Studies on polymer-appended free base porphyrins with ether linkage and their copper complexes

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Monohydroxy- and tetrahydroxyporphyrins have been anchored on crosslinked polystyrene matrices through ether linkage. Ortho, meta and para substituted polymeric porphyrins have been synthesised from chloromethyl polystyrene and suitably substituted porphyrins and the products characterised by spectral studies. The interesting features of the electronic spectra of polymer anchored porphyrins like split soret bands are explained by the orientational variation in ortho-, meta- and para-isomers and the effect of polymer-porphyrin interaction on the electronic levels of porphyrin macrocycle. The copper complexes of these polymer-bound porphyrins are synthesised and analysed spectroscopically. Electronic and ESR spectra show interesting results and these are explained based on the electronic modification of porphyrin systems on a rigid macromolecular backbone.

The highly delocalised π-electron framework of planar porphyrin molecules make them a finely tunable molecular system in terms of their electronic characteristics. Among various factors which modulate these key properties the major ones are known to be the type of substituents on the porphyrin periphery, the nature of the central metal atoms of metalloporphyrins and the coordination number of the metal ion concerned. Studies on innumerable varieties of polymeric porphyrins and their metallo derivatives were carried out by several workers. Crosslinked polymers obtained by the polymerisation of suitably designed monomers find extensive use as support materials for a wide variety of catalysts, reagents and functional fragments to carry out novel reactions by extremely simple synthetic strategy. The idea of porphyrin supported on crosslinked polymer offers innumerable probabilities for the structural and electronic modification of the porphyrin system by varying the porphyrin, polymer and the nature and position of polymer-porphyrin linkage. The present study covers the synthesis of polymeric porphyrins with ether linkage, metallation with copper(II) ions and the chemical and spectral analysis of these polymeric systems.

Materials and Methods

2% Divinylbenzene (DVB)-crosslinked polystyrene was prepared by the suspension co-polymerisation of styrene and DVB in the required ratio. Chloromethyl polystyrene [A], 5,10,15,20-tetrakis(hydroxyphenyl)porphyrins I and 5-(hydroxyphenyl)-10,15,20-triphenylporphyrins I' were synthesised following the literature procedure. The chlorine capacity of the polymers was estimated by the modified Volhard's method. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer operating in the range 4000-400 cm⁻¹ using KBr disks. Solid state electronic spectra were recorded on a Cary-2390 UV-vis-near IR spectrophotometer and ESR spectra on a Varian E-12 spectrophotometer.

Polymer-bound porphyrins [A1 and A1']

General procedure. DVB-crosslinked chloromethyl polystyrene (2%, 1 g) was suspended in the mixture of chloroform-methanol (3:1). Hydroxyporphyrin (I or I') (500 mg) was dissolved in methanol and was added to the above mixture. Triethyl amine (1 mL) was then added and the mixture refluxed for 8 hr. After cooling, the resin was filtered, washed...
repeatedly with hot methanol, water, acetone and chloroform until a colourless filtrate was obtained. The resin was then dried in an air oven.

Differently substituted polymer-bound porphyrins were prepared by using ortho-, meta- and para-substituted hydroxyporphyrins. IR(KBr): 1260 cm\(^{-1}\) (Ar-O-C), 1150 cm\(^{-1}\) (–CH\(_2\)-O–).

**Preparation of copper complexes of A1 and A1**: General procedure. The copper complex was prepared by the reaction of the polymer-bound porphyrin (1 g) swelled in methanol and chloroform (50 mL, 1:1) with a solution of copper(II) acetate (20 mg/20 mL water). Acetic acid (0.1 mL) and sodium acetate (50 mg) were added. The mixture was refluxed for 2 hr, cooled, filtered and washed well with water and methanol.

**Results and Discussion**

Substituents on the phenyl groups of porphyrin system lie in a plane orthogonal to the porphyrin frame\(^9\). It is possible to synthesise porphyrins with functional groups attached to various positions (ortho, meta and para) on the mesophenyl groups by reacting with appropriate starting materials. In analogy with the observation on low molecular systems it was proposed that by appending such position isomers of functionalised porphyrins on polymer supports, the orientation of porphyrin π-frame with respect to polymer support can be controlled at varying angles depending on the position of the linkage. Thus, on grafting ortho-substituted H\(_2\)TPP’s the bulky polymer matrix would feel the porphyrin plane quite close and face-to-face leading to intense steric interaction. As a result, there can be expected significant distortion (puckering) on the porphyrin moiety to ease the steric action. In the case of species appended through meta-substituted porphyrin, the proximity of porphyrin frame and the polymer support would not be close enough and hence only moderate puckering is expected. On the other hand, the system with para-substituted porphyrin attached to the polymer support is expected to have only the minimum puckering. In the –O-linked polymeric porphyrins there can be some amount of non-rigidity or flexibility especially with regard to the rotation of porphyrin frame about the connecting single bond or bending about the intervening bonds. These ‘flexible’ bonds are likely to cause distortion on porphyrin by steric interaction (especially on the ortho- and meta-isomers).

Polymers with monohydroxy- and tetrahydroxy-tetraphenylporphyrins having different phenyl substituent positions were prepared (Scheme I) and the number of functional groups on the porphyrin ring appended on to the polymer matrix were determined by estimating the residual chlorine capacity of the polymer. It was estimated that 0.6 to 0.95 meq of chlorine/g of the polymer was replaced by the porphyrin groups for the compounds A1ortho, A1meta and A1para.

Characterisation of the polymer-bound porphyrins were done by spectral analysis. IR spectroscopy provides a clear evidence for the bonding pattern in the compounds. The IR spectrum of compound A1 shows a broad band in the region 3380-3450 cm\(^{-1}\) corresponding to the O-H stretching vibrations. This is due to the free hydroxyl groups of the porphyrin moiety. A1' compounds do not show this peak indicating the absence of free hydroxyl groups. The peaks observed at 1260 and 1150 cm\(^{-1}\) are corresponding to the aryl ether and CH\(_2\)-O vibrations, respectively. The latter indicate the formation of ether linkage between the polymer support and the porphyrin system.

Electronic spectra of the polymeric porphyrins...
Al$_{ortho}$, Al$_{meta}$, Al$_{para}$, Al$'_{ortho}$, Al$'_{meta}$ and Al$'_{para}$ exhibit characteristic etio type spectra with the appearance of Q-bands and soret band. The presence of polymer matrix in these derivatives impart some remarkable change on the electronic properties of the porphyrin macrocycle. On appending the porphyrin through their hydroxy substituents to the polymer backbone, some well-distinguishable observations were obtained for the soret band of the spectra of Al compounds. Here the soret bands get splitted and appear as an intense band with a shoulder. These spectral changes are depicted in Figure 1. The split soret band is more pronounced for the para-substituent.

Apart from the inestimable backbone effect of the polymer, the absorption spectra helps to give us a deeper insight into the electronic and steric interactions in the porphyrin systems. Tetrahydroxy-tetraphenylporphyrins are bonded to the support material through an ether linkage and in this process, a considerable extent of hydroxyl groups remain free. Though the hyperentropic factor is operative in functional polymers, the interaction of the porphyrin core unit and unreacted phenolic groups is quite possible due to the coiling effect of the backbone. In such situations, the porphyrins can be protonated by the presence of a close, suitably oriented phenolic group. This will perturb the electronic ordering in the porphyrin core. The presence of protonated and non-protonated porphyrin systems is responsible for the split soret bands.

Another interesting and important observation was derived by comparing the absorption spectra of ortho-, meta- and para-isomeric systems Al$_{ortho}$, Al$_{meta}$ and Al$_{para}$. No systematic variation could be observed in these cases though it was expected due to the systematic steric participation of polymer in ortho, meta and para-isomers. The meta-isomer showed a blue shift compared to the ortho (Table 1). Protonation of the porphyrin system by phenolic groups and the electron redistribution of the resultant phenoxy ion with its porphyrin core is again clearly evident from these results. In ortho- and para-isomers, higher extent of electron delocalisation is possible due to conjugation and hence the absorption band is shifted to longer wavelength region.

On the other hand, electronic spectra of Al$'$ compounds show some systematic change on going from Al$'_{ortho}$ to Al$'_{para}$ (420, 421 and 423 cm$^{-1}$ for ortho, meta and para compound respectively). This is due to the pure steric interaction of the polymer backbone on the electronic levels of porphyrin system. Split soret bands observed in Al compounds were absent in Al$'$ compounds. This is because of the absence of free or unreacted hydroxyl groups which facilitate protonation in the case of Al compounds.

The polymer-bound porphyrins, Al and Al$'$ were metallated and the formation of the metal complexes of Al is represented in Scheme II (where M=Cu).

The formation of the copper complexes were confirmed by spectral measurements. The optical absorption spectra of these polymer-bound copper complexes gave the characteristic etio type spectra for metalloporphyrins. The absorption spectra of Al (Cu) complexes show an intense soret band and two Q-bands (Table II).

For the free base Al compounds a split soret band was observed. This splitting was absent in their copper complexes. Metallated porphyrins cannot be protonated and as a result, the phenomenon of soret band splitting was not observed in Al (Cu) complexes. Absorption spectra of Al$_{ortho}$ (Cu), Al$_{meta}$ (Cu) and Al$_{para}$ (Cu) were analysed and a systematic red shift was observed (Table II). The varying degree
of steric participation in ortho-, meta- and para-isomers is responsible for this systematic spectral change.

The ortho, meta and para derivatives of Al' (Cu) complexes were also synthesised and analysed spectroscopically. The nature of polymer-porphyrin interaction was deducible from the spectral results. A systematic change was observed in the λ_{max} values of Al_{ortho} (Cu), Al_{meta} (Cu) and Al_{para} (Cu) complexes (418.5, 420 and 421 cm^{-1} for ortho, meta and para respectively) which is a measure of the strain experienced by the π-electron framework. Al' (Cu) complexes showed strong red shift when compared to their Al (Cu) counterparts. This is because of the higher degree of steric effect created in Al (Cu) complexes.

The electronic modification brought about by the polymer support can also be studied by ESR spectroscopy. Copper tetraphenylporphyrin in powder form, which is a magnetically concentrated system is capable of providing only isotropic X-band ESR spectra. This is because, the neighbouring copper ions in this sample interact well leading to the dipolar broadening of the resonance lines. Two methods have already been suggested to minimise the dipolar interaction between the neighbouring copper ions. The magnetic dilution can be achieved either by using suitable solvent or by a diamagnetic solid solvent. In Al (Cu) and Al' (Cu) complexes, magnetic dilution is attained by covalently attaching the porphyrin systems to an insoluble polymer support. The copper complexes of Al (Cu) and Al' (Cu) gave well-defined ESR spectra even at room temperature in the solid state. The spin Hamiltonian parameters showed a systematic variation as we go from ortho to para (Tables III and IV).

Tables III and IV show that the greater steric effect on the ortho compound is evidenced by the increase in α^2 value compared to meta and para. Compared to Al (Cu) compounds, α^2 values are higher for Al' (Cu) complexes. Again, it was found that on moving from Al_{ortho} (Cu) to Al_{para} (Cu) or Al'_{ortho} (Cu) to Al'_{para} (Cu) the metal nitrogen bond strength increases.

**Conclusion**

The macromolecular structural features of the polymeric support material have been proved to contribute significantly to the reactivity of the
attached functions. The nature of the interaction between the polymeric backbone and the functional species is either physical or chemical in nature. Electronic properties of porphyrins and the catalytic behaviour of metalloporphyrins are controlled by the sensitive $\pi$-electron framework of the porphyrin core unit. The polymer support of polymeric porphyrins is used to regulate the electron distribution and thereby impart specific characteristics to the system. By varying the position and nature of polymer-porphyrin linkage, any desired situation can be created in the porphyrin system. The synthesis and electronic studies of polymer-bound porphyrins with flexible ether linkage were presented here.

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References