

Copper(II) and Silver(II) Complexes of Polymer-Bound Porphyrins with Schiff Base Linkage

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Received 4 June 1997; accepted 3 September 1997

ABSTRACT: Two percent divinylbenzene (DVB)–crosslinked polystyrene was prepared and functionalized to obtain its aldehyde analog. Amino porphyrins were anchored on this polymer support by Schiff base condensation. The anchoring positions were adjusted so as to obtain *ortho*-, *meta*-, and *para*-isomeric systems. The polymer-bound free-base porphyrins were metallated to obtain the corresponding Cu(II) and Ag(II) complexes by treating them with the corresponding metal salt solutions. The products were characterized chemically and spectroscopically. Electronic and ESR spectral analysis shows the microenvironmental participation of the polymer network on the electronic levels of the porphyrin system. The extents of steric and electronic participation were evaluated and are presented. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 89–93, 1998

Key words: polymer, porphyrins, metalloporphyrins, schiff base

INTRODUCTION

Metalloporphyrins find wider applications as catalysts and biological models.^{1–3} Free-base porphyrins exhibit remarkable ligation characteristics toward metal ions and thus derivatives of porphyrins with almost all metals and semimetals have been synthesized.^{4–6} The type of the central metal ion has a very pronounced effect on the electronic property of the porphyrins.⁷ The nature of the interaction between the metal ion and the porphyrinato systems is such that both species mutually influence the electronic levels. In the majority of cases where the metalloporphyrins exhibit catalytic activity, the main reactive site is the central metal ion. The present study dealt with copper(II) and silver(II) complexes of polymer-bound porphyrins with rigid polymer–porphyrin linkage.

They were studied in detail by ESR and electronic spectra to characterize and evaluate the electronic modification brought about in various polymer-bound porphyrins. There were significant changes in the electronic properties depending on the extent of distortion thrust upon the porphyrin macrocycle by the polymer matrix at different linking positions.

EXPERIMENTAL

General

Two percent divinylbenzene (DVB)–crosslinked polystyrene was prepared by the suspension copolymerization of styrene and DVB in the required ratio. Chloromethyl polystyrene, polymeric benzaldehyde [A], and 5-(aminophenyl)10,15,20-triphenyl porphyrins [I] were synthesized following the literature procedure.^{8–10} The chlorine capacity of the polymers was estimated by the modified Volhards method. IR spectra were recorded on a

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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 were recorded on a Varian E-12 spectrometer.

Polymer-bound Porphyrins [AI]: General Procedure

Two percent DVB-crosslinked polybenzaldehyde (2 g) was suspended in chloroform (50 mL). A solution of aminoporphyrin [I] (100 mg) dissolved in chloroform (5 mL) was added to this and the reaction mixture was refluxed for 6 h. After cooling, the resin was filtered and washed with chloroform and methanol until a colorless filtrate was obtained. The resulting polymer was finally dried in an air oven. *Ortho*-, *meta*-, and *para*-substituted aminoporphyrins were used for the preparation of differently substituted AI.

Synthesis of Metal Complexes of Polymer-bound Porphyrins: General Procedure

The metal complex was prepared by the reaction of the polymer-bound porphyrin (1 g) with a solution of the metal salt (20 mg/20 mL water) in a mixture of methanol and chloroform in a 1 : 1 ratio. Acetic acid (0.1 mL) and sodium acetate (50 mg) were added. The mixture was refluxed for 2 h. This was then cooled, filtered, and washed well with water and methanol. The salts employed for the preparation were copper(II) acetate for the copper complex and silver(II) acetate for the silver complex.

RESULTS AND DISCUSSION

In polymer-supported porphyrins, the support material and porphyrins are so designed that, on linking them covalently, the linking unit between them bears bonds which are either rigid or flexible with regard to rotational and/or bending motions of the end units. Evidently, the nature of the linking unit becomes an important factor in deciding the electronic nature of porphyrins. Because both polymer and porphyrin fragments are bulky, there could arise very significant steric interaction, the spacer moiety often having the ability to modulate the strain by bond flexing. It is possible to design several such linkages which could result in systems with a variety of linking modes.

Monoamino-substituted tetraphenyl porphyrins were anchored to the polymer matrix through a Schiff base linkage. The bonding positions were adjusted to obtain various isomeric systems. AI_a, AI_b, and AI_c are the *ortho*, *meta*, and *para* derivatives of polymer-bound monoamino porphyrins, respectively. The products were analyzed by chemical and spectroscopic methods. IR spectral studies indicate that the porphyrins are chemically bound to the polymer system. The peak observed at 1640 cm^{-1} represents the >C=N- stretching absorption of the Schiff base linkage. A broad band was obtained at 3440 cm^{-1} , corresponding to the -N-H stretching vibration. This is due to the unreacted amino groups in the porphyrin system. The >C=O stretching absorption of the free aldehyde group was observed at 1700 cm^{-1} (Fig. 1).

Solid-state electronic spectra (reflectance spectra) gave interesting results. A systematic red shift was expected on moving from the *ortho* to the *para* derivative, due to the increasing steric participation observed for polymer-bound porphyrins with amino or ether linkage.^{11,12} But for AI compounds, no systematicity was observed in the electronic spectra. The Soret bands of AI_a, AI_b, and AI_c gave peaks at 420, 417.5, and 425 nm, respectively. The Q bands also showed similar trends. These results show that the polymer-porphyrin interaction is not purely steric for AI compounds. For these compounds, the steric effect is somewhat masked by the extensive conjugation of the π -electron framework of the porphyrin moiety to the polymer chain. This is because the bonding of the porphyrin to the polymer matrix is through a >C=N- bond. This conjugative effect is greater for *ortho*- and *para*-substituted systems.¹²

AI(Cu) complexes were synthesised by the general preparative method (Scheme 1, where $M = \text{Cu}$). Various spectral techniques were employed for their structural and electronic characterization.¹³ All the AI(Cu) complexes showed the characteristic electronic spectra of metalloporphyrins (Fig. 2). The spectrum shows two bands in the visible region and an intense Soret band in the near-UV region. Depending on the position of attachment of the polymer function (*ortho*, *meta*, or *para*) on the phenyl group of the porphyrin, the spectral data show characteristic shifts in their values.

It is clear that for AI_a(Cu) and AI_c(Cu) the λ_{max} values are red-shifted compared to AI_b(Cu). This is because of the highly delocalized π -electron framework of the planar porphyrin molecules

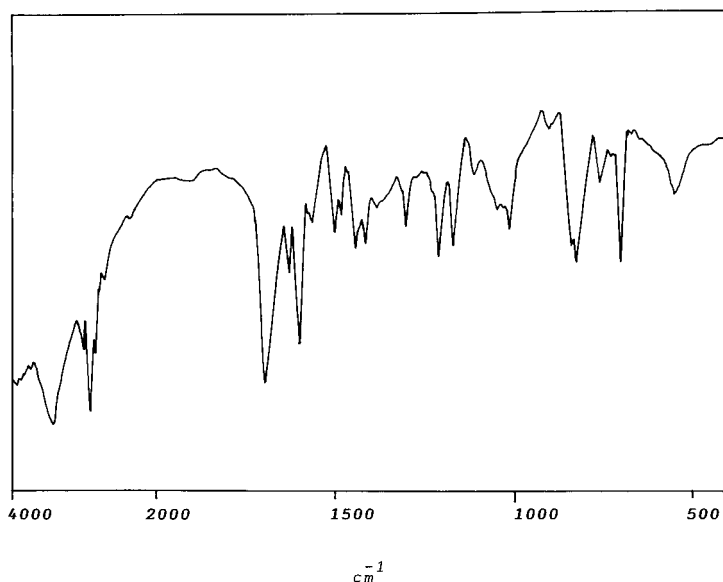


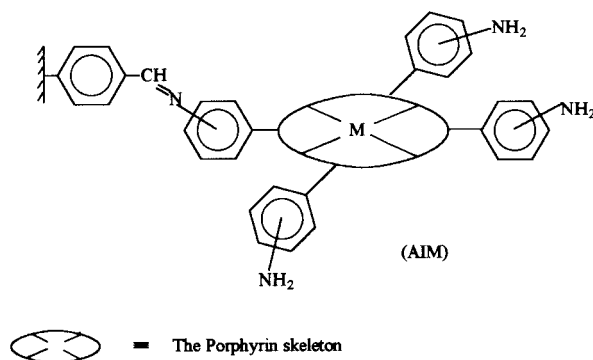
Figure 1 IR spectrum of polymer-bound Schiff base porphyrin.

which are extensively conjugated with the polymer chain through the Schiff base linkage. Thus, for the $Al_a(Cu)$ complex, a combined effect of steric and conjugative factors are operating, but for $Al_b(Cu)$, the steric effect is pronounced, and for $Al_c(Cu)$, the effect of conjugation is much more prominent. All these observations are in good agreement with the spectral data of corresponding free-base AI compounds.

ESR spectra of all polymer-bound copper complexes were recorded at room temperature in the solid state. The simulation technique was employed to determine the spin Hamiltonian parameters (Table I).

Figure 3 gives the ESR spectrum of a typical AI(Cu) species recorded at room temperature, which shows both parallel and perpendicular

parts separated. The superhyperfine features are manifested in the perpendicular component, while these could be observed in the parallel component on increasing the gain. One noteworthy feature of these polymer-supported copper complexes is that they give well-resolved anisotropic ESR spectra in the solid state at room temperature.¹⁴ The occurrence of anisotropic spectra is essentially due to the wide separation among magnetic nuclei which avoids dipolar interaction, and one can extract all the electronic features at room temperature. On comparing the spin Hamiltonian parameters of these copper complexes, which have only directional variation (of the porphyrin plane with the polymer matrix surface), very distinct changes were recorded. The variation in g and A values, as seen from Table I, indicates the domi-



Scheme 1 Structure of the metal complex of polymer-bound porphyrin with Schiff base linkage.

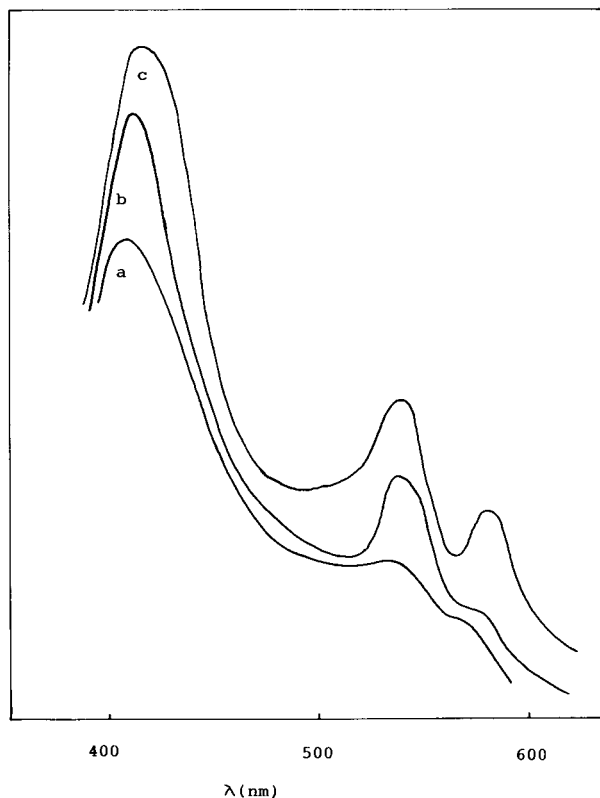


Figure 2 Electronic spectra of Al(Cu) complexes.

nation of a conjugative effect over a steric effect in the case of Al_a(Cu) and Al_c(Cu) compared to Al_b(Cu).

Changes in σ -bonding between the metal and four nitrogen atoms are expected for this series of complexes. In the case of Al(Cu) complexes, α^2 values show a decrease for *ortho*- and *para*-substituted polymeric porphyrins when compared to *meta*, that is, the metal nitrogen bond strength is increased for the Al_a(Cu) and Al_c(Cu) complexes compared to the Al_b(Cu) complex. These observations confirm that, besides the systematic structural distortion brought about by the macromolecular system on the porphyrin framework appended on the polymer, extensive conjugation of the porphyrin macrocycle to the polymer chain

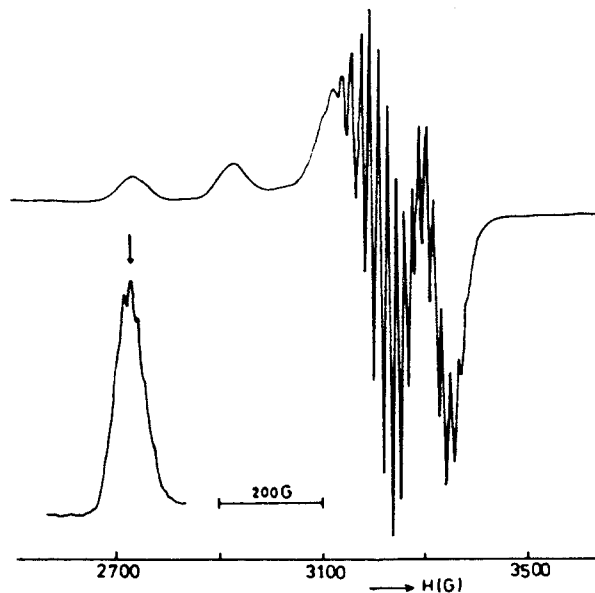


Figure 3 ESR spectrum of Al(Cu) complex.

plays a key role in the electronic energy levels of Al(Cu) complexes.

The G values for Al(Cu) complexes are greater than 4. This important observation suggests that, in these copper complexes, the copper-copper interaction is negligible. This is supporting evidence for the fact that on appending the porphyrin moiety to a polymer chain the porphyrin molecules are effectively isolated from each other and so the polymer effect is evident.¹⁵

Silver Complexes of Al

Silver complexes of Al with a porphyrin-polymer Schiff base linkage were prepared by refluxing the required polymeric porphyrin with silver acetate in the chloroform-methanol mixture containing traces of acetic acid and sodium acetate (Scheme 1, where $M = Ag$). Electronic spectral data were carefully analyzed and compared with the correspondingly designed copper porphyrins. The unique nature of the Schiff base linkage is a deci-

Table I Spin Hamiltonian Parameters of Al (Cu) Complexes

Compound	g_{\parallel}	g_{\perp}	$A_{\parallel}^{\text{Cu}}$ (G)	A_{\perp}^{Cu} (G)	A_{\parallel}^{N} (G)	A_{\perp}^{N} (G)	α^2	G
Al _a (Cu)	2.1863	2.0282	190.0	33.3	13.0	16.6	0.7603	7.03
Al _b (Cu)	2.1898	2.0311	188.5	32.5	12.5	15.8	0.7610	6.10
Al _c (Cu)	2.1786	2.0258	192.5	35.0	14.0	17.0	0.7584	7.42

Table II Spin Hamiltonian Parameters of AI (Ag) Complexes

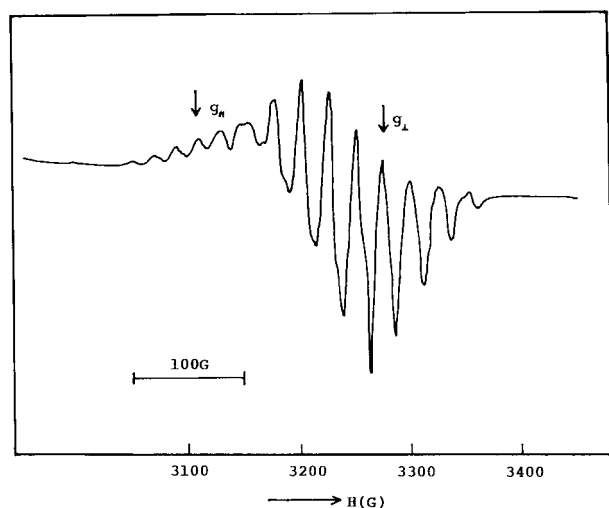
Compound	g_{\parallel}	g_{\perp}	$A_{\parallel}^{\text{Ag}}$ (G)	A_{\perp}^{Ag} (G)	A_{\parallel}^{N} (G)	A_{\perp}^{N} (G)
AI _a (Ag)	2.1236	2.0251	56.5	28.0	18.9	24.0
AI _b (Ag)	2.1250	2.0262	60.0	29.3	20.0	25.0
AI _c (Ag)	2.1241	2.0259	58.5	28.7	19.2	24.5

sive factor in the electronic modification of a porphyrinic system. The Soret band of the *meta* derivative of AI(Ag) was recorded at 426 nm, while the other two isomers showed red shifting in λ_{max} values [427.5 nm for AI_a(Ag) and 428 nm for AI_c(Ag)]. The conjugative effect gained predominance over the steric effect in these cases.

Electron paramagnetic measurements gave well-resolved lines with superhyperfine splitting, indicating the existence of well-separated porphyrin groups. The irregularity, observed in the g values and hyperfine tensors of the *ortho*, *meta*, and *para* isomers, is not explainable with pure steric participation of the backbone support. The ESR parameters are in agreement with the electronic spectral data and these spectral results show the competition between steric hindrance at the *ortho*, *meta*, and *para* positions and conjugative interaction of the polymer and porphyrin macrocycle at the *ortho* and *para* positions. The ESR data of the AI(Ag) complexes are given in Table II. A typical ESR spectrum of the AI(Ag) complex is shown in Figure 4.

CONCLUSION

Polymer-bound porphyrins and their metalloderivatives are compounds of theoretical importance

**Figure 4** ESR spectrum of AI(Ag) complex.

and for catalytic applications.^{1-3,14} The highly sensitive π -electron system of porphyrins brings immense possibilities for structural modification by solid polymer matrices. Porphyrin, bonded to the crosslinked polymeric network through a Schiff base linkage, provides a highly useful porphyrin-polymer association with interesting structural and electronic properties. The syntheses of a series of such polymer-bound porphyrins and their copper and silver complexes were discussed in this article. The interesting features of the IR, electronic, and ESR spectra were also discussed.

REFERENCES

1. M. N. Hughes, *The Inorganic Chemistry of Biological Processes*, 2nd ed., Wiley, New York, 1981.
2. R. P. Hanzlick, *Inorganic Aspects of Biological and Organic Chemistry*, Academic Press, New York, 1976.
3. E. I. Ochiai, *Bioinorganic Chemistry*, Allyn and Bacon, Boston, 1977.
4. D. Dolphin, Ed., *The Porphyrins*, Vols. I-VII, Academic Press, New York, 1979.
5. B. Meunier, *Chem. Rev.*, **92**, 1411 (1992).
6. G. Pratviel, J. Bernadot, and B. Meunier, *Angew. Chem. Int. Ed. Engl.*, **34**, 746 (1995).
7. K. M. Smith, Ed., *The Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, 1975.
8. P. Hodge and D. C. Sherrington, *Polymer Supported Reactions in Organic Synthesis*, Wiley, New York, 1980.
9. V. K. Haridasan, A. Ajayaghosh, and V. N. R. Pillai, *J. Org. Chem.*, **52**, 2662 (1987).
10. A. D. Alder, F. R. Longo, F. Kamps, and J. Kin, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
11. T. Mathew and M. Padmanabhan, in *Polymer Science: Recent Advances*, Vol. 1, I. S. Bhardwaj, Ed., Allied, New Delhi, 1994.
12. T. Mathew, M. Padmanabhan, and S. Kuriakose, *Ind. J. Chem. B*, **34**, 903 (1995).
13. K. Kano, M. Takei, and S. Hashimoto, *J. Phys. Chem.*, **94**, 2181 (1990).
14. T. Mathew, M. Padmanabhan, and S. Kuriakose, *J. Appl. Polym. Sci.*, **59**, 23 (1996).
15. J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, **9**, 135 (1976).