process involves the synthesis of conjugated polymers followed by incorporating the required charge carrier in desired concentration.

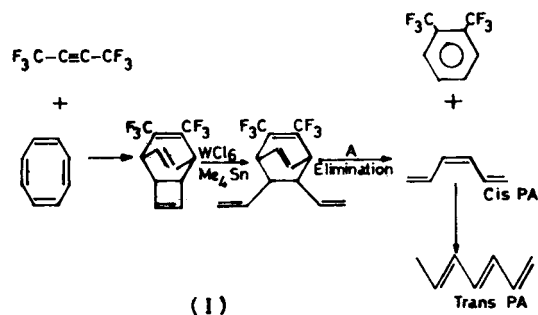
The electrical conduction behaviour in these polymers has been extensively studied. Novel conduction mechanisms involving coupling of electronic excitations to nonlinear conformations have been proposed^{1,2,4}. Dopant induced bond alterna-

tion defects such as solitons, polarons and bipolarons are associated with bulk electrical conductivity which is enhanced by doping or photo excitation^{2,12-14}.

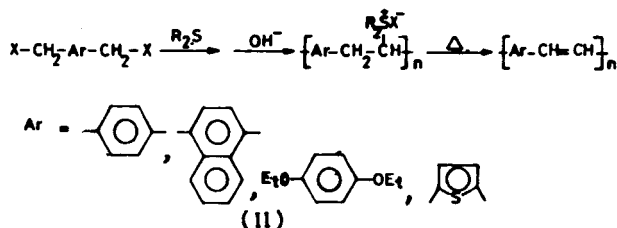
Organic conjugated polymers are synthesized either by direct or by indirect approach. The direct approach involves the conversion of the monomer to polymer by either addition or condensation polymerisation. The indirect route involves the preparation of the precursor polymer (either through addition or condensation polymerization), followed by a variety of reactions such as elimination, addition, isomerization, etc. The most popular conductive polymer, viz., polyacetylene (PA), is made by addition polymerization of acetylene gas, which is passed through a solution containing Ziegler catalyst, $\text{Ti}(\text{OBu})_4\text{-Al}(\text{Et})_3$, or Luttingers catalyst, $\text{NaBH}_4 + \text{Co}(\text{NO}_3)_2$ (refs 15-17). Depending upon the temperature of polymerization, *cis* or *trans* PA can be obtained. Film

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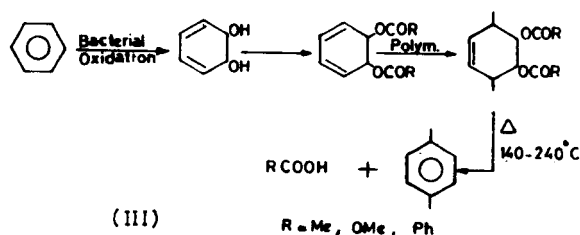
thickness can be controlled by the pressure of acetylene gas, time of reaction and amount of catalyst used^{18,19}. The electrochemical route gives conjugated polymers as peelable films on an electrode surface. It offers precise control on the thickness and electrical conductivity of the film, which is effected by varying the current density, solvent, supporting electrolyte, nature of electrolytes, etc.²⁰. Other conjugated polymers like poly(*p*-phenylenes) (PPP), polyphenylene sulphide (PPS), polyquinolones (PQL), and ladder polymers of the benzimidazo benzophenanthrolene (BBL) type are prepared by condensation polymerization²¹. The polymers made by either addition or condensation routes via chemical or electrochemical polymerization techniques are intractable, and hence efforts are now concentrated on the preparation of melt and solution processible polymers with minimum defects and a high degree of chain alignment. One of the most innovative and useful techniques for the preparation of conducting polymers has been the synthesis of highly soluble precursor polymers, that can be easily handled in solution, purified and then later converted to the less tractable conducting polymer. The first example was the dehydrohalogenation of polyvinyl chloride (PVC)²². This reaction, like most elimination reactions on polymers, rarely goes to completion. The Durham route to polyacetylene (PA) developed by Feast *et al.*²³ involves meta-thesis polymerization of Diels Alder adduct of cyclooctatetraene and substituted acetylene to give a soluble and thermally unstable polymer precursor. This undergoes retro-Diels Alder reaction slowly at room temperature or more rapidly at 80°C, yielding amorphous PA eliminating a substituted benzene as shown in (I) (ref. 23).



By choosing the appropriate monomers, retro-Diels Alder reaction can be controlled. Poly(phenylene vinylene) (PPV) has been synthesized²⁴ via a soluble precursor route, yielding the product via the elimination of HCl and dimethyl sulfide as shown in (II).



Poly-*p*-phenylene has also been synthesized via polymerisation of soluble derivatives of 5,6-dihydroxycyclohexa-1,3-diene, which is prepared by bacterial oxidation of benzene. These derivatives are polymerised using free radical initiators to give soluble precursors, which on thermolysis yield poly-*p*-phenylenes as shown in (III) (ref. 25).



Methods of doping organic conducting polymers

The conjugated polymers are made conductive by doping which is carried out through chemical route, electrochemical route, or photochemical route. Doping reactions are characterized by charge transfer from the dopant to the polymer or vice versa. An ionic state of the polymer, delocalised along the backbone, is formed with a counterion derived from the dopant. Conductivity of the doped material is varied and controlled by the amount of dopant used. Polymers such as polyacetylene (PA), polyphenylene (PPP), polyphenylene sulphide (PPS), polypyrrole (PPy), polythiophene (PT) and polyquinolene (PQL) are doped by either chemical or electrochemical means and conductivity ranging from 1 to 2000 S/cm has been achieved^{19,26-35}. Stretch orientation of doped polyacetylene has improved the electrical conductivity to values above 10⁵ S/cm (ref. 36). Highly conjugated polyparaphenylene (PPP) has been shown to have a conductivity of 10⁴ S/cm (ref. 37).

In electrochemical doping, the polymer to be doped is used as one of the electrodes in an electrolytic cell in which the electrolyte contains the ion for doping. For p type doping, the polymer is used as anode, while for n type doping the polymer acts as cathode. The degree of doping depends on the dopant concentration, voltage applied and the amount of charge passed.

Polymers that become conductive upon doping

can be classified into two categories³⁸. The first category is that in which polymers form simple charge transfer complexes with donors or acceptors, e.g. PA doped with Na forms n-type semiconductor or PPP doped with AsF₅ forms p-type semiconductor. These polymers are useful for applications where variable conductivity is needed, i.e., the polymer is used both as a conductor and as a non-conductor. The switching of non-conductive state to conductive state is reversible and this is controlled by the amount of dopants. This phenomenon is made use of in secondary batteries, visual displays and variable transmission shields. This category of polymers is characterised by broad valence band and low ionisation potential for p-type conductors and by broad conduction band and high electron affinity for n-type conductors. In the second category, the polymers become highly conductive due to formation of new covalent bonds either during the doping process or during other treatment. When polyphenylene sulfide is doped with AsF₅, the latter introduces covalent bonds or crosslinking in addition to partial oxidation. The polymer undergoes irreversible changes during the doping process. The polymerization energy decreases and the band width increases on doping. While these polymers are not suitable where doping/dedoping process is required for specific applications, they can be easily processed.

Photochemical doping calls for a compound whose photoproducts are effective dopants, e.g., diaryl iodonium salts³⁹, which on photolysis yield a proton acid which serves as a dopant. The method is selective; specific parts of the polymer can be doped. In most of the doped polymers, solitons (radical ions) or polarons form the chemical basis for their electrical conductivity as in other molecular metals¹⁶.

Most of the doped polymers have certain limitations^{1,2,11,13,14,16}: (i) they exhibit stable conductivity only as long as the dopants remain in the system, (ii) dopants often migrate out of the bulk of the polymer over a period of time and the conductivity of the polymer varies with the variation in the dopant concentration, (iii) the doped polymers have poor stability against heat, light, moisture and air, (iv) some of the dopants like I₂, AsF₅, Na, SO₃ are corrosive, and (v) the doped polymers have poor processability and show metal to semiconductor transition (Peierl's instability) at low temperatures.

Thermal treatment of polymers

Thermal treatment is also a method which is

used for the improvement of electrical conductivity of polymers⁴⁰⁻⁴⁸. This method appears to be advantageous, as conductivity can be controlled by varying the conditions of treatment. These systems have excellent stability towards environmental conditions such as heat, light, moisture and air. Improvement in electrical conductivity occurs due to the build-up of ordered polycondensed rings, allowing charge transport through charge-hopping and tunnelling between aromatized rings. These charge carriers are generated through formation of radical defects during the heat treatment. These materials show good thermal stability and stable conductivity and may find potential applications in the fabrication of devices and as matrix materials for advanced composites^{49,50}. Although they show large improvement in thermal properties and electrical conductivity, most of these polymers have poor processability.

Improvements in processibilities of conducting polymers

Various attempts have been made to improve the environmental stability of the doped polyacetylenes and its copolymers through external protection of the polymer by encapsulation in oxygen barriers such as glass, silicone rubber, polyethylene, polyurethanes, epoxy resins and poly-*p*-xylylene⁵¹⁻⁵⁵. The stability of conducting polyacetylenes and substituted polyacetylenes has also been improved to a limited extent by the use of classical antioxidants such as phenols and hindered amines⁵⁶⁻⁵⁸.

The choice of counter ion (anion or cation) has a major effect on the stability of conducting polymers⁵⁹⁻⁶³, in addition to its effect on mechanical properties. In air, the perchlorate and tetrafluoroborate salts of polypyrrole decompose and lose conductivity above 150°C, but polypyrrole-*p*-toluene sulfonate salts remain stable up to 280°C. The electro-polymerization of pyrrole in aqueous solution, in the presence of sulfonated cobalt phthalocyanine, form highly tractable films which exhibit better stability in air as compared to perchlorate doped material. The conductivity of the composite increased from 4 to 400 S/cm during 2 months of exposure to air⁶⁴. Pyrrole has been polymerized in the presence of the sodium salt of metallophthalocyanine polymer which exhibits stable electrical and electrochemical properties⁶⁵.

Electrical conduction requires conjugated structure, but this in turn makes the chain rigid and insoluble. The insolubility makes the polymer difficult to purify or properly characterize. Hence the

interest is in making soluble conducting polymers^{65b}.

The major requirement for making useful gadgets out of conducting polymers is to make them tractable. Some of the approaches that are adopted for this purpose are⁶⁶:

(i) the preparation of blends, dispersions and composites, (ii) the synthesis of random, graft and block copolymers, (iii) the use of precursor polymers that can be converted to conducting polymers by thermal and reactive treatments and, (iv) the use of solvents like molten iodine and $\text{AsF}_5\text{-AsF}_3$, that render some of the conductive polymers soluble.

Polypyrrole films formed in the presence of *p*-toluene sulfonate in acetonitrile gave a flexible polymer. Pyrrole electro-polymerized in the presence of a sulfonated styrene and hydrogenated butadiene yields a flexible polymer that can be melt-pressed to form conducting polymer plaques⁶⁷. Dodecylsulfate anion doped polypyrrole renders flexible conducting films with tensile strength of the order of 10 MPa (ref. 68).

Polymer blending or alloying is yet another approach to processible polymers. This can be achieved either by chemical or electrochemical means. For example, suspensions of polypyrrole have been prepared by chemical polymerization using ferric chloride in an aqueous solution of a high molecular weight polymer such as methyl cellulose or polyethylene oxide. They are used for making polymer composites used in all polymer secondary batteries⁶⁹.

Another technique for preparing soluble derivatives of intractable polymers is to add solubilising substituents to the monomer. Thus, insoluble polyphenylenes have been rendered soluble in common solvents such as chloroform by suitable substitution on the phenyl ring. They are rendered water soluble by introducing carboxyl terminals⁷⁰. Chemical and electrochemical polymerization of N-substituted pyrroles gave polymers of substantially lower conductivity as compared to that of unsubstituted polypyrrole⁷¹. Substituted pyrrole or thiophene having alkyl or alkoxyl group substitutions at 3 or 4 positions gave soluble and processible polymers⁷¹⁻⁷³. But long alkyl groups at the 3 or 4 positions reduces the conjugation length and hence the electrical conductivity due to steric effects^{74,75}. Dialkoxy substituted thiophene vinylene copolymers in which the vinylene units act as "spacer" to reduce steric interactions of substituents show improved processibility and electrical conductivity. The doped polymers are also transparent^{76,77}. By incorporating sulphonic or car-

boxylic acids in the alkyl substituent of the 3-alkylthiophenes, water soluble thiophenes have been prepared with excellent tractability and conductivity⁷⁸. To obtain highly conducting substituted polyheterocycles, an alkyl spacer is used to suppress electronic inductive effect of the hetero elements and avoid the effects of steric hindrance of the bulky groups on polymerization and conjugation in the macromolecules⁷⁹. Polypyrroles with enhanced redox reversibility by substitution of polyether chains at 3 position have been synthesized⁸⁰. Bipolymer complexes of polyethers and other conjugated polymers like polypyrrole and poly 3-methylthiophene are useful in sensors and activators^{10b}.

Phthalocyanines and their properties

Phthalocyanines and their polymers are known to have highly aromatic structures and excellent stability against heat, light, moisture and air. Moreover, they are soluble without decomposing in strong acids. Hence, they have attracted a great deal of attention in the search for environmentally stable electrically conducting materials⁸¹⁻⁸⁵. The electrical conductivity in these materials is associated with thermal or optical excitation of mobile pi electrons from the valence band containing the highest occupied molecular orbitals to the conduction band containing the lowest unoccupied molecular orbitals^{86,87}.

Simple monomeric phthalocyanines are insulators and they form stable and highly conductive charge transfer salts when partially oxidised with iodine⁸⁸. In these compounds the phthalocyaninato ligand (dianionic ligand) forces the central metal atom in a square planar configuration. The highly conductive material is built up of stacks of metallophthalocyanine units and chains of polyhalide anions, e.g., nickel phthalocyanine forms a complex with iodine whose formula is written as $(\text{NiPc})^{0.33+}(\text{I}_3^-)^{0.33}$ (ref. 89).

The single crystals of this compound show metallic conductivity, i.e., $d\sigma/dT$ is negative. In most of such compounds the electrical conduction occurs mainly through overlap of pi orbitals along the stacks of the ligands⁸⁸. Martinson *et al.*⁹⁰ have shown that in partially oxidised cobalt phthalocyanine (CoPcI_x), the conduction pathway is through metal-metal overlap, similar to that in Krogman salts⁹¹, where electron delocalisation occurs along the overlapping d_{z^2} orbitals of closely packed Pt atoms (Pt-Pt 2.9 Å) in the $\text{Pt}(\text{CN})_4^{2-}$ chains. The Co-Co spacing is 3.12 Å (ref. 89). This type of one-dimensional conductors is different from simple organic charge transfer complexes⁹², in which

strong electron donors, such as tetrathiofulvalene (TTF), are combined with strong electron acceptors like tetracyanoquinodimethane (TCNQ). In the latter, the transfer of electronic charge from the donor to the acceptor results in the formation of cation and anion radicals, which stack together as alternating columns within the crystal. The overlap of pi orbitals along these columns of radical ions causes their electrical conductivity. The electrical conductivity is very sensitive to the presence of impurities in the system⁹³. At low temperatures these charge transfer complexes including partially oxidised metallo macrocyclic compounds and doped conjugated polymers undergo metal to semiconductor transition (Peierl's transition)²⁸. This phenomenon is common to all one dimensional conductors.

Phthalocyanine polymers

Monomeric phthalocyanines are generally prepared by heating aromatic *ortho*-dinitriles or aromatic anhydrides in the presence of metal or metal salts, urea and catalysts^{85,94}. When the reaction is carried out with aromatic tetranitriles or dianhydrides such as 1,2,4,5 tetracyanobenzene (TCNB) or pyromellitic dianhydride (PMDA) instead of the difunctional dinitriles or anhydrides, polymeric phthalocyanines are formed⁹⁵⁻¹⁰⁰. The structural uniformity of the polymers obtained de-

pends on the reaction conditions and the method of recovery of the final polymer⁸¹.

There are several types of phthalocyanine polymers (Fig. 1a-d). Some of them are listed below:

1. Polymers in which benzene rings of phthalocyanine moieties are joined through one bond as in biphenyls¹⁰¹ and biphenylenes (Fig. 1a & a').
2. Polymers in which monomeric units are joined through substituents on benzene rings^{42,46,102,103} (Fig. 1b).
3. Those in which benzene rings of neighbouring phthalocyanine moieties are shared in common^{94,95,98,99} (Fig. 1c).
4. Those in which phthalocyanine rings are connected through atoms or ligands at the central metal atom, as washers threaded on to a shaft (bridge stacked polymers)¹⁰⁴⁻¹⁰⁸ (Fig. 1d).
5. Those in which phthalocyanine compounds are bonded to polystyrene or its copolymers^{81,109}.

The conductivity of different types of phthalocyanine polymers are given in Table 1. From Table 1 it is obvious that the electrical conductivity of the polymeric phthalocyanines is higher than that of unsubstituted monomeric phthalocyanines. This is probably due to the increase in extent of conjugation in the polymeric phthalocyanines which causes intramolecular charge transfer. Polymers of Type 2, in which phthalocyanine mo-

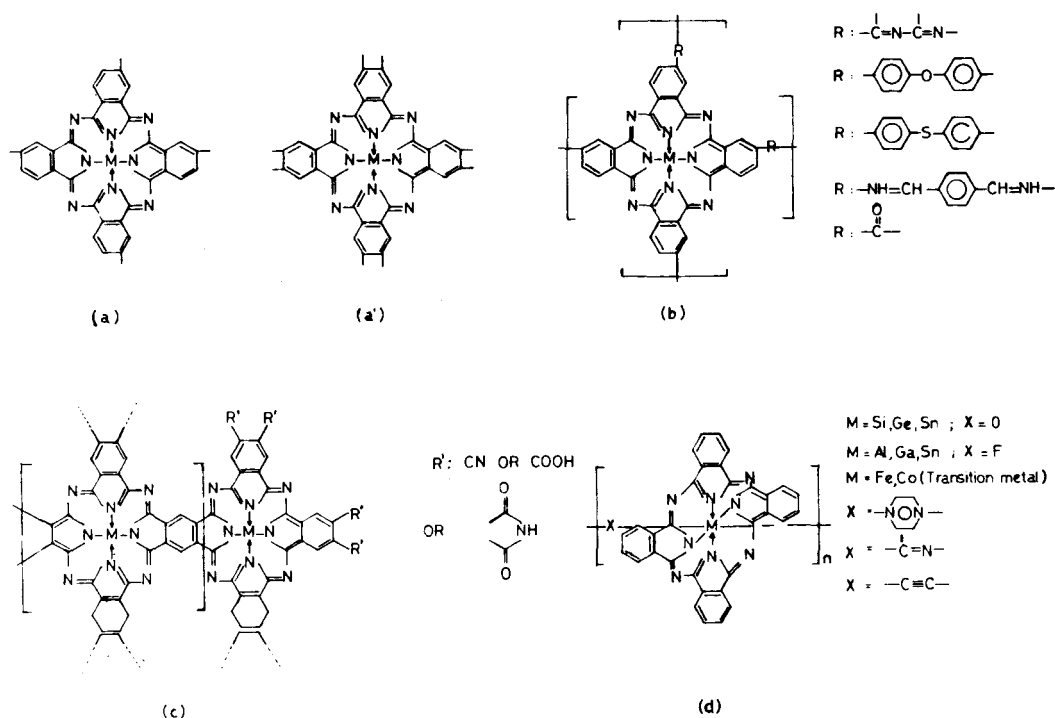
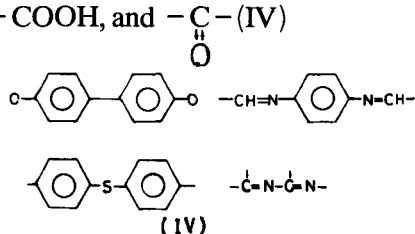


Fig. 1—Types of phthalocyanine polymers [a, Type 1; b, Type 2; c, Type 3; d, Type 4]

Table 1—Electrical conductivity of polymeric phthalocyanines

Compound	Type	Electrical conductivity (S/cm)	Ref.
Copper phthalocyanine Nickel phthalocyanine	Monomer	10^{-11} – 10^{-15}	88
Polymeric copper phthalocyanine	Polymer type 1	2×10^{-8}	101
Poly (copper octacyanophthalocyanine)	Type 2	6×10^{-7}	46
Polymer of bis-phthalonitriles (Thermally treated)	Type 2	10^2	41, 42
Poly copper phthalocyanine			
(i) with cyano end groups	Type 3	10^{-2}	124
(ii) with COOH end groups	Type 3	10^{-3}	124
Monomeric (phthalocyaninato silicon) dihydroxide, $\text{PcSi}(\text{OH})_2$	Monomer	6×10^{-9}	124
Polymeric (phthalocyaninato-1-siloxane), $(\text{PcSiO})_n$	Type 4	3×10^{-7}	124
μ -Cyano(phthalocyaninato cobalt III)	Type IV	4×10^{-2}	108
Octacyano copper phthalocyanine	Monomer	2×10^{-2}	124

ieties are connected through groups such as $-\text{CN}$, $-\text{COOH}$, and $-\text{C}(=\text{O})-$ (IV)



show large improvement in conductivity on heating^{41,42,46,110-112}.

Poly(copper octacyanophthalocyanine)⁴⁶ in which phthalocyanine moieties are connected through conjugated $-\text{C}\equiv\text{N}-\text{C}\equiv\text{N}-$ linkages (Type 2) has a conductivity of 10^{-7} S/cm. This increases by 8 orders of magnitude (10 S/cm) on heating, due to formation of conjugated network structures through opening of peripheral cyano groups.

Polymers of Type 3, that are prepared by heating pyromellitic dianhydride with metal salts, form sheet-like structures¹³ and have conductivities more than those of monomeric ones. The conductivity in polymers prepared from tetracyanobenzene¹¹⁴ is due to simple thermally activated hopping between adjacent sites and varies approximately as the square root of the applied pressure. The metallised polymers have higher conductivity than the unmetallised ones. Similar to monomeric phthalocyanines, polymeric phthalocyanines show improvement in electrical conductivity on doping with iodine¹¹⁵. In the latter case, however, the improvement in conductivity is only by 2-3 orders of magnitude as compared to monomeric phthalocyanines which show in conductivity of the order often on doping⁸⁸.

The conductivity of doped phthalocyanine po-

lymers depends on the nature of stacking of donor and acceptor units, their orientation and their repeat distances. Hence, the nature of stacking and the crosslinked structure of the polymeric phthalocyanine system are likely to introduce more randomness leading to lower conductivities¹¹⁵.

Polymers in which neighbouring phthalocyanine rings are cofacially stacked through substituent atoms such as F, O or ligands such as $-\text{C}\equiv\text{C}-$, $-\text{C}\equiv\text{N}-$, pyrazine, 4,4'-bipyridine, 1,4-dicyanobenzene attached to the central metal atom (Type 4), show large improvement in electrical conductivity on doping^{28,84,85,108,116}. Hanack *et al.*¹⁰⁸ have shown that cofacially stacked polymers of Fe, Co, Ru phthalocyanines through ligands such as pyrazine, 4,4'-bipyridine and 1,4-dicyanobenzene show both metal and phthalocyanine centered electrical conductivity. These polymers in which phthalocyanine moieties are joined through $\text{Si}-\text{O}-\text{Si}$ linkages with metal-to-metal distance of 3.33 Å has a conductivity of 10^{-7} S/cm, which improves to 1 S/cm on doping with iodine due to formation of segregated stacks of metallomacrocyclic cations and parallel arrays of polyhalide counteranions. In these metallomacrocyclic polymeric conductors, the pathways of conduction is through the pi system in the ligand columns. The conduction band of the partially oxidised $(\text{PCSiO})_n$ is composed of carbon p_π orbitals located near the macrocyclic core^{117,118}. It has been shown that there occurs minimal mixing between carbon p_π orbitals and Si or O orbitals in the highest occupied molecular orbital and the Si-O units do not play any direct role in the electronic conduction¹¹⁷⁻¹¹⁹. Variable temperature conductivity data in these systems have been fit-

ted to a fluctuation induced tunnelling model which is based on tunnelling between small metal particles in an insulating medium¹²⁰. The model is consistent with inhomogeneous nature of doping in these systems.

Theoretical studies on the bridge stacked metallophthalocyanines have shown that when the bridging group is an atom e.g., O, F and the central metal in the macrocycle is a non-transition metal, e.g., Al, Si, the inter-ring spacing determines the band structure. Both overlap and inter-ring spacing are also important for atom bridged polymers with a non-transition metal atom in the macrocycle. For diatomic and polyatomic bridging groups, e.g., $-C\equiv C-$, $-C\equiv N$, pyrazine, the band structure is determined by the overlap of the d_{xz} and d_{yz} orbitals of the metal and the pi orbitals of the bridging ligand¹²¹.

These materials have been incorporated in high strength polyamide fibre, e.g., Kevlar, and doped before and after extrusion to yield air stable conductive fibres which demonstrate conductivities upto 5 S/cm with metal-like properties (i.e., $d\sigma/dT$ is negative)^{122,123}.

Replacement of the central silicon atoms by Ge or Sn causes increase in metal-metal distance, and hence there is decrease in electrical conductivity due to diminishing of the intramolecular charge transfer^{120,124}. These doped bridge-stacked polymers retain their electrical conductivities only as long as the dopant molecules remain in the system. Like all other one-dimensional conductive polymers these polymers also are predicted to un-

dergo metal to semiconductor transition at low temperatures¹²⁰.

The metal to semiconductor transition in most of the one dimensional system can be overcome by improving interchain interactions. Such interactions in phthalocyanine polymers would be favoured by introducing electron-withdrawing substituents such as cyano group in the phthalocyanine rings. These substituents improve interchain charge transfer, e.g., low molecular weight octacyanophthalocyanines show high electrical conductivities of the order of 10^{-1} S/cm (Table 1) due to intermolecular charge transfer¹²⁴.

Thermal and chemical refinements of electrical and magnetic properties of polymeric phthalocyanines

In our laboratory different types of polymeric phthalocyanines have been synthesised and their electrical conductivity improved by effecting refinements in the polymers via thermal and reactive treatments^{110,112,125,126}. Polymeric phthalocyanines containing Cu, Ni and Co in which benzene rings are shared in common with macrocyclic phthalocyanine rings (Type 3) containing peripheral COOH groups have been prepared (Fig. 2). Thermal treatment of these polymers results in increase in the number of charge carriers and extended conjugated structures through decarboxylative polymerization reactions of the terminal COOH groups. The Co polymer exhibits larger conductivity (10 S/cm) than the Ni and Cu analogues. The ESR line width, magnetic susceptibility and electrical conductivity of the phthalocyanine polymers before and after thermal treatment are given in Table 2 (ref. 112).

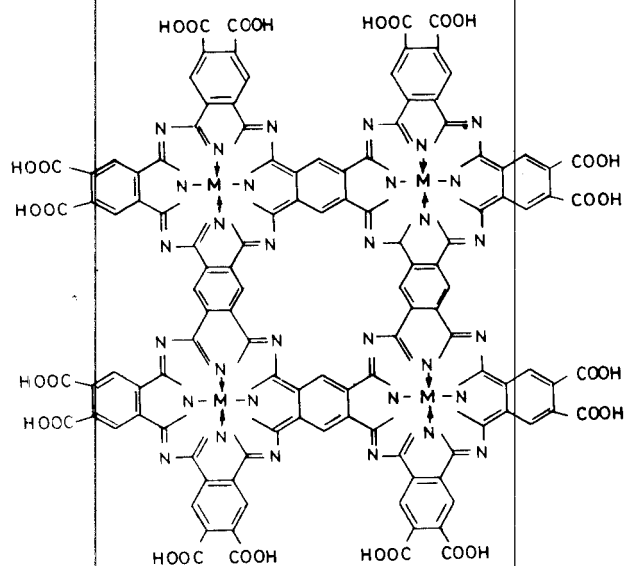


Fig. 2—Structure of metallophthalocyanine oligomers
[M = Cu, polymer IA; M = Ni, polymer IIA;
M = Co, polymer IIIA]

Table 2—Electrical conductivity, ESR linewidth and magnetic susceptibility of phthalocyanine polymers at 298 K (ref. 112)

Polymer†	Electrical conductivity (S/cm)	Peak to peak linewidth (mT)	Magnetic susceptibility (emu/g)
Polymer I A	9.8×10^{-6}	7.0	5.00×10^{-6}
Polymer I B	8.0×10^{-1}	15.0	1.80×10^{-5}
Polymer II A	4.0×10^{-7}	3.0	-3.12×10^{-7}
Polymer II B	2.33	144.0	3.12×10^{-4}
Polymer III A	2.0×10^{-8}	90.0	4.6×10^{-5}
Polymer III B	8.0	No signal	8.82×10^{-5}

†Polymer IA, IIA, and IIIA contain Cu, Ni, and Co respectively as the central metal atoms. Polymer IB, IIB and IIIB represent the corresponding heated samples.

In the heated polymers^{110,112}, the ESR line width decreases with increase in temperature, as in the case of lightly doped polyacetylene^{127,128}. The magnetic susceptibility of these polymers exhibits Curie-like behaviour^{110,112}, similar to polarons, bipolarons, solitons, etc.¹²⁷⁻¹³² in doped conjugated polymers like PA and PPP. The variable temperature study of ESR line width and intensity of the ESR signal width helps in understanding the nature of the charge carriers and confirms the presence of spinless dipolar charge carriers in the system¹¹⁰⁻¹¹².

The three-dimensional octacyanophthalocyaninato polysiloxane polymer (Fig. 3), on thermal treatment causes both lateral overlap of pi orbitals through formation of polycondensed ring structure via opening of terminal cyano groups, and, longitudinal overlap of phthalocyanine orbitals via formation of more Si—O—Si linkages¹¹¹. The bond-alternation structures are also shown in Fig. 3. Polymers possessing locked-in ladder type structures have also been prepared by condensing the terminal carboxyl groups of polymeric phthalocyanines with aromatic *ortho*-substituted tetraamines¹²⁵ (Fig. 4). The electrical conductivity and magnetic properties as well as ESR behaviour indicate the presence of spinless dipolar charge carriers. ESCA measurements on the phthalocyanine polymers before and after heat treatment also in-

dicate the formation of extended conjugated structures. The binding energies for N and metals shift to lower values in the heat-treated phthalocyanine polymers indicating the formation of extended conjugated structures in the latter.

Although thermal treatment imparts large stable conductivities, the rigid structure of the resulting polymers makes them poorly processable. Hence attempts have been made to incorporate these polymers in a suitable polymer base such as polyimide, polyamide, polypyrrole, etc., by chemical or electrochemical means to obtain composites of improved electrical and electrochemical behaviour^{64,65,81}. Li and Guarr¹³³ have electrochemically prepared thin films of tetraamino metallophthalocyanines. Since the prepolymer containing COOH groups is soluble in polar solvents like dimethylacetamide, it can be incorporated into processible polymers capable of forming films, e.g., polyamic acid of N,N'-p,p'-oxydiphenylene pyromellitimide⁸². The polymeric copper phthalocyanine containing peripheral carboxyl groups has been converted into the corresponding polyimide by condensing the anhydride of the latter with 4,4'-diaminodiphenyl ether in our laboratory¹³⁴. The electrical conductivity of the polymer improves (10 S/cm) on heating to 520°C in vacuum (10 mT). This method, thus yields coatings based on polymeric phthalocyanine, which could find

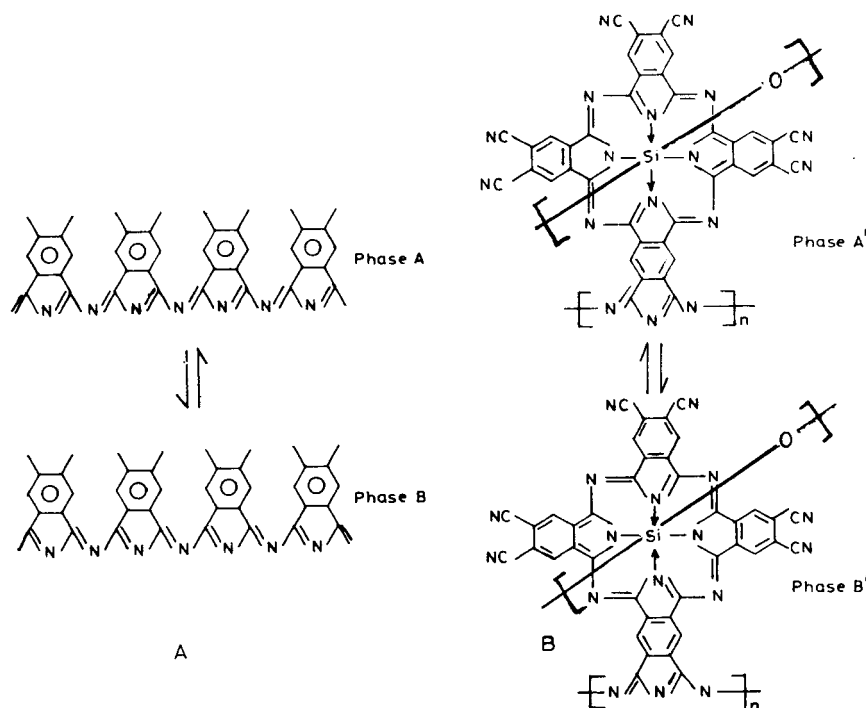


Fig. 3—Bond alternation structures of (octacyanophthalocyaninato polysiloxane) polymers $(C_{40}H_8N_{16}SiO)_n$

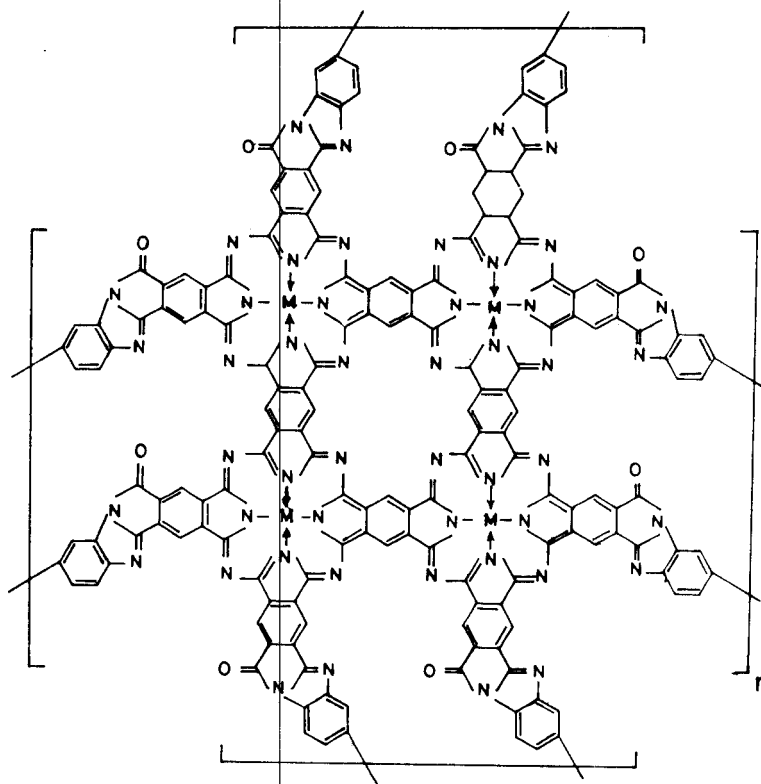


Fig. 4—Structure of metallophthalocyanine polymers containing pyrrone type ladder moieties [M = Cu, Ni]

application in the prevention of electrostatic charging of spacecrafts and rockets.

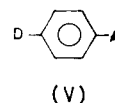
NLO properties of organic materials and conducting polymers

The development of new nonlinear optical (NLO) materials which allow frequency multiplication and mixing of UV-vis-IR radiation for laser and electro-optics applications (optical processing/computing, image analysis, switches, modulators), has been extended to conjugated polymers^{4-6,135-137}. Highly delocalized pi electron systems not only exhibit large electrical conductivity but also show large nonlinear optical effects, which make them useful materials for photonic applications. Organic conjugated polymers exhibit photo-induced absorption, bleaching and photoluminescence which occur in picoseconds¹⁸. This implies that photon absorption by these polymers causes structural distortions in the system due to which major shifts in oscillator strengths occur within picoseconds.

Nonlinear optical properties originate primarily due to the response of a dielectric material to a strong electromagnetic field. Polarization is induced by the electromagnetic field. The polarization response of a molecule is given by

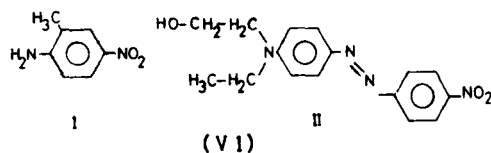
$$P_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l +$$

where α , β , γ , etc. are tensor quantities relating the induced polarization vector components P_i , to the appropriate field components, and where E_j , E_k , etc. and i,j,k and l refer to the molecular coordinate system. α, β, γ , etc., are also called molecular hyper polarizabilities. The odd-order ranked tensors such as β require that the molecule providing the response has no centre of inversion symmetry; otherwise its contribution to the induced polarization is zero in the dipole approximation^{137,138}. Molecules with low-lying charge-transfer states of the appropriate symmetry can give very large β . In general molecules exhibiting large β have the structure (V).



where D and A are electron donating or electron accepting substituents that provide a substantial charge-transfer resonance interaction through the aromatic ring. Approaches to increasing the β of compounds, include placement of strong electron donor and electron acceptor groups at opposite ends of a conjugated electron system and increas-

ing the conjugation length¹³⁹⁻¹⁴¹. Examples are 2-methyl,4-nitroaniline (MNA) (structure I) and azodye disperse Red (structure II) as shown in (VI).



Katz *et al.*¹⁴² have introduced the use of cyano-vinyl electron acceptor groups and dithiolydene methyl electron donor group. Polarization induced in bulk media (liquids and solids) can be expressed by the following expansion:

$$P_i = \chi^{(1)}E_i + \chi^{(2)}E_jE_k + \chi^{(3)}E_jE_kE_l$$

where the coefficients $\chi^{(n)}$ have meanings similar to their molecular counterparts but are scaled to the properties of the medium. Construction of a bulk material possessing a large bulk susceptibility requires not only molecular constituents with large microscopic susceptibilities, but also a non-centrosymmetric system where the orientation of the molecular species results in constructive additivity of β . A number of approaches to construct bulk materials with large nonlinearities are known. These include crystal engineering, LB film preparation, electric field poling of polymeric systems, development of molecular composites and aggregates and the preparation of fibres with crystalline organic materials on the core¹⁴³. Crystal engineering approaches for NLO materials suffer from inherent difficulties. For example, symmetry and orientation of molecular units within the unit cell affect the noncentrosymmetry of the system. Noncentrosymmetric organization of the molecules can be achieved by techniques such as Langmuir Blodgett (LB) technique, guest host technique and side chain liquid crystalline polymer technique¹⁴⁴⁻¹⁴⁶.

The LB technique is one of the well-known methods available for manipulating the architecture of an assembly of organic molecules. It may be regarded as an organic analogue of molecular beam epitaxy, which is extremely important to solid state electronics as a means of fabricating precise micro structures with novel transport properties. The LB technique offers the means to construct one organic mono layer at a time with precise geometries (molecular orientation and thickness). Very few materials are suitable for LB film formation and these molecules contain both hydrophobic and hydrophilic end groups such as long alkyl and carboxylic groups¹⁴⁴⁻¹⁴⁶. One prob-

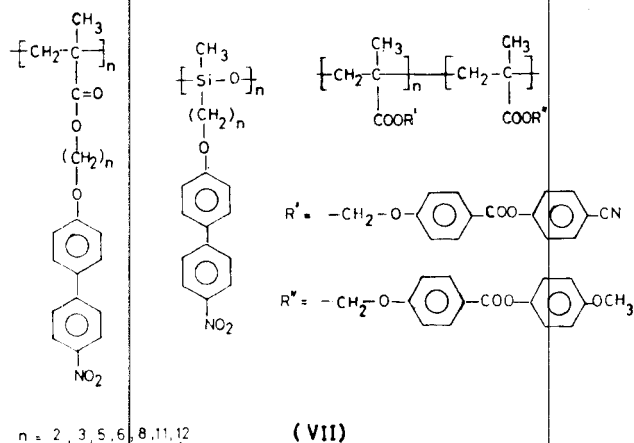
lem with LB films in optical applications is that they are not truly single crystalline materials and this limits applications in nonlinear and guided wave optics.

NLO of poled polymers and side chain liquid crystalline polymers

In the guest/host method, the NLO compound (guest) under investigation is dissolved in a polymer host and spin coated on a substrate. The NLO polarizable molecules are oriented by applying a DC electric field across the polymer just below its glass transition temperature (T_g) to give large molecular hyper polarizability¹⁴⁷⁻¹⁴⁹. The poling can be effected by contact or corona poling. Stability of the polar orientation after cooling the polymer well below the T_g depends on the polymer used and the methods used for increasing the degree of polar orientation. NLO effects are obtained when the medium is illuminated by a very intense laser beam. The advantage of such a system is that it can be manufactured in different shapes—cylinder, fibres or films. A typical example is the field induced alignment of the azo dye disperse Red I in PMMA. Using disperse red molecule number density of $2.74 \times 10^{20}/\text{cm}^3$, the system gives a $\chi^{(2)}$ of 3×10^{-6} esu at a poling field of 0.6×10^6 V/cm. This value agrees with the theoretically predicted value¹⁴⁵. The guest-host technique suffers from limited solubility of active species in host polymer which lowers the achievable level of NLO properties. In addition to these, problems such as phase separation, nonuniformity of dispersion and evaporation of the active species also exist. Many of the above difficulties are removed when the NLO active species are chemically attached to polymer chains, e.g. the guest molecule Red dye I is attached to the monomer MMA and then copolymerized with MMA¹⁴⁵. The resulting polymer is poled just above its T_g and then cooled in its polar orientation. This technique allows incorporation of high concentration of active moiety in the system. If the concentration is increased, higher $\chi^{(2)}$ values are obtained¹⁴⁵. It can be manipulated by various processing techniques into different shapes, sizes and degree of orientation and would enable the use of these materials for many devices and applications of second order NLO phenomena. Moreover, their long relaxation times can be utilized to maintain the desired structure at ambient temperature for an indefinite period^{145,150,151}.

Due to the tensorial character of NLO coefficients, alignment and the extent of noncentrosymmetry of NLO moieties in NLO materials are cri-

tically important for maximizing the NLO response. For example, the value of $\chi^{(3)}$ for an unoriented polymer containing long axially symmetric NLO unit is increased by a factor of 5, by orienting all the NLO units along the same axis¹⁵². Unoriented polymers are by definition centrosymmetric and have no $\chi^{(2)}$ properties, whereas orienting high β moieties in the same direction produces high $\chi^{(2)}$ values. Thus, by controlling the orientation and symmetry of polymeric materials different types of NLO responses can be realized. The liquid crystalline polymer chains are typically composed of three parts: backbone, side chain spacer groups and mesogens. Intermolecular interaction between the mesogens, and to a lesser extent, between spacer groups results in mesophase formation in the melts of these polymers. The function of the spacer group is to decouple the side chain motion from that of the backbone, since otherwise the latter will affect phase stability. The requirements are the same as that required for mesogens in a liquid crystalline polymer for a highly active NLO molecule. Hence one can use NLO molecules as mesogens while maintaining the other molecular structure unchanged. By appropriate manipulation of the backbone, spacer and NLO group, a variety of mesophases can be realized in these polymers. Nematic, cholesteric, smectic A and smectic C have been observed in side chain liquid crystalline polymers¹⁵². The following types of side chain liquid crystalline polymers represent some of the systems that have been studied^{151,152} (VII).



In addition, as polymers these materials also possess glass transition temperature and hence the molecular order for a given phase may be frozen for use over a wide range of temperature. For NLO applications side chain polymers are favoured because of their high orientational order

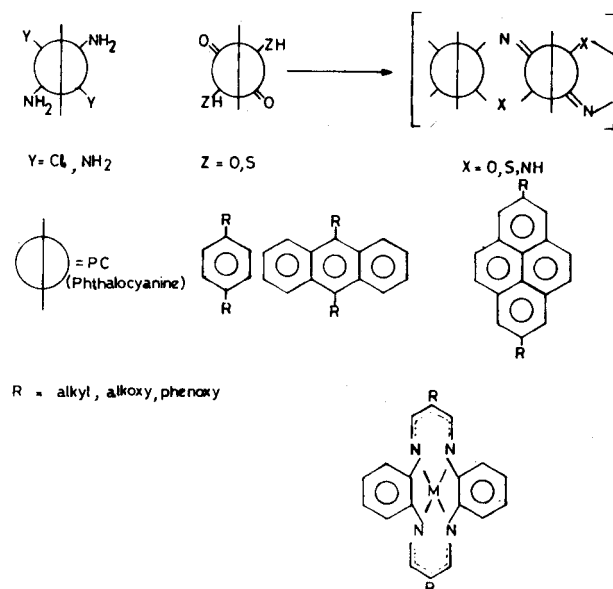
in the melt phase. Utilizing slow relaxation characteristics of polymers, different NLO characteristics, viz., unoriented $\chi^{(3)}$ material, oriented $\chi^{(3)}$ material by cooling an aligned smectic A structure and oriented $\chi^{(2)}$ material by poling under a high electric field, of the sample can be obtained. Low concentration of dopant is dispersed in a nematic liquid crystalline thermoplastic polymer¹⁵². The polymer should show nematic behaviour above T_g in addition to it being homogeneous and alignable in an external applied field^{150,151}. The sample is heated to nematic regions and an electric field is applied producing axial alignment of the nematic medium. The dopant molecule is now in an anisotropic environment and its degree of alignment will be determined by the superposition of the alignment field E_d on the anisotropic potential of the medium^{150,152}. In yet another approach, large nonlinear optical properties are found in molecules covalently bound in a polar polymer chain in an otherwise isotropic medium¹⁵⁰. In this approach, extended polymer chains are treated with nonlinear chromophores as part of the repeat unit. For example, polybenzyl- γ -glutamate (PBG) dissolved in a helix forming solvent and subjected to an electric field forms a rigid extended helix and has a large dipole moment owing to the asymmetric placement of repeat units in the rigid polymer chain. Hence it shows total field induced polar orientation at modest field strength. The β for the monomer repeat unit is 2×10^{-31} esu while for the individual chains it is 500×10^{-30} esu. It is therefore possible to have a molecular design approach in which polar polymer chains would contain a repeat unit of a chromophore with large and permanent field induced polar alignment of polymer chains.

Importance of ladder polymers and phthalocyanine polymers for NLO applications

In view of the large electron displacement in conjugated electron system, the conjugated polymers offer better nonlinear properties than the current inorganic systems like LiNbO_3 , KH_2PO_4 (KHP) and III-V semiconductors GaAs or InSb (ref. 5). In addition to their large architectural flexibility, conjugated organic polymers have been valued for their ultra fast switching times, third order NLO susceptibilities and high optical damage thresholds^{4,6}. Among the conjugated polymers, polydiacetylenes (PDA) are one of the most extensively studied polymeric systems because of the processibility and capability to exhibit phase transition in the solution state¹⁵³⁻¹⁵⁶. Since various changes are possible in its backbone

structure a number of substituted PDAs have been studied¹⁵⁷. Recently a number of other conjugated polymers including polythiophene, polyaniline, and poly(phenylene vinylenes) have also been examined¹⁵⁸⁻¹⁶¹.

The $\chi^{(3)}$ values for the present day electroactive polymers are too small for applications such as receiver protection and for a variety of components necessary for optical information processing⁴⁻⁶. As optical nonlinearity increases with increase in conjugation or electron delocalisation, ladder polymers give maximum overlap and delocalisation, and hence are best candidates for large $\chi^{(3)}$ (refs 162, 163). Ladder polymers are also characterized by excellent thermal and chemical stabilities and frequently exhibit exceptional mechanical strength. However, they are well-known for their poor solubility and hence are difficult to process. The present day efforts¹⁶⁴⁻¹⁶⁸ focus upon the preparation of derivatized monomers and the effects of solvent and temperature upon the rates of the various condensation reactions. Schluter *et al.*¹⁶⁹ have described a Diels-Alder route for synthesizing soluble ladder polymers. The general methodology for the production of high symmetry ladder polymers by condensation of derivatized quinones with aromatic di- and tetra-substituted amines as mentioned by Dalton¹⁶⁵ is given in the following Scheme:



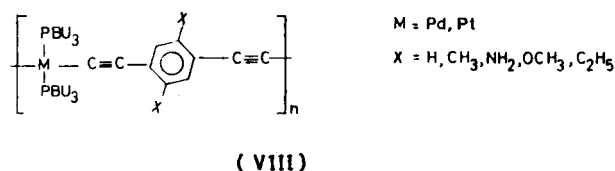
The results of Dalton's work suggest that the substituent does not strongly influence the electron delocalisation and this is not expected to influence $\chi^{(3)}$ (ref. 165). It also indicates that $\chi^{(3)}$ will

not increase with increasing polymer length after a certain chain length.

Odd parity susceptibilities such as $\chi^{(1)}$, $\chi^{(3)}$ are always present in any material. In pi electron conjugated polymers which exhibit large $\chi^{(3)}$, the presence or otherwise of centre of symmetry does not pose any problems. Theoretical calculations suggest^{4-6, 164, 170, 171} that the extent of electron delocalisation influences third order optical susceptibility $\chi^{(3)}$.

Although electrical conduction property and nonlinear optical properties are based on extended pi conjugation (or even σ conjugation in silanes), conductivity is found only in doped polymers and is influenced by interchain and intrachain charge transfer while large $\chi^{(3)}$ is found only in neutral polymers. Based on these observations it has been realised that conducting polymers may find application as fast nonlinear optical materials. The NLO property in conjugated polymers is primarily a microscopic one. As oxidation/reduction is expected to affect optical properties, it is worthwhile to direct future research on the NLO of doped polymers.

Another class of compounds that exhibits NLO behaviour is the transition metal organic compound with extended pi electron delocalisation^{172, 173} as shown in (VIII).



Their behaviour is analogous to nonlinear phenomena observed in purely organic compounds having similar electronic characteristics. Third harmonic generation and power limiting measurements corroborate the presence of large third order susceptibility in these metallopolymers. The extent of orbital overlap is determined by the proximity and relative energies of the combining orbitals of the correct symmetry¹⁷⁴. In addition to these parameters, conformational issues also exist. For the pi electrons of aromatic ring to overlap effectively with the pi electrons of acetylene moiety, which interact in turn with two of the d_{z^2} orbitals of the metal, the plane of the benzene ring must be perpendicular to the metal phosphorous bonding axis¹⁷². The arene plane however, rotates about the bond between one of the acetylene carbons and the connecting carbon of the benzene rings so that at any given moment only a fraction of the benzene rings in the polymer chain

is correctly oriented to provide good orbital overlap. This negates the expected hyperpolarizability enhancement due to extended delocalisation. To prevent rotation, polyynes with substituent aromatic rings are required. Free standing pure polymer films of good optical quality are expected to be of considerable use in NLO applications.

Phthalocyanines and their polymers possessing -CN and -COOH terminals have suitable extended structures that facilitate solitonic, polaronic and bipolaronic conformational deformations^{110,112,126} and hence are expected to show large ultrafast nonlinear optical properties. The peripheral functional groups can be used for structural modifications to improve processability and allow fabrication of various device structures such as film, channel waveguides and planar waveguides, etc. The presence of macrocyclic structures in these polymers provide mechanical, thermal, and environmental stabilities. Moreover, the optical damage threshold of these polymers is also expected to be much higher than that of simple, low molecular weight materials. The terminal anhydrides of phthalocyanine polymers are condensed with aromatic and aliphatic diamines to give polyamic acids which are imidized thermally to form electroactive films¹³⁴. Condensation of the anhydride units with tetramines gives semi-ladder or ladder type polymers possessing pyrrole type structures¹²⁶. The combination of σ and π electron systems in polymeric phthalocyanine structures can stabilize the excited electronic state, which allows these polymers to undergo redox processes in a wide potential range^{65,81,175,176}. These properties make them useful as semiconductors, electrochemical catalysts and materials for nonlinear optics. The excitation of polymer chains is strongly coupled to local bond order and therefore a strong nonlinear response is shown. These polymers can be easily incorporated electrochemically into other conducting polymer matrices^{64,65} so that polymeric thin films possessing both processability and electrochemical properties can be realized.

In view of the similarities in the requirements for structural and NLO applications, one must attempt synthesis of the heterocyclic ladder polymers with extensive aromatic rings to increase the conjugation, and with suitable backbone substituents, to increase the processability. To obtain maximum tensile properties and stability in a light weight material for structural applications, the clear choices are organic, conjugated, aromatic or hetero aromatic and rigid structures to give ordered or isotropic materials¹⁷⁷. The poly-conden-

sation of substituted diquinones and diamines in a solvent yields a soluble precursor which on heating is converted to fully cyclized material¹⁶⁵. It is possible to enhance $\chi^{(3)}$ by more than an order of magnitude by chemical and electrochemical doping and values up to 10^{-7} esu has been achieved in ladder polymers. Polymers possessing phthalocyanine structures are shown to have large $\chi^{(3)}$ values^{158,170,178,179}. Cyclic voltammetry shows electro-chromic and redox properties of the system^{64,65,175,176}. Magnetic and optical measurements show that the charges are associated with generation of polaron and bipolaron states^{110,112}.

Semiconductor devices from phthalocyanines and other conducting polymers

Organic conducting polymers have very different conductivity in the reduced and oxidised state and their conductivities are controlled by the dopant concentration, applied potential, etc.^{1,2,4}. This makes them useful for a wide ranging applications such as electrochemical insertion electrodes, high conductivity low density metals, materials for NLO applications and semiconductors. The extended π conjugated structure provides the self localised states, which determine the operation of a wide variety of semiconductor devices, metal-insulator semiconductor (MIS) devices, metal-insulator-semiconductor field effect transistors (MIS-FET), etc. In these devices the charge can be introduced into the region of surface charge at the semiconductor/insulator interface by the application of a strong electric field across the insulator, for example two terminal devices such as Schottky diode and MIS structure. FETs based on polyacetylene, polypyrrole, polythiophenes and metallophthalocyanines¹⁸⁰⁻¹⁸⁶ have been fabricated and analysed. These FETs operate through formation of accumulation layers generated through band bending at the insulator semiconductor interface which is controlled by the applied voltage. These devices require fabrication as a series of layers. For example, to construct a MIS structure a silicon wafer is needed as a substrate with a doped layer to act as gate and the native oxide layer on top as insulator. This structure has to be coated with the polymer and finally capped with an evaporated thin gold top contact. For MISFET structures, it is convenient to put the source and drain contacts into the insulator layer and the polymer layer on top as the last stage of fabrication. Source and drain contacts may be poly-*n*-silicon or Au structures. The mode of operation of organic conjugated polymer based FET shows¹⁸⁷ that in addition to carrier mobility, the ohmic

contribution to the drain current must also be taken into account. The mobility/conductivity ratio appears as the determining factor and hence, short conjugated oligomers such as polysequisquithienylene¹⁸⁸ which possess a high carrier mobility and low conductivity would make them potentially interesting. In these systems, charge trapping by structural defects may play a prominent role in limiting the charge transport properties¹⁸⁹. Petit *et al.* have made insulated gate FETs with metallophthalocyanine based active semiconductors whose performance is comparable to that of amorphous silicon based devices¹⁸⁶. Schottky barrier diodes have been made and formation of space charge regions in $M_1/PcM/M_2$ cells have been proved by Andre *et al.*¹⁹⁰

Conclusion

The non-resonant $\chi^{(3)}$ values observed in conjugated polymers are less than 10^{-9} esu (ref. 170). For practical purposes, the values has to be increased so that devices using small switching energies can be fabricated. In order to enhance the $\chi^{(3)}$ values, suitable structural modifications and spectral responses of NLO coefficients are needed. In order to make use of organic materials in NLO devices such as wave guides (used to confine intense light over sizable distances), processability and optical clarity are as important as large nonlinear optical response. For example, though polyacetylene has large $\chi^{(3)}$ it is practically useless because of high scattering losses. Optical quality of the materials is important for integrated optical applications which will involve wave guide configurations. The best optical media is provided by silica although they have low $\chi^{(3)}$. A composite structure of glass and polyphenylene vinylene (PPV) with optical clarity has been obtained by chemical processing of oxide glass using a sol-gel process. Up to 50% of PPV has been incorporated into the composite¹⁹¹. Similar approaches are possible with phthalocyanine polymers possessing functional terminals.

Crystalline materials offer a natural way to reducing scattering losses but their birefringence may hinder bending of wave guide structures. It seems that glassy materials would make a workable compromise. But chemical reactivity of the organic materials could pose problems. In all these aspects metallophthalocyanine polymers seem to offer good thermal, chemical and photochemical stabilities for use in a wide range of temperature and environments. Hence, in order to realize useful and viable materials for electronic and photonic applications, the theoretical under-

standing of third order optical nonlinearity and stability of poled $\chi^{(2)}$ molecules dispersed in polymer matrices and a thorough study of these effects in metallophthalocyanine based systems have to be undertaken. In the organic conducting polymer based MISFET structures, the accumulation or inversion layer is confined to the interface between the polymer and the insulator and is very sensitive to the surface structure of the polymer. Hence, control of the electronic structure of the conjugated polymer on which the accumulation layer or inversion layer is formed is very important for the improved performance of the devices.

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