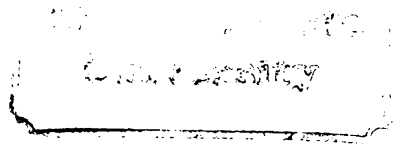

This is to certify that the

dissertation entitled

SYNTHESIS AND CHARACTERIZATION OF

POLYMER-BOUND METALLOPORPHYRINS

presented by

Frederick Russell Batzer

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Carl H. Brubaker, Jr.
Major professor

Date May 12, 1982

SYNTHESIS AND CHARACTERIZATION OF POLYMER-BOUND METALLOPORPHYRINS

By

Frederick Russell Batzer

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1982

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF POLYMER-BOUND METALLOPORPHYRINS

By

Frederick Russell Batzer

Several methods of covalently attaching porphyrins to 20% divinylbenzene-polystyrene copolymer beads were investigated to determine which of the various methods lends itself to the preparation of polymer-attached porphyrins. The Friedel-Crafts acylation and alkylation of 20% divinylbenzene-polystyrene copolymer beads were investigated. Aminated, 20% divinylbenzene-polystyrene copolymer beads were used to bind two different porphyrins. Chloromethylated, 20% divinylbenzene-polystyrene copolymer beads were used to bind three different porphyrins. These resins were metallated with metal salts in hot N,N-dimethylformamide. The radial distributions of these resins were determined by scanning electron microprobe analysis. The distributions varied with the relative reactivity of the functional group on the porphyrin.

The ESR spectra of the polymer-bound copper complexes indicated that there is varying degrees of interactions between the polymer-bound copper porphyrins. These spectra were qualitatively related to the loadings and radial distributions of the polymer-bound metalloporphyrins and to the ESR spectra of a series of dilutions of TTPCu in $TTPH_2$.

In addition, the assisted autoxidation of cyclohexene and the assisted autoxidations of benzaldehyde and of butanal were investigated. The polymer-bound metalloporphyrins were not as effective as the soluble metalloporphyrins in assisting the autoxidations. In addition, the decomposition of the porphyrin ring was observed in all cases.

To my daughter, Trista

Acknowledgements

I would like to thank the Department of Chemistry at Michigan State University for providing financial support in the form of a teaching assistantship. I would also like to express my appreciation to Professor Carl H. Brubaker and to all of the group members for all of their help and friendship.

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LIST OF ABBREVIATIONS

$TPPH_2$	5,10,15,20-tetraphenylporphyrin
$TTPH_2$	5,10,15,20-tetrakis(4-methylphenyl)porphyrin
$TPP(CO_2H)_4H_2$	5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin
$TPP(CO_2Et)_4H_2$	5,10,15,20-tetrakis(4-carboethylphenyl)porphyrin
$TPP(CO_2hexyl)_4H_2$	5,10,15,20-tetrakis(4-carbohexylphenyl)porphyrin
$TPP(CH_2OH)_4H_2$	5,10,15,20-tetrakis(4-hydroxymethylphenyl)porphyrin
$TPP(CH_2OH)_{4-x}(CH_2Cl)_xH_2$	partially chlorinated $TPP(CH_2OH)_4H_2$
$T_3P(OC_5Br)H_2$	5-(2-(5-bromopentoxy)phenyl)-10,15,20-tris(4-methylphenyl)porphyrin
$T_3P(OH)H_2$	5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)-porphyrin
$T_3P(py)H_2$	5-(4-pyridyl)-10,15,20-tris(4-methylphenyl)porphyrin
$T_3P(NHAc)H_2$	5-(4-acetamidophenyl)-10,15,20-tris(4-methylphenyl)porphyrin
$T_3P(NH_2)H_2$	5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl)-porphyrin
2% P_1	2% divinylbenzene-polystyrene copolymer beads
P_1	20% divinylbenzene-polystyrene copolymer beads
P_2	Aminated, 20% divinylbenzene-polystyrene copolymer beads
P_3	chloromethylated, 20% divinylbenzene-polystyrene copolymer beads
DMF	N,N-dimethylformamide
THF	Tetrahydrofuran

I. INTRODUCTION

A. General Introduction

In recent years there has been considerable interest in the attachment of various types of compounds to polymers in order to form useful catalysts and synthetic reagents. Polymer-bound catalysts are often either more active, more selective, or more easily recovered than the original catalysts which are not attached to a polymer matrix[1]. Polymer-bound synthetic reagents can be easily separated from the reaction products and have found extensive service as a protecting group such as in polypeptide syntheses[2].

One important aspect of attachment of these compounds to polymers is that the polymer matrix can serve to isolate individual molecules from each other. This isolation can substantially reduce any interactions that can arise between adjacent molecules. This results in hindering the catalyst from forming dimers or higher aggregates. For example, it has been shown that Wilkinson's catalyst can form halogen-bridged dimers when it is attached to either 2% or 20% divinylbenzene-polystyrene copolymer beads[3]. From EXAFS it was shown that dimerization was lessened in the 20% cross-linked copolymer.

In biological systems, porphyrins are found in polymeric matrices and perform many important biological functions. In these polymers the porphyrins are well isolated from each other such as in hemoglobin.

Therefore, it is not surprising that porphyrins and analogous macrocycles such as phthalocyanines and Schiff base complexes have been attached to polymers. Much of this work has involved the study of reversible oxygenation of polymer-bound cobalt and iron porphyrins and Schiff base complexes of cobalt. Some work has also been done with polymer-bound metalloporphyrins, metallophthalocyanines, and Schiff base complexes as oxidation catalysts.

The attachment of porphyrins and related compounds to polymers has been undertaken in an effort to isolate monomers effectively. The formation of dimers and higher aggregates is known to occur for many of the naturally occurring[4] and synthetic porphyrins[5]. The ability of these compounds to form aggregates is best exemplified by chlorophyll[6], a closely related chemical species. It is these dimers and aggregates which often retard the metalloporphyrins' effectiveness in performing various functions. As an example, the irreversible oxidation of simple iron(II) porphyrins is known to be bimolecular[7]. This process has been retarded by the synthesis of sterically hindered iron(II) porphyrins. Examples of these complexes are the crowned[8], capped[9], strapped[10], and picket-fence prophyrins[11]. Two of these, Chang's crowned porphyrin[8] and Collman's picket-fence porphyrin[11], point out the need of isolation by bulky groups whether consisting of side chains or of polypeptide chains. With polymer-bound iron(II) porphyrin complexes, reversible oxygenation has been realized by Bayer and Holzbach with a water soluble polymer containing covalently-bound iron(II) protoporphyrin and porphyrin- and polymer-attached imidazole residues[12].

There are only a few reports of polymer-bound porphyrins and their analogs functioning as oxidation catalysts. Lautsch and coworkers used their polymer-bound, iron porphyrins as oxidation catalysts in the oxidation of substrates such as cysteine[13]. In similar work, Rollmann used polymer-bound, cobalt porphyrins in the oxidation of 1-butanethiol[14]. The cobalt porphyrin was reported to be decomposed to some extent during the oxidation reaction. In other work, hydroquinones were oxidized to quinones by polymer-bound, cobalt protoporphyrin[15]. The analogous polymer-bound cobalt phthalocyanine has been used in thiol oxidation[16] and the polymer-bound cobalt Schiff base complex of Drago has been used in the oxidation of 2,6-ditertiarybutylphenol[17].

B. Classification of Porphyrin-Containing Polymers

Porphyrin-containing polymers may be classified as to how the porphyrin is bound to the polymer. The porphyrin may be bound as a coordination complex in which the central metal atom of the metalloporphyrin is coordinated to a ligand which is covalently attached to a polymer. Collman et al. have formed this type of linkage between 2% divinylbenzene-polystyrene copolymer which contains covalently bound imidazole and iron and cobalt porphyrins[18,19]. Secondly the porphyrin may bind covalently to the polymer and this has been done in several ways. A pre-formed polymer such as polyethyleneimine and a porphyrin acid chloride may be coupled together to form an amide linkage[13]. This has also been done with amine-containing polystyrene copolymers[20]. Polymers containing covalently bound porphyrins have also been formed when an appropriate porphyrin is included in the polymerization step.

For example, Lautsch and coworkers have copolymerized protoporphyrin and styrene[13]. Another way of forming polymer-bound, covalently-attached porphyrins is to form the porphyrin by condensation of appropriate reagents to a polymer-bound residue. This has been done with a 2% divinylbenzene-polystyrene copolymer containing benzoyl chloride groups which have been treated with either 3- or 4-hydroxybenzaldehyde. This polymer was then reacted with para-tolylaldehyde and pyrrole in propionic acid. Lastly, there are polymeric porphyrins which are formed from aldehydes and meso-substituted porphyrins. Polyesters and polyamides may be formed with polyfunctional porphyrins. Examples of these are mostly dimers and trimers. Polyphthalocyanines could also be viewed as examples of polymeric porphyrin analogs.

1. Coordination Polymers of Metalloporphyrins and Related Compounds

The formation of coordination complexes between metalloporphyrins and polymers containing ligating groups is well represented in the literature. These polymers may be divided into two groups: polymer-embedded and polymer-attached. In general, these polymers have greater coordination equilibrium constants than the analogous unbound ligands.

In 1958, Wang reported the formation of a polystyrene embedded complex between 1-(2-phenylethyl)imidazole and iron(II) protoporphyrin IX diethyl ester[22]. The embedded heme was found to reversibly bind dioxygen and carbon monoxide.

More recently, Collman and coworkers have used chloromethylated, 2% divinylbenzene-polystyrene copolymer as a support for imidazole[18]. The formation of a coordination complex between the polymer-bound

imidazole and TPPFe in benzene resulted in the formation of a six-coordinate complex of TPPFe and two of the imidazole residues in the polymer. The polymer-bound complex was found to bind carbon monoxide but treatment of either the polymer-bound bisimidazole TPPFe or polymer-bound imidazole TPPFe carbon monoxide complexes with dioxygen resulted in the leaching of $(TPPFe)_2O$ from the polymer. TPPCo has also been shown to form a five-coordinate complex with the polymer-bound imidazole groups[19]. This complex was shown to oxygenate more readily than complexes such as TPPCo(1-methylimidazole). The cobalt complexes of picket-fence porphyrin and hemoglobin were also shown to bind dioxygen to a much greater extent than TPPCo(1-methylimidazole). The polymer-bound imidazole complex with iron(III) TPP was shown to form a more stable complex with benzenethiol than the analogous 1-methylimidazole complex[23].

Tsuchida and coworkers have investigated the interactions of soluble polymers containing covalently-bound pyridine and imidazole groups with iron porphyrins. Overall, they have found that the equilibrium constant for the ligation of iron porphyrins with the polymer-bound ligand is greater than that of the unbound ligand with iron porphyrins in solution equilibria studies.

Their results with heme and partially quaternized poly(4-vinylpyridine) in aqueous solution show that the five-coordinate pyridine complexes for both iron(II) and iron(III) porphyrins are the predominate species[24]. The equilibrium constants are also much greater by a factor of 10^2 for the polymer-bound ligand than for the monomeric analog in water at room temperature. This polymer-bound ligand was used to

study the oxygenation of heme in aqueous solution. Polymer effects were studied by adding agents such as NaCl, sodium lauryl sulfate, poly(methacrylic acid) and poly(styrenesulfonic acid). These additives were found to affect the viscosity of the polymer solution by shrinkage of the polymer. The polymer effect on the stability of the oxygenated ferroprotoporphyrins can be seen from the fact that those solutions with the least viscosity (most shrinkage) contained the most stable oxygenated complex. Here again the polymer is seen to increase the stability of the oxygenated complex because of its steric effects.

Tsuchida and coworkers have also prepared polymers containing covalently-bound imidazole and pyridine to which various cobalt and iron porphyrins have been coordinated. It was found heme could reversibly bind dioxygen when coordinated to either poly(4-vinylpyridine) or poly(N-vinylimidazole) while in a DMF solution[25]. A copolymer of styrene and N-vinylimidazole was also found to bind cobalt protoporphyrin IX dimethyl ester and that the resulting complex was able to bind dioxygen[26]. In addition, a copolymer of 4-vinylpyridine and styrene[27] was found to bind cobalt protoporphyrin IX dimethyl ester and the cobalt Schiff base complexes, ethylenebis(salicylideniminato)cobalt(II), Co(II) salen, and N,N'-[1,1,2,2-tetramethyl]ethylenebis(3-tert-butylsalicylideniminato)cobalt(II), Co(II) tBsalten. All of these complexes bind dioxygen to a much greater extent than that of the analogous monomeric pyridine complexes.

Allcock and coworkers have prepared water-soluble polyphosphazenes which contains covalently bound imidazole groups[28]. Iron(II) protoporphyrin forms the bisimidazole complex with this polymer as was

determined by Mossbauer spectroscopy. From Mossbauer spectroscopy, this complex appears to be irreversibly oxidized by dioxygen and then reduced by excess reducing agent or the polymer itself.

Imidazole has also been covalently bound to silica gel by Basolo and coworkers[29]. They have found that the heme complex does reversibly bind dioxygen at -127°C and all dioxygen was lost by -78°C. The carbon monoxide complex was found to be much more stable.

2. Covalent Attachment of Porphyrins Directly to a Polymeric Support

The formation of covalent attachments of porphyrins to polymers began with Lautsch and coworkers in 1957 and has continued ever since. Included in this group, are the analogous polymer-bound cobalt phthalocyanines of Zwart[16,30,31] and Schiff base complexes of Drago[17]. The covalent linkages which have been reported to date for porphyrins are amide[13,20,32-34], amine[14], ester[14,21,33], ketone[14], alkyl[13,14], and sulfonamide[20]. These linkages have been formed either during copolymerization or to an already existing polymer. One other method reported had the porphyrin prepared by condensation of the appropriate reagents to a polymer-bound residue[21].

It is perhaps the pioneering work of Lautsch that has set the scope of methods of covalent attachment of porphyrins to polymers[13]. His early work dealt with several schemes which could be utilized in the covalent attachment of porphyrins to polymers. Amide linkages could be formed between mesoporphyrin IX and polyethylenimine. Amide linkages to polyphenylalanine were produced by the copolymerization of 4-benzyl-2,5-dioxazolidine and mesoporphyrin IX diazide. The alkyl linkage was

formed during the copolymerization of protoporphyrin IX dibenzyl ester and styrene (with mole ratios of 1 to 10^3-10^5). Each of these polymer-bound porphyrins was converted into the respective iron complexes. Crosslinked, polyethylenimine-bound iron(III) mesoporphyrin and the polyphenylalanine-bound analog oxidized cysteine at comparable rates to that of their unattached analogs.

Rollmann used porous, macrorecticular divinylbenzene-polystyrene copolymer beads (XAD-2) which were supplied by Rohm and Haas as a polymeric support for covalently attaching various porphyrins to the polymeric matrix[14]. In his work, he exclusively used functionalized $TPPH_2$ derivatives as the porphyrin moiety and various functionalized polymers in addition to the original copolymer. The chloromethylated copolymer was treated with 5,10,15,20-tetrakis(4-aminophenyl)porphyrin to form the amine-linked, porphyrin-containing copolymer. The chloromethylated copolymer was also hydrolyzed and then treated with 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin in the presence of a catalytic amount of concentrated sulfuric acid to form an ester-linked, porphyrin-containing copolymer. Rollmann also attached 5,10,15,20-tetrakis(4-chlorocarbonylphenyl)porphyrin to the divinylbenzene-polystyrene copolymer beads with $AlCl_3$ used as a Friedel-Crafts catalyst in the acylation of the polymer's phenyl groups.

These porphyrin-containing copolymers were metallated with the acetate salts of cobalt, nickel, copper, and zinc in refluxing chloroform:acetic acid (1:1). The copper complexes of the copolymer-bound $TPP(NH_2)_4H_2$ and the ketone-linked, porphyrin-containing copolymer were each characterized from their ESR spectra at room temperature and at

77°K. The ESR spectra show well-defined nitrogen and copper hyperfine structure at room temperature and nitrogen perpendicular lines are also observed at 77°K. This is characteristic of magnetically dilute copper porphyrins and suggests that the copper porphyrin is well dispersed within the polymer.

Rollmann reports that, for the autoxidation of thiols, the polymer-bound metalloporphyrins are not all active. He found that the cobalt complex was active and also susceptable to decomposition due to radical attack on the porphyrin periphery.

In the work of King and Sweet[20], porphyrins were covalently attached to aminated, 20% divinylbenzene-polystyrene copolymer beads through an amide linkage and a sulfamide linkage with $TPP(COCl)_4H_2$ and $TPP(SO_2Cl)_4H_2$, respectively. Little control was found over the amount of porphyrin that could be bound to the copolymer. Their experiments show little variation in porphyrin loading as the relative amounts of reagents were changed. The cobalt complexes of these copolymers were also effective in catalyzing the rearrangement of quadricyclane to norbornadiene.

In similar work, LeDon formed the amide linkage between $TPP(COCl)_4H_2$ and either of the copolymers made from 5% p-aminosytrene, 20% p-divinylbenzene, and 75% styrene or 5% p-aminostyrene, 30% p-divinylbenzene, and 65% styrene[32]. The insertion of iron was performed by using the general procedure of Adler in which an iron(II) salt is used in hot DMF. The resulting iron(III)complexes were then reduced to iron(II) by piperidine. In the case of the 20% divinylbenzene cross-linked copolymer, the heme irreversibly bound dioxygen and the infra-

red spectrum of the oxidized product was that of the μ-oxodimer. On the other hand, the heme-containing 30% divinylbenzene cross-linked copolymer reversibly bound dioxygen through at least 12 cycles.

LeDon has also attached chloroiron(III)-deutero[mono(histidyl methyl ester)amide]porphyrin to the 30% divinylbenzene cross-linked copolymer mentioned above[34]. Its attachment was effected with dicyclohexylcarbodiimide, (DCCI), as the linking reagent between the acid side chain of the porphyrin and the amino groups of the copolymer. In this way, LeDon was able to form a polymer-bound iron(II) "tail-base" porphyrin. The iron(II) complex reversibly bound dioxygen through at least 10 cycles at room temperature.

In a similar approach, Bayer and Holzbach have used DCCI to attach hemin to the hystidyl amine of a water soluble polymer[12]. Next (3-(5-imidazolyl)propylamine was coupled to the remaining propionic acid group. With this polymer-bound, "tail-base" iron(II) porphyrin, it was possible to reversibly bind dioxygen in aqueous solution at 25°C through several cycles. Furthermore, the oxidized, hemin-containing polymer could be reduced with the enzyme, methemoglobin reductase, and again reversibly bound dioxygen.

Tsuchida and coworkers have also synthesized polymers containing covalently attached porphyrins. In their procedure, a free base porphyrin containing a vinyl group is copolymerized with styrene or styrene and N-vinylimidazole with azobisisobutyronitrile as a radical

initiator[27,35,36]. In particular, N,N'-bis(p-vinylphenyl)-7,12-divinyl-3,8,13,17-tetramethylporphyrin-2,18-dipropylamide, 5-mono(p-acrylamidophenyl)-10,15,20-triphenylporphyrin, 5,10,15,20-tetra-(α,α,α,α-o-methacrylamidophenyl)porphyrin, and N-(p-vinylbenzyl)-N'-(imidazolylpropyl)-7,12-divinyl-3,8,13,17-tetramethylporphyrin-2,18-dipropylamide have been utilized in the formation of soluble, porphyrin-containing polymers. The latter porphyrin provided a polymer-bound, "tail-base" porphyrin similar to LeDon's[34] and Bayer and Holzbach's[12]. All of these polymers form relatively stable, oxygenated iron(II) complexes.

Another approach that has been used to form covalently attached porphyrins to a polymer is to synthesize the porphyrin onto an appropriately substituted polymer. In this way, Leznoff and Svirskaya were able to prepare a 2% divinylbenzene-polystyrene copolymer containing benzoyl chloride groups to which either 3- or 4-hydroxybenzaldehyde were coupled[21]. With this polymer-bound aldehyde group, both 5-(3-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin and 5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin were prepared. The ester linkage could then be hydrolyzed after the beads had been extracted to remove any $TTPH_2$ which was trapped in the polymer matrix. The two mono-substituted porphyrins could be then obtained without the extensive chromatography required when Little's mixed aldehyde synthesis was used. Furthermore, the yield of the two porphyrins is comparable to Little's, in that yields of 2% and 4%, respectively, were obtained.

This approach has also been used by Drago in the preparation of polymer-bound, chelating amine and Schiff base complexes[17]. Starting with a copolymer of styrene, p-divinylbenzene, and p-chloromethylstyrene as the polymer matrix, bis(2-cyanoethyl)amine was used to displace the chloride of the benzyl groups. Next, the nitriles were reduced with $BH_3 \cdot THF$. The resulting polymer-bound triamine was then converted into a Schiff base complex with salicylaldehyde. The Mn(II), Fe(III), Co(III), Ni(II), Cu(II), and Zn(II) complexes were characterized and the cobalt complex used as an oxidation catalyst for 2,6-dimethylphenol.

Examples of polymer-bound phthalocyanines come from the work of Zwart. In his work, cobalt 4,4',4",4'''-tetraaminophthalocyanine was attached to aminated, Merrifield resin (a chloromethylated, 2% divinylbenzene-polystyrene copolymer) and Enzacryl AA (a cross-linked polyacrylamide with aniline-substituted acrylamide groups) via cyanuric chloride[16,30]. In addition, cobalt 4,4',4'',4'''-tetracarboxyphthalocyanine was coupled to polyvinylamine with DCCI used as the coupling agent[31]. These cobalt phthalocyanine-containing resins were used as oxidation catalysts for the oxidation of 2-mercaptoethanol.

Recently, Gebler reported the attachment of various metallocomplexes of poly-sulfonatophthalocyanines to 20% divinylbenzene-polystyrene copolymer beads[37]. An aluminum chloride-catalyzed sulfonation of the above mentioned copolymer resulted in the formation of a sulfone linkage between the polymer and the metallophthalocyanine. A sulfamide linakge was also formed between aminated, 20% divinylbenzene-polystyrene copolymer beads and the sulfonyl chloride of the metallophthalocyanines. These resins were used to assist the autoxidation of alkenes

like cyclohexene.

3. Polyporphyrins.

This category includes such compounds as porphyrin dimers, trimers, and higher polymers. Examples of dimers with only one linkage are found in the work of Dolphin[38], Paine and Dolphin[39], Anton[40], and Little[41]. Dimers with two linkages have been reported by Collman[42,43], Chang[44], and Ogoshi[45]. A dimer with four linkages has also been prepared by Kagan, Mauzerall, and Merrifield[46]. Trimers have been prepared by Anton[40]. Von Maltzen has prepared dimers, trimers, and higher polymers of meso-tetramethylporphyrinatonickel(II) from its reaction with acetals[47].

C. Conclusion and Statement of Research Goals

It has been shown that there is a wide variety of polymeric materials containing porphyrins and related macrocyles. In the case of the coordination polymers, these polymers are of limited use for the central metal atom of the porphyrin must be able to bind to the ligating group and not all metalloporphyrins bind ligands in the 5th and 6th sites. Although the equilibrium constants are greater for iron porphyrins by factors of about 10^{2} [24], this may not prevent the iron porphyrin from migrating and this may be partially, at least, the cause for the leaching of $(TPPFe)_2O$ in Collman's work[18].

Since the main emphasis of attaching porphyrins to polymers was to reduce the incidence of dimerization, the work undertaken in this dissertation has involved only the covalent attachment of porphyrins chiefly to 20% divinylbenzene-polystyrene copolymer beads. In this way, the metalloporphyrin can no longer migrate from one site to

another. The only movement of the porphyrin can only result from the thermal motion of the polymer, itself, thus reducing the likelyhood of dimerization.

The main purpose of this work has been to develop and characterize the synthetic procedure used in the formation of the covalent attachment of the porphyrin moiety to the copolymer. The ease of use of the method and its loading characteristics were considered and evaluated.

The work of Rollmann[14] was reinvestigated so as to provide new insight into the Friedel-Crafts acylation and alkylation of divinylbenzene-crosslinked, polystyrene copolymers. The use of aluminum chloride as the catalyst was brought into question since aluminum porphyrins are known to be highly stable to demetallation and therefore the question of contamination by aluminum ions has been addressed.

The use of chloromethylated, 20% divinylbenzene-polystyrene copolymer beads as the polymer matrix was also investigated. Rollmann used 5,10,15,20-tetrakis(4-aminophenyl)porphyrin to form an amine-linked porphyrin to the chloromethylated copolymer[14]. In this work, only monofunctionalized, mesotetraarylporphyrins were used to replace the chloride. 5-(4-Hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, 5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin, and 5-(4-pyridyl)-10,15,20-tris(4-methylphenyl)porphyrin were used to form the ether, amine, and pyridinium linkages, respectively, to the copolymer. This was done in order to insure that no increase in the cross-linking of the copolymer resulted which is known to cause the beads to become more brittle.

Finally, aminated, 20% divinylbenzene-polystyrene copolymer beads were prepared as in the procedure used by King and Sweet[20]. These beads were then treated with $TPP(COCl)_4H_2$ as was done by King and Sweet, to form the amide-linked porphyrin to the copolymer. The aminated beads were also reacted with a partially chlorinated porphyrin to form the amine-linkage.

These samples were metallated in DMF and the metal content was determined by electron scanning microprobe analysis as the radial distribution of a midsection of the bead. The radial distribution varied from method to method which had been used to attach the porphyrin to the particular copolymer. This variation affected the resolution of the copper ESR spectra and also the rate of dioxygen uptake in the assisted autoxidation of cyclohexene by the cobalt complexes of these resins.

II. RESULTS

A. The Synthesis of Porphyrins and Metalloporphyrins

The methods of Adler and coworkers[48,49] or the mixed aldehyde synthesis of Little[50] were used to prepare the meso-tetraarylporphyrins that were used in this study. The procedure of Adler and coworkers[51] was used to metallate the porphyrins that were prepared. In addition, several of these porphyrins have been altered at their functionalized sites by one of several synthetic procedures.

5,10,15,20-tetrakis(4-methylphenyl)porphyrin, $TTPH_2$, and 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, $TPP(CO_2H)_4H_2$, were synthesized from p-tolylaldehyde, and p-carboxybenzaldehyde, respectively, and pyrrole in refluxing propionic acid. The latter porphyrin was converted into its tetrahexyl ester via treatment of the tetra acid in a refluxing solution consisting of 10% concentrated sulfuric acid in n-hexanol (V:V). The purification of the tetrahexyl ester on an alumina column was then performed with dichloromethane as the elutent. The porphyrin tetrahexyl ester, $TPP(CO_2hexyl)_4H_2$, was subsequently recrystallized from dichloromethane and methanol. In addition, the tetraethyl ester was prepared in a similar manner. The hydrolysis of $TPP(CO_2hexyl)_4H_2$ was accomplished in a refluxing mixture of porphyrin in tetrahydrofuran and aqueous potassium hydroxide. $TPP(CO_2H)_4H_2$ was then used as its tetra acid chloride in the Friedel-Crafts acylation of

20% divinylbenzene-polystyrene copolymer beads and also in the formation of an amide with aminated, 20% divinylbenzene-polystyrene copolymer beads.

Cobalt complexes of $TTPH_2$, $TPP(CO_2Et)_4H_2$, and $TPP(CO_2hexyl)_4H_2$ were prepared in refluxing DMF with $CoCl_2 \cdot 6H_2O$ as the source of cobalt. $TPP(CO_2Et)_4Co$ was used to study the autoxidation of aldehydes. TTPCo and $TPP(CO_2hexyl)_4Co$ were utilized as standards for comparison with the polymer-bound cobalt complexes in the assisted, autoxidation of cyclohexene. TTPFeCl was also prepared and used in the study of the autoxidation of cyclohexene. TTPCu was prepared and used in an ESR study. In addition, $TPP(CO_2H)_4Cu$ was used in an attempted Friedel-Crafts acylation of 20% divinylbenzene-polystyrene copolymer beads.

The procedure which was used by N. Datta-Gupta to reduce $TPP(CO_2$-methyl$)_4H_2$ with lithium aluminum hydride[52] was used to reduce $TPP(CO_2$-hexyl$)_4H_2$. 5,10,15,20-Tetrakis(4-hydroxymethylphenyl)porphyrin, $TPP(CH_2OH)_4H_2$, was obtained in a very good yield of about 90% as compared to 35% for the Datta-Gupta method. The major difference in yield is believed to be due to filtration through celite which resulted in considerable amounts of the hydroxyporphyrin being adsorbed onto the celite. This adsorption does not occur when paper filtration is used.

The copper complex of $TPP(CH_2OH)_4H_2$ was used in the Friedel-Crafts alkylation of 20% divinylbenzene-polystyrene copolymer beads. $TPP(CH_2$-$OH)_4Cu$ was prepared in a refluxing solution of the free-base porphyrin and copper acetate in a 1:1 solution of tetrahydrofuran and pyridine.

$TPP(CH_2OH)_4H_2$ also served as starting material for the synthesis of a hoped for tetra(chloromethylphenyl)porphyrin. Several attempts

were made in which thionyl chloride was used as the chlorinating reagent. Thionyl chloride was added to a THF solution of the porphyrin at ambient temperatures and the reaction was terminated after 3 hours. The resulting product was determined from a study of its ^{1}H NMR spectrum to be a mixture containing both hydroxy- and chloromethyl groups. Next $TPP(CH_2OH)_4H_2$ was treated at ambient temperatures for 12 hours in thionyl chloride. Again the product was a partially chlorinated porphyrin. When the porphyrin was refluxed with thionyl chloride for 24 hours, a different product was obtained and it did not contain hydroxy groups. Its ^{1}H NMR spectrum showed that the β-pyrrole hydrogens were no longer equivalent for a multiplet was now present.

Since benzyl alcohol has been converted into benzyl chloride in a refluxing solution of triphenylphosphine and carbon tetrachloride[53], the chlorination of $TPP(CH_2OH)_4H_2$ was also attempted with triphenylphosphine and carbon tetrachloride in refluxing THF. Here again, the ^{1}H NMR spectrum of the product shows that only partial chlorination has occurred and therefore a mixture resulted. The mixed chloro- and hydroxymethylporphyrin was used in the Friedel-Crafts alkylation of 20% divinylbenzene-polystyrene copolymer beads and in an S_N2 substitution reaction with aminated, 20% divinylbenzene-polystyrene copolymer beads.

The mixed aldehyde synthesis of Little[50] has been used to prepare mono-functionalized tetraphenylporphyrin derivatives which were subsequently utilized in the formation of covalent linkages to chloromethylated, 20% divinylbenzene-polystyrene copolymer beads. The porphyrins, 5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(OH)H_2$,

5-(4-acetamidophenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(NHAc)H_2$, and 5-(4-pyridyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(py)H_2$, were prepared. $T_3P(NHAc)H_2$ was subjected to acid hydrolysis in order to obtain its free amine derivative which was used to form the amine linkage to the chloromethylated copolymer.

The mixed aldehyde synthesis of Little[50] was also used to prepare 5-(2-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(2-OH)H_2$. $T_3P(2-OH)H_2$ was then reacted with 1,5-dibromopentane and anhydrous potassium carbonate in DMF to form 5-(2-(5-bromopentoxy)phenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(OC_5Br)H_2$. $T_3P(OC_5Br)H_2$ was then used in the Friedel-Crafts alkylation of 20% divinylbenzene-polystyrene copolymer beads.

B. Friedel-Crafts Acylation and Alkylation of Divinylbenzene-Polystyrene Copolymers

The Friedel-Crafts acylation and alkylation of divinylbenzene-polystyrene copolymers offered a simple and direct procedure for the preparation of covalently bound porphyrins and metalloporphyrins to these copolymers. Rollmann has acylated a divinylbenzene-polystyrene copolymer (XAD-2 from Rohm and Haas) with $TPP(COCl)_4H_2$ and $AlCl_3$[14]. These samples which were prepared by Rollmann had metal contents of about 0.01%. Gebler also used this procedure to attach metal phthalocyanines to 20% divinylbenzene-polystyrene copolymer beads by the formation of the sulfone linkage[37].

The Friedel-Crafts acylation of divinylbenzene-polystyrene copolymer beads was carried out on copolymers containing 2% and 20% divinylbenzene. The reactions were carried out in either nitromethane or

1,1,2,2-tetrachloroethane at either ambient temperatures, 50°C, or 100°C. The $AlCl_3$-catalyzed acylations were performed with $TPP(COCl)_4H_2$ as the acylating reagent.

The Friedel-Crafts acylation of 20% divinylbenzene-polystyrene copolymer beads with $TPP(COCl)_4H_2$ and $AlCl_3$ as catalyst yielded light tan to brown beads. From a qualitative point of view, the highest loadings were obtained in nitromethane at a temperature of 50°C. These samples were reddish brown and visibly darker than the other samples. Metallation of the beads with either $Cu(OAc)_2 \cdot H_2O$ or $CoCl_2 \cdot 6H_2O$ in hot DMF afforded the respective metal complexes, P_1-CO-porCu and P_1-CO-porCo. P_1 is used to designate the copolymer, 20% divinylbenzene-polystyrene copolymer beads, and -CO- to indicate the ketone linkage.

Elemental analyses of these samples were performed on the cobalt and copper complexes, P_1-CO-porCo and P_1-CO-porCu. The results are in Table 1. The results are from elemental analysis, neutron activation analysis, and scanning electron microprobe analysis. From elemental analysis, P_1-CO-porCo contained 0.05% Co and 0.42% N which gave a nitrogen to cobalt ratio of 35 to 1. Furthermore, neutron activation analysis of P_1-CO-porCo indicated the presence of aluminum in the beads. Its content was 0.035% aluminum. When the nitrogen to total metal (Co + Al) ratio was determined, it was found to be 14 to 1.

In order to reduce or eliminate contamination from aluminum, the Friedel-Crafts acylation of 20% divinylbenzene-polystyrene copolymer beads was again performed. But this time, $TPP(COCl)_4Cu$ was used in place of the free base porphyrin. The reaction was carried out under similar reaction conditions and light tan beads were obtained. No ESR

Table 1

Elemental Analysis for Polymer-Bound Metalloporphyrins
Resulting from Friedel-Crafts Reactions
(Neutron Activation Analyses)

Sample	% M	% N	% Al	N/M
2% P_1-CO-porCu	0.83	e	0.195	—
P_1-CO-porCo	0.085(0.05)[b]	(0.42)[b]	0.035	35.3
P_1-CO-porCo(B)	0.015(0.013)[c]	e	a	—
P_1-CO-porCu	0.068	e	0.026	—
P_1-CO-porCu(c)	0.000	e	0.009	—
P_1-CH_2-porCu	0.018	e	0.010	—
P_1-CH_2-porCo	0.017(0.02)[b]	(0.18)[b]	a	37.9
P_1-CH_2-porCu(B)	0.030(d)[c]	e	0.078	—
P_1-C_5-O-porCo	(0.006)[c]	e	e	—

[a] below reliable detection level
[b] elemental analysis
[c] scanning electron microprobe analysis
[d] at or below background count
[e] not analyzed

signal for the copper porphyrin could be found so an attempted metallation of these beads with $Cu(OAc)_2 \cdot H_2O$ in hot DMF was made. Again no ESR signal could be found for a copper porphyrin. Furthermore, the filtrate from the acylation reaction did not contain any copper porphyrin. This can be seen from the visible spectrum of the filtrate for no Soret band is present (Figure 1). Neutron activation analysis of this sample showed that no copper was present but that 0.009% aluminum was.

In an effort to increase the amount of porphyrin attached onto the divinylbenzene-polystyrene copolymer beads, 1.8% divinylbenzene-polystyrene copolymer beads were acylated with $TPP(COCl)_4H_2$ and $AlCl_3$ as catalyst. The reactions were carried out in either nitromethane or 1,1,2,2-tetrachloroethane at ambient temperatures, 50°C, or 100°C. The best results were obtained at 50°C in 1,1,2,2-tetrachloroethane. In all cases, the resulting porphyrin-containing copolymer was more efficiently acylated but the resultant beads were brittle and easily pulverized. The copper complex of one sample was analyzed by neutron activation analysis and it contained 0.83% Cu and 0.195% Al. Since these samples were easily pulverized, the usage of 1.8% divinylbenzene-polystyrene copolymer beads was not pursued further even though enhanced loading was found.

As an extension of this work, the Friedel-Crafts alkylation of 20% divinylbenzene-polystyrene copolymer beads was also investigated in an effort to study this reaction when it is catalyzed by $AlCl_3$. Both haloalkyl- and hydroxyalkyl-containing porphyrins were used. 5-(2-(5-Bromopentoxy)phenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(OC_5Br)H_2$, a mixture of partially chlorinated porphyrins from $TPP(CH_2OH)_4H_2$, and $TPP(CH_2OH)_4Cu$ were used in the alkylation reactions.

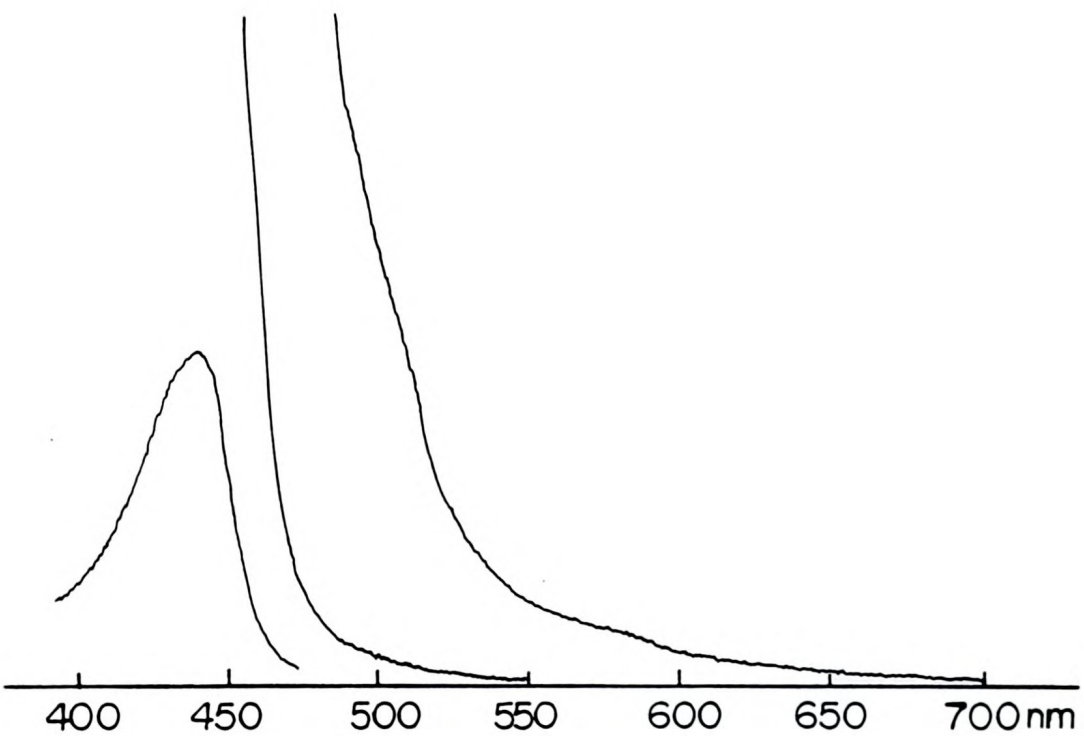

Figure 1. UV-VIS spectrum of decomposition product from $TPP(COCl)_4Cu$ acylation attempt.

In the case of $T_3P(OC_5Br)H_2$, Friedel-Crafts alkylation catalyzed by $AlCl_3$ provided a light tan colored sample after 7 days at 100°C in 1,1,2,2-tetrachloroethane. The beads were metallated with $CoCl_2 \cdot 6H_2O$ in hot DMF. The beads contained 0.01% Co. This result was obtained as the average value from the scanning electron microprobe analysis which provided low results for other samples (see Table 1).

For the partially chlorinated porphyrin, a light tan colored sample was obtained after 2 days at 100°C in 1,1,2,2-tetrachloroethane. Metallation with $Cu(OAc)_2 \cdot H_2O$ and $CoCl_2 \cdot 6H_2O$ in hot DMF produced P_1-CH_2-porCu and P_1-CH_2-porCo respectively. Elemental analysis of P_1-CH_2-porCo showed that the cobalt content was 0.02% and that of the nitrogen was 0.18%. This gave a nitrogen to cobalt ratio of 38 to 1. Neutron activation analysis showed that aluminum was present but below the level of reliable detection. Neutron activation analysis of P_1-CH_2-porCu gave a copper content of 0.015% and an aluminum content of 0.010%.

For $TPP(CH_2OH)_4Cu$, the Friedel-Crafts alkylation was attempted with BF_3 and with $AlCl_3$ as catalysts. When catalysis with BF_3 was attempted, no reaction between $TPP(CH_2OH)_4Cu$ and 20% divinylbenzene-polystyrene copolymer beads could be confirmed. No ESR signal for copper porphyrins could be found for this sample. When catalyzed by $AlCl_3$, the copper porphyrin yielded reddish brown colored beads with 20% divinylbenzene-polystyrene copolymer beads. P_1-CH_2-porCu(B) was analyzed by neutron activation analysis which gave a copper content of 0.030% and an aluminum content of 0.078%.

C. Preparation of Aminated, Divinylbenzene-Polystyrene Copolymers

Two groups have used amine-containing copolymers of divinylbenzene and styrene as the support to which $TPP(COCl)_4H_2$ has been covalently bound by an amide linkage. King and Sweet nitrated and then reduced the nitro groups to form their aminated, 20% divinylbenzene-polystyrene copolymer beads[20]. On the other hand, LeDon copolymerized mixtures of 5% p-aminostyrene, 20% p-divinylbenzene, and 75% styrene, and of 5% p-aminostyrene, 30% p-divinylbenzene, and 65% styrene[32].

In this work, the procedure of King and Sweet[20] was followed in the preparation of aminated, 8%- and aminated, 20% divinylbenzene-polystyrene copolymer beads. The beads were first nitrated with nitric acid in acetic anhydride. Next, reduction of the nitro groups with stannous chloride produced the aminated copolymers. During nitration and reduction, the 8% divinylbenzene-polystyrene copolymer beads were found to be brittle and pulverized to some extent. Therefore, these beads were not used any further. The aminated, 20% divinylbenzene-polystyrene copolymer beads, P_2, were not shattered and therefore have been used in subsequent research.

D. Aminated, 20% Divinylbenzene-Polystyrene Copolymer Beads as Support for Porphyrins

As mentioned, $TPP(COCl)_4H_2$ has been attached to amine-containing copolymers of divinylbenzene and styrene[20,32]. Therefore, $TPP(COCl)_4H_2$ was attached to P_2 which was prepared in this work. Dark, red-colored beads were obtained which were extensively washed before metallation. These beads were metallated at 120°C with $Cu(OAc)_2 \cdot H_2O$ and $CoCl_2 \cdot 6H_2O$ in DMF. In the case of the copper complex, P_2-NH-CO-porCu, a bright red

product was obtained. The cobalt complex, P_2-NH-CO-porCo, was more of a red-brown color. See Table 2 for analyses.

P_2 was also used as the support for the formation of an amine-bound porphyrin. The partially chlorinated porphyrin from $TPP(CH_2OH)_4H_2$ was used as the porphyrin. The reaction was carried out at 100°C in DMF. The product is red-brown. Metallation of P_2-NH-CH_2-porH_2 with $Cu(OAc)_2 \cdot H_2O$ and $CoCl_2 \cdot 6H_2O$ was performed in hot DMF (120°C). Again the copper complex is much redder than the corresponding cobalt complex. See Table 2 for analyses.

E. Chloromethylated, 20% Divinylbenzene-Polystyrene Copolymer Beads as Support for Porphyrins

Chloromethylated, divinylbenzene-polystyrene copolymers have been extensively used as supports for covalently attaching many different chemical species to a divinylbenzene-polystyrene copolymer. Reviews of some of these applications have been given by Grubbs[1] and by Crowley and Rapoport[2]. In the area of porphyrin chemistry, two examples are known. Collman used chloromethylated, 2% divinylbenzene-polystyrene copolymer beads as a support for covalently binding imidazole to the copolymer[18]. The imidazole-containing copolymer was then used as a coordination polymer for cobalt[19] and iron[18,23] porphyrins. $TPP(NH_2)_4H_2$ was covalently attached by Rollmann to a chloromethylated, XAD-2 copolymer of divinylbenzene and styrene[14].

Chloromethylated, 20% divinylbenzene-polystyrene copolymer beads, P_3, were purchased from Strem Chemical Company. These beads were then used as the polymer matrix to which porphyrins could be covalently bound.

Table 2

Elemental Analyses for Metalloporphyrins Bound to Aminated, 20% Divinylbenzene-Polystyrene Copolymer Beads (Neutron Activation Analyses)

Sample	% M
P_2-NH-CH_2-porCu	0.393
P_2-NH-CH_2-porCo	0.430(0.113)[a]
P_2-NH-CO-porCu	0.153
P_2-NH-CO-porCo	0.358(0.225)[a]

[a] scanning electron microprobe analysis

As mentioned earlier, three mono-functional, meso-tetraarylporphyrins were prepared as candidates for covalent attachment to P_3. These porphyrins are 5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(OH)H_2$, 5-(4-acetamidophenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(NHAc)H_2$, and 5-(4-pyridyl)-10,15-20-tris(4-methylphenyl)porphyrin, $T_3P(py)H_2$.

The covalent attachment of $T_3P(OH)H_2$ to P_3 was carried out under conditions similar to those employed in the preparation of alkoxyphenylporphyrins[41,50]. $T_3P(OH)H_2$, P_3, and anhydrous potassium carbonate were mixed together in DMF and the reaction was carried out at room temperature for 7 days. The beads that were obtained, P_3-CH_2-O-porH_2 were dark, red-brown.

P_3-CH_2-O-porH_2 was metallated with various metal salts in hot DMF. The vanadyl complex is red-brown on the polymer. The manganese(III) chloride complex is dark green on the polymer. The iron(III) chloride and cobalt complexes are both red-brown on the polymer. Copper imparts a bright red color to the polymer. See Table 3 for analyses.

The covalent attachment of $T_3P(NH_2)H_2$, which had been obtained from the hydrolysis of $T_3P(NHAc)H_2$, to P_3 was effected under conditions similar to those employed by Rollmann in the attachment of $TPP(NH_2)_4H_2$ to chloromethylated XAD-2[14]. The porphyrin and P_3 were mixed together in DMF and the mixture was heated at 100°C for 24 hours. A green-brown colored sample was obtained. Metallation of P_3-CH_2-NH-porH_2 with $Cu(OAc)_2 \cdot H_2O$ was carried out in DMF. The resulting copper complex, P_3-CH_2-NH-porCu, imparts a red color to the beads and had a copper content of 0.352%.

Table 3

Elemental Analyses for Metalloporphyrins Bound to Chloromethylated, 20% Divinylbenzene-Polystyrene Copolymer Beads
(Neutron Activation Analyses)

Sample	% M	% N	N/M
P_3-CH_2-O-porCu	1.363	____	____
P_3-CH_2-O-porCu(B)	0.238	____	____
P_3-CH_2-O-porMnCl	0.861	____	____
P_3-CH_2-O-porFeCl	(0.83)[a]	____	____
P_3-CH_2-O-porCo	(0.61)[a](0.182)[b]	(0.72)[a]	4.96
P_3-CH_2-NH-PorCu	0.352	____	____
P_3-CH_2-py-porCu	0.310	____	____

[a] elemental analysis
[b] scanning electron microprobe analysis

$T_3P(py)H_2$ was similarly attached to P_3 in DMF at 100°C. The resulting beads were again green-brown. Metallation with $Cu(OAc)_2 \cdot H_2O$ results in the preparation of red P_3-CH_2-py-porCu which had a copper content of 0.310%.

In an effort to prepare a polymer-bound porphyrin by a more direct route, 4-hydroxybenzaldehyde was covalently attached to P_3. The polymer, P_3, and 4-hydroxybenzaldehyde were mixed together in the presence of anhydrous potassium carbonate in DMF and the mixture was stirred for 24 hours. The resulting beads, P_3-CH_2-O-Ph-CHO contained 2.17 mmole of the attached aldehyde per gram of beads. P_3-CH_2-O-Ph-CHO was then treated with pyrrole and p-tolylaldehyde in refluxing propionic acid for one hour. The beads were recovered and extensively washed with methanol and then soxhlet extracted with dichloromethane to remove any impurities and $TTPH_2$ which might be in the beads. The resulting beads, P_3-CH_2-O-porH_2(B), are black. Leznoff also reported the formation of a black, porphyrin-containing copolymer[21]. Metallation of P_3-CH_2-O-porH_2(B) with $Cu(OAc)_2 \cdot H_2O$ in DMF yielded a black sample, P_3-CH_2-O-porCu(B) with a copper content of 0.238%.

F. Scanning Electron Microprobe Analysis of the Porphyrin-Containing Copolymer Beads

Scanning electron microprobe analysis, SEM analysis, has been used previously to determine the radial distribution of an element across a cross section of a divinylbenzene-polystyrene copolymer bead. Grubbs and Su have used this method to determine the radial distribution of phosphorous in 1.8% and 20% divinylbenzene-polystyrene copolymer

beads[66]. Gebler has also utilized SEM analysis to determine the metal content and the radial distribution of metallophthalocyanines bound to 20% divinylbenzene-polystyrene copolymer beads[37].

The radial distribution of polymer-bound, metalloporphyrins was determined by SEM analysis in order to evaluate the various methods of attachment of porphyrins to copolymers of divinylbenzene and styrene. The results are in Table 4. I_c is the ratio of the intensities at the center to that at the surface of the bead. These intensities refer to the number of counts that was measured as the cross section of the bead was scanned for the K_α line of the desired element.

From the data, it is observed that all of the Friedel-Crafts reactions are characterized by a low value for I_c. This is indicative of low penetration of the bead by the reactive porphyrin.

For the Friedel-Crafts acylation of P_1 with $TPP(COCl)_4H_2$, the cobalt porphyrin distribution of P_1-CO-porCo was determined by SEM analysis. The value of I_c was 0.28 which indicated low penetration of the polymer by the porphyrin. This is clearly seen from the SEM scan of P_1-CO-porCo shown in Figure 2. This result is also consistent with results obtained by Gebler in the Friedel-Crafts sulfonation of 20% divinylbenzene-polystyrene copolymer beads[37].

In the Friedel-Crafts alkylation of P_1, one of the porphyrins that were used had produced a porphyrin-containing copolymer with a low value of I_c. For P_1-C_5-O-porCo, a value of 0.00 was obtained for I_c (Figure 3). For P_1-CH_2-porCo and P_1-CH_2-porCu(B), no results were obtained for the recorded intensities of the x-rays resulting from the K_α lines for

Table 4

Radial Distribution of Polymer-Bound Metalloporphyrins

Sample	Edge[a]	Center[a]	I_c
P_1-CO-porCo	72	20	0.28
P_1-CH_2-porCu(B)	——[b]	——[b]	——
P_1-CH_2-porCo	——[b]	——[b]	——
P_1-C_5-O-porCo	121	0	0.00
P_2-NH-CO-porCo	1818	45	0.025
King and Sweet	2500	9	0.004
P_2-NH-CH_2-porCo	177	177	1.00
P_3-CH_2-O-porCo	405	261	0.65
P_3-CH_2-NH-porCu	230	230	1.00
P_3-CH_2-py-porCu	200	200	1.00
P_3-CH_2-O-porCu(B)	316	26	0.08

[a] counts for K_α line
[b] at or below background

Figure 2. SEM scan of P_1-CO-porCo.

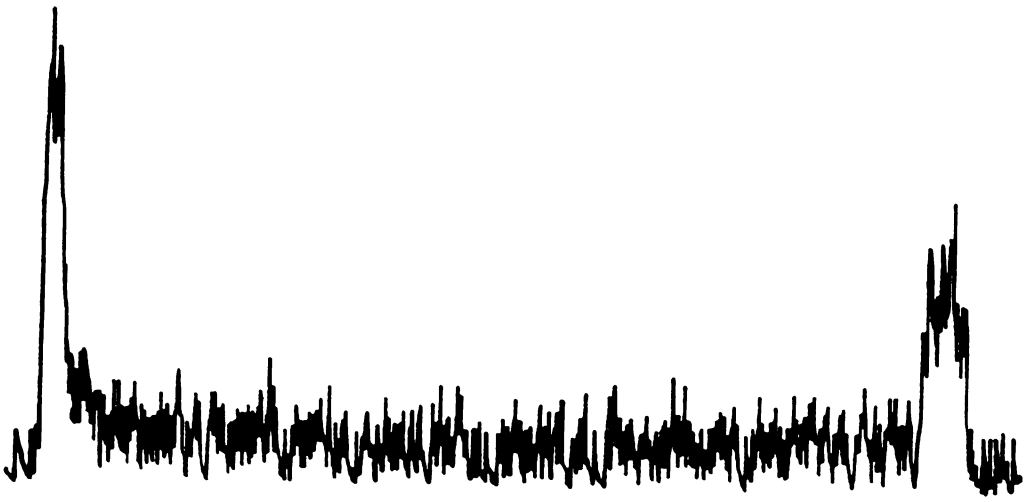

Figure 3. SEM scan of P_1-C_5-O-porCo.

cobalt and copper, respectively, were at the background level. For P_1-CH_2-porCu(B), this is the result of the low sensitivity in measuring the K_α line for copper.

P_2-NH-CO-porCo was shown to have an I_c value of 0.025 and the SEM scan is shown in Figure 4. A low value of I_c was also found for a similarly prepared sample donated by King and Sweet. This result of low I_c was also borne out by results of Gebler for the sulfamide-linked metallophthalocyanines to aminated, 20% divinylbenzene-polystyrene copolymer beads[37].

For P_2-NH-CH_2-porCo, the SEM scan is shown in Figure 5. From this figure, it is observed that the cobalt is evenly distributed throughout the bead. The I_c value for this sample was 1.00.

In the case of those porphyrins attached to chloromethylated, 20% divinylbenzene-polystyrene copolymer beads, the values of I_c are near one. For P_3-CH_2-O-porCo, a value of 0.65 was obtained and its SEM scan is shown in Figure 6. For P_3-CH_2-O-porCu(B), a value of 0.08 was obtained (see Figure 7). In the case of both P_3-CH_2-NH-porCu and P_3-CH_2-py-porCu, an I_c value of 1.00 was found. The SEM scan for P_3-CH_2-NH-porCu is shown in Figure 8 and that of P_3-CH_2-py-porCu is shown in Figure 9.

G. Electron Spin Resonance Spectra of Some Polymer-Bound Metalloporphyrins

The ESR spectra of the vanadyl and the copper complexes of the polymer-bound porphyrins provided strong evidence for the presence of the metalloporphyrins attached to the divinylbenzene-polystyrene copolymers. These complexes gave ESR spectra which are typical of the

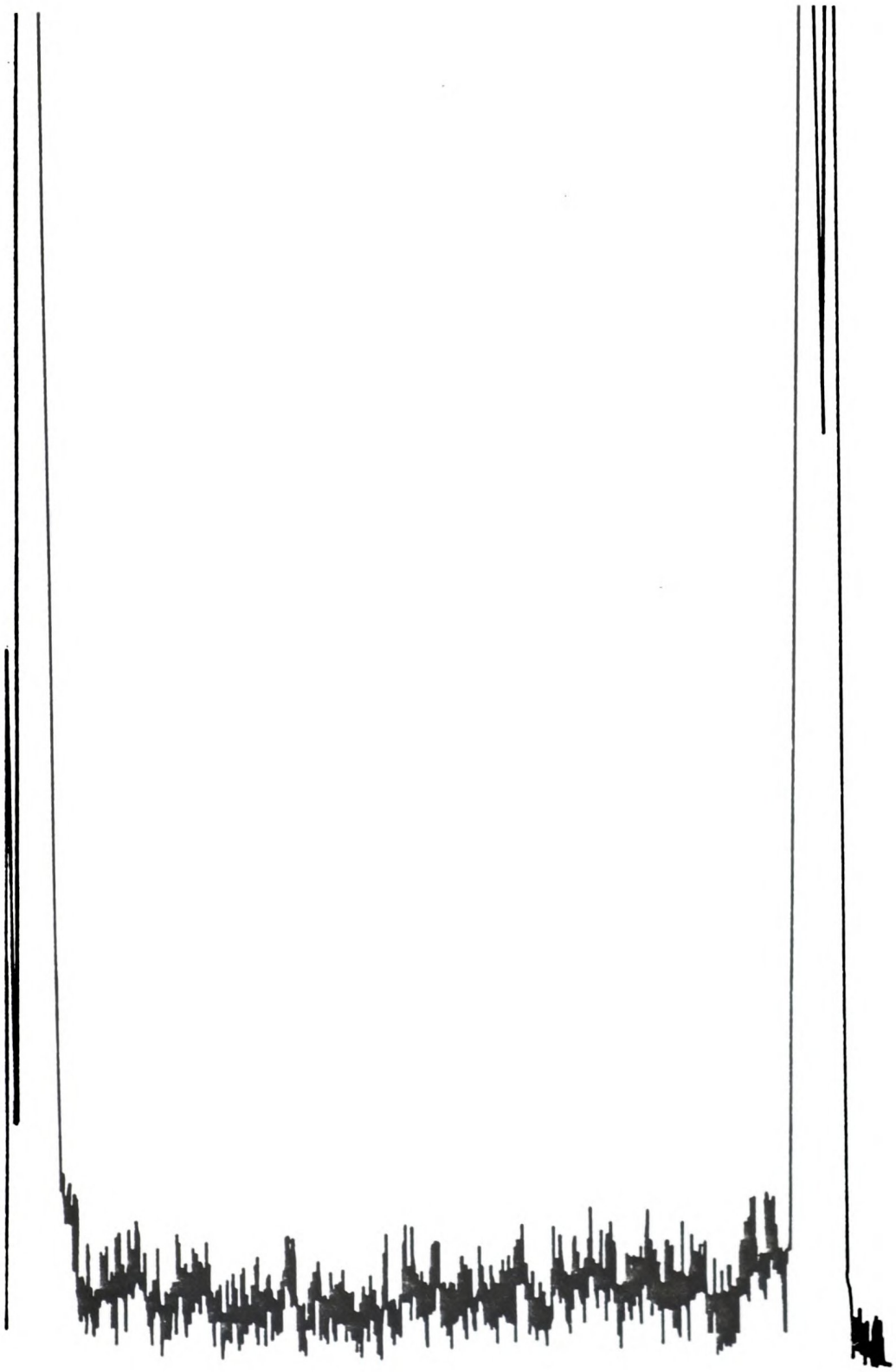

Figure 4. SEM scan of P_2-NH-CO-porCo.

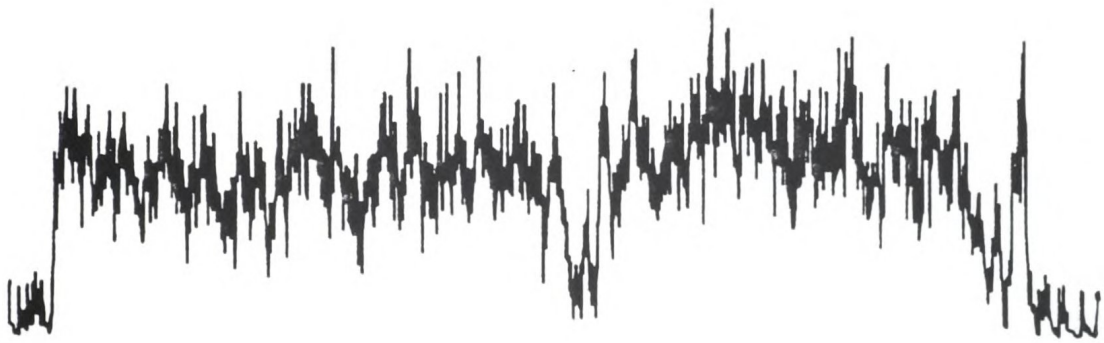

Figure 5. SEM scan of P_2-NH-CH_2-porCo.

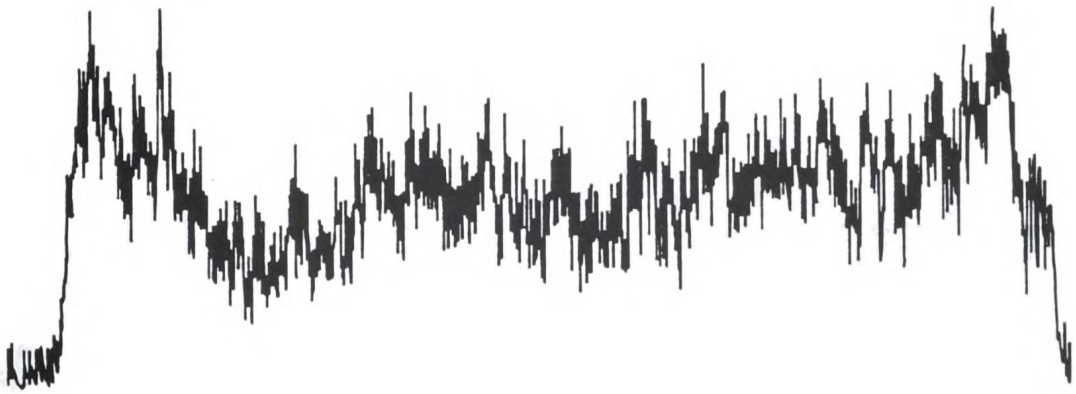

Figure 6. SEM scan of P_3-CH_2-O-porCo.

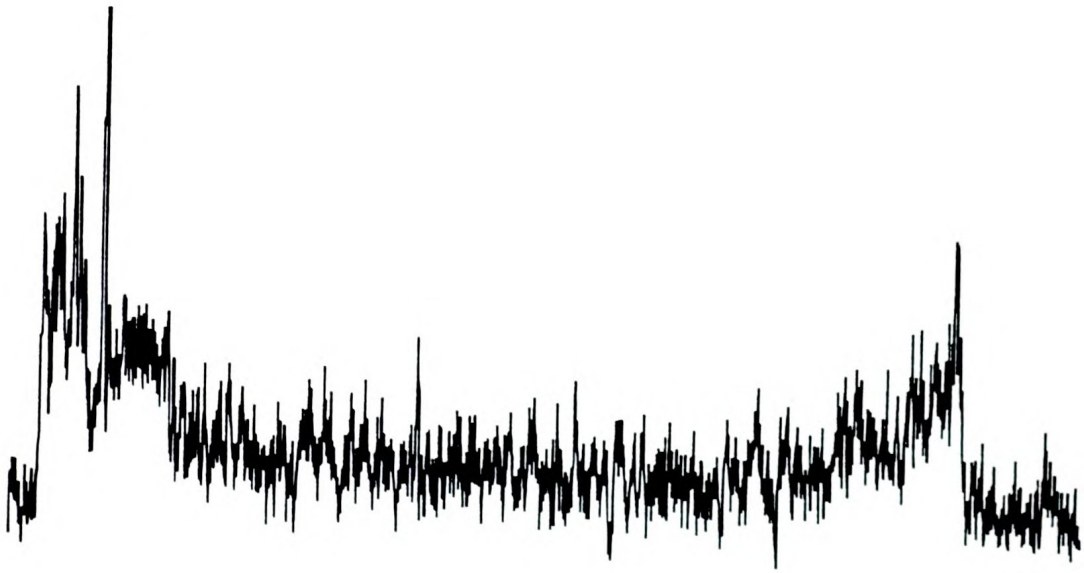

Figure 7. SEM scan of P_3-CH_2-O-porCu(B).

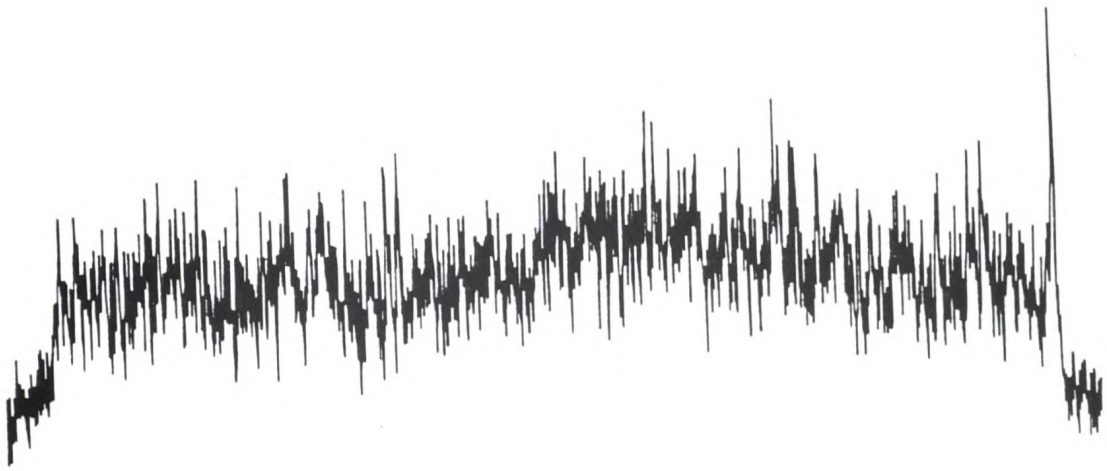

Figure 8. SEM scan of P_3-CH_2-NH-porCu.

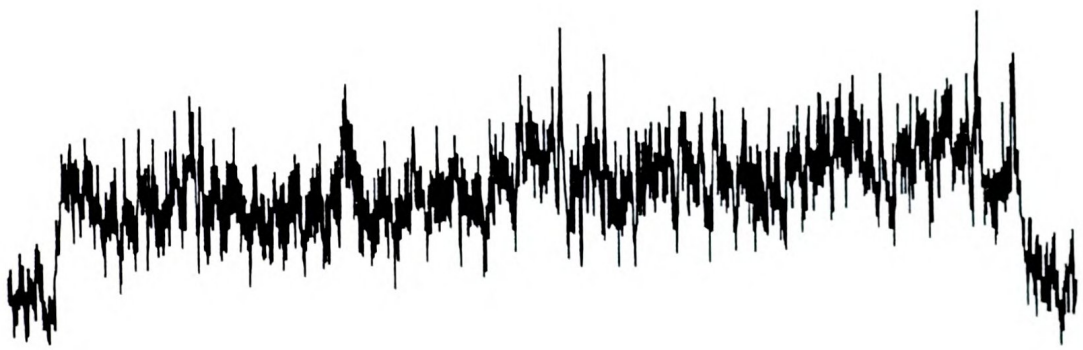

Figure 9. SEM scan of P_3-CH_2-py-porCu.

metalloporphyrins concerned. This can be readily observed from the data in Tables 5 & 6 which contain the g values and other parameters for the above mentioned metalloporphyrins and from the spectra themselves.

The vanadyl complex, P_3-CH_2-O-porVO, has a well defined signal at room temperature (Figure 10). Its spectrum is comparable to spectra of TPPVO in $CHCl_3$ at 78°K[67] or of polycrystalline samples diluted with the free base porphyrin taken at either room temperature or 77°K[67,68]. The lineshape of the ESR spectrum of P_3-CH_2-O-porVO is nearly identical to those that have been reported previously. P_3-CH_2-O-porVO is experimentally observed to have $g_{||}$ = 1.956 and $g_{\perp}$ = 1.988 which are similar to values reported by Assour[67]. The $V_{||}$ and $V_{\perp}$ lines are well resolved with no superhyperfine splitting due to the porphyrin's four nitrogens. This is not unusual for only Sato and Kwan have ever reported nitrogen superhyperfine structure for TPPVO[69]. Lastly the spectrum is observed to be second order because of the unequal spacings between the hyperfine splittings. This is true of other spectra reported in the literature[67-69].

In the case of the copper complexes' ESR spectra, it is apparent that the copper porphyrins are present and are magnetically dilute for most of the samples. The ESR spectra of the polymer-bound copper porphyrins are characterized by relatively well resolved $Cu_{||}$ lines and nitrogen superhyperfine splitting from the porphyrins' nitrogens.

As would be expected from the low metal content of P_1-CO-porCu, the ESR spectrum of this complex is well resolved with most of the expected features being observable (Figure 11). Only the nitrogen perpendicular

Table 5

ESR Data for Vanadyl Porphyrins

	$g_{\parallel}$	$g_{\perp}$	$V_{\parallel}$ (a)	$V_{\perp}$ (a)
P_3-CH_2-O-porVO	1.956	1.988	170	56
TPPVO in $TPPH_2$ [b]	1.966	1.985	161	55

[a] in gauss
[b] ref 67

Table 6

ESR Data for Copper Porphyrins

	$g_{\parallel}$	$g_{\perp}$	$Cu^{a}_{\parallel}$	$Cu^{a}_{\perp}$	$\langle N \rangle^{a}$
P_1-CO-porCu	2.162	2.046	200	31	15.3
P_1-CH_2-porCu	2.158	2.046	205	33	16.2
P_1-CH_2-porCu(B)	2.169	2.039	210	36	17.6
P_2-NH-CH_2-porCu	2.166	2.048	205	36	17.2
P_2-NH-CO-porCu	2.162	2.038	215	37	17.1
P_3-CH_2-O-porCu	2.159	2.037	205	36	17.5
P_3-CH_2-O-porCu(B)	2.169	2.040	205	36	17.3
P_3-CH_2-NH-porCu	2.167	2.052	210	35	17.2
P_3-CH_2-py-porCu	2.166	2.052	210	35	17.2
Cu Res-NH-TPP-NH_2[b]	2.182	2.049	199	42	17
Cu Res-CO-TPP-COOH[b]	2.157	2.07	220	40	15
TPPCu in $TPPH_2$[c]	2.187	2.045	202	33	15

[a] in gauss
[b] ref 14
[c] ref 68

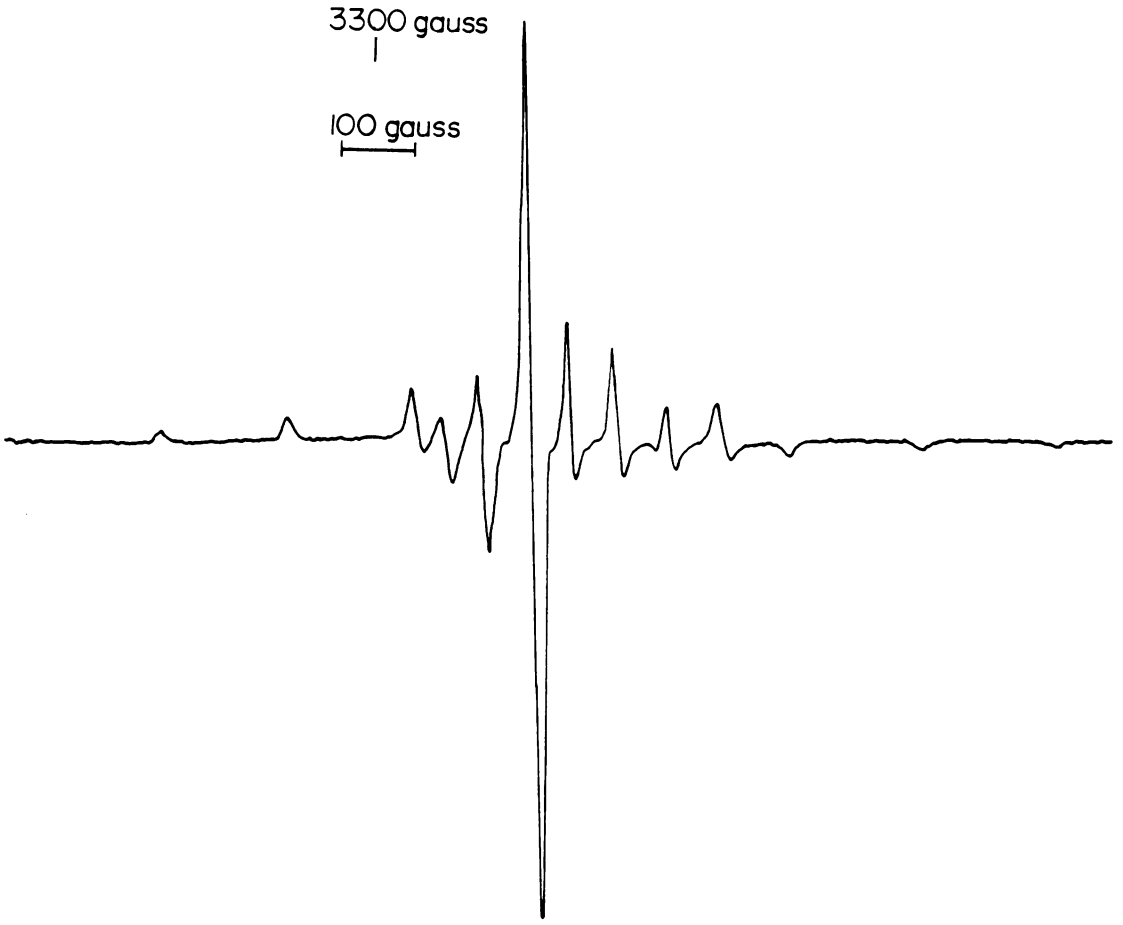

Figure 10. ESR spectrum of P_3-CH_2-C-porVO.

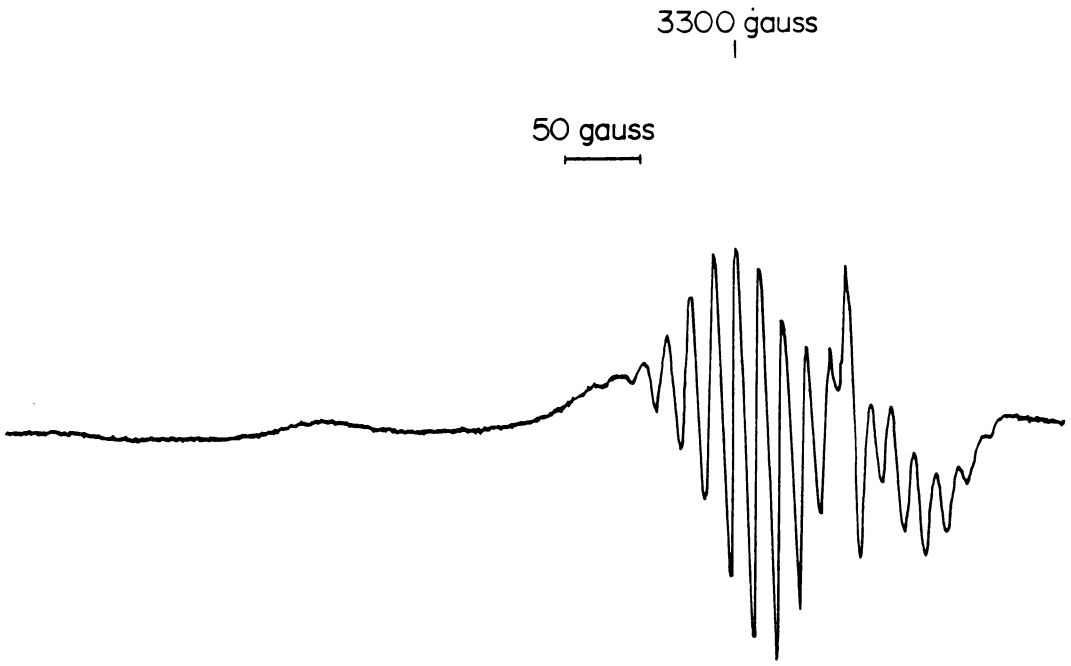

Figure 11. ESR spectrum of P_1-CO-porCu.

features are not observed in the room temperature spectrum of this complex. Some of the pertinent data are given in Table 6. It will be noted that the ESR parameters for this complex are very similar to those of TPPCu in $TPPH_2$ and those reported by Rollmann for a similarly prepared polymer-bound copper porphyrin[14].

For P_1-CH_2-porCu prepared from $TPP(CH_2OH)_{4-x}(CH_2Cl)_xH_2$, the polymer-bound copper complex gives a well resolved ESR spectrum (Figure 12) very similar to that of P_1-CO-porCu. In the case of P_1-CH_2-porCu(B) prepared from $TPP(CH_2OH)_4Cu$, the spectrum is again well resolved in Figure 13 although the ESR parameters are somewhat different (see Table 6). Neither of these samples show nitrogen perpendicular splittings at room temperature or at 77^oK.

The copper complex, P_2-NH-CO-porCu, has an ESR spectrum that is the least resolved of all of the polymer-bound copper porphyrins except perhaps that of P_3-CH_2-O-porCu(B) which was prepared from P_3-CH_2-O-Ph-CHO as the starting material. Despite the poorer resolution of P_2-NH-CO-porCu's ESR spectrum, the $g_{||}$, $g_{\perp}$, $Cu_{||}$, $Cu_{\perp}$, and the average value of the nitrogen superhyperfine splitting were still observable in Figure 14.

P_2-NH-CH_2-porCu has an ESR spectrum that is relatively well resolved with all but the nitrogen perpendicular superhyperfine structure being apparent at room temperature (Figure 15). Values of $g_{||} = 2.166$ and $g_{\perp} = 2.048$ were easily determined from the spectrum. Also $Cu_{||}$ and $Cu_{\perp}$ and $\langle N \rangle$ were easily obtained.

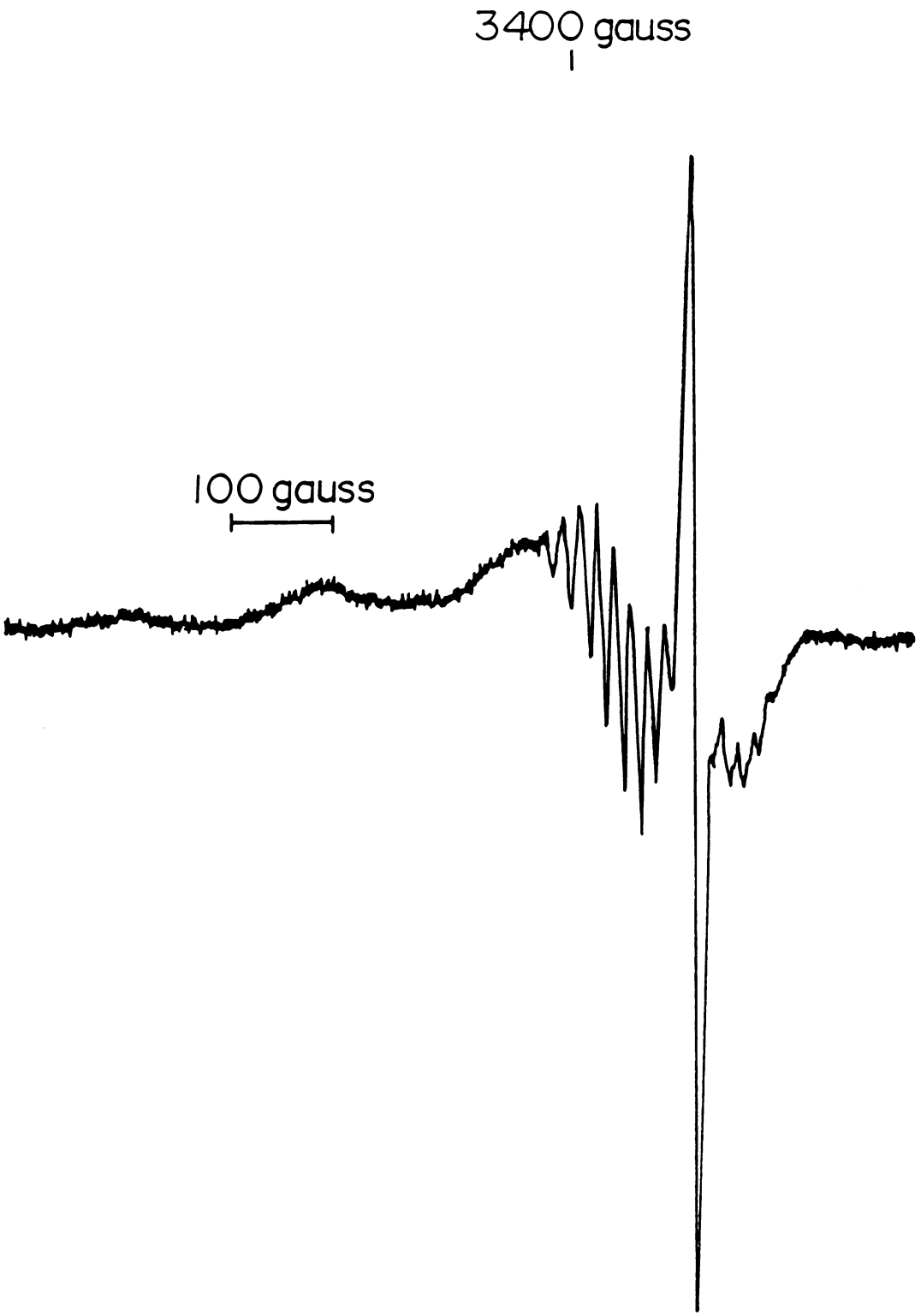

Figure 12. ESR spectrum of P_1-CH_2-porCu.

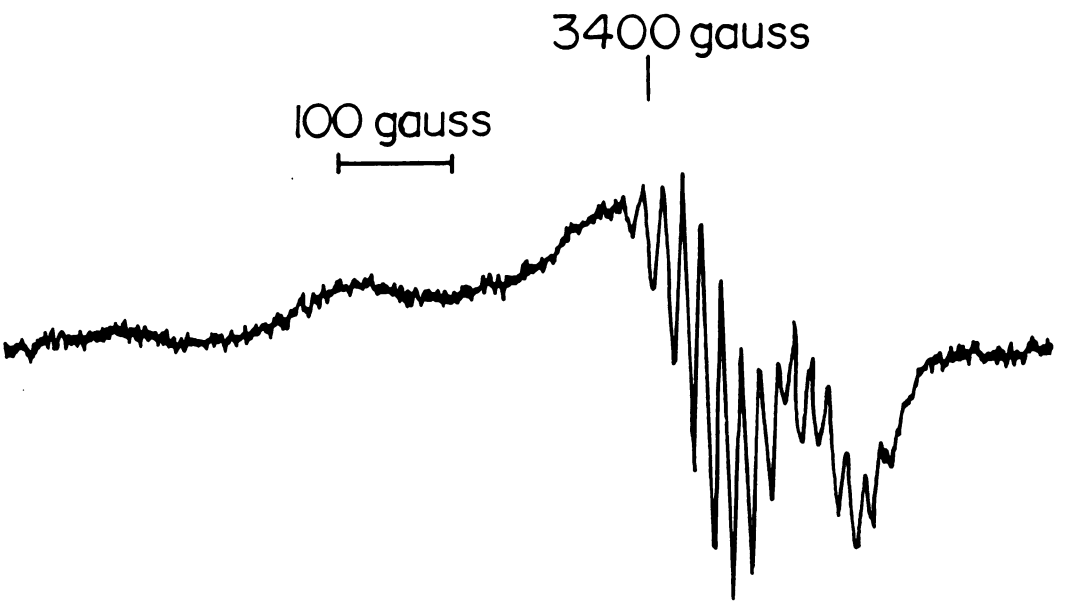

Figure 13. ESR spectrum of P_1-CH_2-porCu(B).

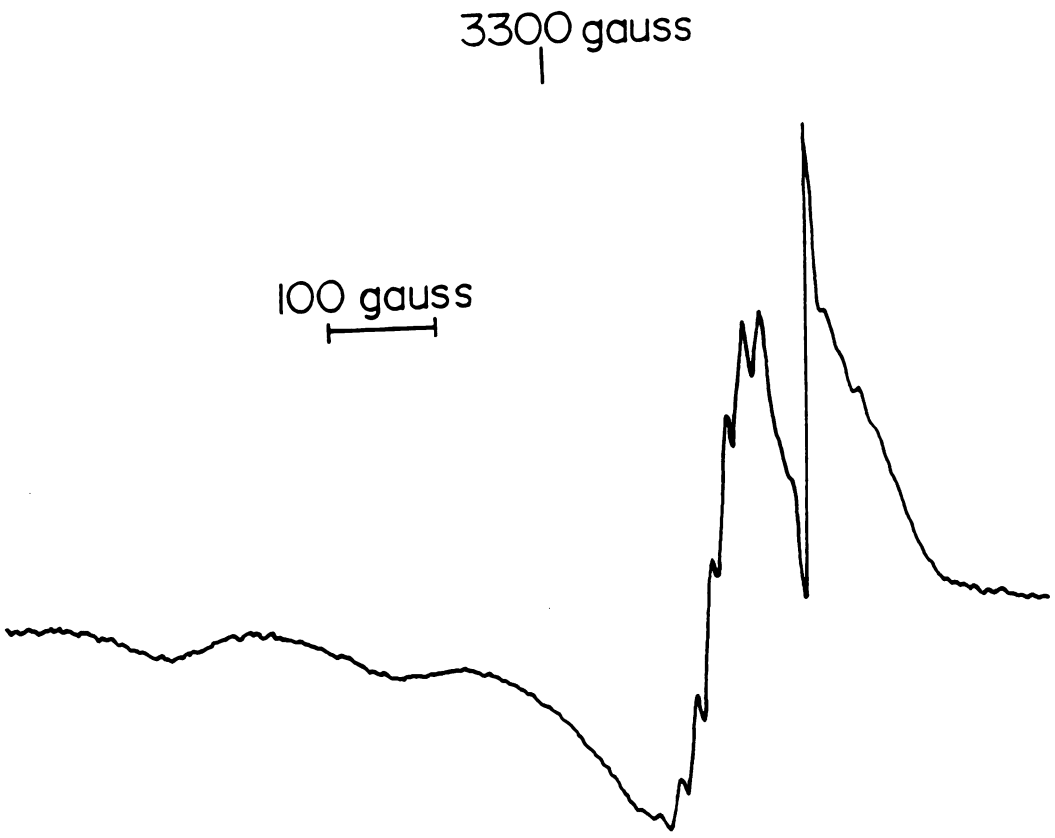

Figure 14. ESR spectrum of P_2-NH-CO-porCu.

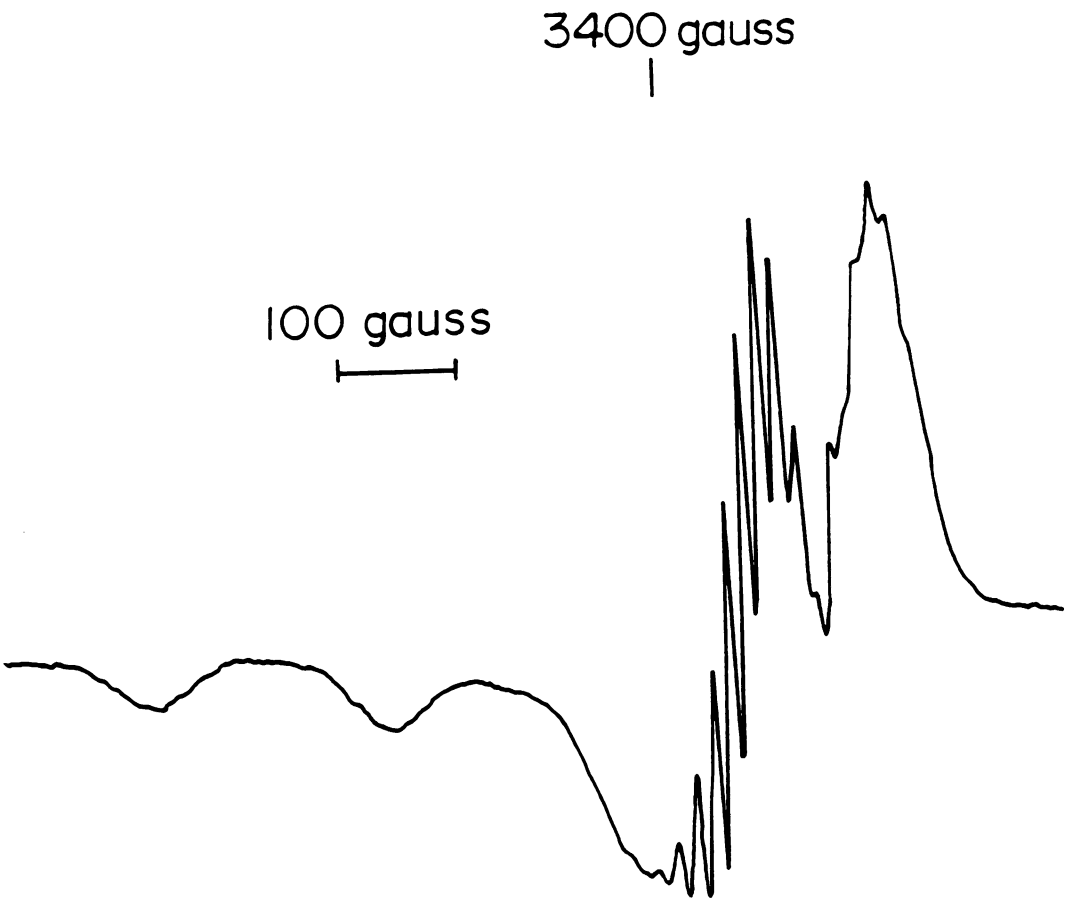

Figure 15. ESR spectrum of P_2-NH-CH_2-porCu.

P_3-CH_2-O-porCu and P_3-CH_2-O-porCu(B) have surprisingly different copper ESR spectra which must reflect the two methods that were used in their preparations. P_3-CH_2-O-porCu has a relatively well resolved ESR spectrum in Figure 16, whereas P_3-CH_2O-porCu(B) does not (Figure 17). Despite these differences, the two complexes have similar ESR parameters (see Table 6). In addition to the usually observed lines, nitrogen perpendicular superhyperfine splittings are observable for P_3-CH_2-O-porCu at room temperature. These lines are found on the m = -3/2 and -1/2 lines of the $Cu_{||}$ features.

In the case of P_3-CH_2-NH-porCu and P_3-CH_2-py-porCu, the ESR spectra are very well resolved and clearly show all of the characteristics expected for a copper porphyrin. At room temperature, spectra of both complexes are found to have nitrogen superhyperfine lines on the $Cu_{||}$ features of m = -3/2 and -1/2. These features are easily seen in Figures 18 and 19, respectively.

H. The Assisted, Free-Radical Autoxidation of Cyclohexene as a Probe for Reactivity of Polymer-Bound Metalloporphyrins.

The free-radical oxidation of alkenes and of cyclohexene, in particular, has been shown to be initiated by metalloporphyrins,[33,72-75] metallophthalocyanines,[37] and various other transition metal complexes.[76,77] The commonly obtained oxidation products for cyclohexene are cyclohexene oxide, 2-cyclohexenone, and 2-cyclohexenol (with the latter two being the major products).

Vanadyl porphyrins, cobalt porphyrins, and iron porphyrins have been shown to be effective initiators in the free-radical autoxidation of alkenes. An ESR study by Fuhrhop indicates that activation of

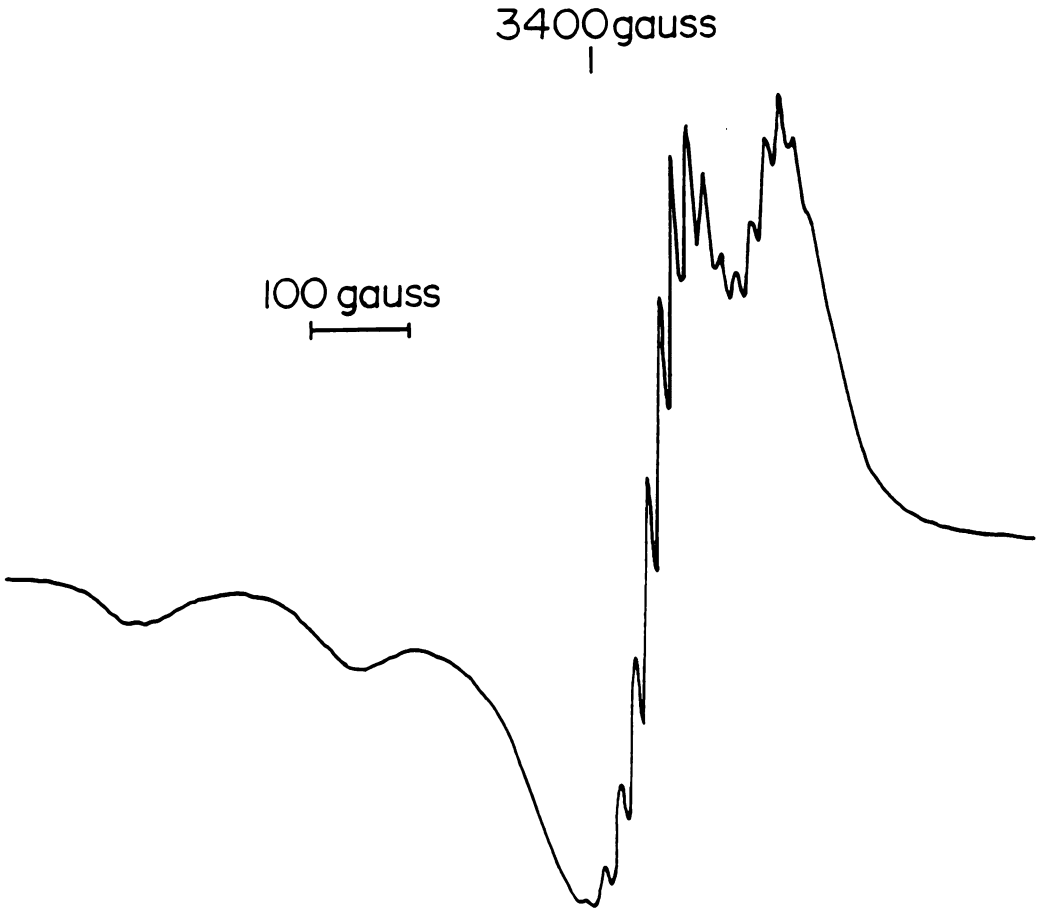

Figure 16. ESR spectrum of P_3-CH_2-O-porCu.

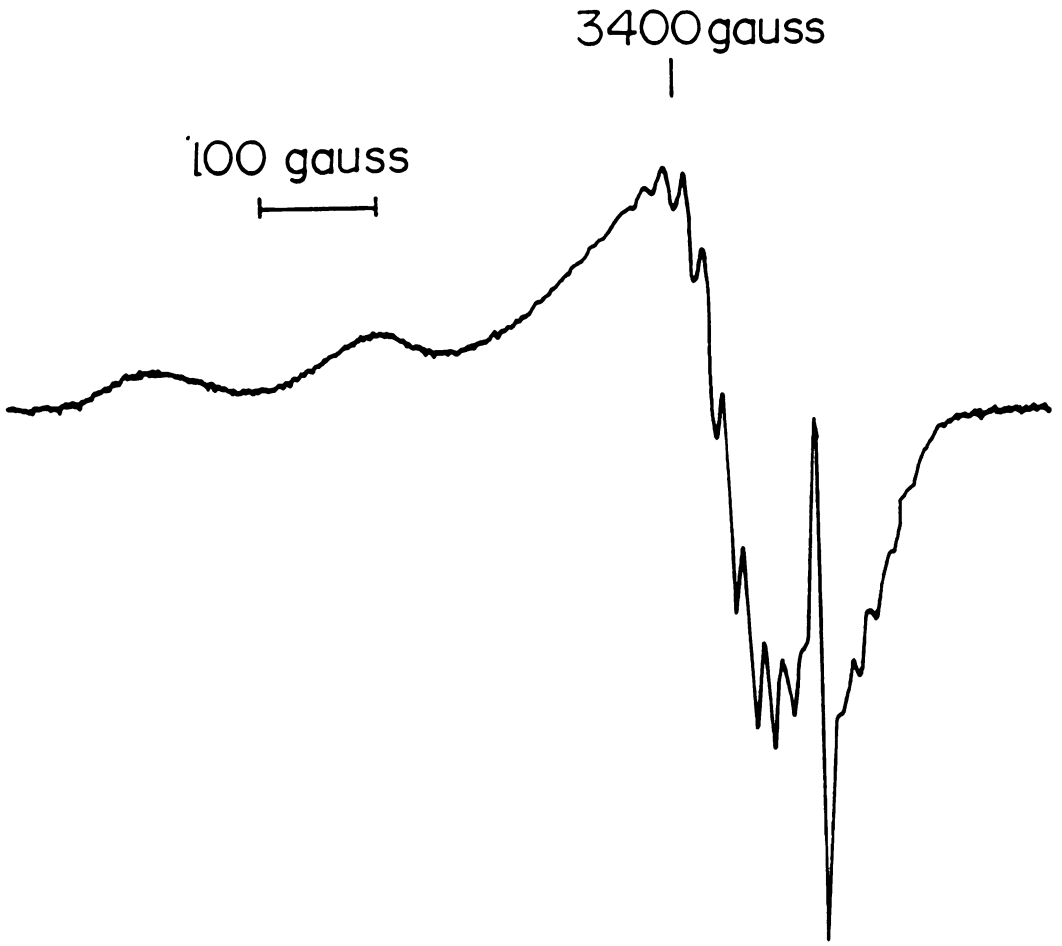

Figure 17. ESR spectrum of P_3-CH_2-O-porCu(B).

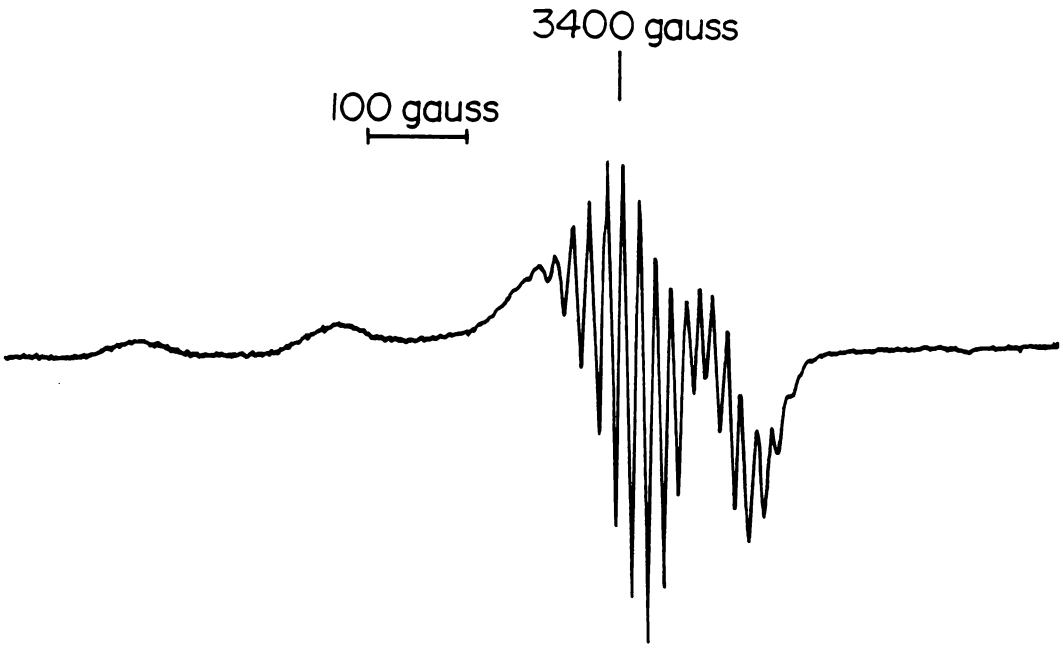

Figure 18. ESR spectrum of P_3-CH_2-NH-porCu.

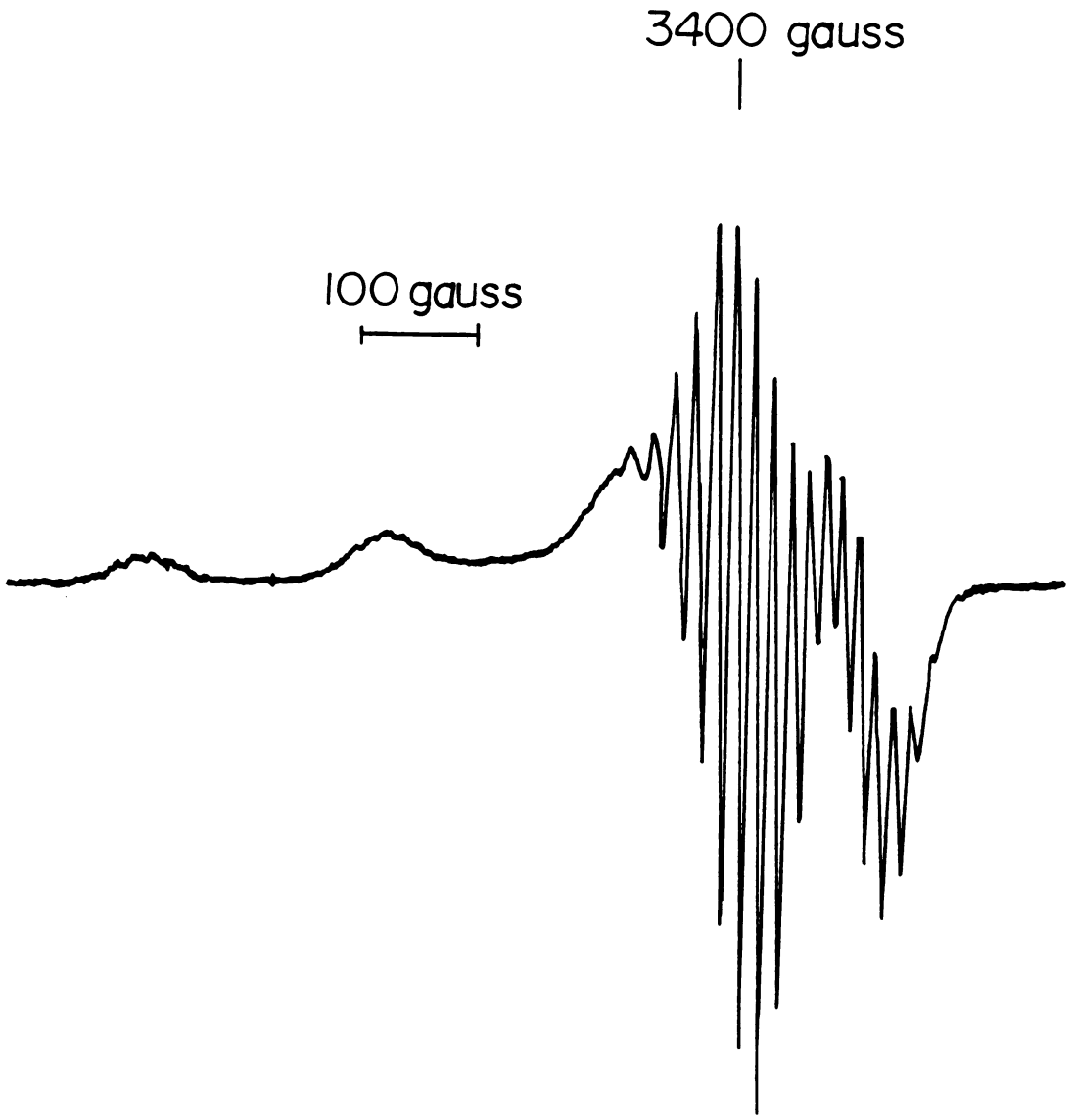

Figure 19. ESR spectrum of P_3-CH_2-py-porCu.

cyclohexene by cobalt(III) porphyrins is the most likely candidate for the initiation step in the autoxidation of cyclohexene.[73,74] Fuhrhop has also shown that the incubation period for the autoxidation of cyclohexene by cobalt(II) porphyrins is eliminated when the cobalt(III) porphyrin is used in place of the cobalt(II) porphyrin.[73,74] LeDon,[33] Paulson,[72] and Fuhrhop[73,74] have shown that the μ-oxo iron(III) porphyrin dimer is necessary for any oxidation of cyclohexene to occur.

The initiation of the free-radical autoxidation of cyclohexene by TTPCo, TPP(CO_2hexyl)$_4$Co, and TTPFeCl was studied as standards for the polymer-bound metalloporphyrins; P_3-CH_2-O-porCo, P_2-NH-CO-porCo, and P_3-CH_2-O-porFeCl, respectively. These reactions were run in cyclohexene at 60°C in one atmosphere of dioxygen and the reaction was followed with the aid of a gas buret. The products and their relative distributions were determined with a gc.

TTPCo was found to initiate the autoxidation of cyclohexene immediately at 60°C. The rate of dioxygen uptake was followed for two hours by which time the rate had reached a maximum. The rate of dioxygen uptake was found to be 2040 mL of dioxygen min^{-1}mmole of Co^{-1} at 60°C (Table 7). The reaction products were analyzed after 2 hours and after 24 hours. The product distribution after 2 hours was found to be similar to that reported previously with 2-cyclohexenone comprising 70-75% of the oxidized products, 2-cyclohexenol was 20-25%, and cyclohexene oxide was only 2-3%.[72] After 24 hours, the relative amounts of the products had changed considerably. The relative amounts were now 2-cyclohexenone, 20-25%; 2-cyclohexenol, 70-75%; cyclohexene oxide, only a trace (Table 8).

Table 7

Rates of Dioxygen Uptake for the Autoxidation of Cyclohexene at 60°C and 1 ATM

Catalyst	Rate[a]
TTPCO[b]	2040
$TPP(CO_2hexyl)_4Co$[b]	1900
TTPFeCl[b]	940
$P_3-CH_2-O-porCo$[c]	900
$P_2-NH-CO-porCo$[c]	250
used $P_3-CH_2-O-porCo$[c]	570
used $P_3-CH_2-O-porFeCl$[c]	357
ground $P_3-CH_2-O-porCo$[d]	2850
ground $P_2-NH-CO-porCo$[e]	1770

[a] mL of dioxygen $min^{-1} mmole^{-1}$ M
[b] 0.5 mg
[c] 100 mg
[d] 43.4 mg
[e] 76.6 mg

Table 8

Product Distribution

Catalyst	Time (h)	Cyclohexene (%)	Cyclohexeneoxide (%)	2-Cyclohexenone (%)	2-Cyclohexenol (%)	ol/one
TTPCo	2	98.1	trace	1.5	0.4	0.4
	24	60.7	trace	8.4	31.0	3.69
$TPP(CO_2hexyl)_4Co$	2	98.1	trace	1.5	0.4	0.4
	24	61.1	trace	11.1	27.8	2.5
TTPFeCl	24	72.4	1.0	10.9	15.7	1.44
P_3-CH_2-O-porCo						
new	24	44.8	trace	6.7	48.5	7.24
used	24	84.3	trace	4.5	11.2	2.49
ground	24	69.8	trace	6.6	23.6	3.58
P_2-NH-CO-porCo						
new	24	82.7	trace	4.5	12.8	2.84
ground	24	68.1	trace	7.2	24.6	3.42
P_3-CH_2-O-porFeCl						
used	24	97.8	trace	0.4	1.8	4.5

Similar results were found for the autoxidation of cyclohexene when $TPP(CO_2hexyl)_4Co$ was used to initiate the reaction. The rate of dioxygen uptake was 1900 mL of dioxygen min^{-1}mmole of Co^{-1}. Again the product distributions after 2 hours and 24 hours were determined. The relative amounts of each product were similar to the results for when TTPCo was used as the catalyst.

When TTPFeCl was used to initiate the autoxidation of cyclohexene, a very short incubation period of less than 5 minutes was observed. The rate of dioxygen uptake was 940 mL of dioxygen min^{-1}mmole of Fe^{-1}. After 24 hours, the reaction products had a distribution of 2-cyclohexenone, 35-40%; 2-cyclohexenol, 55-60%; cyclohexene oxide, 3-4%.

For P_3-CH_2-O-porCo, the uptake of dioxygen occurred after a short incubation period of less than 10 minutes. The rate of dioxygen uptake was 900 mL of dioxygen min^{-1}mmole of Co^{-1} for unused, whole beads and 2850 mL of dioxygen min^{-1}mmole of Co^{-1} for unused, powdered beads. After 24 hours, the product distribution was 2-cyclohexenone (20-25%), 2-cyclohexenol (70-75%), and cyclohexene oxide (trace). Used, whole beads were less active than the unused beads. The used beads have a dioxygen uptake rate of 570 mL of dioxygen min^{-1}mmol of Co^{-1} which is nearly half the rate of the unused, whole beads.

In the case of P_2-NH-CO-porCo, the uptake of dioxygen began after an incubation period of about 10 minutes. A rate of 250 mL of dioxygen min^{-1}mmole of Co^{-1} was found for dioxygen uptake for the whole beads. Once ground, the copolymer, P_2-NH-CO-porCo, caused a dioxygen uptake of 1770 mL of dioxygen min^{-1}mmole of Co^{-1}. After 24 hours, the product distribution for whole and ground beads was again similar to that of P_3-CH_2-O-porCo after 24 hours.

In comparison to TTPFeCl, P_3-CH_2-O-porFeCl was very sluggish in starting the autoxidation of cyclohexene. At 60°C the polymer-bound iron(III) porphyrin had a very long incubation period before any dioxygen uptake was noted. No uptake was noted for at least 3 hours and only 6 mL of dioxygen had been taken up after a total of 6 hours. In comparison, several experiments for other samples (Co) absorbed about 1 mL of dioxygen in only one minute. Used beads had an incubation period of only 20 minutes and an uptake rate of 360 mL of dioxygen min^{-1}mmole of Fe^{-1}. The ratio of products after 24 hours was similar to those of the other reactions after 24 hours.

In all of these reactions, the metalloporphyrins were susceptible to decomposition. Fuhrhop has indicated that this decomposition can result in colorless solutions.[73] In this work, solutions of the metalloporphyrins and the polymer-bound metalloporphyrins bleached considerably during the 24 hour period (Figure 20), because the porphyrin ring is susceptible to attack by free radicals that are generated in the autoxidation of cyclohexene. Rollmann also reported that the decomposition of TPPCo and the polymer-bound cobalt porphyrins occurs during the free-radical oxidation of butanethiol[14] that can be catalyzed by cobalt porphyrins. From used P_3-CH_2-O-porCo, it is apparent from its rate of dioxygen uptake (Table 7) that a considerable amount of polymer-bound cobalt porphyrin must have decomposed during the first run when its rate is compared to that of the unused beads.

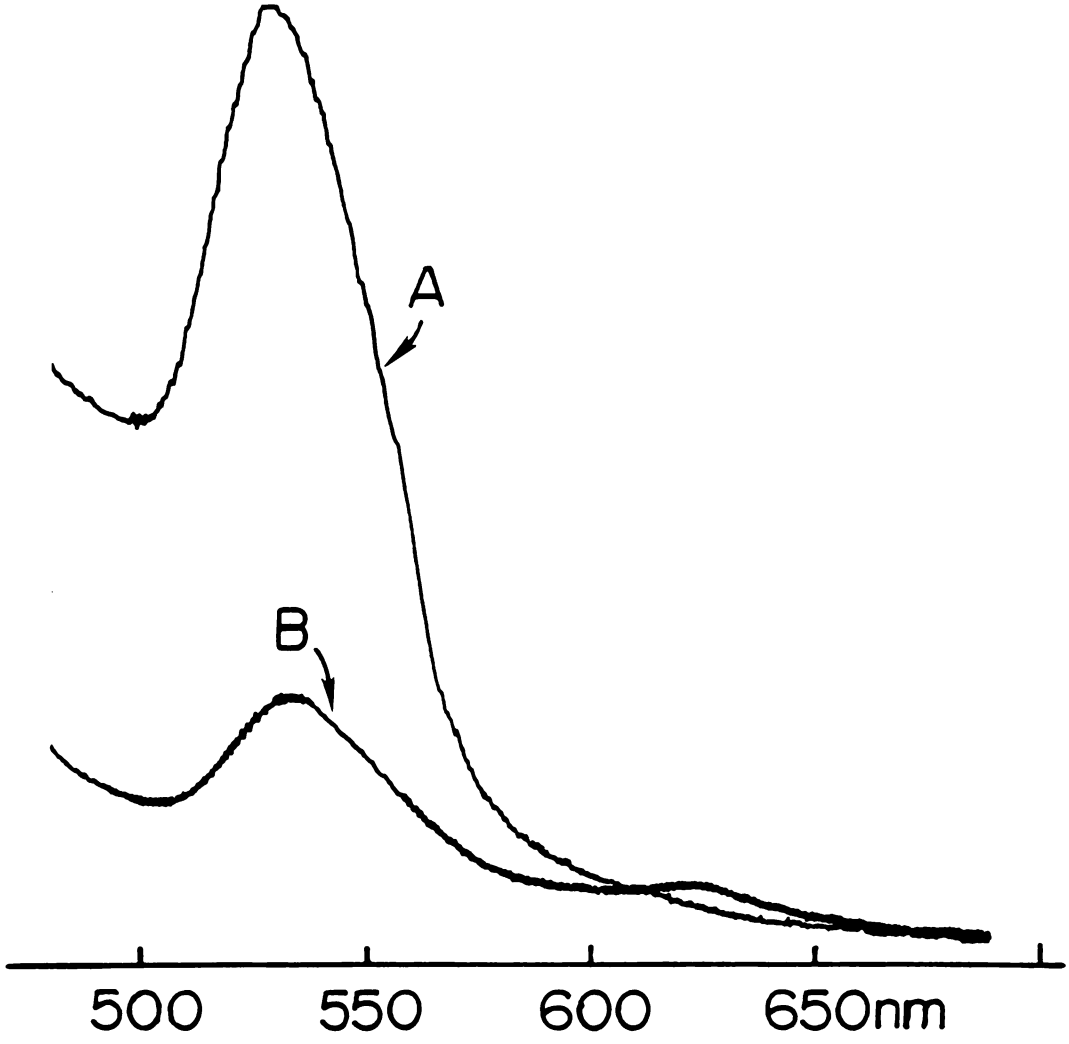

Figure 20. Decomposition of $TPP(CO_2hexyl)_4Co$ during autoxidation of cyclohexene.

I. The Assisted Autoxidation of Aldehydes.

The autoxidation of aldehydes may be initiated either thermally or photochemically, or by metallated polyphthalocyanines and metalloporphyrins. Zaikov and coworkers[79] have investigated both the thermally and photochemically initiated autoxidation of several aldehydes in organic solvents. Osa and coworkers have studied the liquid phase autoxidation of aldehydes in the presence of metallated polyphthalocyanines[80,81] and metalloporphyrins.[81-83]

The autoxidation of benzaldehyde and of butanal were subjected to a preliminary investigation. The autoxidations were carried out in the presence of the following: $TPP(CO_2Et)_4Co$, P_1-CO-porCo(B), and P_1-CO-porFeCl(B). These oxidations of benzaldehyde and butanal to their respective peracids were performed in ethyl acetate which Osa showed was a good solvent for the autoxidation of various aldehydes.[80] The reaction conditions were 25 mL of a solution consisting of 0.09 mM in $TPP(CO_2Et)_4Co$ and 0.5 M in aldehyde at 30°C and 1 ATM of O_2. A 0.100 g portion of beads was used in place of $TPP(CO_2Et)_4Co$ when the polymer-bound metalloporphyrins were used. The rate of dioxygen uptake was determined with the aid of a gas buret and the amounts of peroxides and peracids were determined by titration with a Ce(IV) solution and a thiosulfate solution,[84] respectively.

From the results for the autoxidation of benzaldehyde in Table 9, the reaction conditions resulted in mostly thermal initiation and not photochemical initiation. The rates of dioxygen uptake were the same for blanks run at 30°C in a lighted room and in a darkened room. Zaikov[79] and Cooper and Melville[85] have previously found that the

Table 9

Rates of Dioxygen Uptake for the Autoxidation of Aldehydes at 30°C and 1 ATM O_2

Aldehyde	Catalyst	mL min^{-1}	Rate[a]
PhCHO	-----	1.00[b] 1.00[c]	----
	P_1-CO-porCo(B)	1.63	640
	P_1-CO-porFeCl(B)	0.40	185
	$TPP(CO_2Et)_4Co$	2.00	926
PrCHO	-----	0.80[b]	----
	P_1-CO-porCo(B)	1.70	677
	$TPP(CO_2Et)_4Co$	1.98	918

[a] mL of dioxygen $min^{-1} mmole^{-1}$ M
[b] light
[c] dark

thermal initiation of autoxidation of aldehydes at 30^0C is significant.

In the autoxidation of benzaldehyde and butanal, TPP$(CO_2Et)_4$Co and P_1-CO-porCo(B) showed a slight increase in the rate of dioxygen uptake relative to the unassisted blanks. When the rates for TPP$(CO_2Et)_4$Co and P_1-CO-porCo(B) are calculated on a mL min^{-1}mmole of Co^{-1} basis, TPP$(CO_2$-Et$)_4$Co had an uptake of 926 mL of dioxygen min^{-1}mmole of Co^{-1} and P_1-CO-porCo had 640 mL of dioxygen min^{-1}mmole of Co^{-1} for the autoxidation of benzaldehyde. For butanal, the rates were 918 mL of dioxygen min^{-1}mmole of Co^{-1} and 667 mL of dioxygen min^{-1}mmole of Co^{-1}, respectively. P_1-CO-porFeCl(B) retarded the autoxidation of benzaldehyde relative to the rates for the blank runs and had a rate of dioxygen uptake of only 185 mL of dioxygen min^{-1}mmole of Fe^{-1}.

When the selectivity for the formation of the peracid is considered, the autoxidation of benzaldehyde in the presence of P_1-CO-porCo(B) showed a decrease from about 65% to nearly 30% over a 2 hour period. For butanal, the selectivity went from 40% to 75% over a 2 hour period for P_1-CO-porCo(B) and remained at approximately 50% for TPP-$(CO_2Et)_4$Co for at least 3 hours. Osa and coworkers observed that for the TPPCo-assisted and TTPCo-assisted autoxidations of acetaldehyde that the selectivity remained nearly constant for at least 3 hours at 80%.[82,83] In contrast, the metallated polyphthalocyanines were found to have selectivities which varied with time.[80,83]

As in the autoxidation of cyclohexene, the autoxidations of benzaldehyde and butanal resulted in the bleaching of both P_1-CO-porCo(B) and P_1-CO-porFeCl(B) and of solutions of TPP$(CO_2Et)_4$Co. Therefore, the porphyrin ring was decomposed during the autoxidations of benzaldehyde and butanal.

III. DISCUSSION

A. Friedel-Crafts Acylation and Alkylation of Divinylbenzene-Polystyrene Copolymers.

The Friedel-Crafts acylation of divinylbenzene-polystyrene copolymer beads (XAD-2 from Rohm and Haas) with $TPP(COCl)_4H_2$ and $AlCl_3$ was first investigated by Rollmann.[14] In his work, he indicated that the resulting porphyrin-containing polymer could be metallated, although elemental analysis indicated that the sample had a nitrogen to metal ratio of 25 to 1 for the cobalt complex.[54] This result may be compared with two other samples prepared by Rollmann.[14] When $TPP(NH_2)_4H_2$ was attached to chloromethylated, divinylbenzene-polystyrene copolymer beads (again XAD-2), elemental analysis of its copper complex was found to have a nitrogen to copper ratio of 7 to 1 for one sample and 10 to 1 for another. Theoretically, a ratio of 8 to 1 is expected. From these results, it would appear that metallation is trustworthy but that the Friedel-Crafts acylation of divinylbenzene-polystyrene copolymer beads which was catalyzed with $AlCl_3$ has drawbacks which were not addressed in the original research.

In this work, the Friedel-Crafts acylation and alkylation of 20% divinylbenzene-polystyrene copolymer beads was reinvestigated. Three serious drawbacks to these reactions became apparent. The low loadings associated with these reactions could not be circumvented. The nitrogen to metal ratio was again high as in the work of Rollmann.[14] Lastly, the problem of aluminum contamination of the divinylbenzene-polystyrene copolymer beads was found. The latter two problems will be discussed at this point.

The high nitrogen to metal ratios found in this work and in Rollmann's for the acylation and alkylation reactions indicates an inherent weakness in these $AlCl_3$-catalyzed reactions. This is borne out by Rollmann's results for his samples of Cu[Res-NH-TPP-NH_2] with nitrogen to copper ratios of 7 to 1 and 10 to 1 (theoretical 8 to 1).[14] In this work, P_3-CH_2-O-porCo had a nitrogen to cobalt ratio of 5 to 1 (theoretical 4 to 1). These results indicate that metallation of the polymer-bound porphyrins is not the problem. For P_1-CO-porCo and P_1-CH_2-porCo, the nitrogen to cobalt ratios were 35 to 1 and 38 to 1, respectively. This would suggest that the porphyrin molecule is subject to some form of decomposition. This possibility of decomposition is supported by the complete decompostiion of $TPP(COCl)_4Cu$ during the $AlCl_3$-catalyzed Friedel-Crafts acylation of 20% divinylbenzene-polystyrene copolymer beads.

When the ratios of nitrogen to metal are compared for Rollmann's work[14] and for this work, the ratios for this work are higher for P_1-CO-porCo and P_1-CH_2-porCo than Rollmann's sample which is analogous to P_1-CO-porCo. The higher temperatures which were used in this study may be responsible for this outcome.

Thus far, it has been shown that $AlCl_3$-catalyzed, Friedel-Crafts acylation and alkylation reactions result in the apparent decomposition of the porphyrin. It was also found that the beads were contaminated with aluminum. The question of where the aluminum resides in these porphyrin-containing copolymer beads must be addressed at this point for the aluminum could be either present as an adduct with the phenyl groups of the copolymer or as an aluminum porphyrin.

Neckers has posted a warning which involves $AlCl_3$ and divinylbenzene-polystyrene copolymers.[55] It has been shown that $AlCl_3$ forms a relatively stable chemical entity with 2% divinylbenzene-polystyrene copolymers.[56] These $AlCl_3$-containing copolymers have been shown to remain active as catalysts for acetal,[57] ester,[55] and ether formation[56] and transesterification[55] for periods of at least one year. Furthermore, washing of these samples with water, ether, acetone, hot isopropanol and ether result in beads which contain as much as 3.7% Al.[56] Therefore, Neckers has noted that considerable amounts of $AlCl_3$ may persist after extensive washing of divinylbenzene-polystyrene copolymers which have come into contact with $AlCl_3$.

As mentioned, the other possibility for the location of the aluminum is that it could be present as an aluminum porphyrin. Once formed, aluminum porphyrins are known to be among some of the most stable of metalloporphyrins.[57] Therefore it would not be possible to exchange or remove the aluminum from the porphyrin-containing copolymers with any degree of certainty if it were present as the metalloporphyrin.

Aluminum can also displace many metals from their metalloporphyrin complexes. It has been shown that $AlEt_3$ and diisobutylaluminum hydride can displace such metals as Cu(II), Fe(III), Zn(II), and $Sn(IV)(OAc)_2$ from their octaethylporphyrin complexes[58] and may indicate that $AlCl_3$ could possibly have displaced some of the copper from $TPP(CH_2OH)_4Cu$ in the Friedel-Crafts alkylation of the copolymer, P_1.

When $AlCl_3$ is treated with $TTPH_2$ in carbon disulfide, it formed TTPAlOH in a yield of only 16%. Therefore it is possible for $AlCl_3$ to

react with a porphyrin in a solvent of low polarity to form an aluminum porphyrin. It can be seen that aluminum porphyrin formation is a possibility which could occur during $AlCl_3$-catalyzed Friedel-Crafts reactions.

With this in mind, the infra-red spectra of P_1-CO-porCo and P_1-CH_2-porCu were examined to determine which possibility for aluminum occurred. An absorption at 1650 cm^{-1} has been reported as being characteristic for $AlCl_3$-containing, 2% divinylbenzene-polystyrene copolymers.[56] For P_1-CO-porCo, a strong absorption is observed at 1680 to 1640 cm^{-1}. Since the carbonyl absorption has been reported by Rollmann[14] as being at 1670-1680 cm^{-1} and the absorption for the $AlCl_3$ adduct at 1650 cm^{-1}, it is not clear as to whether the absorption for P_1-CO-porCo is a result of either the carbonyl and $AlCl_3$ adduct or just the carbonyl. For P_1-CH_2-porCu, the carbonyl absorption is not present to obscure the region. Unfortunately, the absorption spectrum for P_1-CH_2-porCu does not clearly show any absorption at or around 1650 cm^{-1}. There may be a weak absorption present but it is of such intensity as to be unreliable for assignment.

Since infra-red spectroscopy could not answer the question of the location of the aluminum, resonance raman spectroscopy was used to determine if aluminum porphyrins are present in these samples. Resonance raman spectroscopy of metalloporphyrins has shown promise in various structural studies. Babcock and coworkers have used this technique to probe the coordination sphere of iron porphyrins[59] in an effort to better understand the coordination sphere in cytochrome oxidase. In addition, several metalloporphyrins other than iron

porphyrins have been investigated with resonance raman spectroscopy. Thus far, resonance raman spectra have been reported for at least TPPMnX,[60] TPPCo,[60] Cu porphine,[62] TPPNi,[63] TPPCu,[63] and PdTPP.[63] Other references are available.[64,65] The use of resonance raman spectroscopy is attractive because of its sensitivity to changes in coordination.

Samples of TTPCu and TTPAlOH in dichloromethane were prepared and used as standards for the resonance raman absorptions of these metalloporphyrins. TTPCu was found to have four major absorptions at 1563, 1362, 1237, and 1076 cm^{-1} (Figure 21). TTPAlOH had absorptions at 1549, 1378, 1259, and 1242 cm^{-1} (Figure 22). The sample, P_1-CH_2-porCu, was found to have absorptions at 1560, 1365, 1228, and 1077 cm^{-1} (Figure 23). This spectrum indicates that a copper porphyrin is present in the powdered copolymer. The base line of P_1-CH_2-porCu was found to fall over the region of 1710 to 1000 cm^{-1} and this was attributed to florescence. Due to the fall of the base line, it was not possible to determine if any aluminum porphyrins were present.

Since infra-red and resonance raman spectroscopies were unable to locate the aluminum, another approach was used to determine if aluminum was incorporated into the porphyrin during the $AlCl_3$-catalyzed Friedel-Crafts reactions. The Friedel-Crafts acylation of ethylbenzene with $TPP(COCl)_4H_2$ was investigated under similar reaction conditions. The reaction was carried out run in nitromethane at 50°C with the same ratio of reactants and solvent.

After the reaction was completed, the product was esterified (at reflux) in 1-octanol with concentrated sulfuric acid added to catalyze

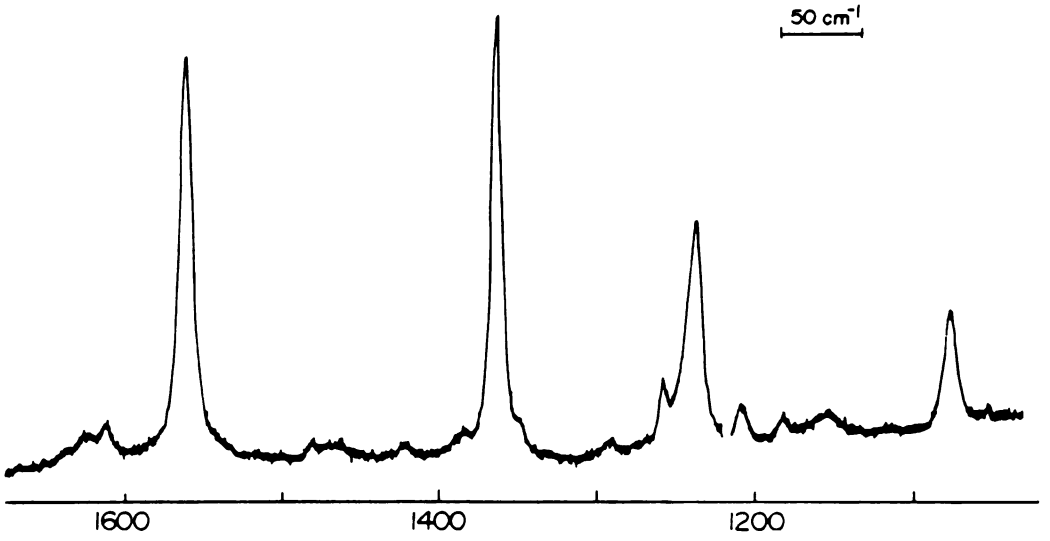

Figure 21. Resonance Raman spectrum of TTPCu.

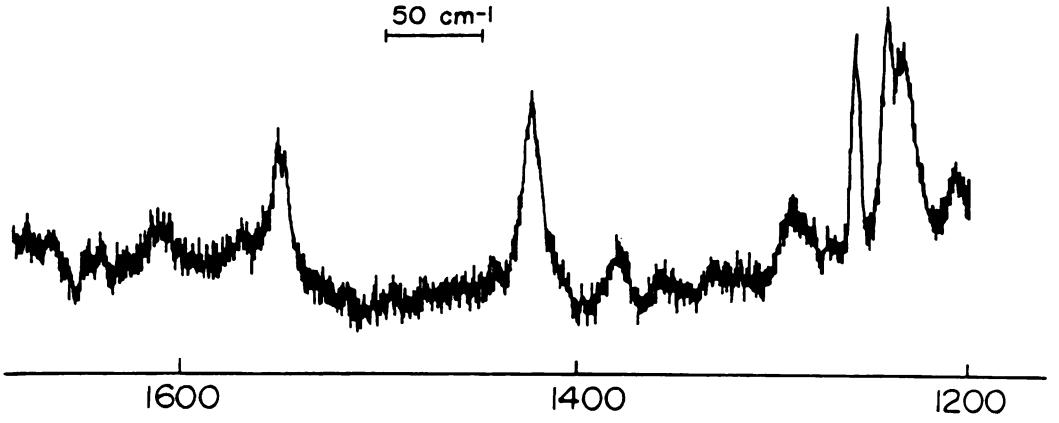

Figure 22. Resonance Raman spectrum of TTPAlOH.

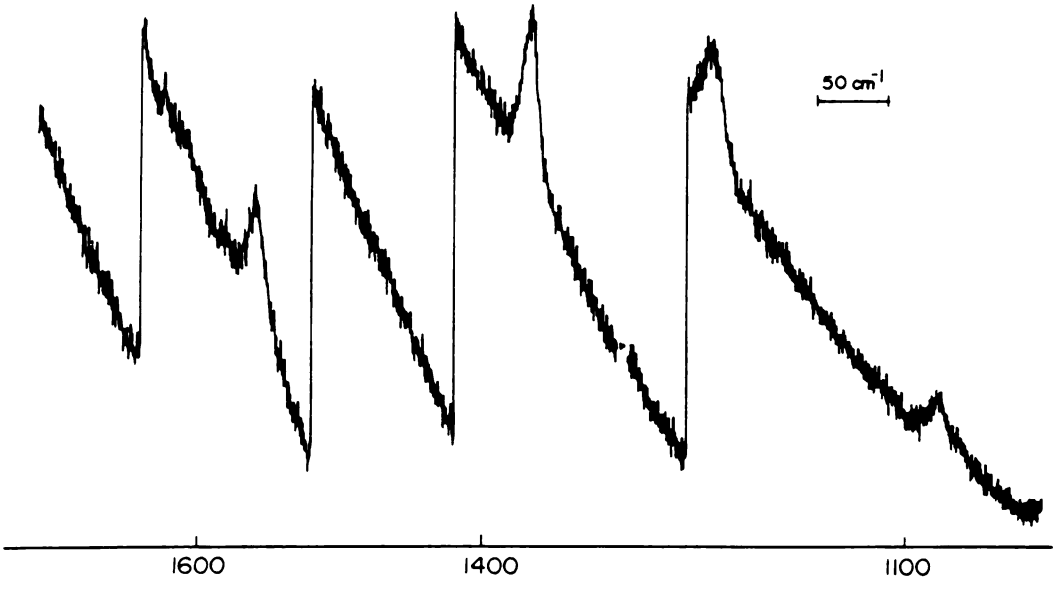

Figure 23. Resonance Raman spectrum of P_1-CH_2-porCu.

the reaction. The resulting ester-containing porphyrin was then chromatographed on alumina. The visible spectrum of each fraction appears to be that of a free base porphyrin (Figure 24). Protonation with trifluoroacetic acid, TFA, reveals that the free base porphyrin is the dominant or only porphyrinic species present for no major absorption at or near 550 nm was observable. This band would have been due to an aluminum complex of a meso-tetraarylporphyrin. The proton NMR spectrum of the first and principle fraction indicates that the ratio of octyl ester groups to ethylphenyl groups is approximately one to one which would mean that only about 50% of the available acid chloride groups were converted into diphenyl ketone groups (Figure 25). The ^{1}H NMR spectrum also shows the presence of the -NH hydrogens. From the integration, their intensity is near what is expected when compared to the intensity of the β-hydrogens of the porphyrin periphery. This may indicate that little if any aluminum was present in this fraction. The remaining fractions consisted of very little material so no ^{1}H NMR was taken for these.

A second effort at the Friedel-Crafts acylation of ethylbenzene was made. This time the resulting product was washed with water and then methanol and dichloromethane. The methanol and dichloromethane soluble fractions were saved. The remaining solid was dissolved with aqueous potassium hydroxide (1N) and reprecipitated with the addition of acetic acid. This was repeated three times to free any aluminum ions from the porphyrins. Each of the resulting fractions, methanol, dichloromethane, and aqueous KOH, were found to contain free base porphyrins (Figures 26-28, respectively). The combined methanol and

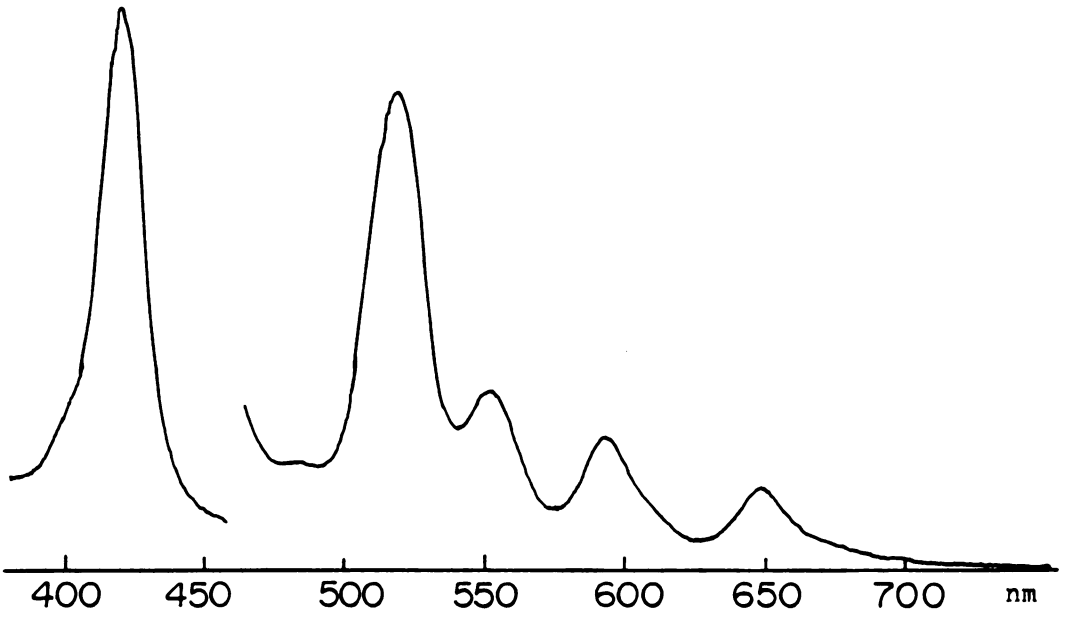

Figure 24. UV-VIS spectrum of $TPP(CO_2octyl)_{4-x}(COC_6H_4C_2H_5)_x$.

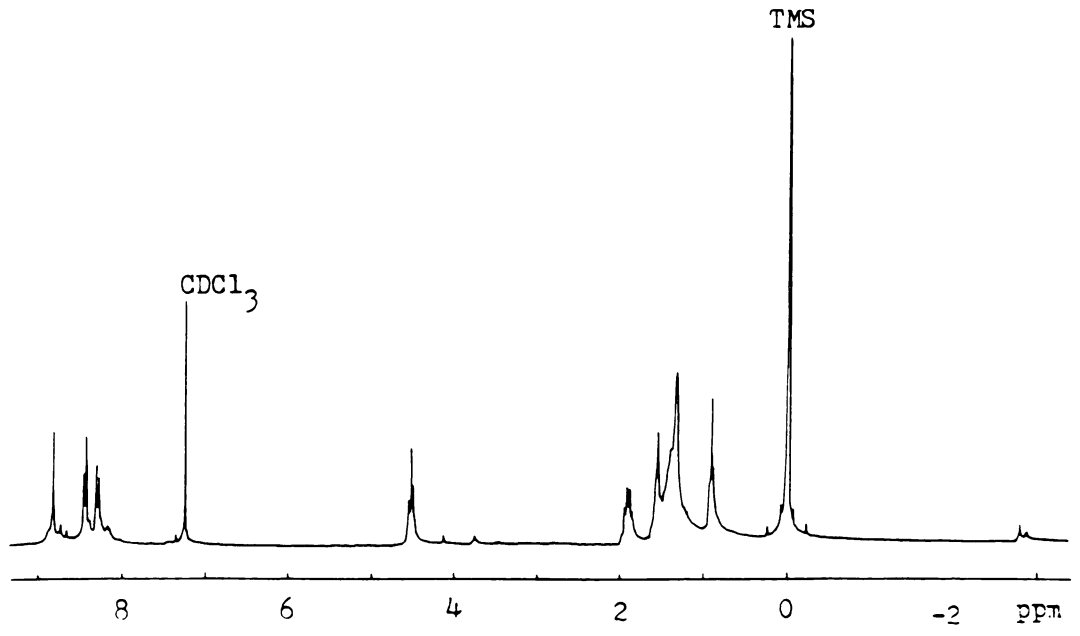

Figure 25. ^1H NMR spectrum of $TPP(CO_2octyl)_{4-x}(COC_6H_4C_2H_5)_x$.

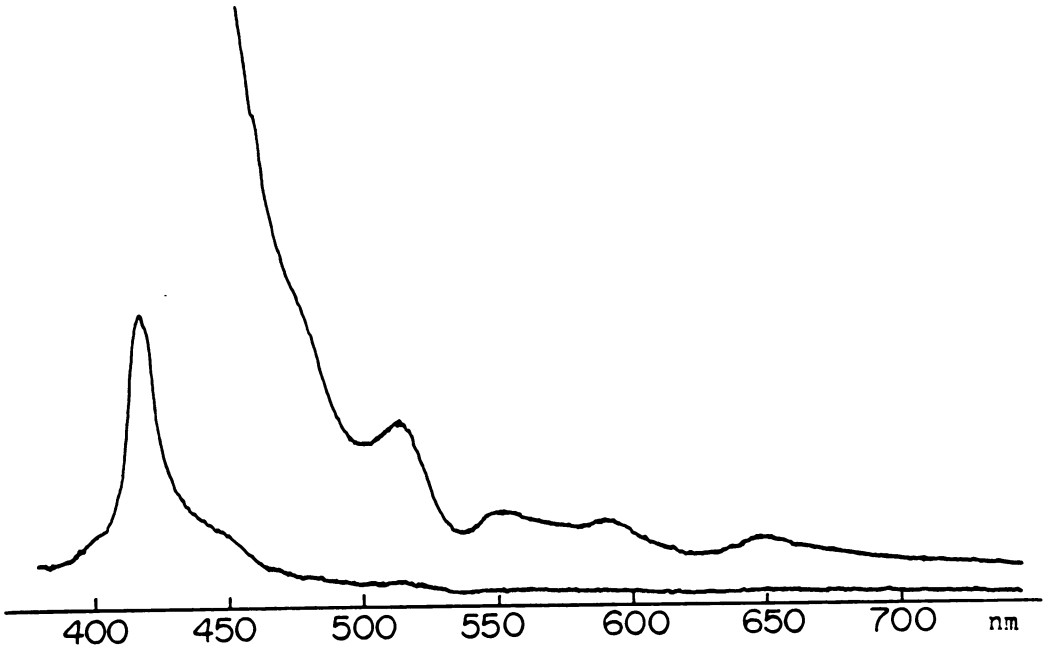

Figure 26. UV-VIS spectrum of methanol solution from $TPP(COCl)_4H_2$ + ethylbenzene.

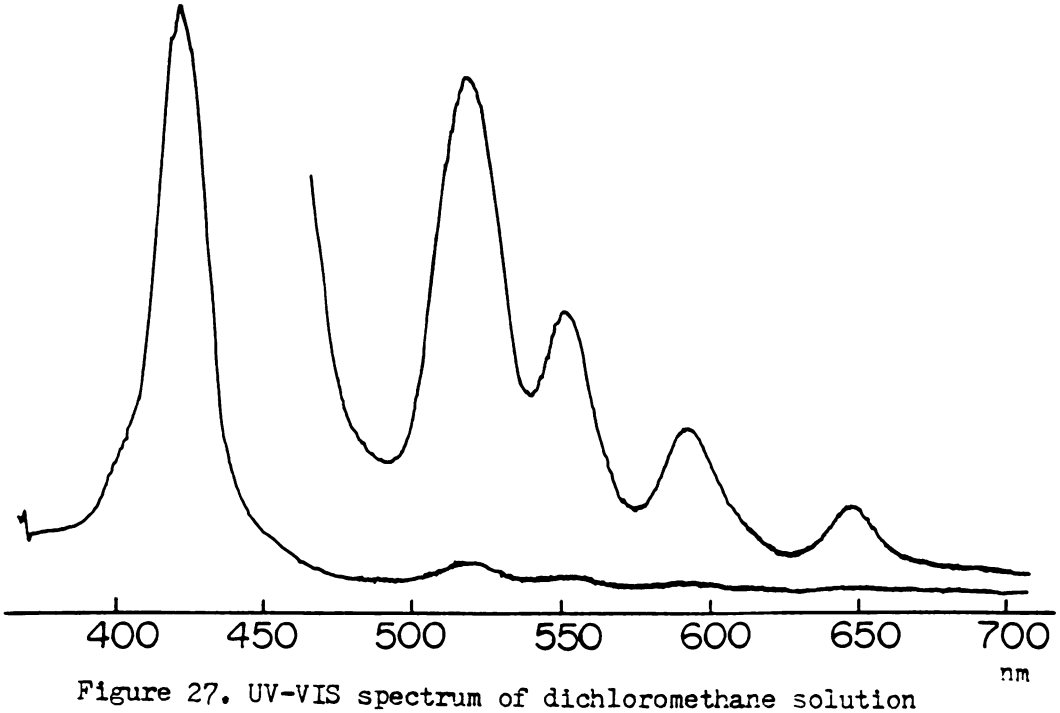

Figure 27. UV-VIS spectrum of dichloromethane solution from $TPP(COCl)_4H_2$ + ethylbenzene.

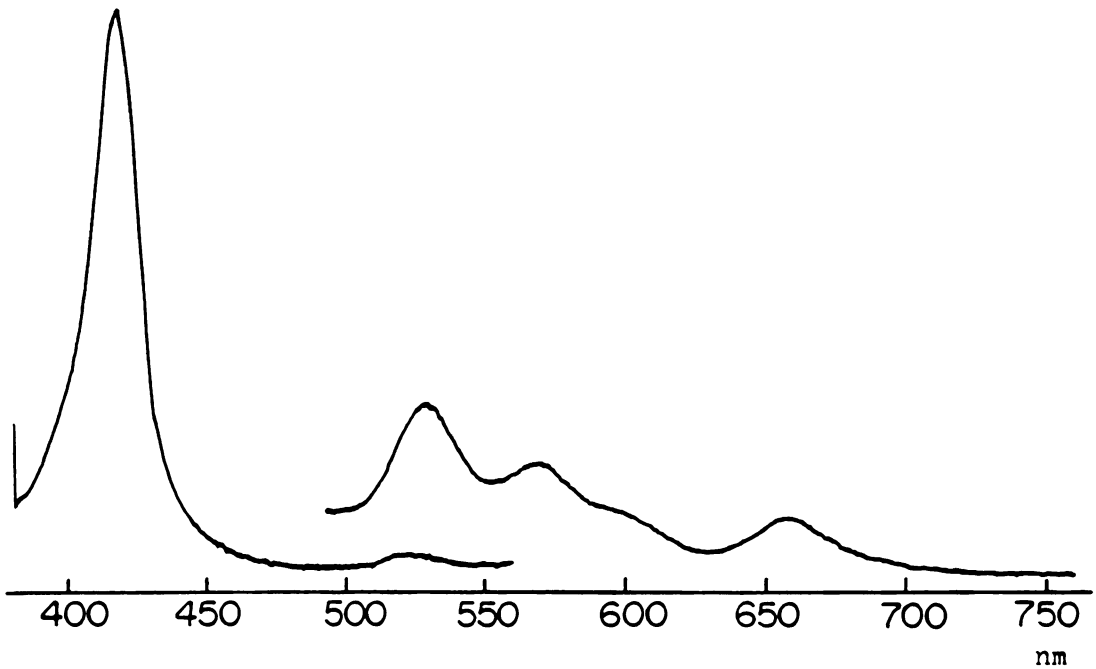

Figure 28. UV-VIS spectrum of $TPP(CO_2H)_{4-x}(COC_6H_4C_2H_5)_x$ in aqueous KOH.

dichloromethane fractions were then evaporated and treated with a solution of 30% H_2O_2 in acetic acid (1 to 2 volume ratio) at reflux for three hours. The resulting solution was tested for the presence of aluminum ions. Aluminon (ammonium aurin tricarboxylate) was used to qualitatively test for aluminum. The test proved to be positive which indicates the presence of Al. Therefore aluminum can be incorporated into the porphyrin moiety during $AlCl_3$-catalyzed, Friedel-Crafts acylation.

In conclusion, the $AlCl_3$-catalyzed, Friedel-Crafts acylation and akylation of 20% divinylbenzene-polystyrene copolymer beads caused to some extent an apparent decomposition of the porphyrin and to also contaminate the copolymer with aluminum. It was found that contamination still occurred for both reactions when $TPP(COCl)_4Cu$ and $TPP(CH_2OH)_4Cu$ were used. Efforts to determine the location of aluminum in the copolymers were not successful. Through analogous Friedel-Crafts acylation of ethylbenzene with $TPP(COCl)_4H_2$, it is apparent that aluminum can be incorporated into the porphyrin during $AlCl_3$-catalyzed Friedel-Crafts acylations and alkylations. Therefore it is believed that the aluminum exists as an aluminum porphyrin in these samples and as an adduct with the 20% divinylbenzene-polystyrene copolymer beads.

B. Scanning Electron Microprobe Analyses

The results from the scanning electron microprobe analyses of metalloporphyrins bound to 20% divinylbenzene-polystyrene copolymer beads show that the radial distribution of the metalloporphyrins varies from method to method used in the attachment. The distributions varied from high loadings at or near the surface to even loadings throughout.

A trend was noticed that the less reactive the functional group of the porphyrin was the more evenly distributed was the resulting bound porphyrin and its metal complex.

SEM scans of P_1-CO-porCo, P_1-C_5-O-porCo, P_2-NH-CO-porCo, and P_3-CH_2-O-porCu(B) were characterized by low values of I_c. These low values of I_c indicate that the penetration of the reactive porphyrin was poor for little porphyrin managed to penetrate into the interior of the beads before reaction had occurred. These samples were prepared from reactive groups in the Friedel-Crafts acylation and alkylation, and amide formation with $TPP(COCl)_4H_2$. For P_3-CH_2-O-porCu(B), reaction time is a more likely factor.

For P_2-NH-CH_2-porCo, its SEM scan shows that the cobalt porphyrin is evenly distributed throughout the bead. This result indicates that the porphyrin had little difficulty in diffusing throughout the bead. Since P_2-NH-CO-porCo does have a low value of I_c, the result for P_2-NH-CH_2-porCo is useful in showing that relative reactivity of the porphyrin's functional groups plays a significant role in determining the radial distribution of the polymer-bound metalloporphyrin on the bead.

The results for P_2-NH-CO-porCo and P_2-NH-CH_2-porCo show that the size of the porphyrin molecule is not the cause for the poor penetration of the porphyrins which was found for P_1-CO-porCo, P_1-C_5-O-porCo, and P_2-NH-CO-porCo. Size would seem to be a poor reason, for 20% divinylbenzene-polystyrene copolymer beads have pore sizes of approximately 1200 Å. This was determined from photographs taken with an electron microscope.[37] Therefore size should not be the reason low values of I_c were obtained but reactivity does seem a pausible explanation.

In the case of the porphyrins attached to chloromethylated, 20% divinylbenzene-polystyrene copolymer beads, these samples were characterized with high values of I_c. For P_3-CH_2-O-porCo, P_3-CH_2-NH-porCu, and P_3-CH_2-py-porCu, the reactivity of the respective porphyrin's functional group is less than that of a porphyrin like $TPP(COCl)_4H_2$. Therefore, these porphyrins were able to effectively diffuse throughout the copolymer before reacting with a chloromethyl group.

In conclusion, the SEM data is able to show that the radial distributions of porphyrins and metalloporphyrins can be affected by the particular reaction which is used to couple the porphyrin to the 20% divinylbenzene-polystyrene copolymer beads. It was shown that the relative reactivity of the functional group had an effect on how well the porphyrin diffused through the 20% divinylbenzene-polystyrene copolymers that were used.

C. Electron Spin Resonance Analyses.

When the ESR spectra of the polymer-bound copper porphyrins are considered in light of the results that were obtained from SEM analysis and elemental anlaysis, there are two noticable trends which affect the resolution of the ESR spectra of the polymer-bound copper porphyrins. The distribution and the amount of the copper porphyrin bound to the divinylbenzene-polystyrene copolymer beads play a significant role in determining the relative degree of resolution of the ESR spectrum for a particular sample.

In those samples with less than 0.1% Cu such as P_1-CO-porCu, P_1-CH_2-porCu, and P_1-CH_2-porCu(B), the copper ESR spectra are well resolved with all but the nitrogen perpendicular superhyperfine lines

being observable at room temperature. For all but P_1-CH_2-porCo and P_1-CH_2-porCu(B) for which no SEM data were obtained, the SEM data indicates that the bulk of the porphyrin was bound at or near the surface of the beads. These levels of loading near the surface did not have any effect on the resolution of the ESR spectra of these samples.

P_2-NH-CO-porCu had a low value of I_c and a copper content of 0.153%. When these numbers are taken together, there must be a considerable amount of copper porphyrin molecules in a small volume of space. It is not surprising that the ESR spectrum of this complex is of such poor resolution. This lack of resolution may be due to the proximity of the copper porphyrin moieties. It has been shown by Barker and Stobart that in a polycrystalline sample of TPPCu that all of the nitrogen superhyperfine splittings were no longer observable at room temperature and at 77°K.[70] This is believed due to dipolar interactions between the nearest neighbors since dipolar interactions were said to be negligible at distances greater than 12 Å. This result may be compared to the ESR spectra of copper octaethylporphyrin, copper meso-mononitro-octaethylporphyrin, copper α,β-meso-dinitro-octaethylporphyrin, and copper α,γ-meso-dinitrooctaethylporphyrin.[71] The ESR spectra of these copper complexes were used to determine the equilibrium constants for dimerization. In comparing the spectrum of P_2-NH-CO-porCu to those in the above cited literature, it became apparent that dimerization is not the main cause for the poor resolution but that dipolar interactions must be occurring between the polymer-bound copper porphyrins. It is these dipolar interactions which must be causing the poor resolution for the ESR spectrum of P_2-NH-CO-porCu.

This must also be true for P_3-CH_2-O-porCu(B). It had an I_c = 0.08 and a 0.238% copper content. This would again result in high local concentrations of copper porphyrin moieties. Its ESR spectrum is very similar to that of the above P_2-NH-CO-porCu and therefore it is probably experiencing a considerable amount of dipolar interactions between neighboring copper porphyrin residues.

In the case of the remaining polymer-bound copper complexes, the value of I_c for each is either near or at unity. These samples are all comprised of materials having a relatively even distribution of the copper porphyrin across the cross section of their respective copolymer beads. For P_3-CH_2-NH-porCu and P_3-CH_2-py-porCu with a copper content of 0.352% and 0.310% copper respectively, the ESR spectra of these complexes are perhaps the best resolved of all of the spectra for the polymer-bound copper porphyrins. It is apparent that the even radial distribution of these beads must effectively isolate the copper porphyrin moieties from each other. This effective isolation then results in obtaining a well defined ESR spectrum for each of these samples.

With P_2-NH-CH_2-porCu, the copper content is 0.393% and the resolution of this complex is less than that of either of the two above complexes. This may reflect the slight increase of copper content but this increase should not affect the ESR spectrum as much as this. When the ESR spectrum of P_3-CH_2-O-porCu is considered, its degree of resolution is qualitatively equal to or greater than that of P_2-NH-CH_2-porCu even though P_3-CH_2-O-porCu has a copper content of 1.363% Cu. From the ESR spectrum of P_3-CH_2-O-porCu, it is evident that the increased content of copper does result in an increase of dipolar interactions between the

copper porphyrins bound to P_3. This is reflected in the decrease of resolution for spectra from P_3-CH_2-O-porCu in comparison to spectra from P_3-CH_2-NH-porCu or P_3-CH_2-py-porCu.

In an effort to observe at what concentration of copper that the dipolar interactions become significant, a series of dilutions of TTPCu in $TTPH_2$ were prepared. This series was prepared by the slow co-crystallization of TTPCu and $TTPH_2$ from a solution of dichloromethane and methanol. Table 10 lists the % Cu of the prepared samples along with pertinent ESR parameters that were taken from the room temperature ESR spectra. In Figures 29 through 34, the ESR spectra of the first six of the series are presented.

In Figures 29 and 30, the ESR spectra of Cu 1 and Cu 2 are presented and are very similar to that reported by Assour for polycrystalline TPPCu in $TPPH_2$ at either room temperature or 77°K.[67] From the data listed, it is quite apparent that these spectra are in all respects comparable to Assour's spectrum for TPPCu in $TPPH_2$.

For Cu 3, the presence of all of the characteristic features are observable (Figure 31). In addition, two sets of four additional lines are visible between the $Cu_{||}$ lines of m = -3/2 and -1/2 and m = -1/2 and 1/2. These lines are also present in the ESR spectrum presented by Assour for polycrystalline samples of TPPCu in $TPPH_2$.[67] The origin of these "extra" lines is unknown. The most important feature of this spectrum is that the resolution of the nitrogen superhyperfine splitting is no longer as sharp in the region of 3200 to 3500 gauss as in the previous samples, Cu 1 and Cu 2.

Table 10

ESR Data for Dilutions of TTPCu in $TTPH_2$

Sample	% Cu	$g_{\parallel}$	$g_{\perp}$	$Cu_{\parallel}$ [a]	<N>[a]	<N> [a]
Cu 1	0.086	2.177	2.049	201	17.5	14.3
Cu 2	0.33	2.177	2.049	201	17.5	14.3
Cu 3	0.79	2.177	2.049	202	17.6	14.2
Cu 4	1.44	2.174	2.049	206	17.0	----
Cu 5	2.00	2.174	2.050	206	16.6	----
Cu 6	2.89	2.172	2.051[b]	208	----	----
Cu 7	3.85	2.171	2.053[b]	209	----	----
Cu 8	4.73	2.171	2.052[b]	209	----	----
Cu 10	8.34	2.164	2.052[b]	212	----	----
Cu 11	8.67	2.164	2.053[b]	210	----	----

[a] in gauss
[b] estimated

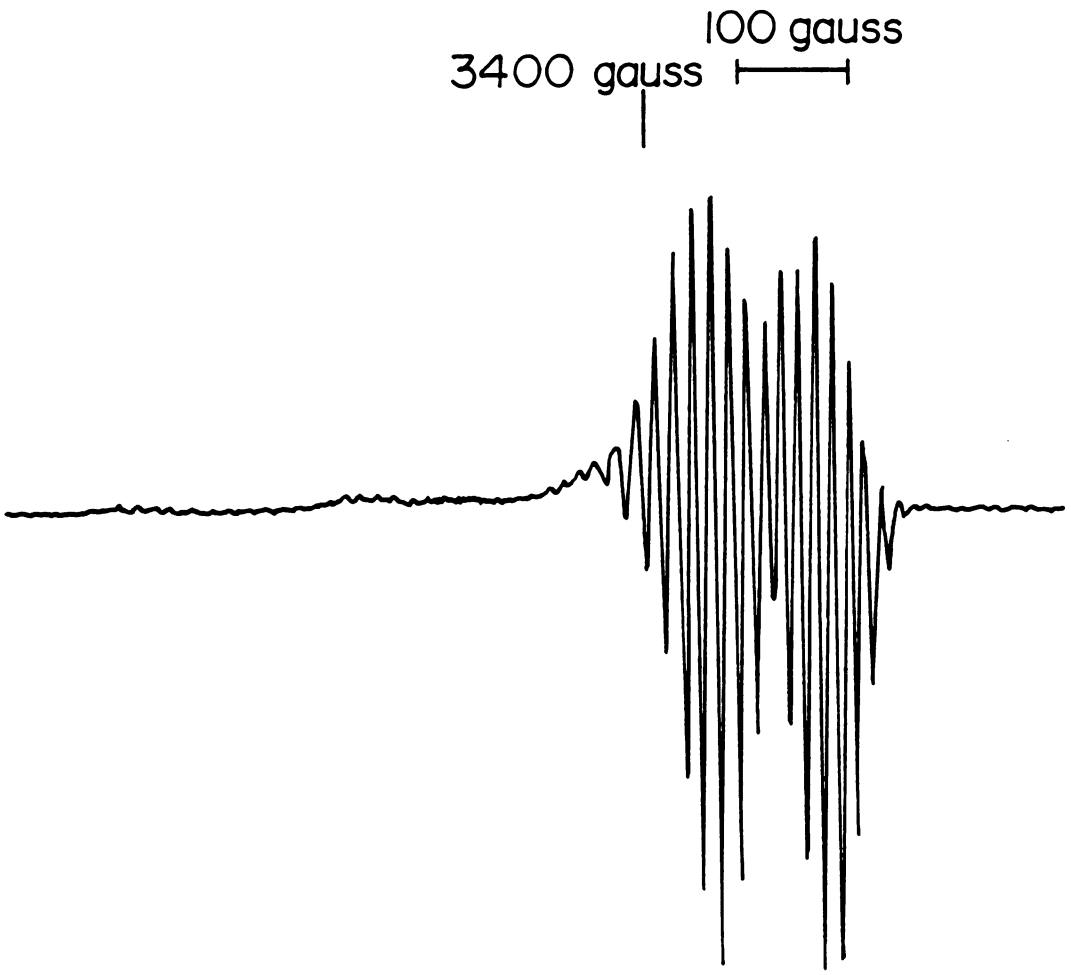

Figure 29. ESR spectrum of Cu 1.

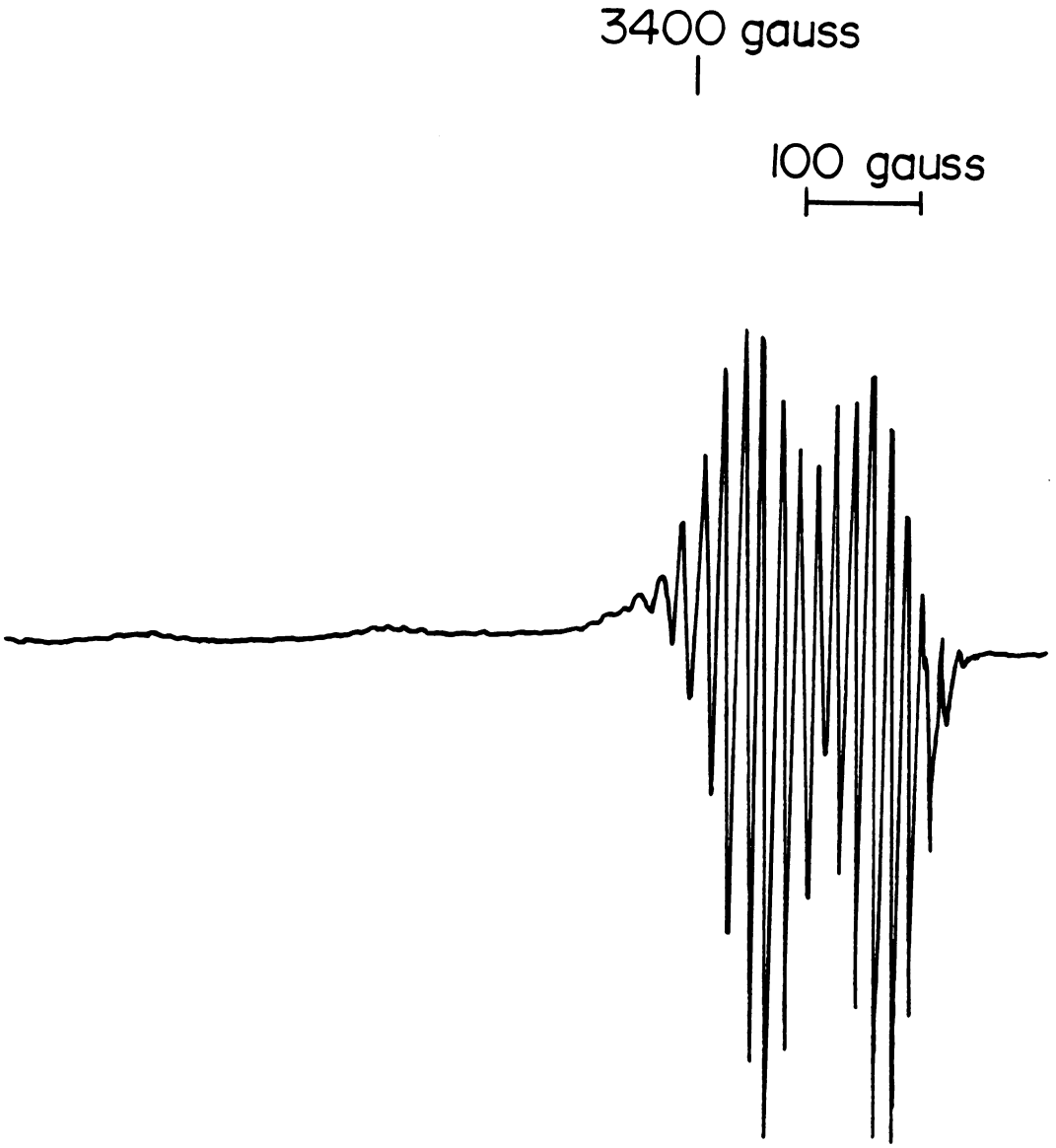

Figure 30. ESR spectrum of Cu 2.

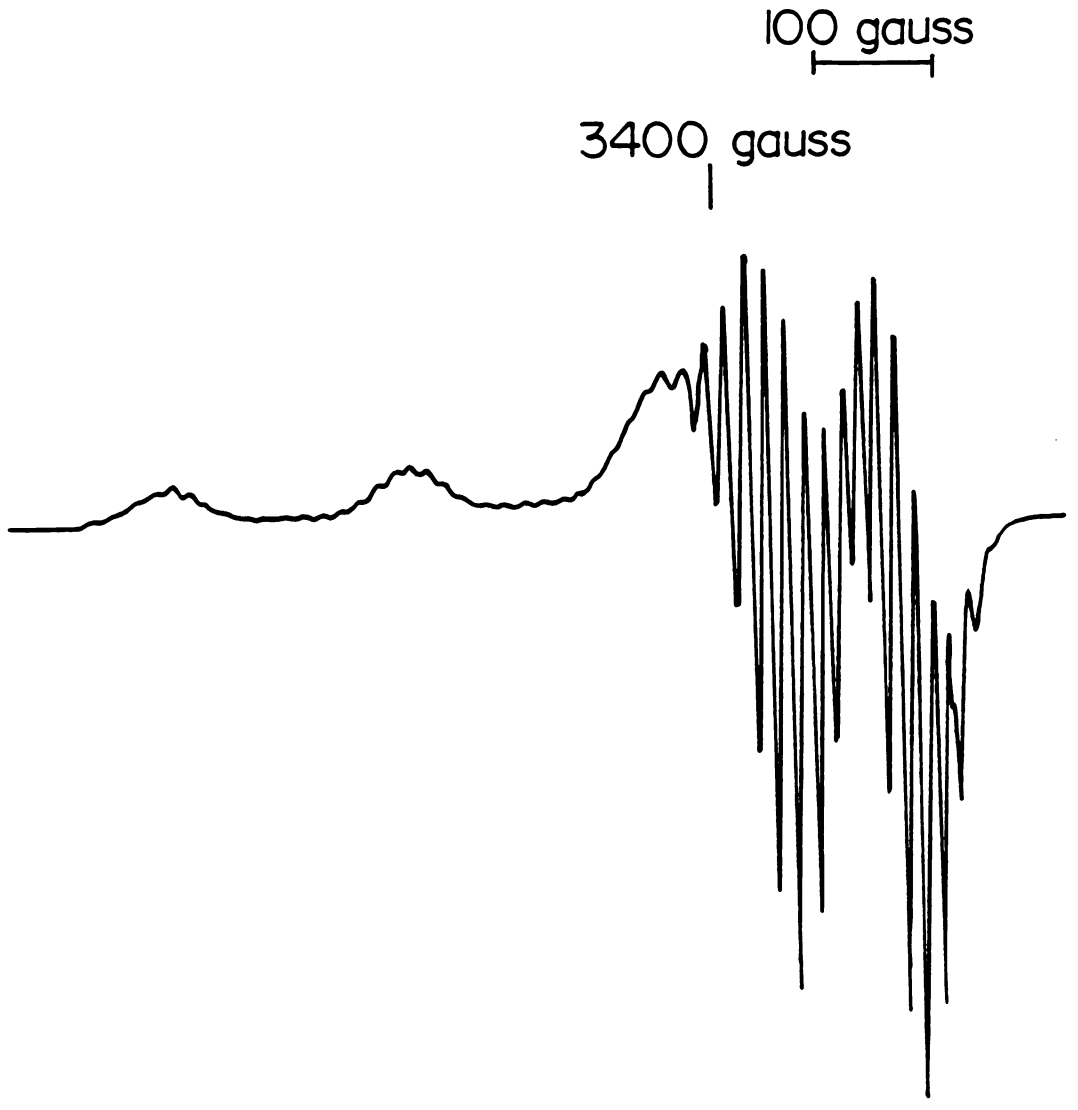

Figure 31. ESR spectrum of Cu 3.

With Cu 4, the nitrogen perpendicular superhyperfine lines are no longer resolved and the "extra" lines are only barely observable in Figure 32. The ESR parameters can still be determined for $g_{||}$, $g_{\perp}$, $Cu_{||}$, $Cu_{\perp}$, and <N>. The nitrogen superhyperfine structure in the region of 3200 to 3500 gauss is of much poorer resolution.

This trend of poorer resolution of the nitrogen superhyperfine lines continues in the next sample, Cu 5. For this sample, the nitrogen superhyperfine lines are still observable but are of very poor resolution (Figure 33). In the next sample, Cu 6, the nitrogen superhyperfine lines are no longer observed in Figure 34. In the remaining samples, Cu 7 through Cu 11, the parallel components of the copper remain visible and there is only moderate changes in the region between 3200 and 3500 gauss. These spectra are in Appendix C.

This series of spectra indicate that the dipolar interactions between neighboring TTPCu molecules increases with the increase of the concentration of TTPCu in $TTPH_2$. These interactions are first noticable at a copper content of 0.79% Cu. At this concentration, the interactions are still of very little consequence but are noticable when its spectrum is compared to the ESR spectra of the first two samples, Cu 1 and Cu 2. With the next sample, Cu 4 has a copper content of 1.44% Cu and the resolution of the nitrogen superhyperfine lines in the region between 3200 and 3500 gauss are considerably affected by the dipolar interactions between the copper porphyrins present in the polycrystalline samples. This is even more true for Cu 5 in which the nitrogen superhyperfine lines are very poorly resolved in comparison to the spectra of Cu 1 and Cu 2. At a copper content of 2.89%, Cu 6 no longer

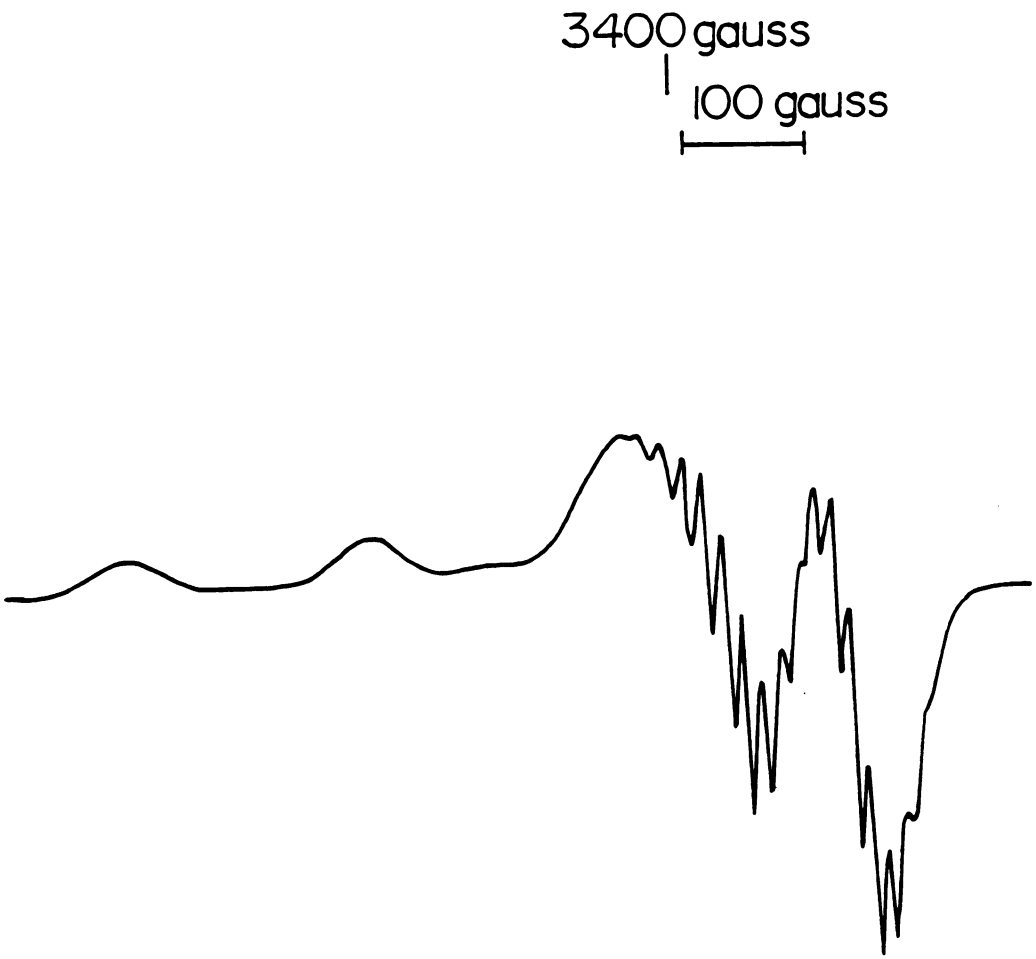

Figure 32. ESR spectrum of Cu 4.

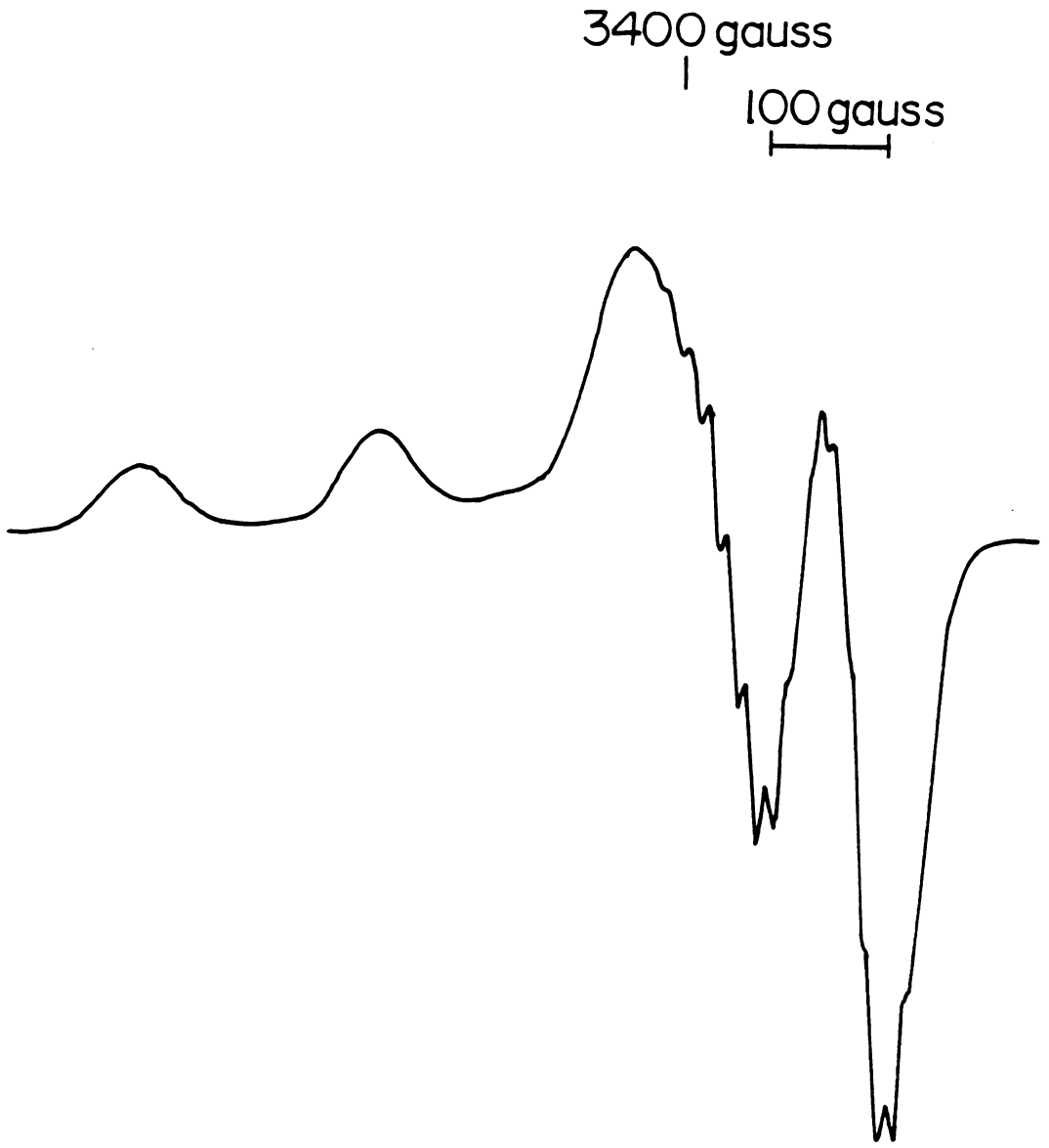

Figure 33. ESR spectrum of Cu 5.

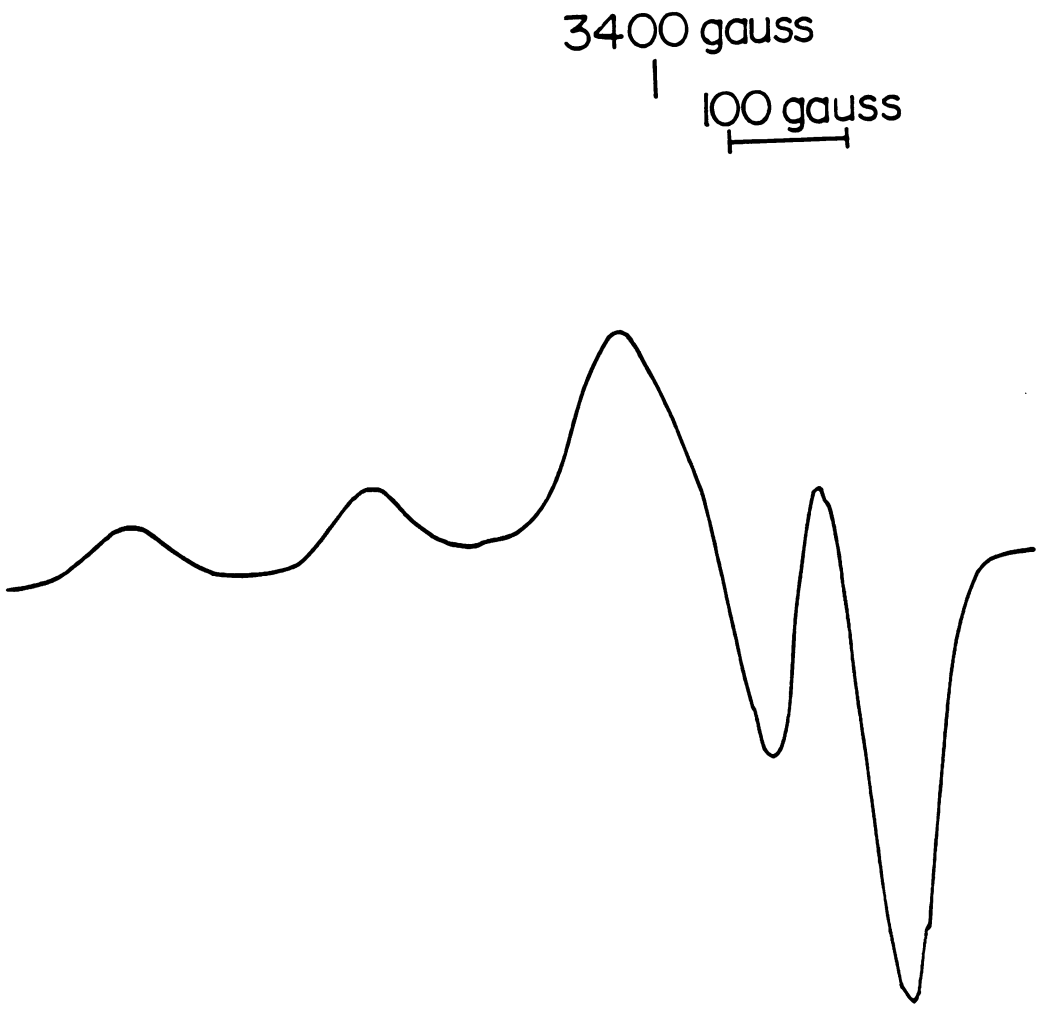

Figure 34. ESR spectrum of Cu 6.

exhibits any nitrogen superhyperfine splitting what so ever. From these results, it is apparent that dipolar interactions start to affect the ESR spectra of copper meso-tetraarylporphyrins at a copper content of around 0.8% and that these interactions can totally eliminate the nitrogen superhyperfine lines from the spectra at about a copper content of 2.9% Cu.

When the polymer-bound copper porphyrins are viewed in light of the results from the spectra for dilutions of TTPCu in $TTPH_2$, it becomes apparent that the polymer-bound copper porphyrins experience greater dipolar interactions than the copper content of these samples would seem to allow. For P_2-NH-CH_2-porCu, the relative resolution of its ESR spectrum is very similar to that of either Cu 4 or of Cu 5. This would mean that P_2-NH-CH_2-porCu (0.393% Cu) has an effective concentration on the polymer matrix of 1.4 to 2.00% copper. In the case of P_3-CH_2-O-porCu (1.363% Cu), its ESR spectrum is very similar to sample Cu 5 with a content of 2.00% copper. For P_2-NH-CO-porCu, this is true also but to an even greater extent. This sample has a copper content of only 0.153% yet its ESR spectrum is very similar to Cu 5's especially near 3200 to 3400 gauss. This result is due to the low I_c value for this polymer-bound porphyrin. Its actual concentration is not known but that of the analogous P_2-NH-CO-porCo was determined with SEM analysis to be 1.16% at the edge. This result may be low for SEM data in this concentration range is low when compared to data obtained from neutron activation analysis (see Table 2). These results suggest a larger effective concentration of porphyrin and metalloporphyrin on the polymer matrix.

This effect of apparently increased concentration of the polymer-bound porphyrins is the result of the polymer structure. Photographs of cross sections of 20% divinylbenzene-polystyrene copolymer beads were taken with an electron microscope.[37] In these photographs, the bead is made up of many small nodules which are fused together. In addition, the beads are porous with pore sizes of as much as 1200 Å. The most likely place for the bound porphyrin is on the surface of these nodules and not deep into the nodule because of size constraints. Therefore the porphyrin moieties are viewed as lining the surfaces of these nodules which make up the bead and thus increasing its effective concentration because of the nodules' and pores' respective dead spaces which are not available for porphyrin binding.

From the ESR data, it has been shown that the polymer-bound copper porphyrins have varying degrees of site-to-site isolation on the polymer matrix. The isolation of copper porphyrins by the polymer matrix was most effective in the samples which are of low loading and/or have even radial distributions of the metalloporphyrin across the copolymer beads. This was found to be true for P_1-CO-porCu, P_1-CH_2-porCu, P_1-CH_2-porCu(B), P_3-CH_2-NH-porCu, and P_3-CH_2-py-porCu. In the case of higher loadings but even radial distributions, intermediate isolation of the porphyrins was evident from the resolution of the ESR spectra of these complexes (P_2-NH-CH_2-porCu and P_3-CH_2-O-porCu). Lastly, the isolation of polymer-bound porphyrins and, in particular, the polymer-bound copper porphyrins is least for P_2-NH-CO-porH_2 and P_3-CH_2-O-porH_2(B) and their copper complexes. This was clearly seen from their ESR spectra.

D. Autoxidation of Cyclohexene

When assisted by metalloporphyrins and polymer-bound metalloporphyrins, the autoxidation of cyclohexene gave the expected products for the free radical autoxidation. In addition, the metalloporphyrins and polymer-bound metalloporphyrins experienced decomposition which resulted from free radicals attacking the porphyrin periphery. When the rates of dioxygen uptake are compared for the homogeneous, soluble metalloporphyrins with those of the polymer-bound metalloporphyrins, the homogeneous, soluble metalloporphyrins have larger rates. Only when ground samples of the polymer-bound metalloporphyrins are used, are the rates of dioxygen uptake comparable to those of the homogeneous, soluble metalloporphyrins. Therefore no advantage is found for using polymer-bound metalloporphyrins as initiators in the autoxidation of cyclohexene instead of the homogeneous analogs.

When the uptake of dioxygen for P_3-CH_2-O-porCo is compared with that of P_2-NH-CO-porCo, it is seen that its rate of dioxygen uptake is 3.5 times greater. This is surprising since TTPCo and TPP(CO_2hexyl)$_4$Co had rates of 2040 and 1900 mL of dioxygen min^{-1}mmole of Co^{-1}, respectively, when dissolved in cyclohexene. This would indicate that the electronegativity of the phenyl substituent should not affect the rate of dioxygen uptake as much as the difference for P_2-NH-CO-porCo and P_3-CH_2-O-porCo used in the assisted autoxidation of cyclohexene.

Since P_2-NH-CO-porCo has a very low value of I_c and P_2-NH-CO-porCu experienced considerable dipolar interactions between neighboring copper porphyrins, the proximity of the polymer-bound cobalt porphyrin moieties to each other is believed responsible for the low rate of

dioxygen uptake found for this polymer-bound cobalt porphyrin. If only diffusion of the substrate into the polymer matrix determined the rate of dioxygen uptake, then P_2-NH-CO-porCo should be more active than P_3-CH_2-O-porCo because of the respective locations of the cobalt porphyrins in the two samples. Since P_3-CH_2-O-porCo is more active than P_2-NH-CO-porCo, the proximity of the cobalt porphyrin residues must be involved in such a way as to retard the autoxidation of cyclohexene.

Two possibilities present themselves as reasons that the close proximity of the cobalt porphyrin moieties would retard the rate of autoxidation of cyclohexene. The formation of μ-peroxo cobalt porphyrin dimers is one possibility that should be considered, especially since LeDon has shown that the μ-oxo iron(III) porphyrin dimer exists in copolymers consisting of 20% divinylbenzene, 5% aminostyrene, and 75% styrene.[32] The other possibility is that the substrate, cyclohexene, may be excluded from the 5th and/or 6th coordination site of the polymer-bound cobalt porphyrin by steric factors, which may arise from the polymer matrix or a neighboring porphyrin residue.

Since oxidation of the μ-peroxo cobalt porphyrin dimer results in the ESR active μ-superoxodicobalt porphyrin dimer, attempts were made to oxidize any of the suspected μ-peroxodicobalt porphyrin dimer with a trace of I_2 and 1-methylimidazole in benzene. The ESR spectra of P_2-NH-CO-porCo before and after treatment with I_2 had very weak lines centered around $g = 2.0$. The linewidths are 15 gauss for the 12 to 14 line pattern. These lines have been found in other samples of the other polymer-bound cobalt porphyrins (Figure 35). Chang has reported an ESR

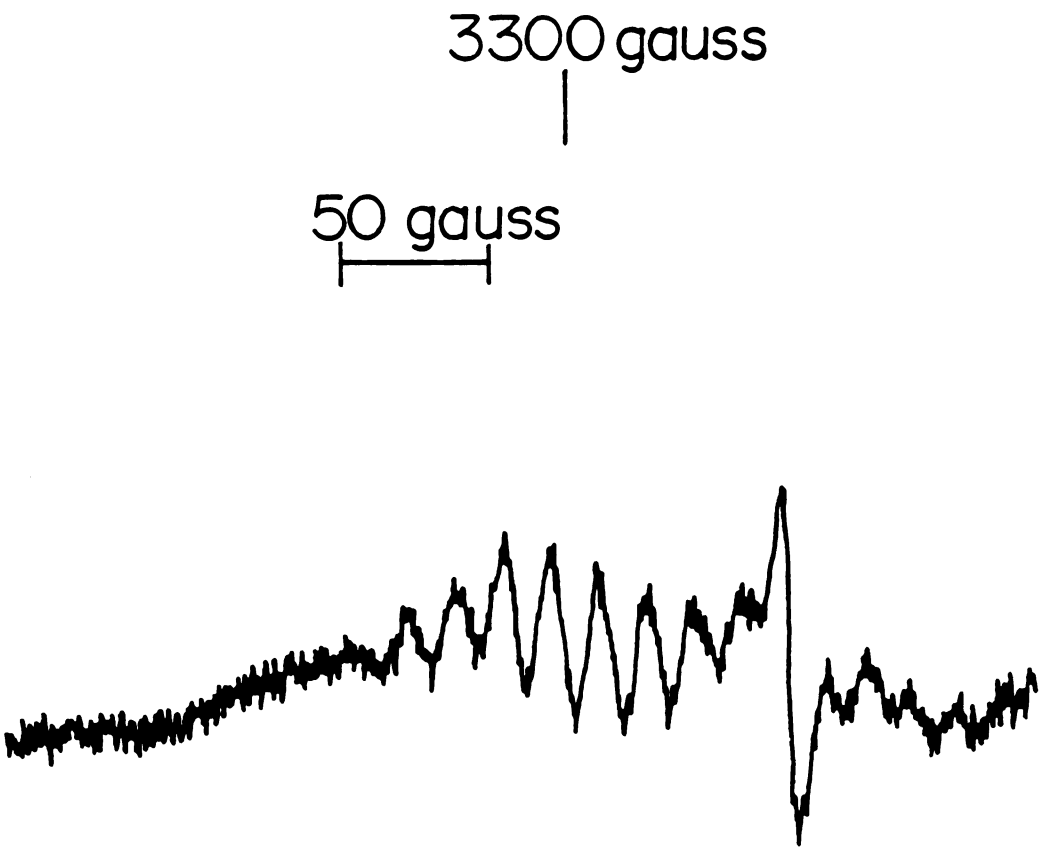

Figure 35. ESR spectrum of a suspected μ-superoxo dicobalt porphyrin dimer.

spectrum for the μ-superoxodicobalt complex of a cofacial diporphyrin.[78]. The spectrum had linewidths of 10 gauss and g = 2.024. In comparison to Chang's data, these lines may or may not be from a μ-superoxo cobalt porphyrin dimer. Therefore, it is unclear why the rates of autoxidation of cyclohexene varied so much for P_2-NH-CO-porCo and P_3-CH_2-O-porCo.

When the results of the autoxidation of cyclohexene are considered for the polymer-bound iron porphyrin, P_3-CH_2-O-porFeCl, and compared with those of TTPFeCl, the most striking difference between these iron complexes is that of the incubation period. At 60°C, TTPFeCl required little or no time before oxidation of cyclohexene started. But when P_3-CH_2-O-porFeCl was used, it required a lengthy incubation period of at least 3 hours before any observable uptake of dioxygen had occurred. The short incubation time for TTPFeCl is very similar to Fuhrhop's finding for OEPFeCl at 60°C.[74] Fuhrhop,[73,74] LeDon,[33] and Paulson[72] have observed that μ-oxo dimers of iron(III) porphyrins did not need incubation periods even at room temperature whereas a complex such as OEPFeCl did (approximately 1 hour).[73,74] These authors have unanimously cited iron(III) porphyrin μ-oxo dimers as being the active species in the initiation of the autoxidation of cyclohexene and other alkenes. For the polymer-bound iron(III) porphyrins, the long incubation time would suggest that the necessary formation of the μ-oxo dimer was retarded by the copolymer matrix of P_3. The once used beads had a shortened incubation period of only 20 minutes, which would suggest that they contained some of the μ-oxo dimer. Therefore the results with P_3-CH_2-O-porFeCl support Paulson, LeDon, and Fuhrhop in that the μ-oxo

dimer is indeed the active species in the autoxidation of cyclohexene. The lengthy incubation time for P_3-CH_2-O-porFeCl indicates that the iron porphyrins are relatively isolated from each other in this sample. Yet the isolation is imperfect for the formation of the μ-oxo dimer must have occurred for used beads have a shorter incubation period.

E. Autoxidation of Aldehydes.

From the results for the autoxidation of benzaldehyde and butanal, little improvement is observed for the dioxygen uptake rates for the cobalt porphyrin-assisted autoxidation of aldehydes relative to the unassisted autoxidation. In addition, $TPP(CO_2Et)_4Co$ is more active than its polymer-bound analog, P_1-CO-porCo(B). Furthermore, P_1-CO-porFeCl(B) retards the uptake of dioxygen. The selectivity of the polymer-bound metalloporphyrins offers no improvement over that of soluble cobalt porphyrins. Finally, the decomposition of the porphyrin ring for the complexes studied indicates that the effort to attach porphyrins to the polymer support is wasted. Therefore no benefit is gained in the attachment of metalloporphyrins to polymer supports and these polymer-bound metalloporphyrins being used in free radical autoxidation reactions.

IV. CONCLUSIONS

It has been shown that porphyrins may be covalently attached to divinylbenzene-polystyrene copolymers. The Friedel-Crafts acylation and alkylation of 2% and 20% divinylbenzene-polystyrene copolymer beads were studied. The use of aminated, 8% and 20% divinylbenzene-polystyrene copolymer beads in the formation of amide and amine linkages were investigated as another means of effecting attachment. Finally chloromethylated, 20% divinylbenzene-polystyrene copolymer beads were used in the formation of ether, amine, and pyridinium linkages to porphyrins.

In the case of $AlCl_3$-catalyzed Friedel-Crafts acylations and alkylations, two problems are found which may seriously limit the utility of these reactions. Aluminum contamination of the copolymer samples had occurred and efforts to pinpoint its location were not entirely successful. In the Friedel-Crafts acylation of ethylbenzene, aluminum had incorporated into the porphyrin ring in a small amount of the sample. Infra-red spectral analysis showed what might have been the $AlCl_3$ adduct of the 20% divinylbenzene-polystyrene copolymer. Therefore the aluminum is believed to be present as an aluminum porphyrin and as an adduct with the copolymer. In addition, the other problem is that of high nitrogen to metal ratios for these samples which suggests that the porphyrin moiety has experienced some form of decomposition during the $AlCl_3$-catalyzed reactions.

Aminated, 20% divinylbenzene-polystyrene copolymer beads were used as the solid support for the formation of amine- and amide-linked porphyrins. For $TPP(COCl)_4H_2$ coupling with P_2, it was found that the resulting polymer-bound porphyrin and its metallated complexes had a very high loading at and near the surface of the beads. ESR spectra of its copper complex indicated that the porphyrin units are relatively close to each other, and causes the poor resolution of the nitrogen superhyperfine lines. The decrease in resolution has been shown to arise from dipolar interactions.[70] The proximity of the cobalt porphyrin units has been suggested as a cause for the reduced rate of autoxidation of cyclohexene relative to that found for P_3-CH_2-O-porCo. In the case of P_2-NH-CH_2-porH_2, it has been determined that the resulting polymer-bound porphyrin and its metallated complexes are evenly distributed in the interior of the copolymer beads. This result indicated that diffusion of the porphyrin molecule is not restricted to as large an extent as might be suggested from the distribution found in P_2-NH-CO-porCo. The ESR spectra of P_2-NH-CH_2-porCu are much better resolved than those of P_2-NH-CO-porCu and is true even though it has a greater loading per gram of beads than does P_2-NH-CO-porCu. From the results of SEM analysis, this is not surprising for P_2-NH-CO-porCu contains most of its copper porphyrin residues at or near the surface of the beads which results in greater dipolar interactions. From the SEM analysis and ESR analysis, these results clearly show that the reactivity of the functional group of the porphyrin plays a role in determining the distribution of the metalloporphyrins along the radii of the beads.

For chloromethylated, 20% divinylbenzene-polystyrene copolymer beads, P_3, it was found that high and uniform loadings were possible. These samples gave some of the best resolved copper ESR spectra for their copper complexes. In comparison to the other methods of attachment of porphyrins to divinylbenzene-polystyrene copolymers, the use of P_3 as the solid support is preferred. The ease of the substitution reaction and the quality of the resulting polymer-bound porphyrins and their metallated complexes makes these beads, P_3, as the preferred choice as starting material for the polymer support for the covalent attachment of porphyrins.

The ESR spectra of the polymer-bound vanadyl and copper complexes show the presence of these complexes attached to divinylbenzene-polystyrene copolymers. These spectra clearly show the result of immobilization of the metalloporphyrin on the copolymer matrix because the spectra resemble spectra of polycrystalline TPPCu in $TPPH_2$ or TPPCu in $CHCl_3$ at 77°K.[67] When the ESR spectra of the polymer-bound copper complexes were compared with those of a series of TTPCu in $TTPH_2$ dilutions, it was shown that the polymer-bound copper porphyrins experienced greater dipolar interactions than might be expected from the concentration of copper in many of the samples. When these results were coupled with those of SEM analysis, it became apparent that the radial distribution and the average loading had an affect on the resolution of the nitrogen superhyperfine splitting.

Resonance raman spectroscopy showed that copper porphyrins were present in P_1-CH_2-porCu(B). Therefore this technique of analysis could be very useful as a companion to ESR spectroscopy in the analysis of

metalloporphyrins bound to polymers. It would be especially useful for the analysis of those polymer-bound metalloporphyrins which do not have ESR signals.

It was found that the polymer-bound cobalt porphyrins are not as effective as the analogous soluble cobalt porphyrins are as catalysts for the autoxidation of cyclohexene or of aldehydes. In these autoxidations, the cobalt porphyrins were susceptible to decomposition. In the case of P_3-CH_2-O-porFeCl, it required an extended incubation period before the uptake of dioxygen began in the autoxidation of cyclohexene. This result supports the findings of Paulson,[72] LeDon,[33] and Fuhrhop[73,74] that the μ-oxo dimer must be present before the autoxidation of cyclohexene can be initiated. The polymer-bound iron complex also underwent decomposition during the autoxidation of cyclohexene as did TTPFeCl. Therefore, since reactivity is lower for the polymer-bound metalloporphyrins and they do undergo decomposition during these free radical chain reactions, their use as catalysts for autoxidation reactions would not seem advisable.

V. EXPERIMENTAL

A. Materials.

Macrorecticular, divinylbenzene-polystyrene copolymer beads were gifts from the Dow Chemical Company. The divinylbenzene content of those beads which were used are 2%, 8%, and 20% divinylbenzene. Chloromethylated, 20% divinylbenzene-polystyrene copolymer beads were purchased from Strem Chemical Company. The aldehydes which were used to synthesize the meso-tetraarylporphyrins were obtained from Aldrich and were used as received. The bulk of reagents and solvents which were used were reagent grade and were used as is. The exceptions are that tetrahydrofuran and cyclohexene were distilled from over sodium.

B. Preparation of Divinylbenzene-Polystyrene Copolymer Beads.

Prior to their use, divinylbenzene-polystyrene copolymer beads were sieved through screens. Beads (28-32 mesh) were used for all further work. These were then washed with the following solvents: 10% aqueous hydrochloric acid (V:V), 10% aqueous sodium hydroxide (W:W), water, 1:1, water/methanol (V:V), methanol, 1:1, methanol/dichloromethane (V:V), and dichloromethane. The beads were dried overnight in a vaccuum at 0.1 mm of Hg and 50^{o}C.

C. Preparation of Aminated, Divinylbenzene-Polystyrene Copolymer Beads.

The procedure of King and Sweet[20] was used in the nitration of divinylbenzene-polystyrene copolymer beads. Below the nitration and reduction with stannous chloride is described for 20% divinylbenzene-polystyrene copolymer beads.

1. Preparation of Aminated, 20% Divinylbenzene-Polystyrene Copolymer Beads.

Acetic anhydride (39 mL) was added to 10 g of beads in a 100 mL round bottom flask. This mixture was cooled to 5°C by immersion in an ice water bath before the addition of a solution of 3.1 mL of 70% nitric acid in 8.5 mL of acetic acid. This mixture was allowed to warm to room temperature after 30 min. of stirring at 5°C. The reaction was stopped after a total of 5 h. The solvents were then removed by suction. The resulting beads were then washed 5 times for 15 min. each with 20 mL of acetic acid. The still wet beads were stirred at 40°C for 3 days with 40 mL of acetic acid and a solution of 11.0 g of stannous chloride dihydrate in 12 mL of concentrated hydrochloric acid. The solution was again removed by suction and the beads were then washed as follows: 5 times with a 3:10 mixture of concentrated hydrochloric acid and acetic acid, 3 times with 3:5:5 hydrochloric acid/tetrahydrofuran/methanol, and 2 times with methanol. These beads were dried at 25°C and 0.1 mm of Hg overnight.

A 2.0 g batch of these beads was then washed twice for 20 min each with a 10% KOH in methanol solution and then five times with methanol and twice with dichloromethane. The beads were dried at 60°C (0.1 mm

Hg) for 4 h. Nitrogen content of the beads was 3.83%.

Before reduction nitro absorptions were observed at 1520 cm^{-1} and 1346 cm^{-1} in the nujol mull of ground and nitrated, 20% divinylbenzene-polystyrene copolymer beads. After reduction, these peaks were reduced in intensity with only the one at 1346 cm^{-1} being easily observed. In addition, the ammonium chloride salt absorptions were observed at 2600 cm^{-1} and 2000 cm^{-1}.

2. Preparation of Aminated, 8% Divinylbenzene-Polystyrene Copolymer Beads.

In the case of 8% divinylbenzene-polystyrene copolymer beads, nitration and reduction of the nitro groups as above resulted in a copolymer which was susceptible to pulverization. Therefore these beads were not studied any further.

D. Preparation of Porphyrins and Metalloporphyrins.

The porphyrins were synthesized from pyrrole and appropriately substituted benzaldehydes in refluxing propionic acid. The procedures of Adler[48,49] and of Little[50] were used to prepare the desired porphyrins. The metalloporphyrins were primarily prepared in a refluxing DMF solution of the porphyrin and the desired metal salt.[51]

1. 5,10,15,20-Tetrakis(4-methylphenyl)porphyrin, $TTPH_2$.

Para-tolylaldehyde (12.0 g) and pyrrole (6.7 g) were added to hot propionic acid (500 mL) and the resulting solution was refluxed for 0.5 h. The solution was allowed to cool and sit overnight before the crystals were collected by filtration. The crystals were then washed with methanol until the washings were colorless. The crude porphyrin was purified by chromatography (alumina/dichloromethane) and

recrystallized by the addition of methanol to a concentrated solution of the porphyrin. The yields were typically 3.5 to 4.6 g (20-27% yields); NMR ($CDCl_3$), δ, -2.79(s, 2H, NH), 2.69(s, 12H, $-CH_3$), 7.53(d, 8H, tolyl-3,5-protons), 8.08(d, 8H, tolyl-2,6-protons), 8.84(s, β-pyrrole H); λ_{max} (dichloromethane) 420, 486 sh, 518, 554, 594, 650 nm. Analysis performed on TTPCu. Calculated for $C_{48}H_{36}N_4Cu$: C, 78.52; H, 4.91; N, 7.63; Cu, 8.94. Found C, 77.93; H, 4.93; N, 7.21; Cu, 9.93.

2. 5,10,15,20-Tetrakis(4-methylphenyl)porphyrinatocopper-(II), TTPCu.

$TTPH_2$ (0.30 g) and $Cu(OAc)_2 \cdot H_2O$ (0.30 g) were mixed together in 30 mL of DMF and then the mixture was refluxed for 30 min. Water (20 mL) was added to the reaction solution after it had cooled down to about 100°C. The copper porphyrin was collected by filtration next day and washed with water. After air drying, TTPCu was chromatographed (alumina/dichloromethane) and recrystallized from dichloromethane and methanol. Analysis. Calculated for $C_{48}H_{36}N_4Cu$: C, 78.52; H, 4.91; N, 7.63; Cu, 8.94. Found C, 77.93; H, 4.93; N, 7.21; Cu, 9.93. λ_{max} (dichloromethane) 417, 541, 575 sh nm.

3. 5,10,15,20-Tetrakis(4-methylphenyl)porphyrinatocobalt-(II), TTPCo.

$TTPH_2$ (0.50 g) and $CoCl_2 \cdot 6H_2O$ (0.50 g) were mixed together in 50 mL of DMF. The resulting mixture was refluxed for 30 min and then allowed to cool to approximately 100°C before 30 mL of water was added. The cobalt complex was collected by filtration and washed with water. After air drying, the cobalt porphyrin was chromatographed (alumina/dichloromethane) and recrystallized from dichloromethane and methanol.

Analysis. Calculated for $C_{48}H_{36}N_4Co$: C, 79.22; H, 4.99; N, 7.70; Co, 8.09. Found C, 80.86; H, 5.34; N, 7.38; Co, 8.41. λ_{max} (dichloromethane) 410, 528, 590 sh nm.

4. Chloro-5,10,15,20-Tetrakis(4-methylphenyl)porphyrinatoiron(III), TTPFeCl.

$TTPH_2$ (0.10 g) and $FeCl_2$ (0.10 g) were mixed together in 25 mL of DMF and the mixture was then refluxed for 20 min. Water (25 mL) was added to the solution after it had cooled to about 100°C. The iron porphyrin was collected by filtration and washed with water. TTPFeCl was recrystallized from dichloromethane. Analysis. Calculated for $C_{48}H_{36}N_4FeCl$: C, 75.84; H, 4.77; N, 7.37; Fe, 7.35; Cl, 4.66. Found C, 77.19; H, 5.03; N, 7.42; Fe, 6.23; Cl, 4.13.

5. Hydroxo-5,10,15,20-Tetrakis(4-methylphenyl)porphyrinatoaluminum(III), TTPAlOH.

a. $TTPH_2$ (0.30 g) was suspended in 200 mL of carbon disulfide at room temperature.[86] $AlCl_3$ (3.5 g) was added in small portions over a 5 min period and the resulting mixture was stirred for another 25 min. The carbon disulfide was then removed at reduced pressure. The residue was dissolved into dichloromethane and chromatographed (alumina/dichloromethane). The first band eluted was $TTPH_2$ and the second band contained TTPAlOH which required 2% methanol in dichloromethane to elute the aluminum porphyrin. Yield 11 mg or 16.0%. λ_{max} 417, 508, 549, 589 nm. TTPAlOH has a resonance raman, metal-sensitive absorption at 1549 cm^{-1} when it is excited with a laser of 413.1 nm.

b. $TTPH_2$ (150 mg) and $AlCl_3$ (150 mg) were mixed together in 20 mL of nitromethane and the mixture was stirred at 50°C for 24 h.

for 24 h. The mixture was poured into 50 mL of water and the porphyrin was extracted into dichloromethane. The green solution was neutralized with 0.1 N aqueous KOH. The porphyrin was chromatographed (alumina/dichloromethane) and only one band was found. This band contained only $TTPH_2$. No TTPAlOH was found.

6. 5,10,15,20-Tetrakis(4-carbohexylphenyl)porphyrin, $TPP-(CO_2hexyl)_4H_2$.

4-Carboxybenzaldehyde (5 g) was added to 335 mL of propionic acid and then pyrrole (2.23 g) was added to the hot solution. After refluxing for 0.5 h, the reaction solution was allowed to cool and sit overnight. The crude porphyrin was collected by filtration and washed with hot water. The crude porphyrin was then dissolved in aqueous NaOH and precipitated by the addition of acetic acid (pH 3). The porphyrin was again collected by filtration and washed with water. Thus treated, the porphyrin was dried at 120°C overnight (35% yield).

Conversion to the tetrahexyl ester was performed to increase the solubility and to facilitate the purification of the porphyrin. This was accomplished when 4.0 g of the crude porphyrin tetra acid was treated with 100 mL of a 10% H_2SO_4 in hexanol solution (V/V). The solution was refluxed for 24 h and then diluted with 300 mL of H_2O and extracted with dichloromethane. The dichloromethane fraction was washed with saturated sodium bicarbonate solution and then concentrated on a rotary evaporator. An equal volume of methanol was then added to the solution to crystallize the porphyrin tetrahexyl ester. The porphyrin tetrahexyl ester was chromatographed (alumina/dichloromethane) and recrystallized from dichloromethane and methanol. Yield from pyrrole was 17%; NMR ($CDCl_3$), δ , -2.79(2, 2H, NH),

0.96(t, $-CH_3$), 1.42(m, 2H, $-CH_2-$), 1.58(m, 2H, $-CH_2-CH_3$), 1.92(m, 2H, $-O-CH_2-CH_2-$), 4.51(t, 2H, $O-CH_2-$), 8.29(d, 8H, tolyl-3,5-protons), 8.45(d 8H, tolyl-2,6-protons), 8.83(s, β-pyrrole H); λ_{max}(dichloromethane) 420, 488 sh, 518, 552, 592, 647 nm. Analysis performed on cobalt complex. Calculated for $C_{72}H_{72}N_4O_8Co$: C, 72.65; H, 6.42; N, 4.73; O, 10.82; Co, 4.98. Found: C, 72.93; H, 6.46; N, 4.61; O, 10.76; Co, 5.24.

7. 5,10,15,20-Tetrakis(4-carboethylphenyl)porphyrinatocobalt(II), $TPP(CO_2Et)_4Co$.

5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin (200 mg) was treated with a solution of 1 mL of H_2SO_4 in 50 mL of ethanol. The resulting solution was then refluxed for 36 h. The solution was neutrallized with aqueous sodium bicarbonate and the porphyrin tetraester extracted with dichloromethane. The dichloromethane was removed at reduced pressure and the porphyrin was then treated with 0.2 g of $CoCl_2$ $6H_2O$ and 10 mL of DMF. The solution was then refluxed for 3 h and after cooling 15 mL of water was added. The precipitated cobalt complex was collected by filtration and air dried. The crude cobalt porphyrin was then chromatographed (alumina/dichloromethane) and recrystallized from dichloromethane and methanol. λ_{max} (dichloromethane) 414, 532 nm.

8. 5,10,15,20-Tetrakis(4-carbohexylphenyl)porphyrinatocobalt(II), $TPP(CO_2hexyl)_4Co$.

$TPP(CO_2hexyl)_4H_2$ (1.0 g) and $CoCl_2 \cdot 6H_2O$ (1.0 g) were mixed together in 100 mL of DMF and heated to reflux. After 45 min, the reaction solution was allowed to cool to approximately 100°C before 75

mL of H_2O was added to the solution. The cobalt porphyrin was collected by filtration and air dried before it was chromatographed twice (once alumina/dichloromethane and then silica gel/dichloromethane) and then recrystallized from dichloromethane and methanol. Analysis. Calculated for $C_{72}H_{72}N_4O_8Co$: C, 72.65; H, 6.42; N, 4.73; O, 10.82; Co, 4.98. Found: C, 72.93; H, 6.46; N, 4.61; O, 10.76; Co, 5.24. λ_{max} (dichloromethane) 414, 532 nm.

9. 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin, $TPP(CO_2H)_4H_2$.

$TPP(CO_2hexyl)_4H_2$ (0.4 g) and KOH (0.8 g) were mixed together in 100 mL of THF and 20 mL of water. The resulting solution was refluxed for 24 h. The THF was removed at reduced pressure and then 3 mL of acetic acid was added to the aqueous solution. The precipitated porphyrin was collected by filtration and washed extensively with water. After initial drying in air, the porphyrin was dried for 5 h in an oven at 140°C. λ_{max} (ethanol) 415, 478 sh, 513, 547, 590, 646 nm.

10. 5-(4-Hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(OH)H_2$.

Para-hydroxybenzaldehyde (4.6 g) and para-tolylaldehyde (13.5 g) were added to 500 mL of hot propionic acid. Pyrrole (10.1 g) was then added and the reaction mixture was refluxed for 1 h. After cooling and standing overnight, the crude porphyrins were collected by filtration and washed with methanol until the filtrate was colorless. The porphyrins were separated by chromatography. The first time alumina/dichloromethane were used. The first band contained $TTPH_2$ and the second band contained $T_3P(OH)H_2$. The second band was rechromatographed on

silica gel with dichloromethane as elutent. Yield of $TTPH_2$ was 1.69 g or 6.7% and the yield of $T_3P(OH)H_2$ was 1.65 g or 6.5%. NMR($CDCl_3$), δ , -2.75(s, 2H, NH), 2.68(s, 9H, $-CH_3$), 7.18 (m, 2H), 7.55(d, 6H, tolyl-3,5-protons), 8.05 (m, 2H), 8.09(d, 6H, tolyl-2,6-protons), 8.85 (s, 8H, β-pyrrole H); λ_{max} (dichloromethane) 421, 486sh, 519, 554, 594, 650 nm.

11. 5-(2-(5-Bromopentoxy)phenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(OC_5Br)H_2$.

2-Hydroxybenzaldehyde (4.6 g) was used in place of 4-hydroxybenzaldehyde. All other details were the same as in the preparation of $T_3P(OH)H_2$. Yield of $TTPH_2$ was 1.92 g or 7.6% and that of the monohydroxyporphyrin was 0.55 g or 2.2%. λ_{max} (dichloromethane) 420, 485 sh, 516, 552, 591, 650 nm.

The porphyrin (0.55 g) was then treated with 4.6 g of 1,5-dibromopentane and 3.0 g of K_2CO_3 in 100 mL of DMF. The resulting mixture was stirred for 2 days at room temperature in a nitrogen atmosphere. The reaction mixture was then poured into 500 mL of water and extracted into dichloromethane. The solution was concentrated and then chromatographed (alumina/dichloromethane). The porphyrin was recrystallized from dichloromethane and methanol. The yield of the porphyrin was 0.65 g (92% yield). NMR($CDCl_3$), δ , -2.82(s, 2H, NH), 0.88(m, 6H, $-CH_2-CH_2-CH_2-$), 2.20(t, 2H, CH_2-Br), 2.63(s, 9H, $-CH_3$), 3.80(t, $-O-CH_2-$), 7.47(d, 6H, tolyl-3,5-protons), 8.02(d, 6H, tolyl-2,6-protons), 7.23(m, 4H, 3,4,5,6-protons), 8.71(s, 8H, β-pyrrole); λ_{max} (dichloromethane) 420, 485 sh, 518, 552, 594, and 651 nm.

12. 5-(4-Pyridyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(py)H_2$.

4-Pyridinecarboxyaldehyde (4.3 g) and para-tolylaldehyde (13.9 g) were mixed together in 500 mL of propionic acid. Pyrrole (10.7 g) was then added to the hot solution and the reaction mixture was refluxed for 1 h. The reaction mixture was then allowed to stand overnight before collecting the crude porphyrins by filtration. They were washed with methanol until the washings were colorless. The porphyrins were chromatographed on alumina with dichloromethane as the solvent. The first band contained $TTPH_2$ and the second band contained the desired porphyrin. The second band was then chromatographed on silica gel with dichloromethane as solvent. The yield of $TTPH_2$ was 2.75 g or 10.2% and that of $T_3P(py)H_2$ was 1.05 g or 4.0%. Analysis. Calculated for $C_{46}H_{33}N_5Cu$: C, 76.60; H, 4.58; N, 9.71; Cu, 9.10. Found: C, 75.75; H, 4.87; N, 9.62; Cu, 10.76. NMR($CDCl_3$), δ, -2.80(s, 2H, NH), 2.69(s, 9H, $-CH_3$), 7.54(d, 6H, tolyl-3,5-protons), 8.08(d, 6H, tolyl-2,6-protons), 8.77(d, 2H, pyridyl-3,5-protons), 9.01(d, 2H, pyridyl-2,6-protons), 8.71(s, 8H, β-pyrrole). λ_{max} (dichloromethane) 419, 486 sh, 518, 553, 592, 648 nm.

13. 5-(4-Pyridyl)-10,15,20-tris(4-methylphenyl)porphyrinatocopper(II), $T_3P(py)Cu$.

$T_3P(py)H_2$ (60 mg) was treated with 60 mg of $Cu(OAc)_2 \cdot H_2O$ in 20 mL of DMF at reflux for 30 min. Water (20 mL) was added after the solution had cooled for 10 min. The precipitated copper porphyrin was collected by filtration and allowed to air dry. $T_3P(py)Cu$ was then chromatographed (alumina/dichloromethane) and recrystallized from

dichloromethane and methanol. λ_{max} (dichloromethane) 416, 541, 574 sh nm. Analysis. Calculated for $C_{46}H_{33}N_5Cu$: C, 76.60; H, 4.58; N, 9.71; Cu, 9.10. Found: C, 75.75; H, 4.87; N, 9.62; Cu, 10.76.

14. 5-(4-Acetamidophenyl)-10,15,20-tris(4-methylphenyl)porphyrin, $T_3P(NHAc)H_2$.

Para-acetamidobenzaldehyde (8.2 g) and para-tolylaldehyde (18.2 g) were mixed together in 500 mL of hot propionic acid. Pyrrole (13.4 g) was then added to the hot solution and the solution was refluxed for 0.5 h. The reaction mixture was then refrigerated overnight and next morning the crude porphyrins were collected by filtration and washed extensively with methanol. The porphyrins were chromatographed on silica gel with dichloromethane as solvent. The first band contained $TTPH_2$. The second band was eluted from the column with 1% methanol in dichloromethane. The second band was rechromatographed as before and then recrystallized from dichloromethane and methanol. The yield of $TTPH_2$ was 1.1 g and 4.3%. The yield of $T_3P(NHAc)H_2$ was 0.80 g and 2.2%. NMR($CDCl_3$), δ, -2.80(s, 2H, NH), 2.31(s, 3H, CO-CH_3), 2.68(s, 9H, -CH_3), 7.53(d, 6H, tolyl-3,5-protons), 8.09(d, 6H, tolyl-2,6-protons), 7.3, 7.8(m, 4H, phenylacetamide), 8.82(s, 8H, β-pyrrole). λ_{max} (dichloromethane) 420, 487 sh, 519, 555, 594, 649 nm.

15. 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinatocopper-(II), $TPP(CO_2H)_4Cu$.

$TTP(CO_2H)_4H_2$ (0.30 g) and $Cu(OAc)_2 \cdot H_2O$ (0.30 g) were mixed together in 30 mL of DMF and the mixture was refluxed for 3 h. After the solution cooled to about 100°C, waster (20 mL) was added to precipitate

the copper porphyrin. Next day, it was collected by filtration and air dried. λ_{max} (aq. KOH) 413, 545, 580 sh nm.

16. 5,10,15,20-Tetrakis(4-hydroxymethylphenyl)porphyrin, $TPP(CH_2OH)_4H_2$.

To a suspension of 0.56 g of lithium aluminum hydride in 50 mL of THF was added dropwise (30 min) a solution of 0.50 g of $TPP(CO_2$-hexyl$)_4H_2$ in 150 mL of THF.[52] After addition was completed, the mixture was refluxed for 1 h before adding an additional 100 mL of THF to the mixture. The reaction was continued at reflux for 0.5 h more before the reaction was allowed to cool to room temperature. Wet THF was then slowly added to the reaction mixture. After the complete decomposition of the excess LAH, the solution was then filtered through Whatman No. 1 filter paper. The THF was removed at reduced pressure on a rotary evaporator. The crude porphyrin crystallized from the remaining water and after collection by filtration, the crude porphyrin was washed with acetone. The porphyrin was recrystallized from pyridine and acetone. Yield of the porphyrin was 300 mg or 92.0% yield. Analysis. Calculated for $C_{48}H_{36}N_4O_4Cu$: C, 72.39; H, 4.56; N, 7.04; O, 8.04; Cu, 7.98. Found: C, 72.05; H, 4.88; N, 7.03; O, 7.94; Cu, 8.10. I.R. spectrum had no absorption at 1680 cm^{-1} for ester.

17. 5,10,15,20-Tetrakis(4-hydroxymethylphenyl)porphyrinato-copper(II), $TPP(CH_2OH)_4Cu$.

$Cu(OAc)_2 \cdot H_2O$ (0.5 g) was added to a solution of 100 mg of $TPP(CH_2OH)_4H_2$ in 50 mL of pyridine and 100 mL of THF. The solution was then refluxed for 2 h before the THF was removed at reduced pressure.

Water (50 mL) was added to the pyridine solution. The copper porphyrin crystallized overnight and was collected by filtration. The copper porphyrin was recrystallized from pyridine and acetone and was collected by filtration and washed with acetone. The sample was first air dried and then dried overnight at 25°C and 0.1 mm of Hg. Yield was quantitative. Analysis. Calculated for $C_{48}H_{36}N_4O_4Cu$: C, 72.39; H, 4.56; N, 7.04; O, 8.04; Cu, 7.98. Found: C, 72.05; H, 4.88; N, 7.03; O, 7.94; Cu, 8.10. λ_{max} (THF) 418, 541, 578 sh nm.

18. Attempted Synthesis of 5,10,15,20-Tetrakis(4-chloromethylphenyl)porphyrin, $TPP(CH_2Cl)_4H_2$.

a. To 100 mg of $TTP(CH_2OH)_4H_2$ in 20 mL of THF:pyridine (1:1) at 0°C was added dropwise thionyl chloride (0.5 mL). After the thionyl chloride was added, the ice bath was removed. After 3 h at ambient temperatures, the reaction was stopped with the removal of excess thionyl chloride and solvents at reduced pressures. The product was then chromatographed (alumina/dichloromethane). Most of the porphyrin remained at the top of the column. NMR of the product indicated that the product was partially chlorinated. NMR($CDCl_3$), δ, -2.81(s, NH), 4.94(s, X-CH_2-Ph), 7.54 and 8.08(d, phenyl protons), 7.76 and 8.19(d, phenyl protons), 8.88(s, β-pyrrole).

b. $TTP(CH_2OH)_4H_2$ (60 mg) was treated with 10 mL of thionyl chloride at ambient temperatures for 12 h. The excess thionyl chloride was removed as before. The product was chromatographed as before and the bulk of the porphyrin remained at the top of the column. NMR again showed a mixture.

c. $TPP(CH_2OH)_4H_2$ (150 mg) was was treated with 10 mL of thionyl chloride at reflux for 24 h. The resulting product was chromatographed as before but most of the porphyrin was eluted. NMR of the product showed that β-pyrrole substitution must have occurred for in place of the usual singlet were two broad multiplets at 8.6 and 8.9.

d. $TPP(CH_2OH)_4H_2$ (40 mg) and triphenylphosphine (150 mg) were mixed together in 10 mL of carbon tetrachloride[53] and 10 mL of THF. The resulting mixture was refluxed for 12 h. The solvents were removed and the porphyrins were chromatographed as before with the bulk remaining at the top of the column. NMR again showed partial chlorination.

19. Friedel-Crafts Acylation of Ethylbenzene with $TPP(COCl)_4H_2$.

Ethylbenzene (1.00 g) and nitromethane (10 mL) were added to $TTP(COCl)_4H_2$ which had been prepared from 150 mg of $TPP(CO_2H)_4H_2$ and thionyl chloride. Then $AlCl_3$ (150 mg) was added to the solution and the reaction was stirred at 50°C for 24 h. The reaction mixture was poured into 50 mL of cold water and 100 mL of ethanol and stirred for 1 h. The crude porphyrin was collected by filtration and allowed to air dry. Workups are as follows:

a. The crude porphyrins were heated at 120°C for 14 h in 25 mL of 1-octanol to which 2 mL of concentrated sulfuric acid had been added. The solution was allowed to cool before a solution of methanolic sodium hydroxide was added. The resulting solution was poured into 50 mL of water and then the octanol layer was separated from the aqueous layer. The octanol layer was placed on top of a column of silica gel.

The column was eluted with pentane to remove some of the octanol. Next THF was used and then toluene. THF eluted the first and major band. Toluene eluted a wide band. The uv-visible spectra of these bands are identical with maxima at 419, 519, 553, 594, and 648 nm. NMR($CDCl_3$), δ, -2.80(s, NH), 0.89(t, $-CH_3$), 1.33($-CH_3$), 1.33-1.63(m, $-CH_2-$), 1.89(q, -Ph-CH_2-), 4.49(t, -O-CH_2-), 8.17(m, Ph), 8.30(d, tolyl-3,5-protons), 8.45(d, tolyl-2,6-protons), 8.82(s, β-pyrrole-H). Integration of signal at 1.89 and 4.49 were of equal intensity.

b. The crude porphyrins were washed with methanol and then dichloromethane. Both solvents dissolved some material. The uv-visible spectrum of the dichloromethane solution had maxima at 421, 518, 551, 593, and 648 nm. For the methanol solution added to isopropanol, maxima were at 417, 514, 554, 590, and 650 nm. The remaining solid was dissolved into aqueous KOH and its maxima are at 416, 529, 568, 595 sh and 655 nm. The methanol and dichloromethane solutions were combined and the solvents were removed. 5 mL of 30% H_2O_2 and 20 mL of acetic acid were added to the porphyrins. The mixture was refluxed for 5 h and porphyrins were decomposed over this time interval.

The resulting solution was then tested for aluminum ions. An aqueous solution of ammonium aurin tricarboxylate (aluminon) was added to a portion of the above solution. A small amount of a red precipitate formed which indicated the presence of aluminum ions.

E. Friedel-Crafts Acylation of 2% Divinylbenzene-Polystyrene Copolymer Beads with $TPP(COCl)_4H_2$.

Reaction conditions, such as the temperature and solvent, were varied. The reaction was run at room temperatue and at 50°C and in

1,1,2,2-tetrachloroethane or nitromethane. When nitromethane was used, only pale tan beads were obtained, whereas red-brown beads were obtained when 1,1,2,2-tetrachloroethane was used as the solvent. Below is given the procedure which resulted in the highest loading.

$TPP(CO_2H)_4H_2$ (150 mg) was treated with 10 mL of thionyl chloride and the resulting solution was refluxed overnight. The excess thionyl chloride was removed at reduced pressure. Next 2% divinylbenzene-polystyrene copolymer beads (1.00 g) were added to the porphyrin tetracid chloride. 1,1,2,2-Tetrachloroethane (10 mL) was added after $AlCl_3$ (150 mg) had been added. The mixture was stirred for 24 h. The beads were collected by filtration and washed with more 1,1,2,2-tetrachloroethane. The beads were then washed with 1 N NaOH, 1 N HCl, water, methanol, and hot DMF. IR, CO = 1655-1675 cm^{-1}. A 0.10 g sample of the partially pulverized beads was treated with 0.10 g of $Cu(OAc)_2 \cdot H_2O$ in 20 mL of DMF and heated to 120°C for 3 h. The resulting polymer is red and completely ground to a powder. The copper content was determined from neutron activation analysis. The copper content was 0.83% Cu and in addition, the polymer contained 0.195% Al. Designated as 2% P_1-CO-porCu.

F. Friedel-Crafts Acylation of 20% Divinylbenzene-Polystyrene Copolymer Beads with $TPP(COCl)_4H_2$.

Reaction conditions were varied as before. In addition, the reaction was also carried out at 100°C. The optimum conditions were found at 50°C in nitromethane. Below is the procedure which gave the best results. IR, (CO) 1655-1675 cm^{-1}.

$TPP(CO_2H)_4H_2$ (150 mg) was treated with thionyl chloride as before. The excess was again removed at reduced pressure. One g of 20% divinylbenzene-polystyrene copolymer beads was added to the residue. $AlCl_3$ (150 mg) was added and then nitromethane (10 mL) was added. The resulting mixture was stirred at 50°C for 24 h. The beads were collected by filtration and washed with nitromethane, 1 N NaOH, 1 N HCl, water, methanol, and hot DMF.

The beads (0.20 g) were mixed together with 0.20 g of $Cu(OAc)_2$ H_2O in 20 mL of DMF. The mixture was then heated at 120°C for 3 h before the beads were collected by filtration. The beads were washed with 0.1 N HCl, water, and methanol. The beads were then soxhlet extracted with methanol for 24 h. The copper complex provided a well resolved ESR spectrum. Neutron activation analysis showed the presence of 0.068% copper and 0.026% aluminum. The sample was designated as P_1-CO-porCu.

1. Preparation of P_1-CO-porCo.

To 0.20 g of the above polymer-bound porphyrin, P_1-CO-porH_2, was added 0.20 g of $CoCl_2$ $6H_2O$ and 20 mL of DMF. The mixture was heated at 120°C for 3 h. After collection by filtration, the beads were washed with 0.1 N HCl, water, and methanol. The sample was soxhlet extracted with methanol for 24 h. Neutron activation analysis showed that 0.085% of cobalt was present. In addition, 0.035% of aluminum was also present. Elemental analysis indicated a cobalt content of 0.05% and a nitrogen content of 0.42%. The nitrogen to cobalt ratio was 35.3 to 1 and the nitrogen to total metal was 10.7 to 1.

2. Preparation of P_1-CO-porCo(B) and P_1-CO-porFeCl(B).

A second batch of P_1-CO-porH_2 was prepared and it was metallated with $CoCl_2 \cdot 6H_2O$ and $FeCl_2$. Neutron activation analysis showed that only 0.015% of cobalt was present and the aluminum content was below the reliable detection levels. They were designated P_1-CO-porCo(B) and P_1-CO-porFeCl(B).

3. Preparation of P_1-CO-porCu(c) from $TPP(COCl)_4Cu$.

$TPP(CO_2H)_4Cu$ (0.160 g) was treated with 10 mL of thionyl chloride and 4 mL of pyridine. The resulting solution was refluxed overnight. The combined solvents were removed at reduced pressure. To the residue was then added 1.00 g of 20% divinylbenzene-polystyrene copolymer beads, 0.150 g of $AlCl_3$, and 10 mL of nitromethane. The reaction was heated at 50°C for 18 h and the beads were collected by filtration and were washed as before. The beads were then extracted with methanol for 3 d and with dichloromethane for 2 d. No ESR signal for copper was detected in the sample. The sample was treated with 0.2 g of $Cu(OAc)_2 \cdot H_2O$ in hot DMF as before. After washing, there was no ESR signal. The visible spectrum of the filtrate from the reaction had an absorption at 440 nm but no Soret band. Neutron activation analysis of this sample showed that the copper content was 0.000% and that of aluminum was 0.009%.

G. Friedel-Crafts Alkylation of 20% Divinylbenzene-Polystyrene Copolymer Beads.

1. Preparation of P_1-CH_2-porH_2.

$TPP(CO_2hexyl)_4H_2$ (200 mg) was reduced with 180 mg of LAH as before. The resulting hydroxymethylporphyrin was then treated with 20

mL of thionyl chloride for 24 h at reflux. The excess thionyl chloride was removed at reduced pressure. The porphyrin was taken up in 30 mL of 1,1,2,2-tetrachloroethane and added to 1.00 g of 20% divinylbenzene-polystyrene copolymer beads and 150 mg of $AlCl_3$. The reaction was heated at 100°C for 2 d. The beads were collected by filtration and washed with dichloromethane and then methanol. The beads are dark green.

2. Preparation of P_1-CH_2-porCo.

P_1-CH_2-porH_2 (0.50 g) and $CoCl_2 \cdot 6H_2O$ (0.50 g) were mixed together in 20 mL of DMF and the mixture was heated at 120°C for 3 h. The beads were collected by filtration and were washed as before. Neutron activation analysis showed that the cobalt content was 0.017% and the aluminum content was below the level of detection. Elemental analysis showed that the cobalt content was 0.02% and the nitrogen content was 0.18%. The nitrogen to cobalt ratio was 37.9 to 1.

3. Preparation of P_1-CH_2-porCu.

P_1-CH_2-porH_2 (0.50 g) and $Cu(OAc)_2 \cdot H_2O$ (0.50 g) were mixed together in 20 mL of DMF and the mixture was heated at 120°C for 3 h. The beads were collected by filtration and were washed as before. The ESR spectrum was well resolved for the copper complex. Neutron activation analysis showed that the copper content was 0.018% and that of the aluminum was 0.010%.

4. Attempted Preparation of P_1-CH_2-porH_2(B) with $TPP(CH_2OH)_4H_2$.

$TPP(CH_2OH)_4H_2$ (0.100 g) and 20% divinylbenzene-polystyrene copolymer beads (1.00 g) were added to a saturated solution of BF_3 in

dichloromethane (10 mL). The porphyrin was not soluble in this solution so 10 mL of nitromethane was added. The green solution was refluxed for 7 d while under nitrogen. The beads were washed with pyridine and tetrahydrofuran to yield a nearly colorless sample.

The beads (0.20 g) were then treated with 0.20 g of $Cu(OAc)_2 \cdot H_2O$ in 20 mL of DMF at 120°C for 3 h. The beads were collected and washed as before. No copper ESR signal was detected.

5. Preparation of P_1-CH_2-porCu(B) from $TPP(CH_2OH)_4Cu$.

A 0.50 g sample of 20% divinylbenzene-polystyrene copolymer beads, 100 mg of $TPP(CH_2OH)_4Cu$, and 150 mg of $AlCl_3$ were mixed together in 10 mL of 1,1,2,2,-tetrachloroethane. The mixture was stirred at 100°C for 2 d. The beads were collected by filtration and washed with 1,1,2,2-tetrachloroethane. The beads were then soxhlet extracted with THF for 24 h. The ESR spectrum is typical of a dilute copper porphyrin. Neutron activation analysis showed that the copper content was 0.030% and the aluminum content was 0.078%. The IR spectrum showed a weak absorption at 1650 cm^{-1} which is characteristic of divinylbenzene-polystyrene copolymer adducts of $AlCl_3$.

6. Preparation of P_1-C_5-O-porH$_2$.

A 1.00 g sample of 20% divinylbenzene-polystyrene copolymer beads, 150 mg of $T_3P(OC_5Br)H_2$, and 150 mg of $AlCl_3$ were mixed together in 20 mL of 1,1,2,2-tetrachloroethane. The reaction was carried out at 120°C for 2 weeks. The beads were collected by filtration and washed with 1,1,2,2-tetrachloroethane, dichloromethane, and methanol. After air drying, the beads are a light tan.

7. Preparation of P_1-C_5-O-porCo.

A 1.00 g sample of P_1-C_5-O-porH_2 and 0.50 g of $CoCl_2 \cdot 6H_2O$ were mixed together in 20 mL of DMF and the resulting mixture was heated at 120°C for 3 h. The beads were collected by filtration and washed with 0.1 N HCl, water, and methanol. The beads were then soxhlet extracted with methanol for 24 h. From results for SEM analysis, the cobalt content is 0.006%.

H. Preparation of Polymer-Bound Porphyrins with Aminated, 20% Divinylbenzene-Polystyrene Copolymer Beads.

1. Preparation of P_2-NH-CO-porH_2

a. A 50 mg sample of TPP(CO_2hexyl)$_4H_2$ and 50 mg of aminated, 20% divinylbenzene-polystyrene copolymer beads were mixed in 20 mL of toluene and the mixture was refluxed for 2 d. The beads were collected by filtration and washed with dichloromethane. The beads were still an off white. No reaction had occurred.

b. A 240 mg sample of TPP(CO_2H)$_4H_2$ was treated with 10 mL of thionyl chloride at reflux for 2 h and then at room temperature for another 3 h. The excess thionyl chloride was removed at reduced pressure and the porphyrin was kept in a vacuum for 4 h so as to remove the last traces of thionyl chloride. TPP(COCl)$_4H_2$ was then mixed with 1.00 g of aminated, 20% divinylbenzene-polystyrene copolymer beads.[20] Dichloromethane (20 mL) and triethylamine (1 mL) were then added. The resulting mixture was stirred at ambient temperatures for 24 h before the beads were collected by filtration. The beads were washed with dichloromethane and then treated with 5 mL of triethylamine and 100 mL of methanol at reflux for 0.5 h. The beads were collected and washed

with methanol. The beads were dried (25°C and 0.1 mm) for 1 h and then extracted with dichloromethane overnight. The resulting beads are a dark red-brown.

2. Preparation of P_2-NH-CO-porCu.

A 0.50 g sample of P_2-NH-CO-porH_2 and 0.50 g of $Cu(OAc)_2 \cdot H_2O$ were mixed togehter in 20 mL of DMF and heated at 120°C for 3 h. The beads were collected by filtration and washed with 0.1 N HCl, water, and methanol. The beads were then soxhlet extracted with methanol for 24 h. Neutron activation analysis showed that the copper content was 0.153%.

3. Preparation of P_2-NH-CO-porCo.

A 0.50 g sample of P_2-NH-CO-porH_2 and 0.50 g of $CoCl_2 \cdot 6H_2O$ were mixed together in 20 mL of DMF and heated at 120°C for 3 h. The beads were collected by filtration and washed with 0.1 N HCl, water, and methanol. The beads were then soxhlet extracted with methanol for 24 h. Neutron activation analysis showed that the cobalt content was 0.358%.

4. Prepartion of P_2-NH-CH_2-porH_2.

A 200 mg sample of TPP(CO_2hexyl)$_4H_2$ was reduced as before and the reduced product was then treated with 10 mL of thionyl chloride. The resulting solution was refluxed for 2 h and then allowed to sit overnight. The excess thionyl chloride was removed at reduced pressure. One g of aminated, 20% divinylbenzene-polystyrene copolymer beads, 0.1 g of $NaHCO_3$, and 20 mL of DMF were added to the porphyrin. The reaction was carried out at 100°C for 16 h. The beads were collected by filtration and washed with dichloromethane. The beads were then soxhlet extracted overnight with dichloromethane. A red-brown product was obtained.

5. Preparation of P_2-NH-CH_2-porCu.

A 0.20 g sample of P_2-NH-CH_2-porH_2 and 0.20 g of $Cu(OAc)_2 \cdot H_2O$ were mixed together in 20 mL of DMF and the resulting mixture was heated at 120°C for 3 h. The beads were collected by filtration and washed with 0.1 N HCl, water, and methanol. The beads were finally soxhlet extracted with methanol for 24 h. The reddish colored beads were analyzed by neutron activation analysis and the copper content was 0.393%.

6. Preparation of P_2-NH-CH_2-porCo.

A 0.10 g sample of P_2-NH-CH_2-porH_2 and 0.20 g of $CoCl_2 \cdot 6H_2O$ in 20 mL of DMF were heated at 120°C for 3 h. The beads were collected by filtration and washed with 0.1 N HCl, water, and methanol. The beads were soxhlet extracted with methanol for 24 h. Neutron activation analysis showed that the cobalt content was 0.430%.

I. Preparation of Polymer-Bound Porphyrins with Chloromethylated, 20% Divinylbenzene-Polystyrene Copolymer Beads.

1. Preparation of P_3-CH_2-NH-porH_2.

A 230 mg sample of $T_3P(NHAc)H_2$ was treated with 120 mL of 6 N hydrochloric acid and 100 mL of 1,2-dichloroethane and the resulting two phase mixture was refluxed for 20 h. After cooling, the organic layer was separated from the aqueous layer. The green organic layer was washed with saturated sodium bicarbonate solution until the free base porphyrin color had returned. The organic layer was dried over anhydrous magnesium sulfate before the 1,2-dichloroethane was removed at reduced pressure. The NMR spectrum indicated that hydrolysis was not complete for an absorption at 2.32 for the methyl of the acetyl group

was present. Integration showed that hydrolysis was about 50% complete.

The mixture of porphyrins from above was dissolved into 20 mL of DMF and added to 1.0 g of chloromethylated, 20% divinylbenzene-polystyrene copolymer beads. The reaction was run at 100°C for 24 h and then the beads were collected by filtration. The beads were then soxhlet extracted with dichloromethane for 24 h and then dried. The beads are a green-brown color.

2. Preparation of P_3-CH_2-NH-porCu.

To 0.40 g of P_3-CH_2-NH-porH_2 was added 0.15 g of $Cu(OAc)_2 \cdot H_2O$ and 20 mL of DMF. The mixture was heated to 120°C and the heating was continued for 3 h. The beads were collected by filtration and then washed with 0.1 N HCl, water, and then methanol. The beads were then soxhlet extracted for 24 h with methanol and then air dried. The resulting copper complex has a well resolved ESR spectrum. Neutron activation analysis showed that the copper content was 0.352%.

3. Preparation of P_3-CH_2-py-porH_2.

A 1.00 g sample of chloromethylated, 20% divinylbenzene-polystyrene copolymer beads and 0.22 g of $T_3P(py)H_2$ were mixed together in 20 mL of DMF and the reaction was run at 100°C for 24 h. The beads were collected and washed with DMF and then dichloromethane. The beads were soxhlet extracted with dichloromethane for 24 h and then air dried. The beads are a green-brown color.

4. Preparation of P_3-CH_2-py-porCu.

To 0.40 g of P_3-CH_2-py-porH_2 was added 0.15 g of $Cu(OAc)_2 \cdot H_2O$ and 20 mL of DMF. The mixture was heated to 120°C and the heating was continued for 3 h. The beads were collected by filtration and then

washed with 0.1 N HCl, water, and then methanol. The beads were then soxhlet extracted for 24 h with methanol and then air dried. The reddish beads have a well defined ESR spectrum for its copper complex. Neutron activation analysis showed that the copper content was 0.310%.

5. Preparation of P_3-CH_2-O-porH_2.

A 1.00 g sample of chloromethylated, 20% divinylbenzene-polystyrene copolymer beads, 1.00 g of $T_3P(OH)H_2$, and 4.00 g of anhydrous K_2CO_3 were mixed together and then 40 mL of DMF was added. The reaction was run at room temperature for 7 d. The beads were then collected by filtration and washed with more DMF and extracted with dichloromethane for 24 h. The dark red-brown beads were allowed to air dry.

6. Preparation of P_3-CH_2-O-porCu.

A 0.20g sample of P_3-CH_2-O-porH_2 and 0.30 g of $Cu(OAc)_2 \cdot H_2O$ were mixed together and 20 mL of DMF was added. The mixture was heated to 120°C and after 3 h, the beads were collected by filtration. The beads were washed with 0.1 N HCl, water, and methanol. The beads were then soxhlet extracted for 24 h with methanol and then air dried. The dark red beads gave a resolved ESR spectrum for its copper complex. Neutron activation analysis showed that the copper content was 1.363%.

7. Preparation of P_3-CH_2-O-porMnCl.

A 0.20 g sample of P_3-CH_2-O-porH_2 and 0.30 of $MnCl_2 \cdot 4H_2O$ were mixed together in 20 mL of DMF and treated as in the preparation of P_3-CH_2-O-porCu. The resulting beads were extracted as before. The beads are a dark green in color which is typical of Mn(III) porphyrins. Neutron activation analysis showed that the manganese content was

0.861%.

8. Preparation of P_3-CH_2-O-porVO.

A 0.20 g sample of P_3-CH_2-O-porH_2 and 0.30 g of $VOSO_4$ were mixed together in 20 mL of DMF and treated as in the preparation of P_3-CH_2-O-porCu. The resulting red-brown beads were extracted with methanol as before. The ESR spectrum of these beads show the presence of magnetically dilute vanadyl porphyrins.

9. Preparation of P_3-CH_2-O-porFeCl.

A 0.20 g sample of P_3-CH_2-O-porH_2 and 0.30 g of $FeCl_2$ were mixed together in 20 mL of DMF and treated as in the preparation of P_3-CH_2-O-porCu. The resulting red-brown beads were extracted with methanol as before. Iron content was 0.83%.

10. Preparation of P_3-CH_2-O-porCo.

A 0.50 g sample of P_3-CH_2-O-porH_2 (a second batch) and 0.30 g of $CoCl_2 \cdot 6H_2O$ were mixed together in 20 mL of DMF and treated as in the preparation of P_3-CH_2-O-porCu. The resulting red-brown beads were extracted with methanol as before. The cobalt content was 0.61% and the nitrogen content was 0.72% N. The nitrogen to cobalt ratio was 4.96 to 1 which is close to the expected 4 to 1.

11. Attachment of 4-Hydroxybenzaldehyde to P_3.

This polymer-bound aldehyde was prepared from 1.00 g of chloromethylated, 20% divinylbenzene-polystyrene copolymer beads, 1.22 g of 4-hydroxybenzaldehyde, and 1.00 g of anhydrous K_2CO_3 in 20 mL of DMF. The mixture was stirred at room temperature for 24 h. The mixture was filtered and the beads were washed with water and then methanol. The beads were extracted with methanol and then dried. Elemental

analysis showed that 6.93% O was present or 2.17 mmole of -O-Ph-CHO per gram of beads were present.

12. Preparation of P_3-CH_2-O-porH_2(B) from P_3-CH_2-O-Ph-CHO.

A 0.50 g sample of P_3-CH_2-O-Ph-CHO, 0.36 g of para-tolylaldehyde, and 0.27 g of pyrrole were mixed together in 100 mL of propionic acid and refluxed for 1 h. The solution was filtered hot and the resulting beads were extensively washed with methanol. The beads were then soxhlet extracted with dichloromethane for 24 h. The beads are black.

13. Preparation of P_3-CH_2-O-porCu(B).

A 0.20 g sample of P_3-CH_2-O-porH_2(B) and 0.20 g of $Cu(OAc)_2 \cdot H_2O$ were mixed together in 20 mL of DMF and treated as in the preparation of P_3-CH_2-O-porCu. The beads were again soxhlet extracted with methanol. The ESR spectrum showed that extensive dipolar interactions between neighboring copper porphyrin units were occurring. Neutron activation analysis showed that the copper content was 0.238%.

J. Elemental Analysis of Porphyrins, Metalloporphyrins, and Polymer-Bound Metalloporphyrins.

The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory. Neutron activation analyses were performed on polymer-bound metalloporphyrins. The TRIGA reacter at MSU was used for these determinations and the operator was Jim Carrick. Reference samples were made up in solution form and the samples of beads were used as whole beads in these determinations.

K. Scanning Electron Microprobe Analysis of Metalloporphyrin-Containing, 20% Divinylbenzene-Polystyrene Copolymer Beads.

Scanning electron microprobe analysis, SEM analysis, was performed on an American Research Laboratories EMX-SM Microprobe. The x-ray intensities were measured from K_α lines of cobalt and copper in order to determine the relative amounts of cobalt and of copper in the divinylbenzene-polystyrene copolymers. The analyses were performed by Viven Schull.

The preparation of the beads consisted of slicing the beads in half and mounting the half bead with its flat surface up on a carbon plate with double sided tape. The half beads were then coated with carbon from a carbon arc in a vacuum before analysis.

The exposed mid-section of the beads were scanned by a moving electron beam and the resulting x-ray intensities were recorded. The % Co was determined after corrections were made for the background and the intensity for a standard was determined.

$$\%Co = (\text{counts for the bead} - \text{counts for the background}) \div \text{counts for standard}$$

The results of analysis for the cobalt and copper were also determined as the ratio of intensity at the center to the intensity at the surface.

L. Resonance Raman Spectroscopy.

The resonance raman spectra were obtained for 55 μM solutions of TTPCu and TTPAlOH in dichloromethane. The sample of P_1-CH_2-porCu(B) was ground to a powder and placed in a 1 mm tube. Its spectrum was obtained with back scattering geometry. The spectra were obtained with a Spectra Physics 164-11 krypton laser and the Spex 1401 Ramalog

spectrometer. The samples were excited with the 413.1 nm line of the laser. The operator was Pat Callahan.

M. Preparation of Samples for ESR Spectral Analysis of TTPCu in $TTPH_2$.

Predetermined amounts of TTPCu and $TTPH_2$ were dissolved in dichloromethane and methanol was slowly added over several days to co-crystallize the two porphyrins. The crystals were collected by filtration and washed extensively with methanol. The crystals were then allowed to air dry for several days. The samples were then placed in tubes and the ESR spectra were obtained at room temperature on a Varian E-4 Spectrophotometer.

The samples of TTPCu in $TTPH_2$ are given in Table 11. The amounts of each are given as well as the % Cu and mole fraction of TTPCu in each of the samples.

N. Experimental Setup and Reaction Conditions for the Autoxidation of Cyclohexene.

The autoxidation of cyclohexene was performed in a constant-pressure, gas manifold equipped with a gas buret, a mercury leveling bulb, a mineral oil bubbler, and a ground joint for the reaction vessel. The reaction vessel was a 50 mL round bottom flask which was equipped with a side arm with a stop cock. The reaction temperature was controlled at 60°C by a thermocouple immersed into an oil bath which was used to heat the reaction vessel. The oil bath was heated by a nichrome immersion coil and the oil bath was stirred by an overhead mechanical stirrer. The contents of the reaction flask were stirred magnetically.

Table 11

Amount of TTPCu in $TTPH_2$

Sample Number	mg TTPCu	mg $TTPH_2$	Mole Fraction	%Cu
Cu 1	1	100	0.009	0.086
Cu 2	1	25	0.035	0.33
Cu 3	3	30	0.085	0.79
Cu 4	4	20	0.155	1.44
Cu 5	6	20	0.216	2.00
Cu 6	10	20	0.314	2.89
Cu 7	12	15	0.423	3.85
Cu 8	12	10	0.523	4.73
Cu 9	20	5	0.787	6.94
Cu 10	25	1	0.958	8.34
Cu 11	25	0	1.000	8.94

When the metalloporphyrins were used, the metalloporphyrin (0.5 mg) was placed into the reaction vessel. Then the system was evacuated and dioxygen was placed into the system. A 10 mL portion of cyclohexene was then injected by a syringe. The volume of dioxygen uptake was then followed for 2 to 4 h. The reaction was either stopped at 2 h or continued for 24 h. In the case of the polymer-bound metalloporphyrins, a 0.100 g portion of the beads were used in place of the metalloporphyrin. All other conditions were the same.

The product composition and identity were determined by gas chromatography. Authentic samples of cyclohexene, cyclohexene oxide, 2-cyclohexenol, and 2-cyclohexenone were used as references to determine retention times on a column of SE-30. The injector temperature was 150°C, the column temperature was 100°C, and the detector temperature was 150°C. The gas chromatograph used was a Varian Aerograph Model 920 Chromatograph with a thermal conductivity detector. The column length was 10 feet long and 0.25 inch in diameter and it contained 10% SE-30 supported on WHP.

O. Experimental Setup and Reaction Conditions for the Autoxidation of Aldehydes.

The autoxidation of aldehydes was performed in a constant-pressure, gas manifold which was equipped as for the autoxidation of cyclohexene. The reaction temperature was regulated at 30°C by a thermocouple immersed into the nichrome coil-heated oil bath. Stirring was as before.

The reaction vessel was charged by the injection of ethyl acetate solution of $TPP(CO_2Et)_4Co$ and the injection of the aldehyde. The amount of aldehyde injected resulted in a 0.50 M solution of the aldehyde in ethyl acetate. Butanal (1.10 mL) and benzaldehyde (1.30 mL) were used with enough of the $TPP(CO_2Et)_4Co$ solution to bring the total volume to 25.0 mL. The molarity of cobalt porphyrin was 0.0872 mM and 0.0865 mM, respectively. The dioxygen uptake was followed with a gas buret. After 0.5, 1.0, and 2.0 h, two mL of the reaction solution was withdrawn and analyzed for hydrogen peroxide and the peracid content. The weighed solution was treated with 150 mL of 5% sulfuric acid and cracked ice.[84] The hydrogen peroxide content was determined by titration with a 0.1 N ceric sulfate solution and with ferroin as indicator. The peracid content was determined with 10 mL of a 10% potassium iodide solution. The liberated iodine was titrated with 0.1 N sodium thiosulfate solution with starch as indicator.

P. Additional Instruments.

In addition to the instruments mentioned already, these spectrophotometers were used. For IR spectra, Perkin-Elmer 457 and Perkin-Elmer 598 were used. For UV-VIS spectra, a Unicam SP 800 was used.

APPENDIX A

APPENDIX A

Other Polymer-Bound Porphyrins and Metalloporphyrins

In addition to the work presented in the main body, coproporphyrin I tetramethyl ester was prepared[87] and then reduced with lithium aluminum hydride in THF[52]. The tetraalcohol was then treated with refluxing solution of thionyl chloride in dichloromethane for 12 hours. The resulting porphyrin was then used in an $AlCl_3$-catalyzed Friedel-Crafts alkylation of 20% divinylbenzene-polystyrene copolymer beads. After 16 hours, the resulting beads were collected by filtration and extensively washed. They were then metallated with $CoCl_2 \cdot 6H_2O$ in hot DMF. The resulting sample, P_1-C_3-porCo, was analyzed with scanning electron microprobe analysis. The scan is shown in Figure 36 and an I_c value of 0.00 was calculated. There was 0.013% Co calculated from the SEM data.

Aminated, 20% divinylbenzene-polystyrene copolymer beads were treated with the sulfonyl chloride of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin[88] in dichloromethane and triethylamine. After 18 hours, green beads were obtained. The beads were metallated with $CoCl_2 \cdot 6H_2O$ in hot DMF. The resulting sample, P_2-NH-SO_2-porCo, was analyzed by SEM analysis and its scan is shown in Figure 37. The sample had an I_c of 0.43 and a cobalt content of 0.076%.

Figure 36. SEM scan of P_1-C_3-porCo.

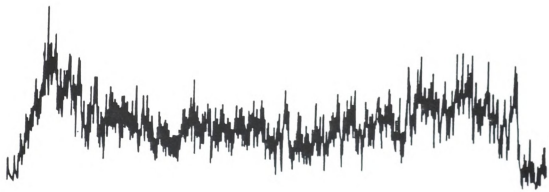

Figure 37. SEM scan of P_2-NH-SO_2-porCo.

The values of I_c for these samples are supporting evidence for the results obtained for the other samples. For P_1-C_3-porCo, I_c of 0.00 again shows that the reactive intermediate in this reaction is unable to effectively penetrate the copolymer matrix. For P_2-NH-SO_2-porCo, its value of 0.43 indicates that diffusion is more efficient. In comparison to P_2-NH-CO-porCo (I_c = 0.025), P_2-NH-SO_2-porCo is more evenly loaded. This again re-enforces the trend of lower reactivity, better penetration for sulfonyl chlorides are more stable than the analogous acid chlorides.

APPENDIX B

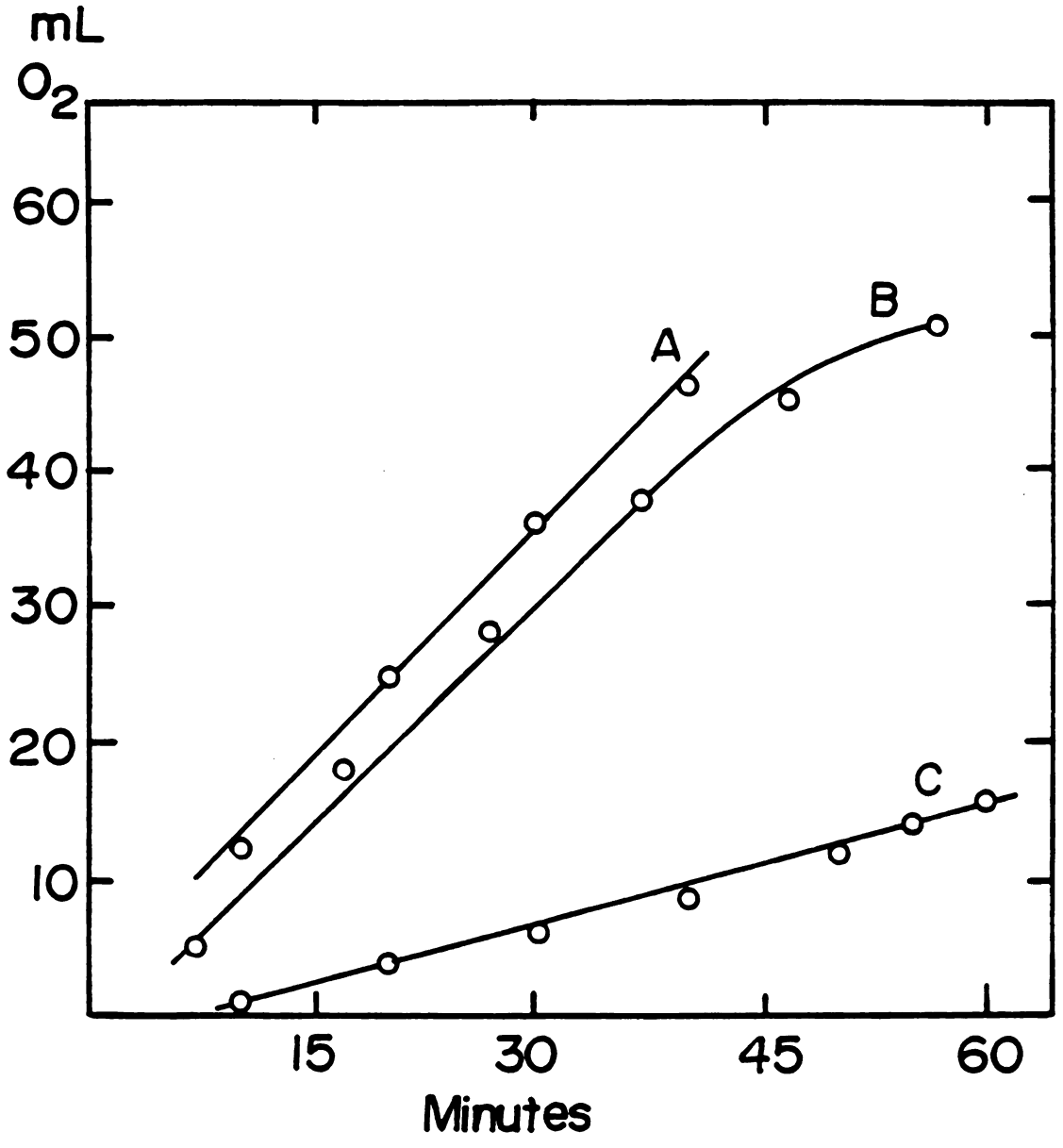

Figure 38. Autoxidation of Benzaldehyde at 30°C under 1 ATM of O_2

A) darkened room

B) lighted room

C) P_1-CO-porFeCl(B).

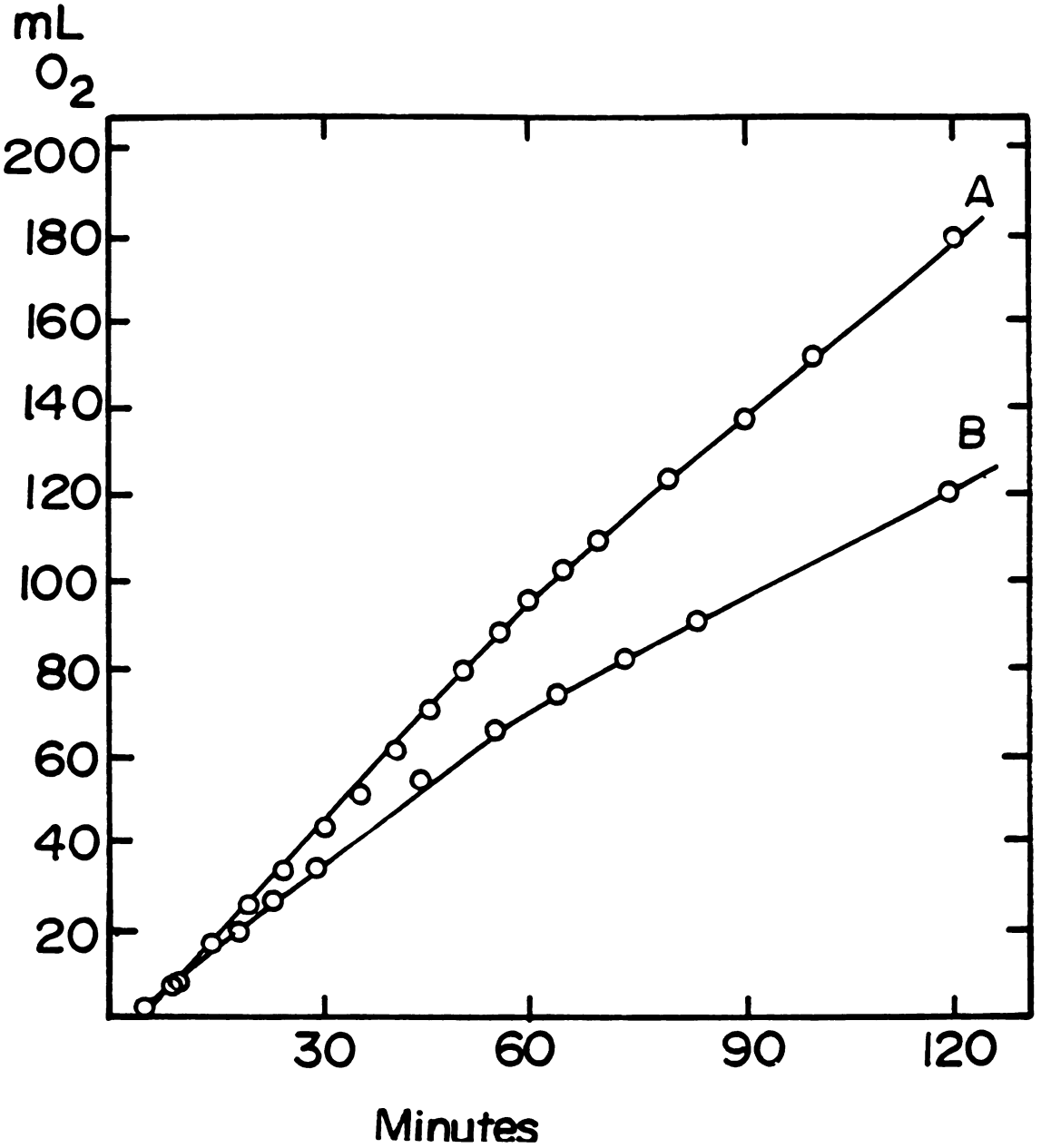

Figure 39. Autoxidation of Benzaldehyde at 30°C under 1 ATM of O_2

A) $TPP(CO_2Et)_4Co$

B) P_1-CO-porCo(B).

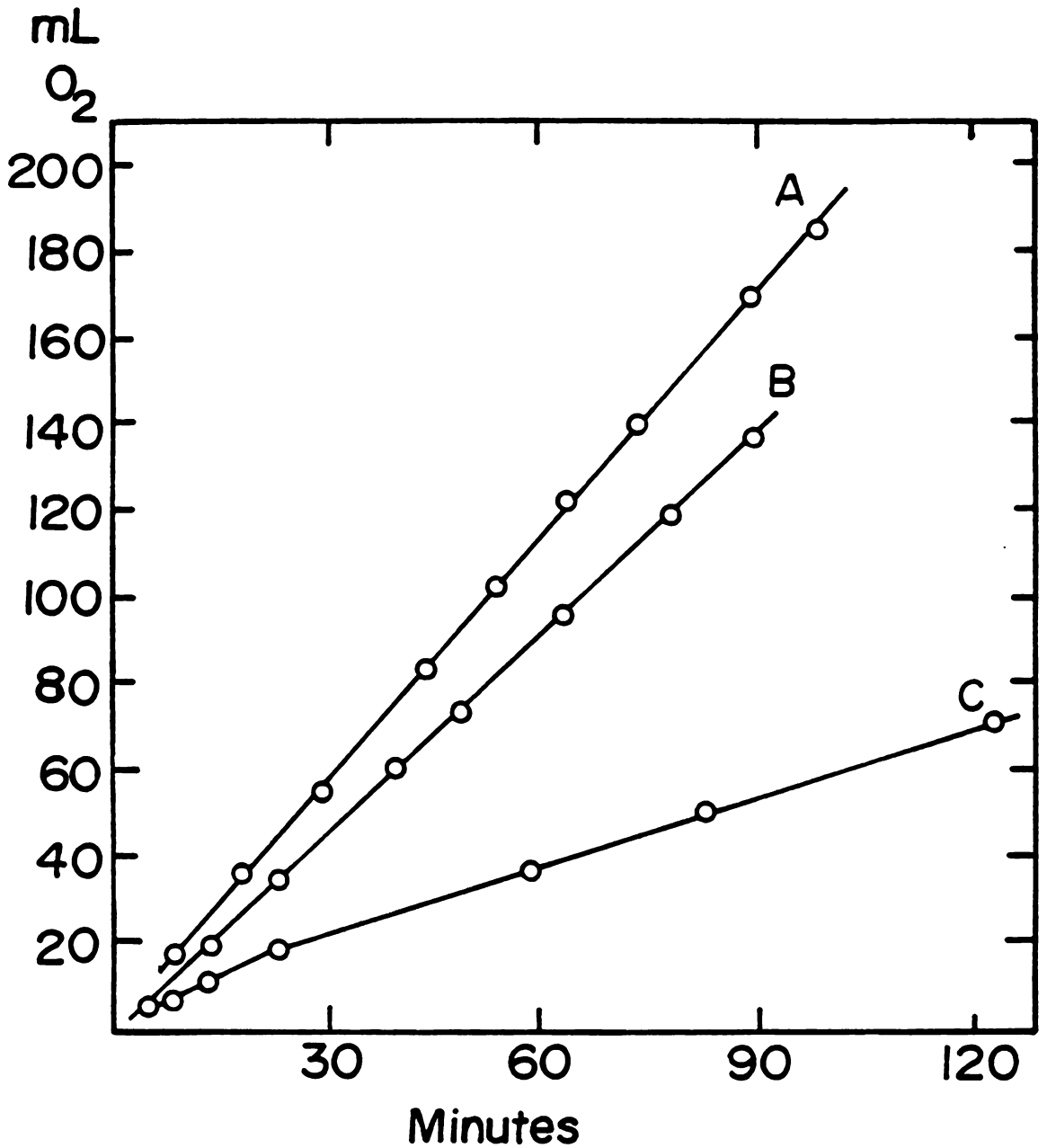

Figure 40. Autoxidation of Butanal at 30°C under 1 ATM of O_2

A) $TPP(CO_2Et)_4Co$

B) P_1-CO-porCo(B)

C) Blank.

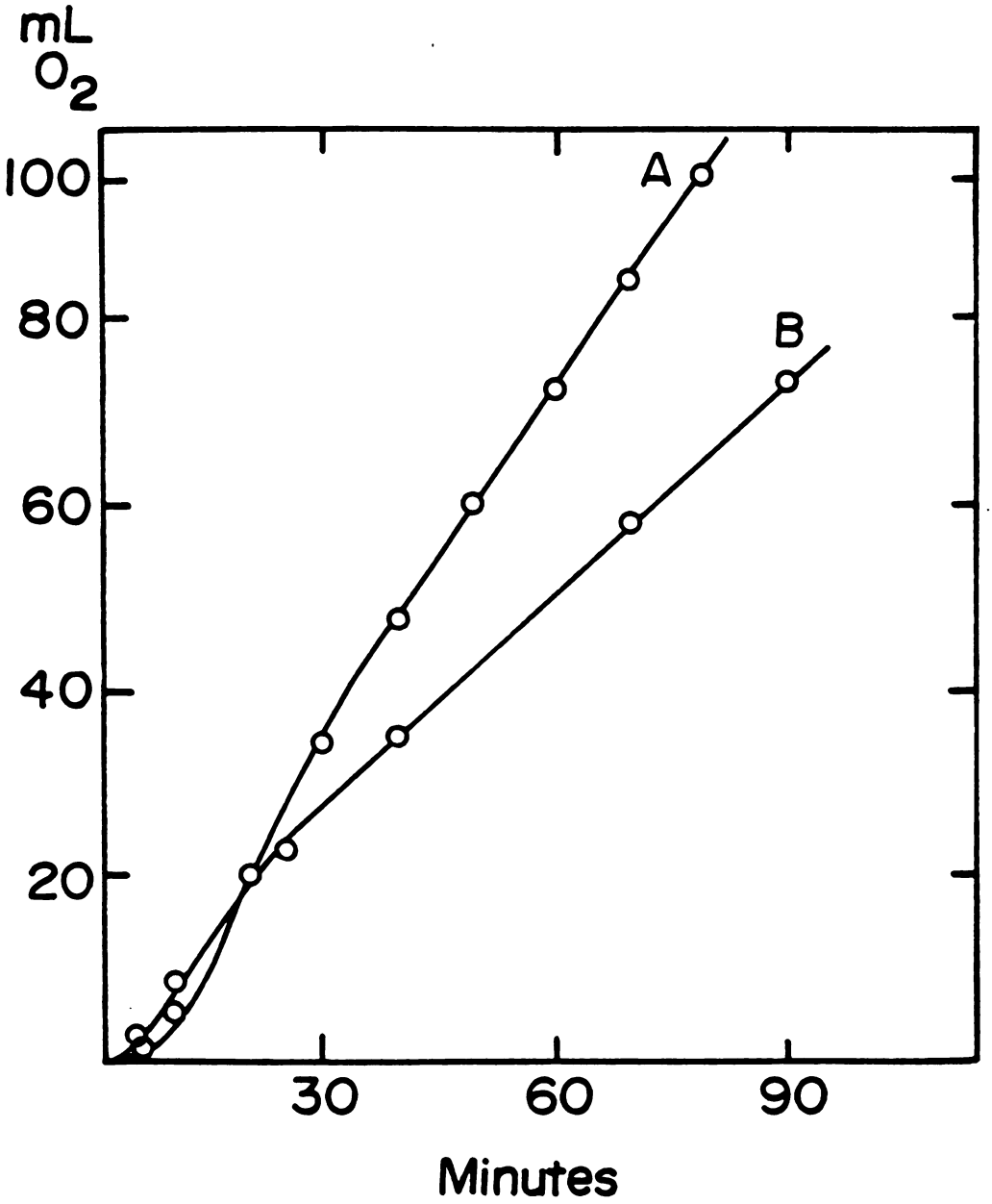

Figure 41. Autoxidation of Cyclohexene at 60°C under 1 ATM O_2

A) TTPCo

B) $TPP(CO_2hexyl)_4Co$.

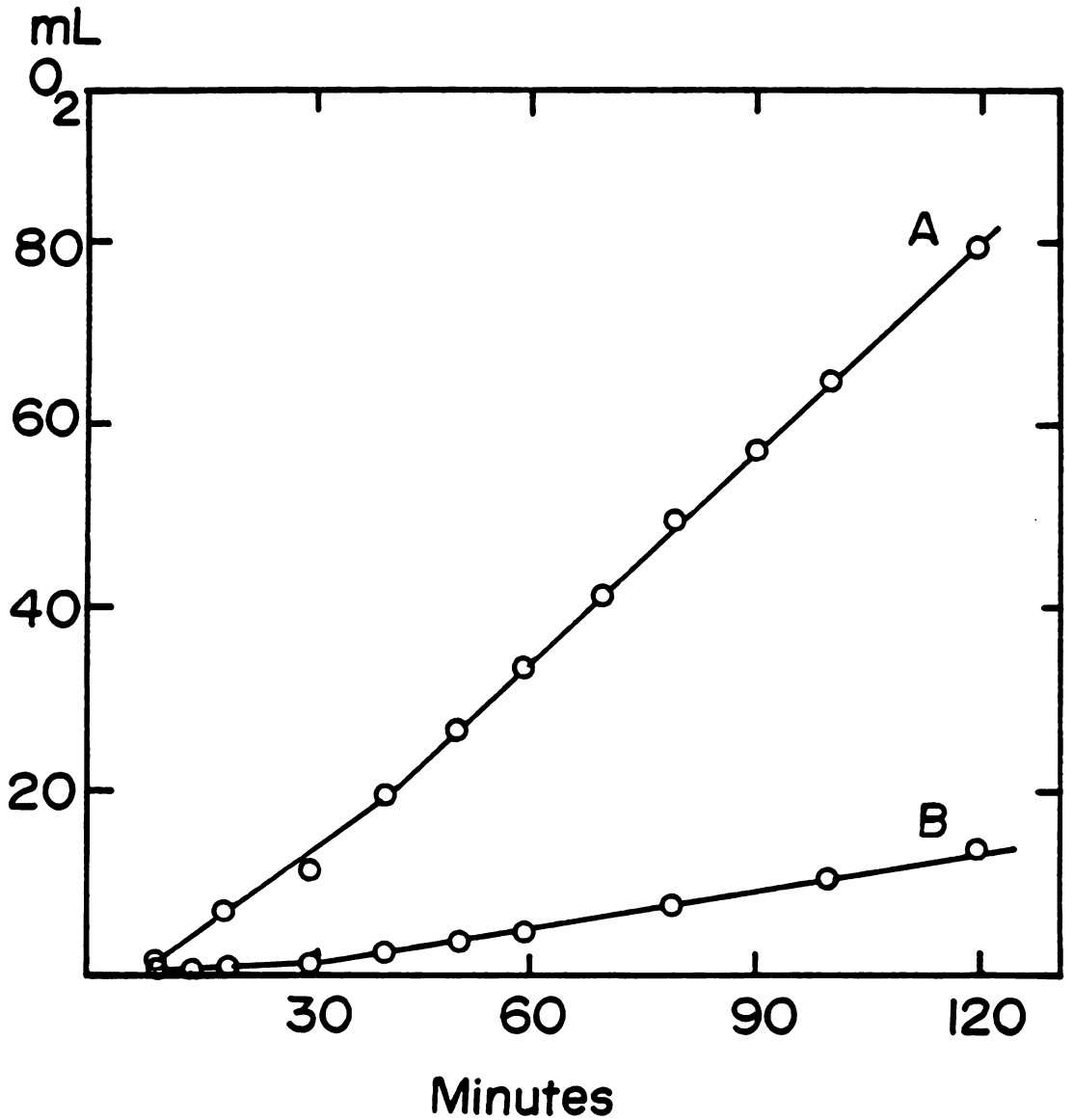

Figure 42. Autoxidation of Cyclohexene at 60°C under 1 ATM O_2

A) P_3-CH_2-O-porCo(whole)

B) P_2-NH-CO-porCo(whole).

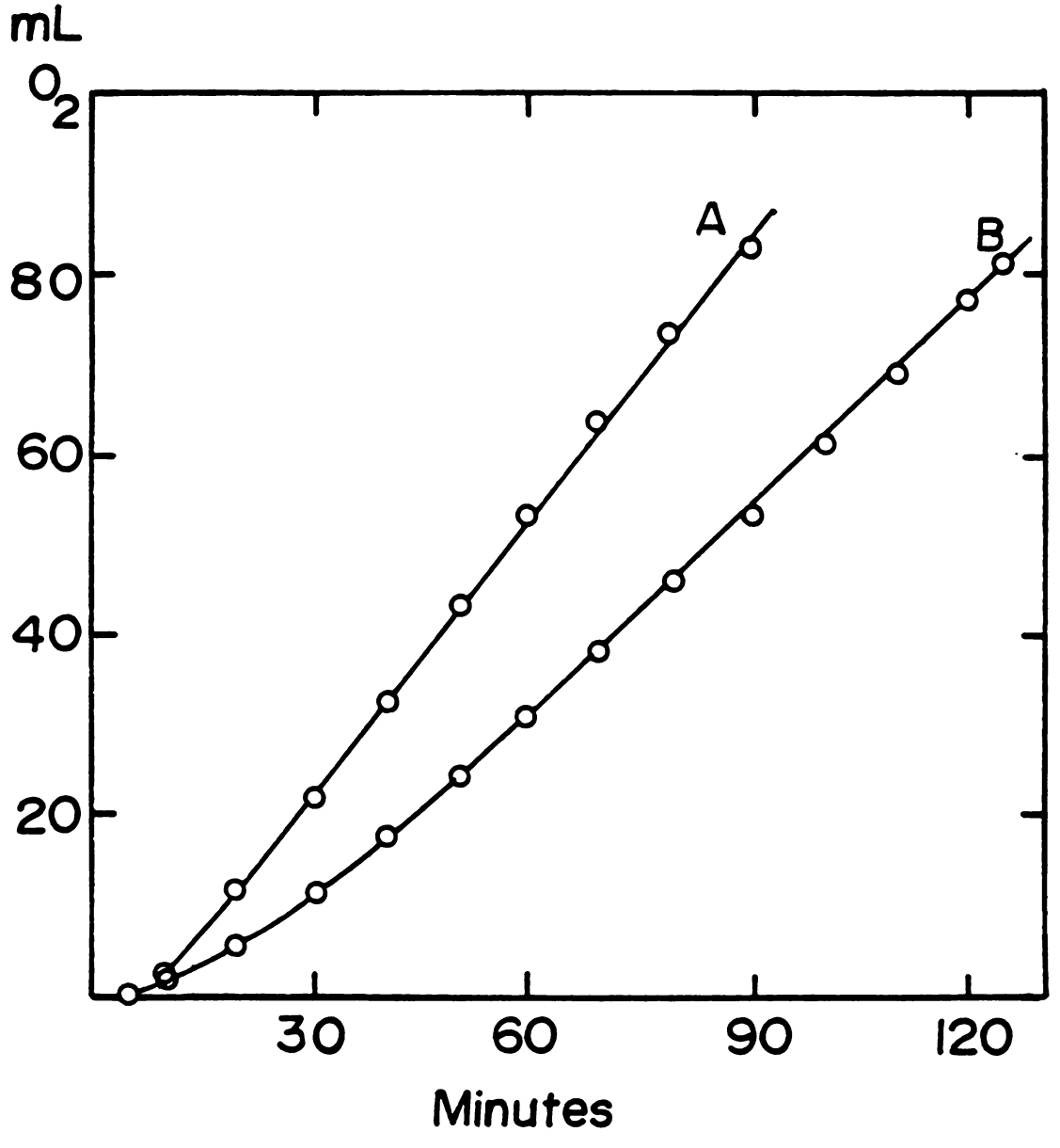

Figure 43. Autoxidation of Cyclohexene at 60°C under 1 ATM O_2

A) P_3-CH_2-O-porCo(ground)

B) P_2-NH-CO-porCo(ground).

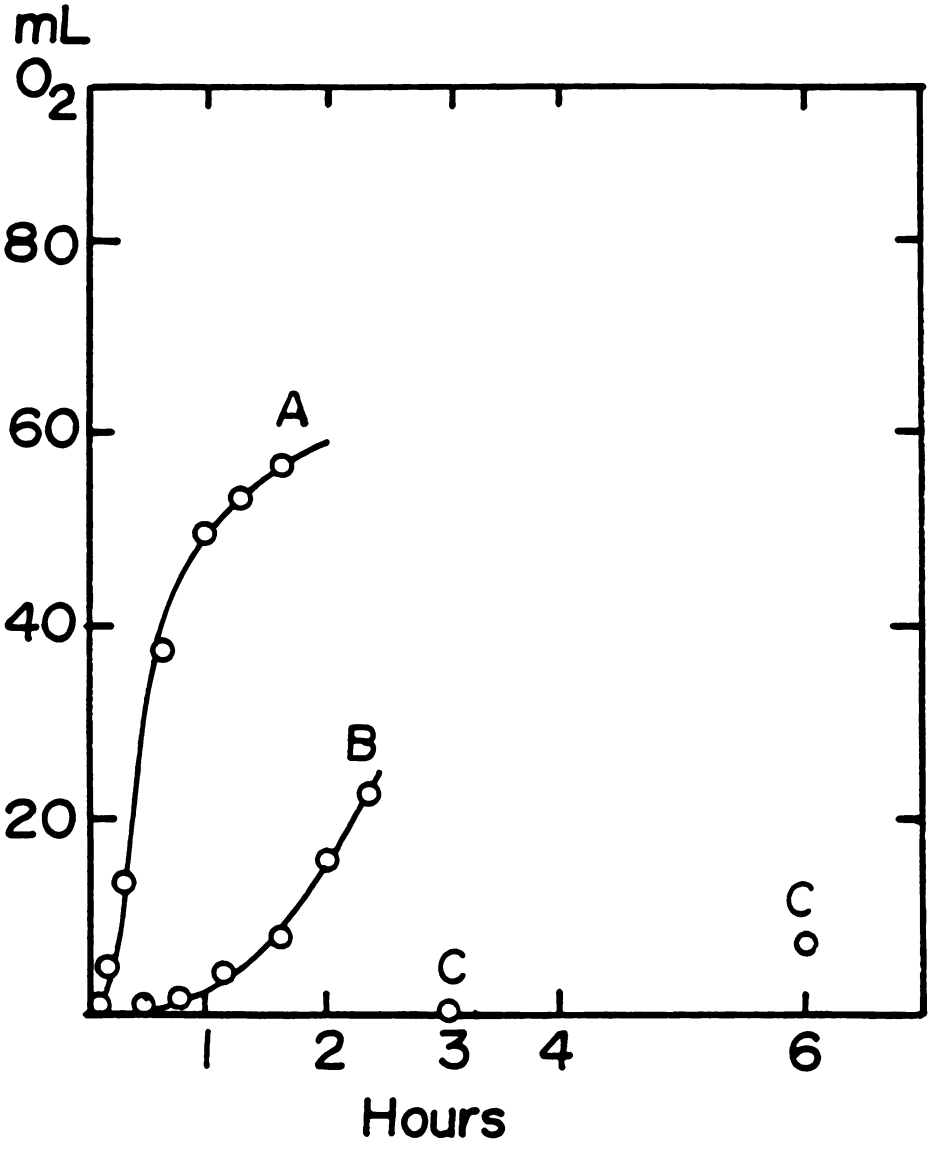

Figure 44. Autoxidation of Cyclohexene at 60°C under 1 ATM O_2

A) TTPFeCl

B) P_3-CH_2-O-porFeCl(used)

C) P_3-CH_2-O-porFeCl(new).

APPENDIX C

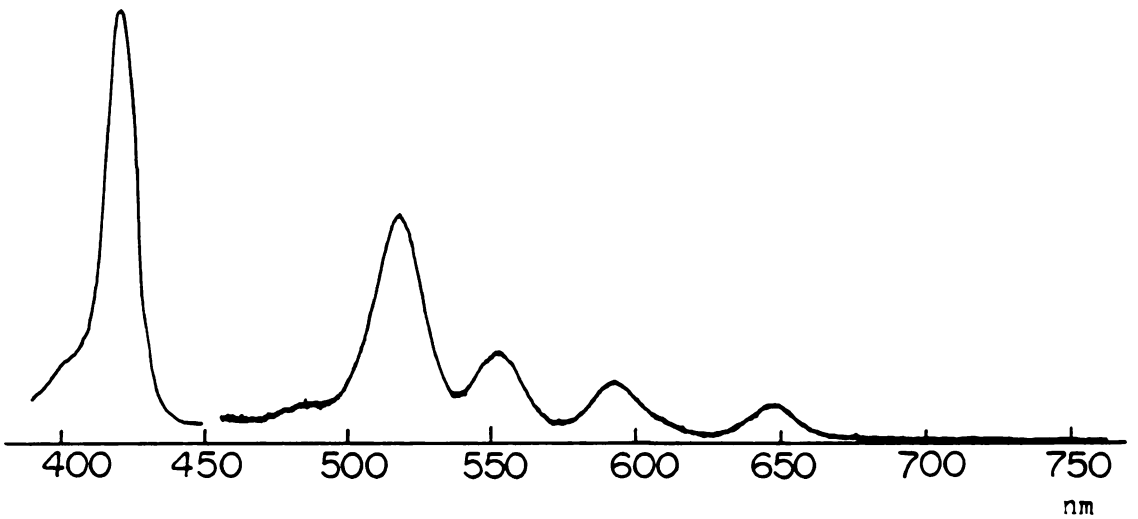

Figure 45. UV-VIS spectrum of TPP(CO_2hexyl)$_4H_2$.

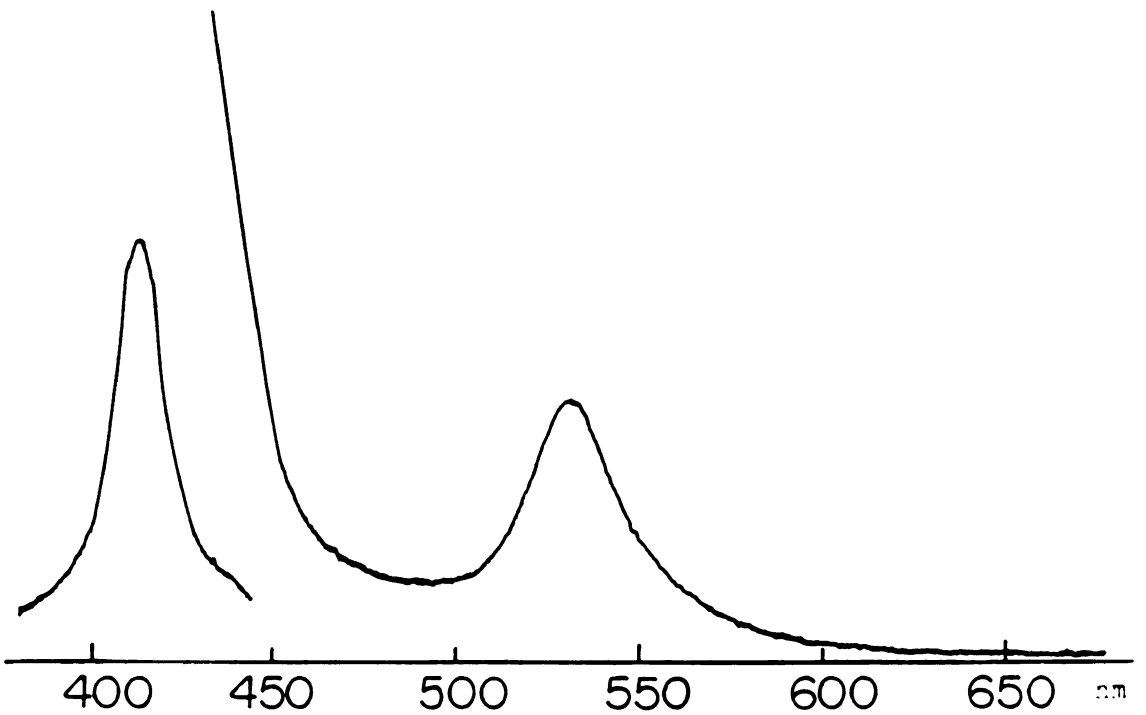

Figure 46. UV-VIS spectrum of TPP(CO_2hexyl)$_4$Co.

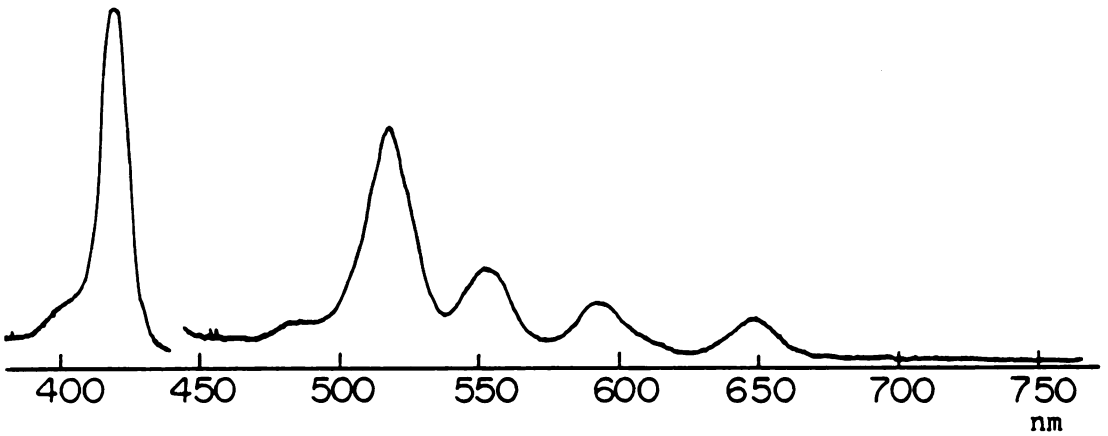

Figure 47. UV-VIS spectrum of $T_3P(py)H_2$.

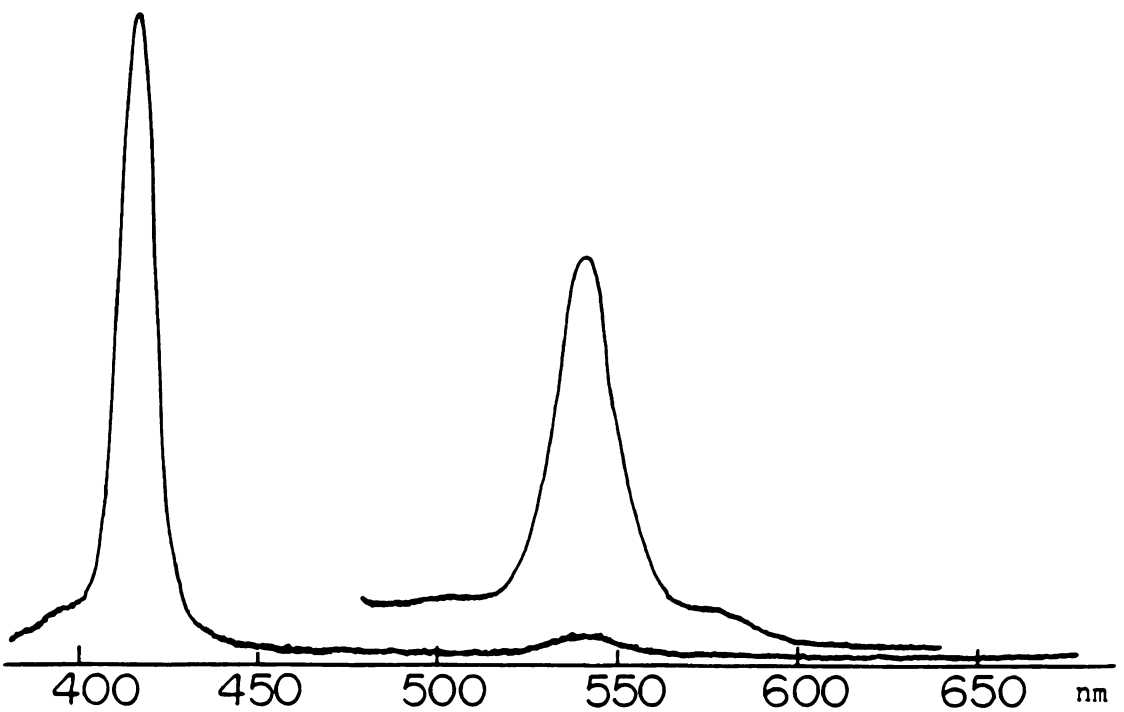

Figure 48. UV-VIS spectrum of $T_3P(py)Cu$.

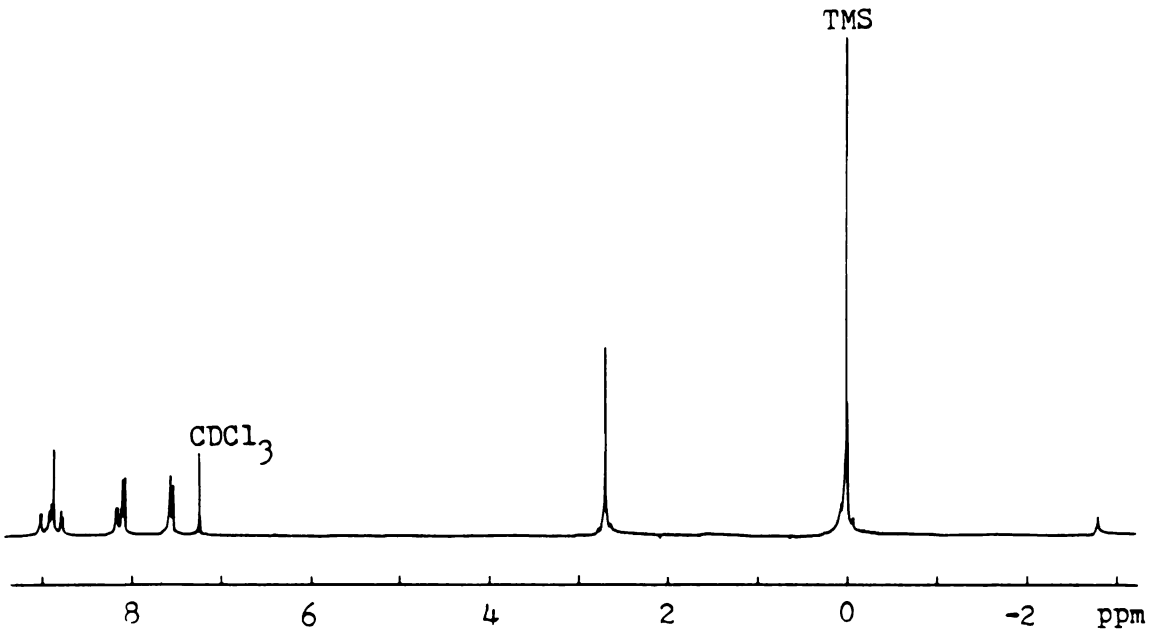

Figure 49. ^{1}H NMR spectrum of $T_3P(py)H_2$.

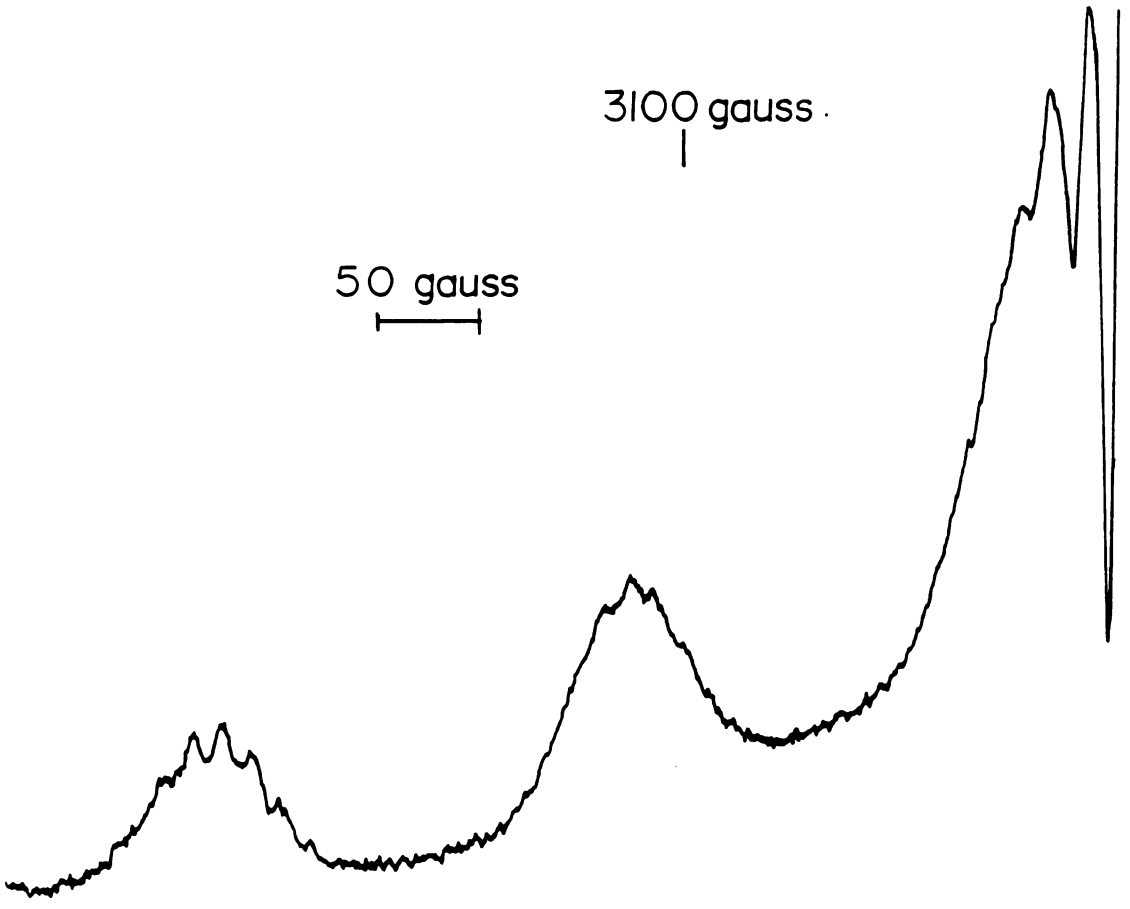

Figure 50. ESR spectrum of P_3-CH_2-py-porCu.

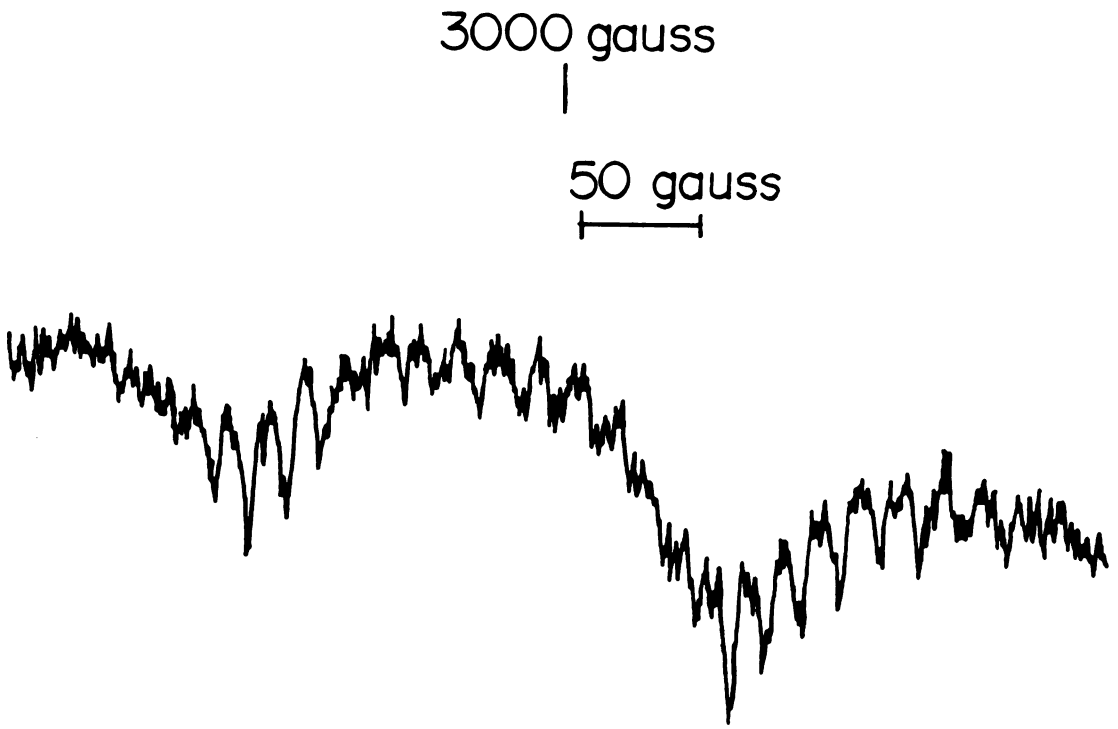

Figure 51. ESR spectrum of Cu 1.

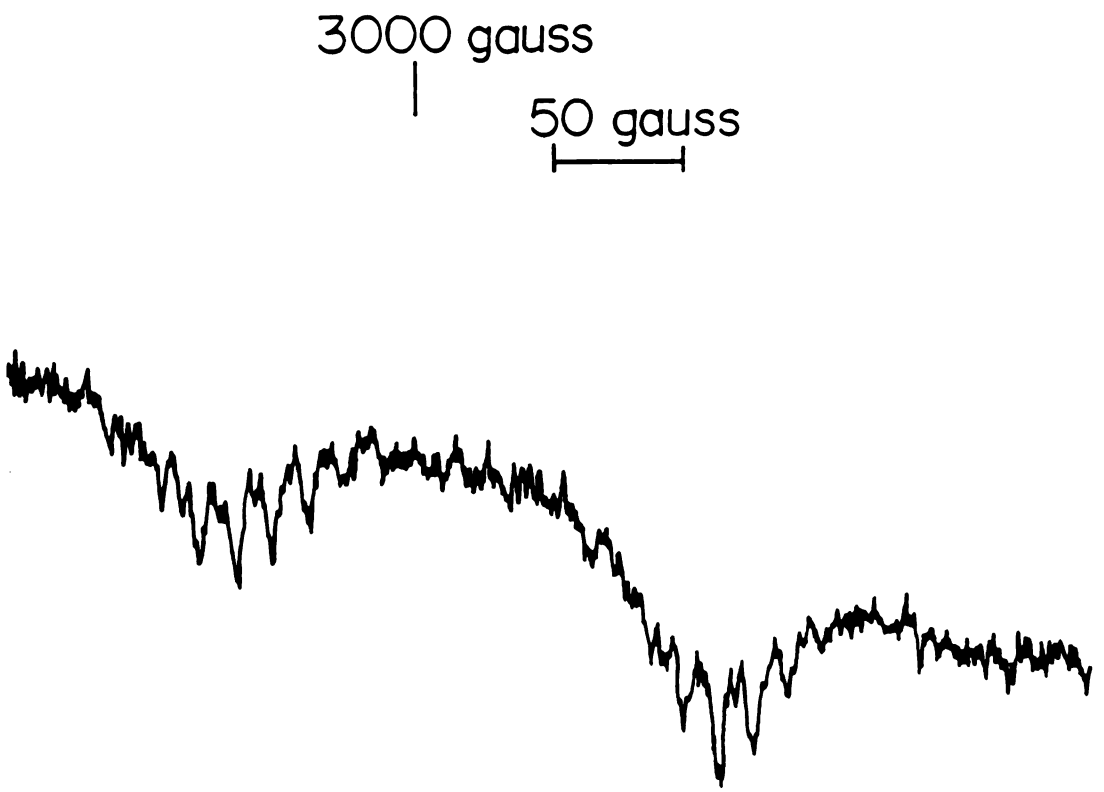

Figure 52. ESR spectrum of Cu 2.

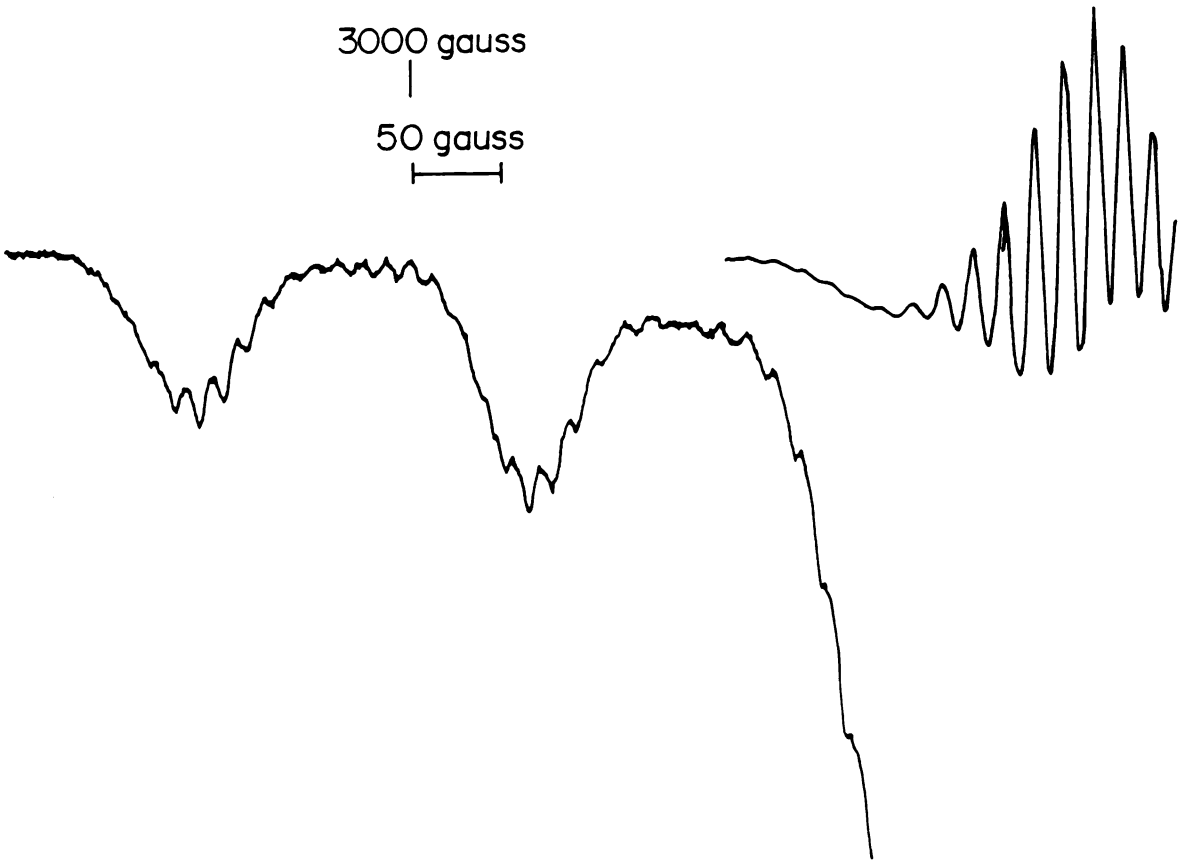

Figure 53. ESR spectrum of Cu 3.

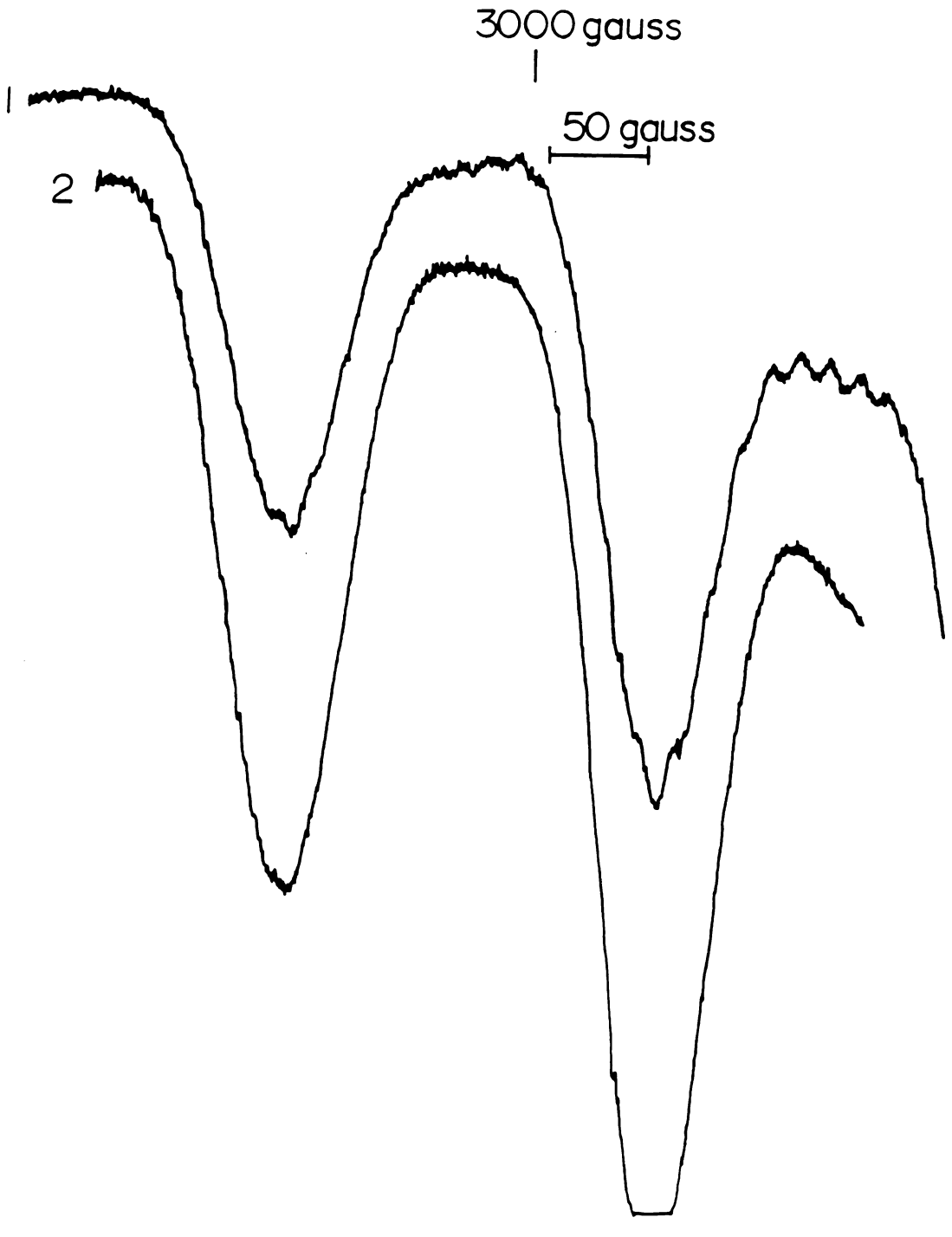

Figure 54. ESR spectra of (1) Cu 4 and (2) Cu 5.

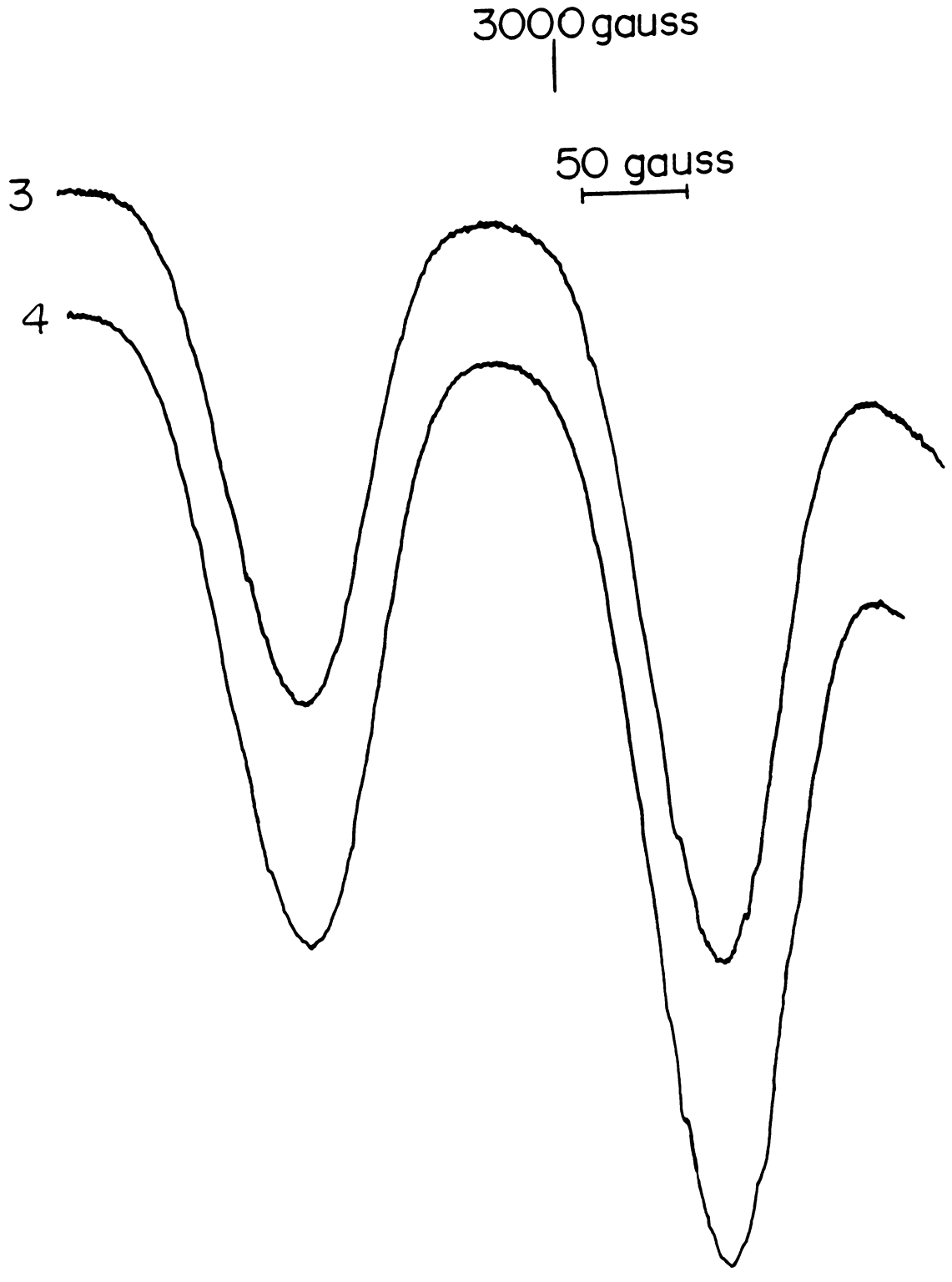

Figure 55. ESR spectra of (3) Cu 6 and (4) Cu 7.

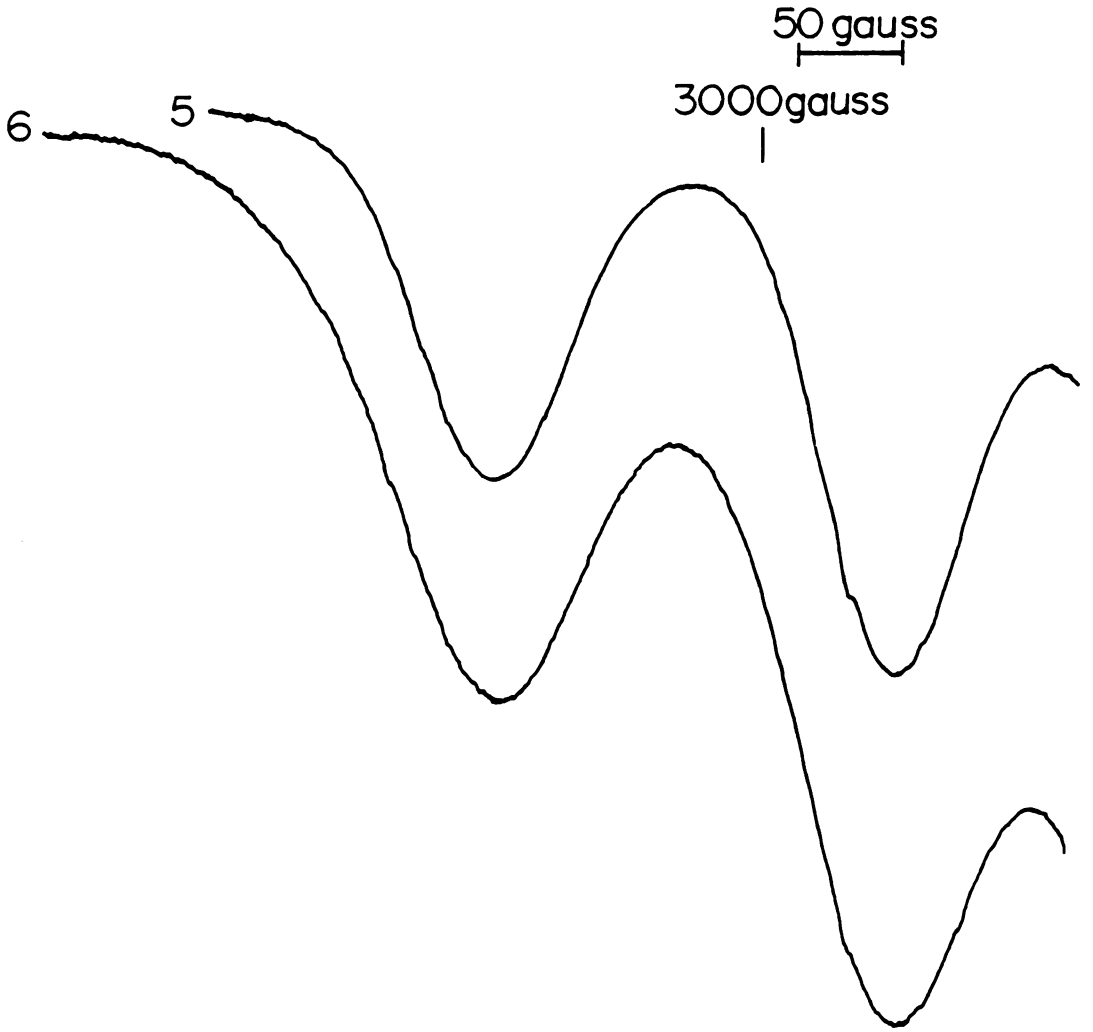

Figure 56. ESR spectra of (5) Cu 8 and (6) Cu 9.

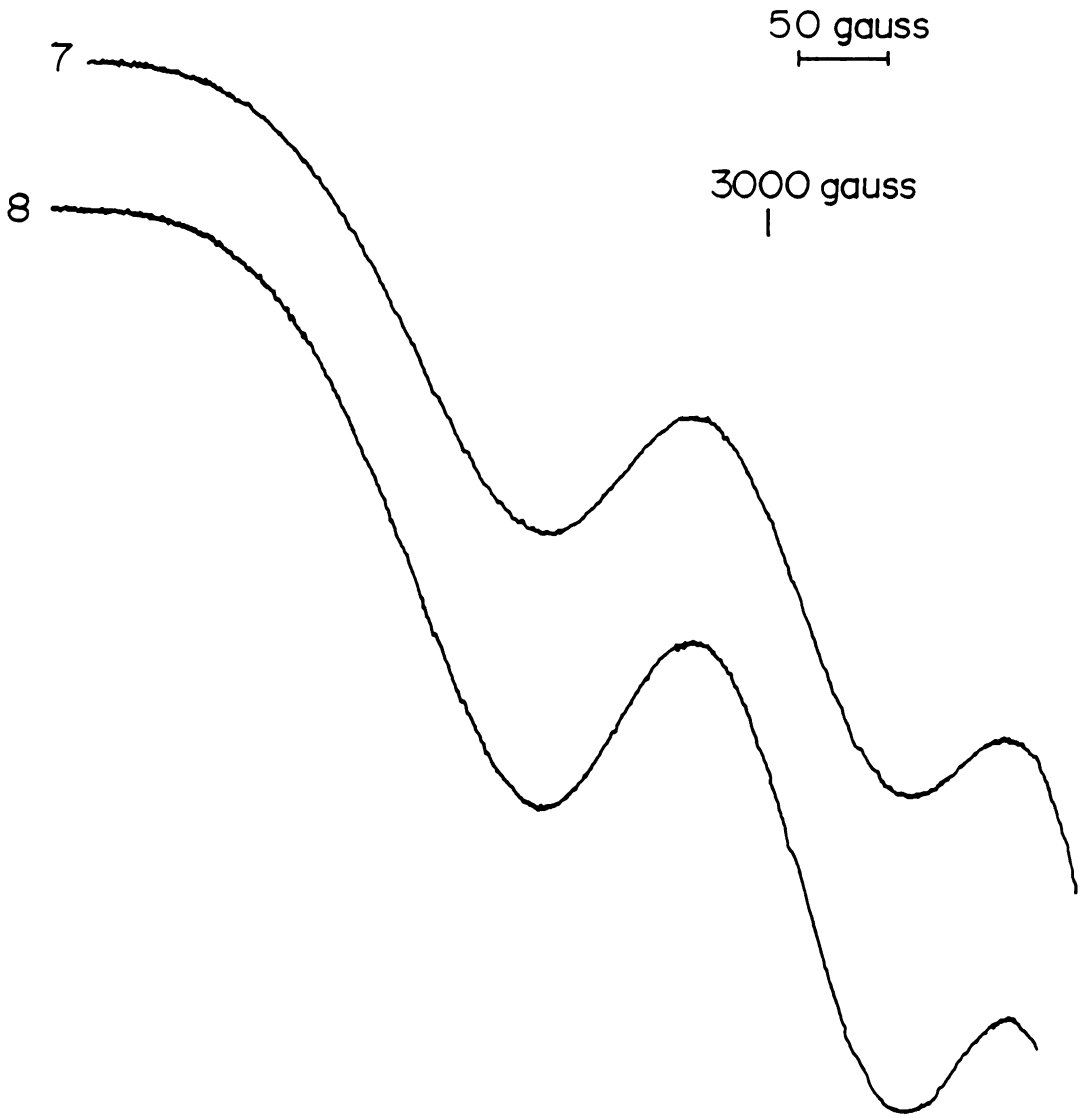

Figure 57. ESR spectra of (7) Cu 10 and (8) Cu 11.

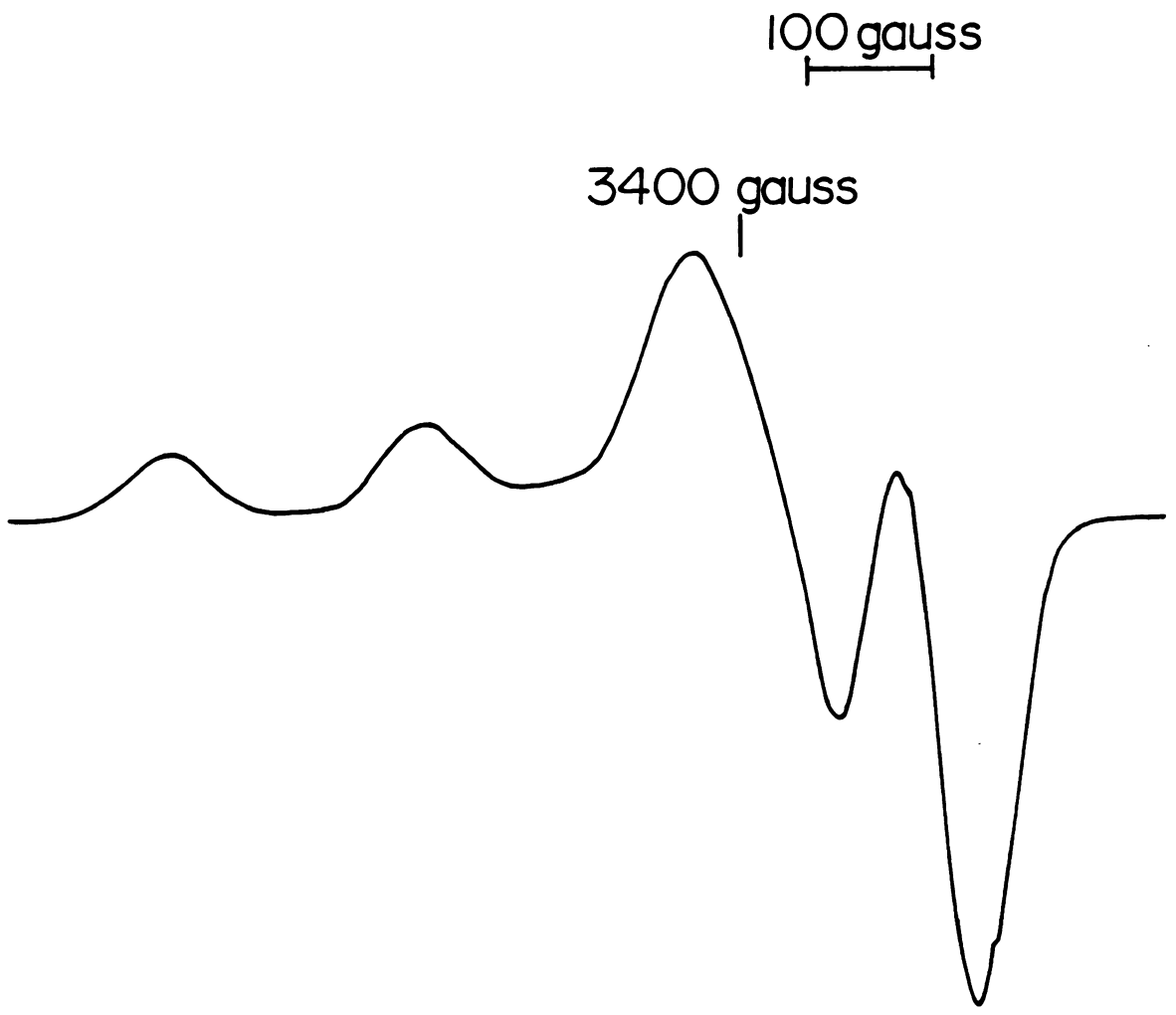

Figure 58. ESR spectrum of Cu 7.

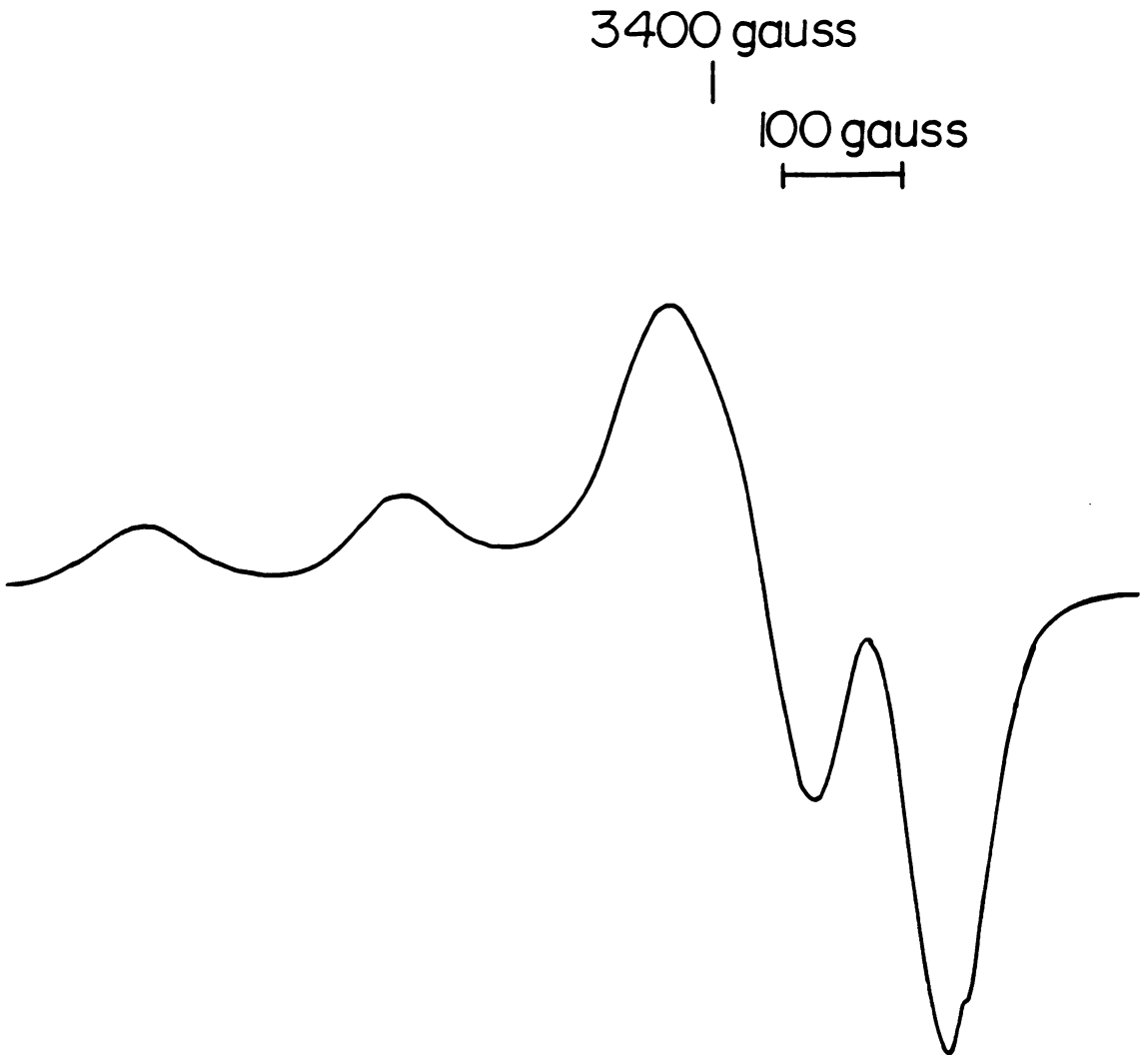

Figure 59. ESR spectrum of Cu 8.

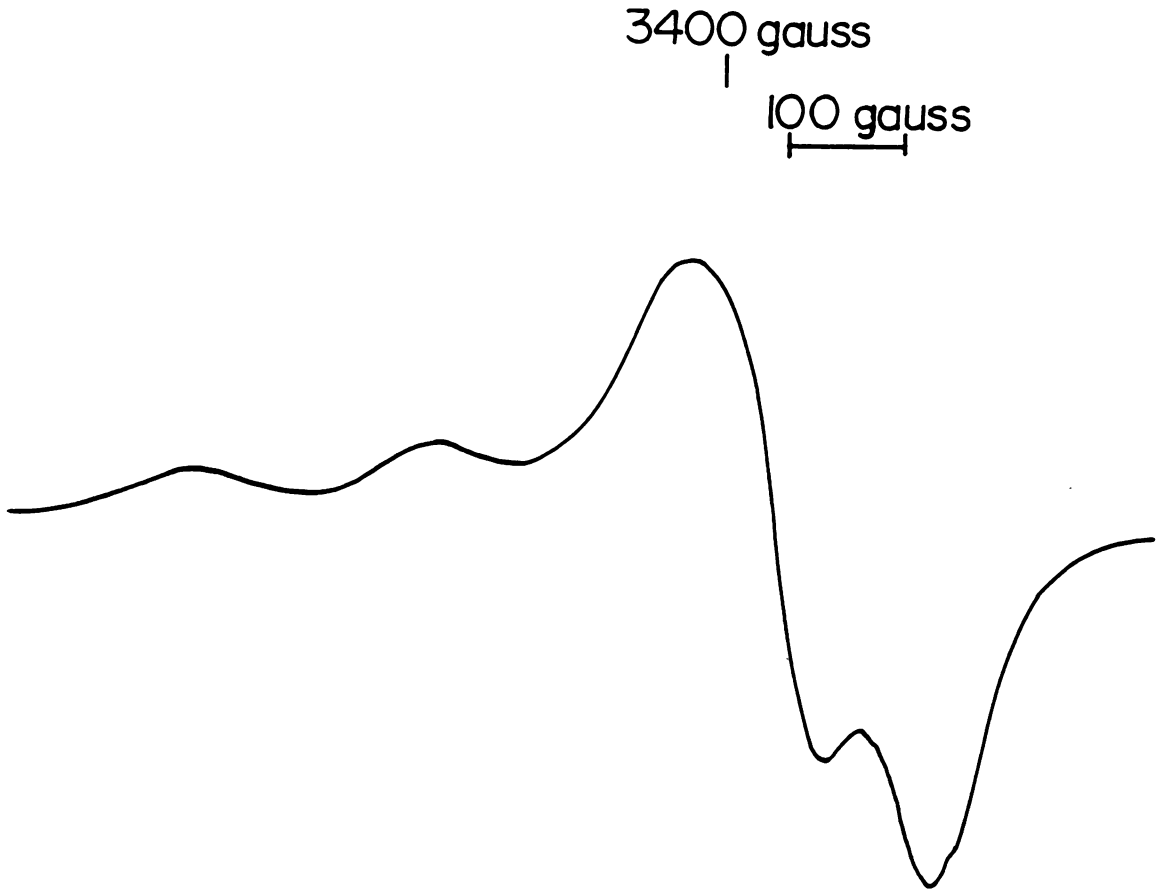

Figure 60. ESR spectrum of Cu 9.

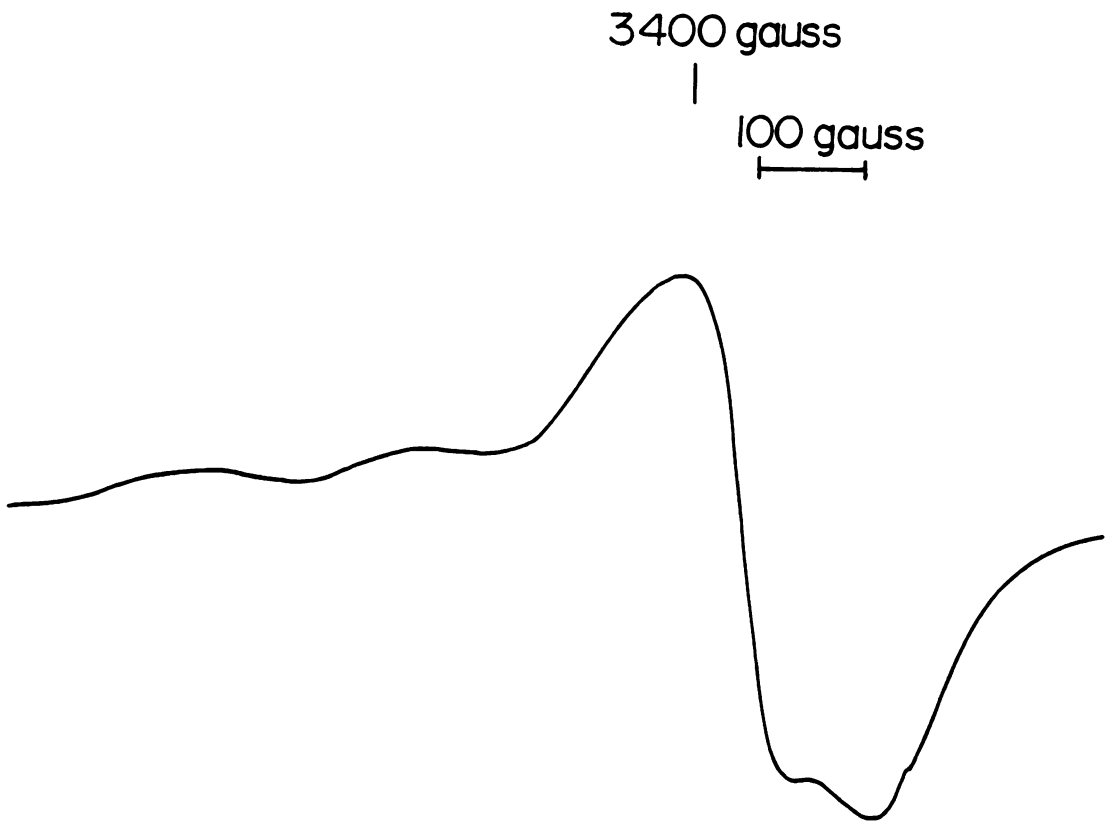

Figure 61. ESR spectrum of Cu 10.

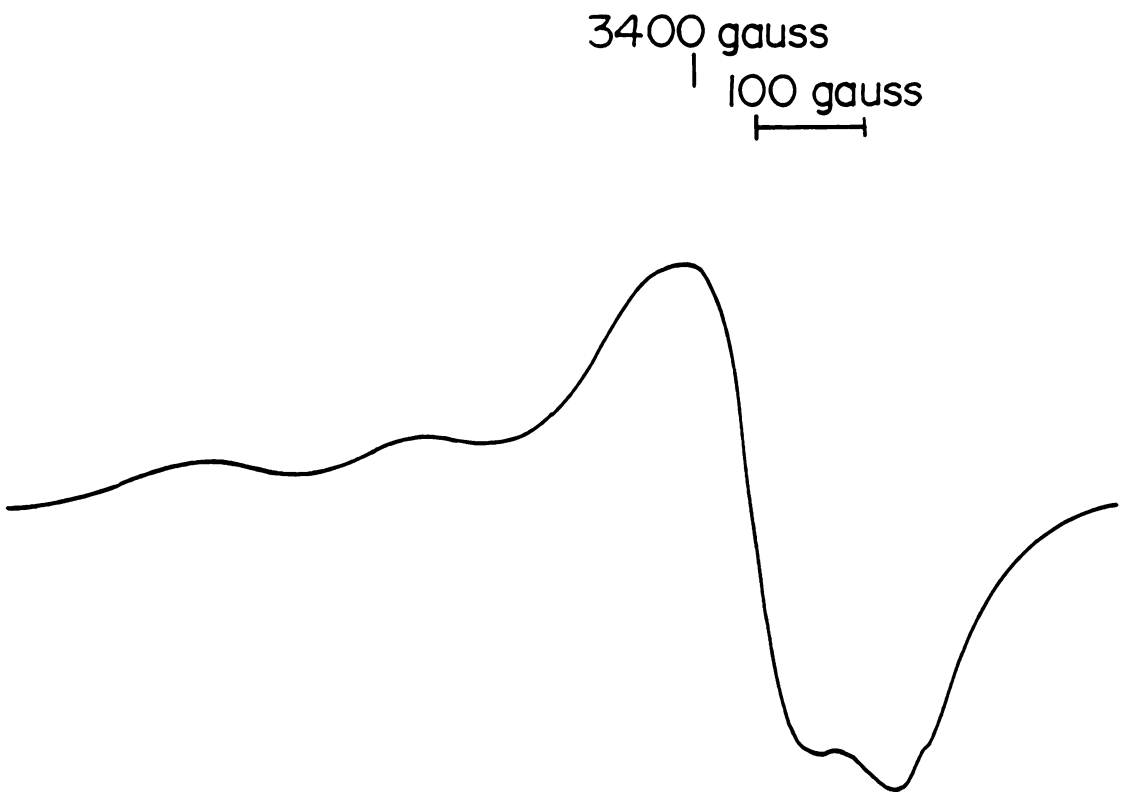

Figure 62. ESR spectrum of Cu 11.

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