CHAPTER 2

Polymer Supported Metalloporphyrins

2.1 Introduction

The development of new catalysts is a field of extreme chemical and industrial challenge and is one of the reasons for the recent surge of interest in metalloporphyrin (MP) chemistry. An efficient catalyst system is expected to be stable towards oxidative destruction during drastic reaction conditions and should exhibit selectivity and specificity to various substrates in the reaction mixture. Metalloporphyrin catalysts in homogeneous conditions suffer serious limitations in this regard, and investigations have pointed out that the performance of these catalysts can be improved if they are heterogeneised by binding them to the surface of a solid\textsuperscript{1-14}. The beneficial effects of the resulting materials would include increased stability, ease of separation from the products, their recovery and reuse. The polymer support could also influence the selectivity of various organic transformations. Supporting the porphyrin system on a synthetic macromolecule can also provide the site of isolation and inhibit any possible binuclear complex formation. Further, it can also provide the required hydrophobic/hydrophilic microenvironment around the catalytic site. Furthermore, since the MPs in enzymatic systems are embedded in a polymeric environment, synthetic porphyrins with a modified environment, especially polymer-bound porphyrins, should be a better model system for mimicking the biological systems than the low molecular weight porphyrins. In addition to catalytic utilities, such polymer-porphyrin systems are also of active interest for developing new materials with unconventional properties. Thus there has been growing and intense scientific and commercial interest in the development of metalloporphyrins, which are bound to solid-macromolecules.
Historically, the area of polymer supported metalloporphyrin catalysts has been approached by the scientific world with three different objectives in mind. The first is to produce polymer-supported systems, which will bind dioxygen reversibly. Such systems might act simply as oxygen carriers or they might be directed specifically towards artificial life-support systems. The second is to produce polymeric mono oxygenase enzyme models, which can function as mild and selective oxidation catalysts without the surrounding globular protein of the natural enzymes. The third is to develop polymer-supported analogues of existing metal complex based industrial oxidation catalysts and indeed other homogeneous catalytic systems, which are currently being researched in industry and academic.

Immobilisation of metalloporphyrins on polymer supports could be generally achieved by (a) covalent binding of MPs to suitably functionalised supports, (b) electrostatic binding of charged MPs to counter charged supports, (c) simple absorption of ionic MPs on solid systems like silica or alumina and (d) to intercalate MPs into layered minerals like clay or zeolite.

2.2 Metalloporphyrins Covalently Bonded to Polymer Support

A variety of methods have been employed to synthesise covalently bonded polymer–porphyrin systems with different environments around the tetrapyrrole system. The effect of such chemical environments (neutral, cationic or anionic) around porphyrin moieties were studied by Wohrle et al. Poly(styrene–co-chloromethylstyrene) 11a, poly(vinyl benzyl–triethyl ammonium chloride) 11b, poly(methacrylic acid) 11c, and poly(N–vinyl pyrrolidone–co– methacrylic acid) 11d were used as polymers in combination with functionalised tetraphenylporphyrins and phthalocyanine.

The covalent interaction of suitably substituted porphyrins [eg. (p–NH₂) TPP] with these polymers resulted in polymer bound porphyrins having neutral, positive or negative charges. The spectral properties of Zn(II)(p–NH₂)TPP were found to be changed on incorporating it into these polymeric environments (Table 2.1).
Table 2.1: Absorption (Soret) and Fluorescent band of polymer grafted Zinc porphyrin systems (DMF/H$_2$O).

<table>
<thead>
<tr>
<th>Porphyrin System</th>
<th>Absorption $\lambda$ (nm)</th>
<th>Fluorescence $\lambda$ (nm)</th>
</tr>
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<tbody>
<tr>
<td>Zn[(p-NH$_2$)TPP]</td>
<td>436.3</td>
<td>636.5</td>
</tr>
<tr>
<td>Zn[(p-NH$_2$)TPP] with 11a</td>
<td>436.2</td>
<td>632.1</td>
</tr>
<tr>
<td>Zn[(p-NH$_2$)TPP] with 11b</td>
<td>447.3</td>
<td>645.7</td>
</tr>
<tr>
<td>Zn[(p-NH$_2$)TPP] with 11c</td>
<td>432.3</td>
<td>621.4/667</td>
</tr>
<tr>
<td>Zn[(p-NH$_2$)TPP] with 11d</td>
<td>435.1</td>
<td>628.1</td>
</tr>
</tbody>
</table>

It was also found that all these polymer bonded porphyrins exhibited a higher triplet life time than the corresponding monomeric porphyrins. In general, the triplet life time increases in the order: monomeric porphyrin $<$ porphyrin on uncharged polymers $<$ porphyrin on negatively charged polymers $<$ porphyrin on positively charged polymers, indicating a strong to very strong shielding effect by the polymer environment. Further, positive charges of the polymer backbone interact strongly with the electron-rich metal chelates, preventing any possible porphyrin-porphyrin interaction. It was also seen that such polymer
binding results in enhanced photo-catalytic activity. The electron-transfer reactions of Mn(III) containing porphyrins using the reducing agent dithionite are also seen strongly influenced by the polymer environment. In contrast to monomeric Mn(III)porphyrins, the polymer containing porphyrins exhibited a two-step reduction which may be due to the change of the conformation of the polymer coil. However, the catalytic epoxidation of 2, 5-dihydrofuran with hypochlorite with the formation of 3, 4-epoxy-tetrahydrofuran, is not seen to be influenced by the polymer environments.

A series of polymer-bonded MPs as in 12a and 12b have been synthesised and characterised by L. D. Rollmann.  

![Chemical Structure 12a](image1.png)

![Chemical Structure 12b](image2.png)
The copper derivatives of these polymer–bonded porphyrins were characterised by ESR spectroscopy. It was observed that the ESR spectra of these systems shows clearly both N- and Cu-hyperfine structures at room temperature. This extensive hyperfine structure suggested that the porphyrin is well dispersed within the polymer, since solid or aggregated CuTPP does not exhibit such hyperfine structure. In the catalytic study it was observed that the Co-derivative of this polymer–porphyrin system which contains both oxidation (cobalt) and proton-acceptor (amine or carboxylate groups) sites are effective catalysts for the oxidation of thiols to disulphides.

Free base/metallodervatives (M = Cu$^{2+}$, Ag$^{2+}$ and Co$^{2+}$) of tetraphenyl porphyrins, which have amino functions either at ortho-, meta- or para- positions of the phenyl group(s) were covalently bonded to solid functionalised polystyrene support by Padmanabhan et al$^{16}$. In these systems, the relative orientation of porphyrin plane with respect to polymer surface is found to cause varying degree of electronic modification in MPs as evidenced from the electronic and EPR studies.

A cytochrome P-450 model was also reported bearing Mn(III) porphyrin on poly(isocyanide)(C = N–CH[CO$_2$H]CH$_2$C$_6$H$_4$OH)$_n$ via formation of phenyl ether linkage$^3$. Cyclohexene was epoxidised by this catalyst using NaOCl in CH$_2$Cl$_2$/H$_2$O diphasic system at 25°C with yields upto 80%. While free N– donor ligands such as pyridine enhanced the catalytic activity considerably, donors like imidazole completely blocked the epoxidation route. In general, the site isolated polymeric catalysts showed higher activity than the free porphyrin analogue, because of the deactivation of the latter by dimerisation.

The catalytic autoxidation of 2-mercapto ethanol has been studied by using a water-soluble polymer containing a Co(II)phthalocyanine complex (13) as the catalyst$^{11}$.
The cationic environment on these polymeric catalyst enhanced enzyme-like activity in the neutral pH region for autoxidation of 2-mercapto ethanol, because of the promotion of substrate dissociation and accumulation of thiolate anions.

A Pd(II) complex of mesotetra(4-hydroxyphenyl)porphyrin immobilized on chloromethylated polystyrene has been reported to catalyze the hydrogenation of cyclohexene\textsuperscript{12}. The catalytic activity is found to be dependent on the polarity of solvent and the reaction temperature.

The electron-transfer properties of polymer bound MPs were investigated using Fe(III) and Mn(III) derivatives of (p-NH\textsubscript{2})TPP bound to a chloromethylated polystyrene\textsuperscript{17}. It was found that the pseudo-first order rate constants for the electron transfer from the polymer-bound Mn(II) complex to the polymer-bound Fe(III) is lower than those for the same process between the corresponding low molecular weight MPs. Also, the activation energy for electron-transfer between the polymer bound MPs (9.2 kJ mol\textsuperscript{-1}) was considerably lower than that corresponding to the reaction between the low molecular weight MPs (16.8 kJ mol\textsuperscript{-1}).

Hemin, protoporphyrin-ferric chloride, isolated from blood, when bonded to polymethacrylic acid (PMAA), (as hemin–PMAA anhydride and bearing upto 1.8 mol % porphyrin) was found to act as a good oxygen absorber\textsuperscript{18}. A co–polymer
of styrene with cobalt(III)protoporphyrin IX styrylamide has been reported to absorb molecular oxygen reversibly in toluene at low temperature\textsuperscript{19}. Similarly a polymer supported metalloprotoporphyrin IX (M = Fe, Mn) has also been found as an efficient model of cytochrome P-450 mono oxygenase\textsuperscript{20}.

A synthetic model system of cytochrome P-450, which incorporates all of the features of the natural enzyme system was also reported by J.Esch et al\textsuperscript{21}. The model enzyme system included (i) a membraneously bound metalloporphyrin, (ii) an axial ligand (N - methyl imidazole) (iii) an electron donor (colloidal Pt-H\textsubscript{2}) (iv) an electron carrier (methylene blue) and (v) a membrane system (a polymerized vesicle bilayer). The Mn – porphyrin, Mn(III)(p-OR)TPP (R = C\textsubscript{16}H\textsubscript{33}) could be distributed equally between the inner and outer surface of the polymerized vesicles. Using this synthetic model of P-450 a variety of olefin epoxidations were carried out and it was reported that the system operates sufficiently well.

### 2.3 Metalloporphyrins Bonded to Ion Exchange Resins

Anionic tetrasulphonated phenylporphyrins (MTPPS) has the ability to interact strongly with anion exchange resins. The incorporation of these MTPPS onto Amberlite IRA 900 (an ion exchange resin derived from poly (vinyl benzene) with ammonium groups) can easily be achieved by shaking the nitrate form of the resin with a solution of MTPPS in a 1:1 mixture of acetone and water for 10 h at 35\textdegree C\textsuperscript{22}. These water soluble porphyrins are strongly held by the resin and cannot be removed from the polymer by acetone or 1M NaCl.

MnTPPS-Amberlite IRA 900 (Am-MnTPPS) is seen to be a good supported catalyst for the dismutation of H\textsubscript{2}O\textsubscript{2} \textsuperscript{22}. The same catalyst has also a strong peroxidase-like activity, which has been evidenced in the co-oxidation of 4- aminoantipyrine and phenol by H\textsubscript{2}O\textsubscript{2} \textsuperscript{23}.

The system was found to be equally efficient for N, N-diethylaniline (instead of phenol) in these peroxidase like oxidations\textsuperscript{24}. Further, Am-MnTPPS and
Am-FeTPPS have been found to act efficiently in modeling of ligninase (an enzyme which degrades lignin, a plant polymer) with stability better than the corresponding soluble catalysts\textsuperscript{25,26}.

A supported Mn-porphyrin system has been reported in which sulphonated Mn-porphyrins were immobilized on poly(vinylpyridinium) matrix with a pyridine of the support acting as proximal ligand as shown in 14\textsuperscript{27}.

\begin{center}
\includegraphics[width=0.5\textwidth]{14.png}
\end{center}

These supported Mn-porphyrin system provides two major advantages, namely, the easy adsorption of anionic porphyrin onto ion-exchange resins and the proximal effect of pyridine. The catalytic oxidation of 1-(3,4-Dimethoxy phenyl) -2-(2-methoxy phenoxy) propane-1, 3-diol (A ligninase model study) by this PVP-Mn porphyrins and Am-Mn porphyrins has been performed and the activity of these supported systems were comparable with the free porphyrins in solution and the major utility of these supported catalysts was their recyclability without much catalyst poisoning. The Mn-TPPS-PVP is also found to be a suitable catalyst for the oxidative chlorination of dimedone (a chloroperoxidase like reaction). This reaction is difficult to mimic using soluble metalloporphyrins\textsuperscript{28}.

FeTPPS or FeTMPS catalysts adsorbed on Amberlite were found to be efficient catalysts in the oxidation of 2,4,6-trichlorophenol or various substituted arenes employing KHSO\textsubscript{4} \textsuperscript{29}. A supramolecular inclusion complex of FeTPPS with \(\beta\)-cyclodextrin crosslinked polymer was also reported and this system mimics horseradish peroxidase (HRP) effectively \textsuperscript{13}.
The catalytic activity of Fe(III)TMPyP adsorbed onto crosslinked polystyrene cation exchange resin has been studied for the epoxidation of cyclohexene or Z-cyclooctene and for the allylic oxidation of cyclohexane. With cyclohexene and cyclooctene, epoxidation was favoured by increased crosslinking of the resin support and was unaffected by changes in the surface area of the support. However adsorption of these metalloporphyrins on the polymeric resin was seen decreasing in the catalyst efficiency when compared with metalloporphyrins in solution. It was proposed that the decrease in catalytic activity arises through the aggregation of the MPs on the resins favouring the inter molecular self oxidation of the catalyst.

Studies were further carried out to investigate the nature of the species that are formed when the cationic Fe(III)TMPyP is bound to three water soluble anionic polymers, namely poly(styrene-4-sulphonate) (15a), poly(vinylsulphonate) (15b), and poly(acrylate) (15c) in water at pH 9.2.

\[
\begin{align*}
\text{15a} & \quad \text{15b} & \quad \text{15c} \\
\text{CH} - \text{CH}_2 \rightleftharpoons \text{CH} - \text{CH}_2 \rightleftharpoons \text{CH} - \text{CH}_2 \\
\text{SO}_3^− \text{Na}^{+} & \quad \text{SO}_3^− \text{Na}^{+} & \quad \text{CO}_2^− \text{Na}^{+}
\end{align*}
\]

GPC studies with Fe(III)TM4PyP and its free base, H₂TM4PyP, showed that the iron porphyrin is bound to the polymers by electrostatic interactions and also by ligation through the metal. Electronic spectra revealed that the porphyrins induce a broadening and blue-shift of the MP Soret band. Spectroscopic GPC and reactivity studies suggested the Fe(III)TM4PyP is extensively aggregated on the anionic polymer chains, probably as μ - oxo x-mers. The product yield from the reaction of Bu'O₂H with polymer–Fe(III)TM4PyP were very similar to those from the analogous reactions with free Fe(III)TM4PyP, although the rate of the former reaction is markedly reduced by aggregation on the polymer chain. UV-Vis spectroscopy also indicated the formation of polymer bound oxo iron(IV) species in the reaction of Bu'O₂H with these supported porphyrins.
Phthalocyaninatocobalt(II)tetrassulphonate(CoPcTS) bonded to crosslinked cationic latexes based on polystyrene, poly(styrene-co-methylmethacrylate) and poly(methylmethacrylate) were found to enhance the rate of autoxidation of 2,6-di-tert-butylphenol in water\(^3\). All CoPcTS – latex catalysts were much more active than the water soluble free CoPcTSNa\(^4\) and the product distribution ratio was found to be affected by the nature of the microenvironment.

### 2.4 Metalloporphyrins Bonded to Inorganic Supports

Silica and alumina are attractive supports for MPs because they are expected to be completely inert, even under drastic reaction conditions. Tanaka et al found that simple FeTPPCl or MnTPPCl adsorbed on silica gel or on silica–alumina, catalyzed the oxidation of cyclohexene to cyclohexanol and cyclohexenol with \(O_2\) and NaBH\(_4\) as electron source\(^3\). Sulfides were selectively oxidized to sulfoxides, without formation of sulfones as observed with the corresponding homogeneous catalyst\(^3\). These neutral MPs are believed to be linked to silica via an Si – O – M bond.

Dioxygen has been found to adsorb reversibly on a Fe(II) prophyrin attached to the imidazole group of silica gel containing 3-imidazoyl propyl groups bonded to surface Si atoms as shown in 16.

![Diagram](image)

The chemisorption of \(O_2\) was seen weak at \(0^\circ\)C, rather strong at \(-78^\circ\)C and irreversible at \(-127^\circ\)C. Each Fe atom adsorb one molecule of \(O_2\), a result in accord with formation of a mono adduct of the type Fe – \(O_2\)\(^3\).
Immobilization of MnTPPCl on to 3-imidazoyl propyl – modified SiO\(_2\) resulted in enhancement of its activity for hydroxylation of cyclohexane\(^\text{35}\). The (Im)SiO\(_2\)–supported catalyst exhibited the highest turn-over of cyclohexane to cyclohexanol and cyclohexanone at 50\(^\circ\)C, which was 31 times as high as that of SiO\(_2\)–supported one. Simple impregnation with these imidazoles was found to be ineffective in promoting the activity; the linking of the imidazoyl moiety to SiO\(_2\) seen to be necessary. Without (Im)SiO\(_2\), MnTPPCl proved to be inactive irrespective of whether imidazole was present or not, suggesting that in homogeneous system, dimerisation of complexes rapidly occurred, resulting in oxidative destruction of the catalyst. The activity of other MPs namely FeTPPCl, CoTPP, NiTPP and CuTPP supported on (Im)SiO\(_2\) was found to be negligible\(^\text{35}\).

Tetracationic Mn porphyrin such as MnTMPyP can be strongly adsorbed on silica and has been found to be very efficient in the PhIO epoxidation of cyclooctene (95% yield) and oxidation of cyclohexane to alcohol and ketone (ol/one ratio 6.5), remarkably higher than those obtained with corresponding soluble Mn–porphyrins. This system was also found to be highly recyclable without much loss of catalytic activity\(^\text{36}\).

An optical sensing film for NH\(_3\) gas has been developed by immobilizing ZnTPP in silicon rubber. The detection of NH\(_3\) can be achieved using both absorbance and fluorescence emission measurements. Spectral changes were observed due to the coordination of NH\(_3\) molecule to Zn(II) ion in the immobilized MP\(^\text{14}\).

### 2.5 Metalloporphyrins Intercalated into Layered Matrices

Metalloporphyrins can be easily immobilized on clays by anion exchange method. The tetracationic Mn(TMPyP) catalyst has been intercalated into the interlayer space of layered mineral like montmorillonite, by simple ion exchange with already present cations\(^\text{6}\). An interesting property of this supported Mn–porphyrin was its particular ability to efficiently catalyse the hydroxylation of heptane or pentane. In fact it gave a better yield for heptane hydroxylation (60%) than the
same Mn–porphyrin simply adsorbed on silica (40%) and Mn–porphyrin alone used as a homogeneous catalyst (3%).

Another interesting property of Mn TMPyP intercalated in montmorillonite was its ability to select substrates of different shapes. On the oxidation of two substrates, adamentane and pentane in competition, the former is seen very much reactive because of its tertiary -CH bonds. Oxidation of a adamentane : pentane (1 : 2) mixture by PhIO in presence of MnTMPyP itself or of MnTMPyP adsorbed on silica showed that the oxidation is exclusively on adamentane (97 : 3). On the contrary, the oxidation of this mixture by PhIO in the presence of MnTMPyP intercalated into montmorillonite led to a clearly different adamentanol: pentanol ratio of (77 : 23), which is much in favour of pentane. This is presumably due to the easier access of pentane, which is much less bulky than adamentane, to the Mn(V)=O active species buried in the interlayer space.6

P4thalocyanatoiron (FePc) complexes may be prepared inside the pore structure of large pore zeolites X or Y. Such species were capable of performing as catalysts in the oxidation of alkanes using PhIO 37. The fact that such catalysis is constrained to occur inside, the size- and shape-selective zeolite crystallities imposed unique selectivities on the distribution of oxidised products. These catalysts preferred to oxidise the smaller of the competitive substrates. In addition, stereoselectivity was apparent in cases of oxidations with diastereotopic C–H bonds. All of the observed selectivities could be explained in terms of the sieving and orienting effects of the zeolite hosts. In all cases, however, pore blockage led to shutdown of the reactivity after few catalytic cycles.

MnTMPyP can also be adsorbed on the surface of a zeolite and has been used as selective catalyst for the electrochemical oxidation of di–t–butyl–phenol 38.
2.6 Immobilization of Metalloporphyrins in Electropolymerized Films – Modified Electrodes.

Metalloporphyrins grafted on polymeric film electrodes has been an intensively researched topic over the past several years\textsuperscript{1}. It is a fruitful strategy for modeling the enzymatic systems electrochemically. Due to the non-conducting behaviour of metalloporphyrins, one of the challenges in developing this concept is the necessity to achieve rapid electron transfer in the enzyme model active site at the electrode surface. Conducting polymers such as polypyrrole, polythiophenes or polyanilines containing porphyrin complexes are attractive candidates for this approach. The principle is based on the electrochemical oxidation (or reduction) of a suitably designed monomer (pyrrole, thiophene or aniline) to form a polymeric film incorporating the porphyrin moiety\textsuperscript{1}. Synthesis of various types of electropolymerised Metalloporphyrin films are briefly discussed below.

2.6.1 Polypyrrole films doped with anionic porphyrins

Polypyrrole films which are prepared on various substrates by electrochemical oxidation of pyrrole form interesting polymer modified electrode because of their ease of preparation, chemical stability and good electro conductivity\textsuperscript{39}. Tetra-sulphonated and tetra carboxy-substituted metalloporphyrins and metallophthalocyanines can be introduced into this poly-pyrrole films as counter ions (or “doping” ions) during the electrochemical growth of polymers in solutions containing pyrrole and anionic complexes as supporting electrolyte. Both the electrochemical polymerisation of pyrrole and the doping of polypyrrole by anionic porphyrins were achieved in one step from aqueous solutions\textsuperscript{40–42}. It was observed that no changes occur in the redox properties of metalloporphyrins by incorporating them on this polypyrrole films\textsuperscript{42}.

2.6.2 Electropolymerisation of pyrrole–substituted metalloporphyrins

The electro oxidative polymerisation of pyrrole–substituted porphyrins (17) is generally seen to yield films having the electrochemical properties corresponding to their monomeric complexes\textsuperscript{1,43–46}.
In most cases, the electrochemical polymerisation of pyrrole-substituted porphyrins was achieved by cyclic voltammetry of acetonitrile or dichloromethane solutions containing the complex monomer and the supporting electrolyte through a well defined potential range. The film gets formed on the electrode as a consequence of electrochemical polymerisation of the attached pyrrole groups.
2.6.3 Electropolymerisation of amino-, hydroxy-, methoxy- and vinyl-substituted porphyrins

Amino-, hydroxy-, methoxy- or vinyl-substituted porphyrins can be employed to create modified electrodes by electrochemical polymerisation \textsuperscript{47-52}. In all these cases, the films were obtained by oxidative electropolymerisation of the cited substituted porphyrins from organic or aqueous solutions. The mechanism of metallo porphyrin film formation was suggested to be a radical cation induced polymerisation of the substituents on the periphery of the macrocycle.

2.6.4 Immobilisation of charged metalloporphyrins into pre-electropolymerised polypyrrole films bearing functional groups

A recent strategy employed for developing modified electrodes involves incorporating water soluble tetra carboxylated and tetra-sulphonated porphyrins into polypyrrole films containing alkyl ammonium groups\textsuperscript{53,54}. Poly(pyrrolealkyl) ammonium, prepared from(3–pyrrole–1–ylpropyl)–triethyl ammonium monomers and (12–pyrrole–1–yldocacyl)–triethyl ammonium monomers (18) exhibit potential independent anion exchange behaviour as well as extraction and binding of organic and inorganic anions from organic and aqueous solutions.

![Chemical Structures]

The adsorption on electrode surface by the amphiphilic monomer produced an irreversibly stable polypyrrole layer; the metalloporphyrins were seen retained on this layer by electrostatic binding. Upon incorporation in the film, a red shift of 12–15nm was observed for the porphyrin Soret band as well as considerable broadening \textsuperscript{53,54}. The available data also showed that, beside their large size, the bulky porphyrins can be efficiently incorporated into the poly-(pyrrole alkyl) ammonium films, until total saturation of all the cationic sites is complete.
2.6.5 Catalytic applications of electopolymerised metalloporphyrin films

The biomimetic hydrocarbon oxidations with molecular oxygen is a field where electopolymerised metalloporphyrin films play a significant role. Mn–porphyrin supported on a polypyrrole film has been found to be an efficient model for cytochrome P–450. The oxidation of cis-cyclooctene, cyclooctane, tetralin, indane and cyclohexane by O₂ has been studied using this polypyrrole doped as well as unsupported Mn – porphyrins. The essential observations were summarized as that (i) the oxidation products are formed with a very good efficiency by the supported catalyst, upto 500 turnovers of the catalyst per hour (ii) the Faradaic efficiency (expressed as the ratio of moles of oxidation products analysed to the electro chemical charge passed) is relatively poor but reached about 99% in some cases; and (iii) the nature of the electrode materials (carbon felt, graphite etc) seem to have a small but significant influence on the chemical and Faradaic efficiencies of the supported catalyst. The high catalytic activity (turnover) of the supported cases was due to either a preferred orientation of the supported catalyst for the approach of the hydrocarbon to the presumed active metal site or to the high local concentration of the catalyst. It was also found that the recovered polymer electrodes retained 95% of the initial activity during the second run and 70% of their initial activity during the third run.

The CoTPPS–polypyrrole film showed excellent electrocatalytic activity in O₂ reduction. It has been reported that this system showed enhanced activity than the electrode coated with simple CoTPPS and the authors proposed this behavior in terms of the high electric conductivity of the polypyrrole doped MP electrode.

It was reported that electropolymerized films of Fe–protoporphyrin IX dimethyl ester are effective catalysts for the electro reduction of HONO / NO۱₂ or NO to N₂O, N₂, N₂OH and NH₃. The electro-oxidation of water, methanol and hydrazine to O₂, CO₂ and N₂ can also be achieved by using an electro-polymerised Ni-porphyrin film as the electrode material. The authors demonstrated high catalytic activity and good effects in the electro oxidation of methanol and hydrazine with over-potentials of 110 and 360 mV respectively.
Stable ordered films of myoglobin and didodecyldimethylammonium bromide (DDAB) on electrode surface were used to catalyse reductions of organohalides with significant lowering of activation free energy. Myoglobin in these films is made to act as redox enzyme. Rates for organohalide reductions in these films were 1000 times larger than in solution and are enhanced further by pre-concentration of organohalides in the films. This method provided a bi-membrane-like environment for these biologically relevant reactions.

A catalytic application of polypyrrole-porphyrin electrodes can be found in the field of oxidation of hindered phenols by molecular O$_2$. In the case of the oxidation of 2,6-di-tert-butyl phenol by molecular O$_2$, catalysed by Mn-porphyrins, the reaction necessitates the reduction of Mn(III) to Mn(II). This reduction could be performed electrochemically with the catalyst supported on the electrode. This electroassisted reaction is schematised in 19.

![Diagram of the reaction](image)

It was found that MnTCPP in polypyrrole film is a good catalyst for this reaction and the yield of product increased with the amount of incorporated porphyrins. Also, whatever the thickness of the film was, no trace of MnTCPP was detected in solution at the end of the electrolysis. This indicated that the porphyrin remains strongly fixed and that the catalytic process is heterogeneous.
2.6.6 Electropolymerised metalloporphyrins—analytical and biological applications

The electropolymerised metalloporphyrins also find applications as electrode materials for anion detection and pH measurements. For example, the electropolymerised aniline-substituted-CoTPP moieties on glassy carbon surface were highly selective towards the detection of thiocyanate and nitrite anions. The mechanism by which these metalloporphyrin electrode sensors operate was probably related to the well known axial complexation capability of the central metal cation of the porphyrin towards different kinds of anions and bases. These ion-selective electrodes have a detection limit of $5 \times 10^{-7}$ M and also have life times of more than 2 months.

As far as biological applications of electropolymerised metalloporphyrin films are concerned, the use of an electropolymerised Ni-porphyrin film for measurement of NO in biological systems was important. The sensor has been applied to amperometric measurements of NO released from a single endothelial cell in a pulmonary artery as well as for the determination of NO in blood and in other biological medium.

Further electropolymerised methoxy, and hydroxy-substituted Cu-TPP films with p-type semiconductor properties were efficient systems for solar energy conversion. In a typical experiment, the porphyrin–polymer was directly illuminated by visible light and the resulting photo current was measured with a plateau at 0.2 $\mu$A/cm; a quantum yield of 21.6% and a conversion efficiency of 0.16 was observed. This calculated conversion efficiency was 10 orders of magnitude higher than those reported for the monomeric porphyrin in homogeneous solution; no decline in efficiency was observed during a 5h run.
2.7 Outline of the Present Work

It is intended to look into the following aspects in the present investigation:

(i) To select and synthesize certain organic polymeric systems which could act as support materials for immobilising porphyrins and their metalloderivatives.

(ii) To surface functionalise appropriately these solid polymer systems so that anchoring of porphyrin system can be done either through covalent bond or ionically or through both. Attempts would be made to develop both cationically (PS) and anionically (PA) functionalised polymer systems.

(iii) In some cases it is intended to estimate the functionality of the polymer systems to get an idea of the nature and extent porphyrin deposition on to the polymer surface.

(iv) To synthesise chemically stable porphyrins and metalloporphyrins and functionalise them suitably so that grafting can be done effectively. The basic porphyrin system selected for the studies are mesophenylporphyrins (H$_2$TPP) and the mesopyridyl analogues (H$_2$TPyP) respectively. These would be further derivatised to get either anionic (H$_2$TPPS) or cationic (H$_2$TMPyP) porphyrins.

(v) All the free-base (metal-free) porphyrins would be complexed with a series of metal ion/carriers to synthesise their metalloderivatives--MTPPS/MTPyP (M= Mn, Fe, Co, Zn, Ag, Cu, Cd).

(vi) Immobilisation of anionic and cationic porphyrins and their metalloderivatives onto the surface--functionalised polymer support by suitable techniques to generate appropriate (PS–MTPPS and PA–MTMPyP) species. Attempt would be made to estimate the extent of uptake of the porphyrins by the polymer surface.
(vii) Characterisation of all the appended porphyrins emphasising on the electronic and redox modifications brought about on them by the polymer matrix. Suitable spectral techniques (IR, electronic and EPR) and cyclic voltammetric methods would be employed.

(viii) It is intended to develop porphyrin systems encapsulated (without any direct chemical bonds) into the polymer matrix. Such systems also would be studied for any possible electronic modification.

(ix) To investigate the enzymatic (catalase) activity of selected PS–MTPPS [M=Fe(III), Mn(III) and Co(III)] systems. It is also intended to investigate the effects of factors like the type of central metal ion, the nature of reaction medium (pH) and temperature onto catalytic efficiency of these systems. Attempts would also be made to decipher the possible mechanism involved in the enzymatic reaction.

(x) To investigate the peroxidase-like activity of PS–MTPPS[M=Fe(III), Mn(III) and Co(III)] systems and to study various contributing factors like the type of metal ion, pH and temperature on to their activity.

(xi) It is also intended to study the photocatalytic activity of some PS–MTPPS systems bearing singlet emitting H₂TPPS, ZnTPPS and CdTPPS with respect to their singlet oxygen generation ability.

(xii) As a first step to develop special coulombically bound dimers, attempts would be made to graft H₂TPyP/MTPyP on chloromethylated polystyrene through quaternisation at one of the mesopyridyl porphyrins to get PS–H₂TpyP⁺/PS–MTPyP⁺ which has porphyrin unit bonded covalently on the support along with the formation of a charged(mono–cationic) centre. The characterisation of various such grafted monomeric(and monoionic) porphyrins would be done.

(xiii) Development of tetraionic (cationic) porphyrins on to the polymer support would be carried out by exhaustive alkylation of PS–H₂TPyP¹⁺ and PS–MTPyP¹⁺ mentioned above. Characterisation
of the resulting highly charged PS–H$_2$TMPyP$^{4+}$/PS–MTMP$_2$TMP$^{4+}$ porphyrin systems would be made by appropriate techniques.

(xiv) Novel diporphyrin systems grafted on to the polymer support would be developed by reacting PS–H$_2$TMPyP$^{4+}$/PS–MTMP$_2$TMP$^{4+}$ with tetra anionic H$_2$TPPS/MTPPS. Quantitative estimation of dimer formation on to the support would be carried out to establish 1:1 identity (cationic:anionic) of the resulting immobilised porphyrins. Porphyrins of several homo–and hetero–dimers would be carried out by this strategy. Characterisation employing electronic and EPR spectral measurements would be done. Attempts also would be made to examine the proximity and the relative disposition of the porphyrin units within these dimer systems.
2.8 References