Declaration

I declare that this thesis is my own composition, that the work of which it is a record was carried out by myself and that it has not been submitted in any previous application for a higher degree.

The thesis describes the results of research carried out in the Department of Chemistry, University of Edinburgh under the supervision of Dr. A.G. Rowley since 1st October 1978, the date of my admission as a research student.
I should like to thank Dr. A.G. Rowley for suggesting the topic of research, and for his constant advice and encouragement throughout the course of the work.

I also wish to thank the technical staff of the Department of Chemistry at the University of Edinburgh for the efficient provision of technical services, and Dr. A.B. MacKenzie of the Scottish Universities Research and Reactor Centre for carrying out the $^{210}$Pb counts. The excellent typing is the work of Mrs. C.G. Ranken to whom I am most grateful.

My thanks are also extended to my husband and parents for their encouragement and support.

Finally, thanks are due to the Science Research Council for financial support.
The following courses have been attended:
Principles and Applications of Spectroscopy in Organic Chemistry (12 lectures), Dr. D. Leaver and Dr. I.H. Sadler;
Organic Electrochemistry (5 lectures), Dr. A. Bellamy;
Strategy of Organic Synthesis (5 lectures), Dr. I. Gosney;
Heavy Metals (5 lectures), Dr. B. Heath;
The Bio-Organic Chemistry of Drugs, Toxins and other Xenobiotics (5 lectures), Dr. A.G. Rowley;
Flash Vacuum Pyrolysis (5 lectures), Dr. H. McNab;
Mass Spectrometry (5 lectures), Professor J.H. Beynon.
The preparation of various polystyrene supported chelating agents and their ability to adsorb metal ions from aqueous solution is described.

Several of the polymers initially investigated were shown to have poor metal adsorption properties. This was usually attributable to the hydrophobic characteristics of the individual polymers.

A material was developed which contained poly(maleic anhydride) units. This was prepared by the polymerisation of maleic anhydride using either polystyryl (diphenylphosphine) or polystyryl (ethyl pyridine) as initiator. Experimental results suggest that this polymer contains carbonyl and carboxylic acid functional groups and that an ion-exchange mechanism is involved in the chelating properties. The ability of this polymer to adsorb metal ions was shown to be particularly pronounced in the case of lead.
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APPENDIX
A. Polymer Supports

In recent years, there has been considerable research into the preparation and properties of chemically active species bound to polymer supports. They have been used as reagents\textsuperscript{1,2} and protecting groups\textsuperscript{3,4,5} in organic synthesis, as supports in solid-phase synthesis,\textsuperscript{6,7,8} and as supports for catalysts.\textsuperscript{9}

Both organic and inorganic materials have been used as the support matrices, but cross-linked polystyrene resins are frequently used because of their relative ease of functionalisation at the aromatic rings and their good mechanical properties.

One of the most important reactions in the functionalisation of cross-linked polystyrene is chloromethylation of the aromatic rings. The chloromethyl group acts as a 'handle' on the polymer which may subsequently be transformed into other functional groups.

Chloromethylation is carried out using a Lewis acid catalyst and chloromethyl methyl ether as solvent and reagent.\textsuperscript{10} Chloroform,\textsuperscript{11-14} methylene chloride,\textsuperscript{15} hexane\textsuperscript{16} and tetrahydrofuran\textsuperscript{17} have also been used as co-solvents. Anhydrous tin (IV) chloride\textsuperscript{10-14} was frequently used as the Friedel-Crafts catalyst, but more recently procedures utilising anhydrous zinc chloride\textsuperscript{15,17} or boron trifluoride\textsuperscript{16,18} as catalyst have been described.
Modification of the chloromethylated resin (1) leads to a wide range of resins carrying other functionalities, a selection of which is shown in Table 1. Of particular importance is the reaction of the chloromethylated polymer with tertiary amines, such as triethylamine and dimethyl-2-hydroxyethylamine, this being the main route for the synthesis of anion-exchange resins.

Another important reaction in the functionalisation of cross-linked polystyrene is lithiation, which may be performed either directly on the polymer using a mixture of n-butyl lithium and N,N,N',N'-tetramethylethylene diamine or indirectly by bromination of the polystyrene followed by a lithium-bromine exchange. Comparison of the two methods shows direct lithiation to be advantageous for its rapidity, whereas the indirect procedure gives better control over the degree of functionalisation as this is controlled by the initial bromination.

Several methods are available for the bromination of cross-linked polystyrene. The method of Heitz and Michels using ferric chloride as catalyst has been frequently used, but is reported to give unreproducible results or highly coloured resins lacking in homogeneity.

A second procedure involving the use of thallium acetate in stoichiometric amount has been described. Although this method produces a cleaner, more homogeneous polymer, it suffers from the drawback of involving an elaborate washing
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**TABLE 1**
procedure to remove any thallium residues. A re-investigation of this method\textsuperscript{47} showed that only a catalytic amount of thallium acetate was required and that the degree of functionalisation was easily controlled by adjusting the amount of bromine used. Aluminium trichloride,\textsuperscript{56} mercuric acetate,\textsuperscript{5} pyridine\textsuperscript{5} and iron powder\textsuperscript{57} have also been used as catalysts for the reaction.

A recent, detailed study\textsuperscript{47} of the lithium-bromine exchange indicates that the conversion depends on the degree of cross-linking in the polymer, its bromine content and the solvent used for the lithiation.

\begin{equation}
\begin{array}{c}
P \\
\text{Li}
\end{array}
\end{equation}

(2)

The lithiated polymer (2) is an important intermediate in the preparation of various functionalised resins (Table 2).

Of particular interest to this research is the use of modified resins in the removal of metal ions from aqueous solution.

Ion-exchange resins have, since their introduction thirty years ago,\textsuperscript{63} been used for the purification of water and pre-concentration of metal ions. Most of these materials are, however, non-specific in their operation and, more recently, resins have been prepared which contain bound chelating groups, several of which have shown good selectivity for particular metals.\textsuperscript{64,65} The major drawback of these resins is
that they are costly due to their production involving multi-stage syntheses. However, although they do not last indefinitely, they can often be regenerated many times, making them a more viable proposition.

Several methods are available for the synthesis of

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<td><img src="image1" alt="Structure1" /> COOH</td>
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<tr>
<td><img src="image2" alt="Structure2" /> CH₂CH₂OH</td>
<td>47</td>
</tr>
<tr>
<td><img src="image3" alt="Structure3" /> CH₂CH₂Br</td>
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<tr>
<td><img src="image4" alt="Structure4" /> SH</td>
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<tr>
<td><img src="image5" alt="Structure5" /> S(CH₂R)₂X⁻</td>
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<td><img src="image6" alt="Structure6" /> SCH₃</td>
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<tr>
<td><img src="image7" alt="Structure7" /> B(OH)₂</td>
<td>47,48</td>
</tr>
<tr>
<td><img src="image8" alt="Structure8" /> PPh₂</td>
<td>18,47,59-62</td>
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<td><img src="image9" alt="Structure9" /></td>
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TABLE 2
chelating resins\textsuperscript{66,67} and these may be broadly classified as follows:

i) Resin impregnates (enclosure compounds). This is probably the easiest and cheapest way of obtaining selectivity due to the simple preparation of the materials.\textsuperscript{68} The resin to be impregnated is soaked in a solution of the desired chelator in a suitable diluent which swells or penetrates the polymer. Once impregnation has been achieved the excess solvent is removed. This method does tend to produce a hydrophobic material,\textsuperscript{69} counteracted to a certain extent by soaking the resin in a dilute solution of sodium lauryl sulphate prior to use.\textsuperscript{70}

These resins have mainly been used in the extraction of copper,\textsuperscript{70-73} uranium\textsuperscript{69,72,74,75} and zinc.\textsuperscript{72,76,77}

ii) Condensation resins incorporating a chelating ligand. One of the first resins of this type produced\textsuperscript{78} was obtained by the polymerisation of an equimolar mixture of 8-hydroxyquinoline and resorcinol with formaldehyde. It was found to be effective in the chelation of copper.

iii) Condensation resins chemically converted to chelating resins. This method is of value when the chelating ligand is not sufficiently stable to survive the polymerisation procedure or where the deactivating effects of the chelating groups are such that the ligand will not enter into a condensation reaction with an aldehyde. An example of this is the o-phenylenebis(oxyacetic acid) resin prepared by Blasius and Kynast\textsuperscript{79} in which
(o-hydroxyphenoxY)acetic acid was condensed with formaldehyde and catechol, as a cross-linking agent, to give an insoluble resin. This was then treated with a hot, alkaline solution of sodium chloroacetate to convert the phenolic groups to phenoxyacetic groups. This resin is reported to have a high selectivity towards zirconium.

iv) Polymerisation of vinyl derivatives of chelate-forming compounds. This method is not of great importance in the manufacture of chelating resins because it is usually difficult and/or expensive to synthesise chelating compounds with vinyl groups attached. A polymer, containing 1,3-diketones, which is selective for iron has been prepared by this method.

v) Cross-linked vinyl polymers chemically converted into chelating resins. This is a main synthetic route to chelating resins, with cross-linked polystyrene being a popular substrate.

In addition to the methods of chloromethylation and lithiation previously discussed, a common route for the introduction of ligands is by nitration of the polymer, and then reduction to the amine followed by diazotisation and coupling of the diazotate to the ligand in alkaline solution. Ligands such as resorcinol, 8-hydroxyquinoline and salicylic acid have been incorporated by this method. This route does, however, tend to produce chelating polymers of low capacity due to the various side reactions which can occur at each stage in the synthesis, giving rise to impurities bound
into the structure, which cannot, of course, be washed out.

vi) Linear polymers chemically converted, in solution, to chelating polymers followed by cross-linking reactions. The starting polymer is usually polystyrene or polyethyleneimine. The latter may be cross-linked with a dihalogen compound such as ethylenedibromide or by reaction with epichlorohydrin to give a cross-linked exchanger, containing basic nitrogen as the sole donor atom, with high affinity for copper but lower affinity for cobalt, nickel and zinc.
B. Soil Organic Matter

The organic matter found in soils and natural waters consists of a mixture of plant and animal products at various stages of decomposition, and of substances synthesised from the breakdown products of these substances by micro-organisms. Soil organic matter is widely regarded as being directly involved in regulating the supply of micro-nutrients available for uptake by plants.

(a) Classification and structure

It is usual for these substances to be divided into two groups, non-humic substances and humic substances.

Non-humic substances are those compounds which still exhibit recognisable chemical characteristics, e.g. carbohydrates, amino acids, fats, proteins, peptides, waxes, resins and pigments. In general, these compounds are relatively susceptible to attack by micro-organisms in the soil and have a relatively short survival time.

The bulk of soil organic matter consists of humic substances. Although they have been known for about two centuries, their actual structure is still the subject of much research. They are amorphous, brown or black, hydrophilic, poly carboxylic acid, polydisperse substances of molecular weight ranging from several hundreds to tens of thousands. Humic substances are further divided into three main groups based on their solubility in acid and alkali as shown in Scheme 1.

Humic substances are not definite, single compounds, but consist of irregular two- or three-dimensional arrays of
SOIL ORGANIC MATTER

HUMIC MATTER

- FULVIC ACID
  - Soluble in acid and alkali
  - M.W. 300-2000

- HUMIC ACID
  - Soluble in acid only
  - M.W. 5000-10 000

- HUMIN
  - Insoluble in acid and alkali
  - M.W. 30 000-100 000

NON-HUMIC MATTER

- e.g. carbohydrates, amino acids, fats

![Scheme 1](image-url)
condensed and broken aromatic rings with no identifiable monomer units. This open structure is held together at least partly by hydrogen bonds among the functional groups.

It has been shown\textsuperscript{86} that fulvic acids have more aliphatic carbon atoms than humic acids and fewer aromatic carbon atoms than humic acids. All humic substances contain a large proportion of oxygen, 30–50\% w/w, most of which is contained in functional groups, in particular as aromatic and aliphatic carboxyl groups, phenolic hydroxyl groups and carbonyl groups.

Schnitzer and co-workers\textsuperscript{89} have used a variety of experimental techniques to ascertain the type and quantity of the functional groups present in fulvic acid. These methods have included functional group analysis, conductivity titrations, back titrations, x-ray diffraction and infra-red spectroscopy. Infra-red spectra have confirmed the presence of a large number of oxygen-containing functional groups, but more specific analysis is hindered as the absorption bands are broadened due to the overlapping of individual absorptions.

From this work, Schnitzer has concluded that the fulvic acid structure may be typically represented in part by Figure 1.

(b) Role of humic substances in soils

It has already been noted that soil organic matter is thought to be involved in the supply of micro-nutrients to plants. Only those micro-nutrients associated with soluble organic matter are likely to be readily available for uptake by plants and most likely means those associated with fulvic
Figure 1
acid. The insoluble organic matter probably acts as a reservoir of micro-nutrients.

It is widely believed that humic substances have a direct influence on the growth of plants.\textsuperscript{90} Again, this will involve the more soluble humic substances, in particular the fulvic acids, as only they are able to move freely between soil and plant.

Preliminary investigations\textsuperscript{90} indicated that it was probably the poly carboxylic acid content of fulvic acid which was involved, but proof was made virtually impossible due to the inability to obtain a pure poly carboxylic acid sample.\textsuperscript{91}

Anderson and Russell\textsuperscript{92} observed that fulvic acid was structurally very similar to the polymer obtained from the pyridine-catalysed homopolymerisation of maleic anhydride. This now made available a source of pure polycarboxylic acid to test the hypothesis.

Experiments have shown that poly maleic acid does possess growth-promoting properties, assayed by the growth response of excised tomato roots, comparable with natural fulvic acid.\textsuperscript{91} Fractionation of the synthetic polymer by ultra-filtration has shown that maximum physiological activity occurs in the weight range 500-1000 which is similar to that found in fulvic acid.\textsuperscript{91,93}

Evidence for the absorption of poly maleic acid through the roots of wheat and tomato plants and translocation into the shoots has been obtained by radioactive tracer techniques.\textsuperscript{94}

It is known that humic substances can absorb 1-17\% of their own weight of metal ion\textsuperscript{95,96} and spectrochemical
analysis\textsuperscript{97} of natural fulvic acids has shown that major amounts of the micronutrient cations iron, manganese, copper, zinc, cobalt and nickel are associated with the polycarboxylic acids. Thus it is proposed that the synthetic polymers may also be able to carry out this function.\textsuperscript{94}

It has been proposed by Gamble et al.\textsuperscript{98} that of the functional groups present in fulvic acid, complexation of any metal ion will involve one or more of three general types. These are:

i) phenolic OH groups which remain unneutralised except by prolonged reaction with concentrated strong base;

ii) carboxylic groups positioned ortho to the phenolic groups;

iii) all other ionisable functional groups, including some carboxyl groups meta to the phenolic groups.

A study of the chelation of Cu$^{2+}$ with model compounds\textsuperscript{99} has suggested that the following two reactions are both possible with fulvic acids:

\[
\text{Scheme 2}
\]
Schnitzer and Skinner\textsuperscript{100} were able to complex more iron and aluminium cations per gram of fulvic acid than could be accounted for by scheme 2 and concluded that Scheme 3 must occur alone or together with Scheme 2.

Further work\textsuperscript{101} involving the selective blocking of the various functional groups has shown that for copper, iron and aluminium, the largest reduction in retention is obtained when both the carboxylic acid and phenolic groups are blocked. This has led to the conclusion that Scheme 2 is the main mechanism for the complexation of these metals. Under these conditions, there was a residual retention of small amounts of these ions, which can be attributed to the incomplete blocking of the sites under investigation rather than being an indication of complexation to other sites.

Infra-red spectroscopic evidence\textsuperscript{102} has also indicated that carboxylate groups are involved in complexation, but such a study cannot invoke the involvement of other functional groups such as phenolic hydroxyl.
The relative stabilities of a series of metal-fulvic acid complexes have been determined\textsuperscript{103} and show the order to be:

\[
\text{Fe}^{3+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}
\]

The magnitudes of these stability constants are considerably lower than those for the same metal ion and a synthetic complexing ligand such as EDTA.
C. The Polymerisation of Maleic Anhydride

The ability to copolymerise maleic anhydride has been known for many years, whereas it was generally accepted that it could not be homopolymerised due to the steric hindrance imposed by the 1,2 disubstitution of the double bond of the monomeric species. Recently it has been demonstrated that maleic anhydride will readily undergo homopolymerisation under gamma- and ultra-violet irradiation as well as in the presence of free radical catalysts and various organic bases. These methods will be discussed in more detail in the following sections, particular attention being paid to the reactions involving free radical or ionic catalysts.

(a) Gamma radiation

Early attempts to polymerise maleic anhydride in the crystalline state using γ-radiation proved unsuccessful, but later experiments by another group of workers showed that irradiation of a melt gave a low yield of polymer.

Solution polymerisation in a variety of solvents was also attempted usually acetic anhydride, benzene and 1,4 dioxane. Poor yields of polymer (ca 20%) were obtained using benzene as solvent and a variety of by-products, including a 2:1 maleic anhydride-benzene adduct (3), carbon dioxide, carbon monoxide and acetylene were also obtained.

Analysis of the polymer showed it to be richer in carbon and hydrogen than would be expected for poly (maleic anhydride) and it is suggested that this is due to the incorporation of
3-4 benzene molecules per 6 maleic anhydride molecules.\textsuperscript{114}

(b) \textbf{Ultra-violet radiation}

A solid coating of maleic anhydride on the inner surface of a glass tube produced the dimer\textsuperscript{115} cis,trans,cis-1,2,3,4-cyclobutanetetracarboxylic acid dianhydride (4) upon irradiation for 10 days.

This product, as well as an oligomer containing four maleic anhydride derived units and one dioxane unit per molecule, was also obtained by irradiation of a dioxane solution of maleic anhydride.\textsuperscript{116}
As in the case of $\gamma$-irradiation, a 2:1 adduct is formed when a solution of maleic anhydride in benzene is photolyzed. It was thus proposed that formation of the adduct follows the same path in both instances (Scheme 4). The initial step being the electronic excitation of the precursor of the 1:1 adduct (5), which is assumed to be either maleic anhydride or its charge-transfer complex with benzene, followed by the formation of the 1:1 adduct and the Diels-Alder addition of maleic anhydride to this adduct (5) to form the 2:1 adduct (3). Later trapping experiments with
tetracyanoethylene\textsuperscript{118} indicated that the 1:1 adduct was not formed during the irradiation of maleic anhydride in benzene. As the excited forms of the 1:1 maleic anhydride-benzene complex are precursors of the final 2:1 photoadduct, it was concluded that the latter resulted from the reaction of a photoexcited 1:1 complex with an unexcited molecule of maleic anhydride. It was also observed that the 2:1 adduct (5) was formed on the addition of the photosensitiser benzophenone to the reaction mixture and the whole exposed to sunlight.\textsuperscript{119}

Further photosensitised reactions of solutions of maleic anhydride\textsuperscript{120} in which chloroform, p-xylene or ethereal solutions of durene, biphenyl, naphthalene or phenol were used in place of benzene produced a near colourless solid polymer consisting mainly of maleic anhydride residues on exposure to sunlight. Although these reactions were only inhibited by the addition of relatively large (up to 5\%) amounts of hydroquinones, it was concluded that the polymerisation was a radical process.

(c) Shock waves

Spontaneous polymerisation of crystalline maleic anhydride has been achieved\textsuperscript{121} by the use of high pressures (>20,000 atm) and has also been observed when the solid monomer is subjected to intense pressures and temperatures in shock waves generated by detonation.\textsuperscript{122} The yield of polymer under these conditions is low\textsuperscript{123} and thus very little work has been carried out to determine the structure of the polymer, although its infra-red spectrum indicates that it
is not the cyclic dimer (4) and shows similarities to the infra-red spectrum of the product of solution polymerisation initiated by γ-rays. 124

(d) Free radical catalysts

Maleic anhydride has been shown to homopolymerise in the presence of free radical catalysts but in poor yield at 'normal' catalyst concentrations (~1 w/w %).

Improved yields of up to 85% can be obtained by the use of higher concentrations of catalyst (up to 25%) and by carrying out the reaction in a suitable solvent, e.g. benzene, toluene, chloroform, decalin, tetrahydrofuran.

Polymerisation of maleic anhydride with varying amounts of dibenzoylperoxide shows a tendency to "dead-end" polymerisation with a significant amount of unreacted polymer remaining even when the initiator proportion is greater than 10%. 125 This is assumed to be due to the rapid consumption of initiator by side reactions. Production of a high molecular weight polymer has been attained by the continuous addition of dissolved catalyst to the reaction mixture. 126

A detailed investigation into the radical initiated homopolymerisation of maleic anhydride was carried out by Braun and co-workers 127 in which they studied the reactions involving azobisisobutyronitrile, dibenzoylperoxide, o-dichlorobenzoyl peroxide, lauroyl peroxide and di-isopropylpercarbonate.

Carbon dioxide evolution had already been observed 128,129 and it was hoped to provide a mechanism for this.

The NMR spectra of the resulting polymers, 127 mainly in
the case of dibenzoyl peroxide as initiator, did not show a single, unique resonance of CH protons as would be expected from a homopolymer resulting from double bond addition (6) but had a number of resonances which indicated that there were CH$_2$ and COOH moieties present in the chain and it was presumed that the polymer contained units of succinic anhydride and cyclopentanone derivatives.

The proposed mechanism (Scheme 5) involves the addition of the initiator radical to a molecule of maleic anhydride. The resulting succinic anhydride radical adds to another maleic anhydride molecule and this is followed by proton transfer to form a free carboxyl group and a cyclopentanone unit. The resulting carboxyl group can be decarboxylated thermally or by reaction with another initiator radical. This is in keeping with the proposal that decarboxylation occurs simultaneously with and as a part of polymerisation.

Results from a recent re-investigation of this work by Backsai$^{130}$ are consistent with the structure of the polymer being an unrearranged poly (maleic anhydride) and not with
the cyclopentanone structure proposed by Braun.

It is well established that the first step in the decomposition of dibenzoyl peroxide is the scission of the oxygen-oxygen band to give two benzoate radicals, which may
further decompose by loss of carbon dioxide to give two phenyl radicals\textsuperscript{131} (Scheme 6).

\[
\text{Ph}\text{C}-\text{O}-\text{O}-\text{C}\text{Ph} \rightarrow 2 \text{PhC}-\text{O}^\cdot \rightarrow 2 \text{Ph}^\cdot + 2\text{CO}_2
\]

Scheme 6

A quantitative investigation of the carbon dioxide evolved during radical induced polymerisation of maleic anhydride showed that the amount generated was less than the maximum which could be accounted for by decomposition of the radical initiator, thus there was no direct evidence for polymer decarboxylation.

In an experiment using di-tert-butylperoxide, which does not form carbon dioxide on decomposition, as initiator, a small amount of carbon dioxide was detected indicating that maleic anhydride decarboxylates slightly during polymerisation. Even if it is assumed that in both cases all the carbon dioxide originates from the maleic anhydride, the extent of decarboxylation is minimal and hence the deviations from the normal poly (maleic anhydride) structure must be minor.

Further evidence that the proposed polycyclopentanone structure is incorrect is provided by the absence of the n.m.r. resonance at 1.46 due to the CH\textsubscript{2} groups of the cyclopentanone structure. Repetition of Braun's experiment
suggests that this resonance is caused by the solvent, decalin, present either as an impurity or as an incorporated solvent oligomer.\textsuperscript{130}

More detailed nuclear magnetic resonance experiments\textsuperscript{132} have shown the structure of the polymer to be poly(2,5-dioxo-tetrahydrofuran-3,4-diyl) (6) and confirm that the mechanism of the initiation step is as shown in Scheme 7.

\[
\text{PhC-O-O-CPh} \rightarrow 2 \text{Ph}^+ + 2 \text{CO}_2
\]

\begin{equation}
\text{Scheme 7}
\end{equation}

(e) Ionic Catalysts

Treatment of maleic anhydride with catalytic amounts
of tertiary amines produced a dark, brittle polymeric material soluble in polar solvents.\textsuperscript{133-139} Evolution of carbon dioxide was observed during the reaction. Analysis of the polymer suggested that the amines were acting only as catalysts as no nitrogen was detected in the product.

As well as the use of tertiary amines as catalysts, some workers have studied the reaction of tervalent phosphorus compounds, in particular tributylphosphine and triphenylphosphine, with maleic anhydride.\textsuperscript{136,140}

Decarboxylation occurred during the reaction of tributylphosphine or triphenylphosphine with maleic anhydride in benzene, tetrahydrofuran or dimethylsulphoxide. The structures of the polymers so produced were complex, but were considered to consist of a mixture of succinic anhydride, cyclopentanone and conjugated keto-olefinic units. By careful control of the reaction conditions, Zweifel and Volker\textsuperscript{140} were able to produce polymers of more defined structure.

The first step in the reaction catalysed by triphenylphosphine is the formation of the previously isolated ylide\textsuperscript{141} (7) which then adds to monomer to produce a structure containing succinic anhydride units (Scheme 8).
Further rearrangement of this structure leads to the presence of cyclopentanone derivatives (Scheme 9).
A polymer consisting entirely of conjugated keto-olefinic units was obtained using tributyl phosphine as initiator (Scheme 10).

A number of workers have studied the polymerisation of maleic anhydride in the presence of pyridine under a variety of conditions, and there are a number of structures proposed for the polymer, and the mechanism by which it is obtained.

The reaction between pure pyridine and maleic anhydride proceeded very slowly with the formation of oligomeric and polymeric products. Protic reagents such as water, maleic acid, acetic acid and pyridinium hydrochloride were found to catalyse the reaction. Radical inhibitors such as sulphur, 2,2-diphenyl-1-picryl hydrazyl, hydroquinone, 1,3,5-trinitrobenzene and anthracene had no influence on the reaction and ESR spectroscopic investigations
proved the absence of ESR signals indicating a radical species.\textsuperscript{138} There is thus general agreement among the various groups of workers that a radical mechanism is not in operation.
As in the case of the tervalent phosphorus initiated reactions, polymers containing conjugated keto-olefinic, succinic anhydride and cyclopentanone units have been proposed. Shopov\textsuperscript{134} has indicated that the polymer obtained with pyridine is a predominantly cis-polyvinylene ketoanhydride structure, formed as a result of a ring-opening polymerisation followed by decarboxylation, (Scheme II) with some cyclopentanone and succinic anhydride units.

\begin{center}
\begin{tikzpicture}
  \node[draw,circle] (circle) at (0,0) {Pyridine};
  \node[draw,rectangle] (rectangle) at (2,0) {Cyclopentanone units};
  \node[draw,rectangle] (rectangle2) at (4,0) {Succinic anhydride units};

  \draw[->] (circle) -- (rectangle);
  \draw[->] (rectangle) -- (rectangle2);

  \node[anchor=west] at (0,-1) {Scheme II};
\end{tikzpicture}
\end{center}
It has recently been suggested\textsuperscript{143} that the structures of and mechanisms proposed for pyridine initiated poly(maleic anhydride) are inconsistent because it has not been taken into account that the polymer can undergo structural changes under the influence of heat or certain solvents e.g. ketones, acetic anhydride. Although these workers have not as yet reported a detailed structure for the polymer, they have spectroscopic evidence for a 2:1 maleic anhydride: pyridine compound as a reaction intermediate (Scheme 12).

Scheme 12
**EXPERIMENTAL**

**A. Symbols and Abbreviations**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p.</td>
<td>boiling point</td>
</tr>
<tr>
<td>m.p.</td>
<td>melting point</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>sh</td>
<td>shoulder</td>
</tr>
<tr>
<td>$T_b$</td>
<td>titre for reagent blank</td>
</tr>
<tr>
<td>$T_s$</td>
<td>titre for sample</td>
</tr>
<tr>
<td>$W_s$</td>
<td>sample weight/g</td>
</tr>
</tbody>
</table>
B. Instrumentation

Nuclear Magnetic Resonance Spectroscopy

a) Routine $^1H$ n.m.r. spectra were recorded on a Varian EM360 spectrometer. 100MHz spectra were obtained using a Varian HA100 spectrometer operated by Mr. J.R.A. Millar. Chemical shifts ($\delta_H$) are measured in parts per million relative to tetramethylsilane (T.M.S.) as internal standard ($\delta=0.0$).

b) $^{13}C$ n.m.r. spectra were recorded on a Varian CFT20 spectrometer operated by Mr. J.R.A. Millar. Chemical shifts ($\delta_C$) are measured in parts per million relative to tetramethylsilane ($\delta=0.0$).

Infra-red Spectroscopy

I.R. spectra were recorded on a Perkin-Elmer 157G grating spectrophotometer. Samples were recorded as potassium bromide discs unless otherwise stated.

Ultra-violet Spectroscopy

U.V. spectra were recorded on a Unicam SP800 spectrophotometer. Solutions of samples were prepared in dry benzene.

Mass Spectroscopy

Mass spectra were recorded on an Associated Electrical Industries MS902 mass spectrometer operated by Mr.D. Thomas.
Atomic Absorption Spectrometry

Analyses of metal ion solutions were obtained using a Hilger Watts Atomspek spectrophotometer and a Pye-Unicam SP 9-800 spectrophotometer.

Melting Points

Melting points of new compounds were obtained on a Kofler hot-stage apparatus. Routine melting points were obtained using open capillary tubes and Gallenkamp apparatus.

Thin-layer Chromatography

Chromatograms were developed on 0.33 mm layers of alumina (Merck, Aluminium Oxide G) or silica (Merck, Silica Gel G) containing Woelm fluorescent green indicator (0.5%). Components of the chromatogram were detected by their quenching of fluorescence under U.V. light or by their absorption of iodine.

Elemental Analysis

Routine carbon, hydrogen and nitrogen microanalyses were obtained using a Perkin-Elmer model 240 analyser operated by Mr. J. Grunbaum. Microanalyses of bromine and phosphorus were carried out by Butterworth Laboratories.

C. Functional Group Analysis

I. Chlorine

Analysis for chlorine in chloromethylated polymers was carried out by a modified Volhard method\textsuperscript{144,145}. 
The resin (~200 mg) was heated in pyridine (3 ml) for 2 h at 100°C. This mixture was then transferred quantitatively to a conical flask using 50% acetic acid (30 ml). Concentrated nitric acid (5 ml) and ferric alum indicator 146 (5 drops) were added and the solution stirred slowly on a magnetic stirrer during the addition of standard 0.1M silver nitrate solution (10 ml). The stirrer was turned off and the mixture allowed to stand for 5 min. Water (50 ml) and toluene (25 ml) were added and the mixture stirred rapidly to coat the precipitated silver chloride with a layer of toluene and thus prevent it reacting further with the thiocyanate ion. The remaining silver nitrate is then back-titrated with standard 0.1M ammonium thiocyanate solution until a permanent, faint red-brown coloration is produced. This is the end-point. It is essential to maintain the vigorous stirring throughout the titration.

A reagent blank should be set up and titrated in a similar manner.

The calculations are as follows:

\[
\frac{(T_b - T_s) \times \text{molarity NH}_4\text{SCN}}{W_s} = \text{mmol chlorine/g of resin}
\]

The amount of ionically bound chlorine is determined by the same procedure except that the initial reaction of the resin with pyridine is omitted.

II. Active hydrogen and total acidity

The sample is allowed to react with an excess of barium hydroxide (Scheme 13).
Ba(OH)$_2$ + 2HA $\rightarrow$ BaA$_2$ + 2H$_2$O

Scheme 13

The barium hydroxide remaining after the reaction is then back-titrated with standard acid.

The resin (≈200 mg) is placed in a ground-glass stoppered conical flask and 0.20N barium hydroxide solution (20 ml) added. The air in the flask is displaced by nitrogen, the flask stoppered and shaken for 24 h at 20°C. A reagent blank consisting of 0.20N barium hydroxide solution (20 ml) only is set up simultaneously.

After 24 h the suspension is filtered and the residue washed thoroughly with carbon dioxide free distilled water. The filtrate and washings are combined and titrated potentiometrically to pH 8.4 with standard 0.5M hydrochloric acid. Nitrogen is bubbled slowly through the solution during the titration.

The calculations are as follows:

\[
\frac{(T_b - T_s) \times \text{molarity HCl}}{W_s} = \text{mequiv total acidity/g of resin}
\]

III. Carboxyl groups

The sample is reacted with calcium acetate and the acetic acid liberated (Scheme 14) is titrated with standard sodium hydroxide solution.
\[ 2 \text{RCOOH} + (\text{CH}_3\text{COO})_2\text{Ca} \rightarrow (\text{RCOO})_2\text{Ca} + 2\text{CH}_3\text{COOH} \]

Scheme 14

The resin (\(\approx 200\) mg) is placed in a ground-glass stoppered conical flask to which is added 1.0N calcium acetate solution (10 ml) and carbon dioxide free distilled water (40 ml), and the flask is then stoppered. A blank is set up at the same time. The mixture is shaken for 24 h at 20\(^\circ\)C, after which time the suspension is filtered. The residue is washed with carbon dioxide free distilled water and the combined filtrate and washings titrated potentiometrically with standard 0.1M sodium hydroxide solution to pH 9.8.

The calculations are as follows:

\[
\frac{(T_s - T_b) \times \text{molarity NaOH}}{W_s} = \text{mequiv carboxyl groups/g of resin}
\]

IV. Carbonyl groups

Carbonyl groups are determined by their reaction with excess hydroxylamine (Scheme 15).

\[
\begin{align*}
\text{R}_1\text{C}=\text{O} + \text{NH}_2\text{OH.HCl} & \quad \rightarrow \quad \text{R}_1\text{C}==\text{NOH} + \text{HCl} + \text{H}_2\text{O} \\
\text{R}_2 & \quad \text{R}_2
\end{align*}
\]

Scheme 15
The hydroxylamine remaining after the reaction is back titrated with standard acid.

To the resin (\(\sim 200\) mg) in a conical flask is added 0.25M 2-dimethylaminoethanol solution (5 ml) and 0.4M hydroxylammonium hydrochloride solution (6.5 ml). A reagent blank is set up simultaneously. The mixture is heated on a steam bath for 1 h, cooled, and a few drops of thymol blue indicator solution added. The solution is then titrated with standard 0.1M perchloric acid, the end-point being detected by the indicator solution changing colour from yellow to red.

The calculations are as follows:

\[
\frac{(T_b - T_s) \times \text{molarity HClO}_4}{W_s} = \text{mequiv carbonyl groups/g of resin}
\]

D. Preparation of Materials

I. Dry solvents

Acetone was heated under reflux with successive quantities of potassium permanganate until the violet colour persisted. It was dried over anhydrous potassium carbonate, filtered from the desiccant and distilled. Benzene was dried over sodium wire. If required 'super-dry', the dry benzene was distilled from lithium aluminium hydride in a dry nitrogen atmosphere and stored over molecular sieve. Carbon tetrachloride and chloroform were passed through a column of alumina.

Dimethoxyethane was stored over sodium hydroxide pellets and then distilled from calcium hydride in an atmosphere of dry nitrogen.

Tetrahydrofuran was distilled from lithium aluminium hydride and stored over molecular sieve.
II. **Reagents**

Except for the compounds described below, reagents were used as commercially available.

Commercial benzaldehyde was washed with portions of 10% sodium carbonate solution until carbon dioxide evolution ceased and dried over anhydrous magnesium sulphate. The filtered benzaldehyde was distilled under reduced pressure.

4-Picoline was stirred with barium oxide overnight, filtered and fractionally distilled under reduced pressure.

Anhydrous potassium carbonate was heated at 100°C in an oven for 2 h, then cooled in a desiccator before use.

---

E. **Alkylation of 8-diketones and related compounds**

I. **Pentane-2,4-dione**

1) **Sodium hydride in dimethoxyethane**

Sodium hydride (3.0 g, 62.5 mmol; 50% dispersion in mineral oil) was added to a stirred solution of pentane-2,4-dione (6.0 g; 60 mmol) in dry dimethoxyethane (50 ml). To this mixture, benzyl bromide (12.0 g; 70 mmol) was added drop-wise and the mixture stirred at room temperature for 17 h. Ether (100 ml) was added and the reaction mixture added cautiously to ice-cold water (100 ml). The ethereal solution was separated, dried over magnesium sulphate and evaporated to give a yellow oil which was distilled on a Kugelrohr apparatus at 125°C at 0.7 mmHg to yield pure 3-benzylpentane-2,4-dione (5.02 g; 26.4 mmol; 38%) (lit\textsuperscript{147} b.p.150°C at 3 mmHg). The distillation residue was recrystallised from
40-60 petrol to yield 3,3-dibenzylpentane-2,4-dione (1.59 g; 5.7 mmol; 16%) m.p. 112-113°C (lit. 148 113.2-113.4°C). This represents a total conversion of 54% based on the alkylating agent.

ii) Potassium carbonate in dimethylformamide

Pentane-2,4-dione (10.01 g; 100 mmol) was added to a stirred suspension of anhydrous potassium carbonate (27.64 g; 200 mmol) in dry dimethylformamide (100 ml). A solution of benzyl chloride (13.42 g; 106 mmol) in dry dimethylformamide (20 ml) was added dropwise over 30 min. The mixture was stirred at room temperature for a further 4 h before being poured onto cold water (250 ml). This was extracted with ether (3x75 ml) and the ether solution itself washed with water (5x50 ml). The organic phase was dried over magnesium sulphate, filtered and concentrated to give a solid which was filtered off and recrystallised from 40-60 petrol to yield 3,3-dibenzylpentane-2,4-dione (1.58 g; 5.6 mmol; 11%) m.p. 112.5-113°C (lit. 148 113.2-113.4°C). Distillation of the filtrate gave pure 3-benzylpentane-2,4-dione (7.54 g; 39.6 mmol; 40%) b.p. 143-144°C at 1.4 mmHg (lit. 147 150°C at 3 mmHg). This is a total conversion of 48% based on the alkylating agent.

iii) Potassium carbonate in acetone

A mixture of pentane-2,4-dione (11.11 g; 111 mmol), benzyl bromide (11.8 ml; 99 mmol) and anhydrous potassium carbonate (13.82 g; 100 mmol) in dry acetone (20 ml) was heated under reflux for 2 h with the exclusion of moisture. The reaction mixture was cooled to room temperature and the solids filtered off and washed thoroughly with acetone (5x50 ml). The solvent
was removed in vacuo, the crystalline solid filtered off and washed with a little cold ether to yield 3,3-dibenzylpentane-2,4-dione (2.46 g; 8.8 mmol; 17.8%) m.p. 110.5-111.5°C (lit148 113.2-113.4°C). The yellow filtrate was distilled under reduced pressure to give 3-benzylpentane-2,4-dione (7.80 g; 41.0 mmol, 41.4%) b.p. 91-92°C at 0.25 mmHg (lit147 150°C at 3 mmHg). The total conversion based on the alkylating agent was 59.2%.

II 2,2,6,6-Tetramethylheptane-3,5-dione (dipivaloylmethane)

i) Potassium carbonate in acetone

Dipivaloylmethane (0.740 g; 4.02 mmol), benzyl chloride (0.625 g; 4.94 mmol) and anhydrous potassium carbonate (0.522 g; 3.78 mmol) were heated under reflux in dry acetone (20 ml) with the exclusion of moisture for 20 h. After cooling to room temperature, the solids were filtered off on a sintered funnel and washed thoroughly with acetone. The solvent was removed and the residue distilled in vacuo to give recovery of the starting materials.

ii) Sodium hydride in dimethoxyethane

Dipivaloylmethane (0.924 g; 5 mmol) in dry dimethoxyethane (3 ml) was added dropwise to a stirred suspension of sodium hydride (0.282 g; 5.9 mmol; 50% dispersion in mineral oil) in dry dimethoxyethane (3 ml). The resulting mixture was stirred and heated under reflux for 3 h, after which time benzyl bromide (0.6 ml; 5 mmol) in dry dimethoxyethane (7 ml) was added dropwise. Reflux was continued for a further 37 h after which time the reaction mixture was cooled
to room temperature and the solvent removed in vacuo. The residue was mixed with ice (20 ml) containing 10% hydrochloric acid (1 ml). The insoluble material was extracted into chloroform (2x10 ml), washed once with water (10 ml) and dried over molecular sieve. Removal of the chloroform in vacuo gave a white, crystalline solid 4-benzyl-2,2,6,6-tetramethylheptane-3,5-dione (1.07 g; 3.9 mmol; 78%) m.p. 66.5-67°C (lit. 149 68-69°C).

III Preparation of 4-amino-pent-3-en-2-one

This was prepared by a modification of the method of Lacey\textsuperscript{150}.

Concentrated aqueous ammonia (30 ml) was added dropwise to pentane-2,4-dione (20 g, 200 mmol) and the mixture left at room temperature overnight. The reaction mixture was saturated with sodium chloride and extracted with ether (5x50 ml). The combined organic phases were concentrated and the residue distilled under reduced pressure. The fore-run consisted of unreacted pentane-2,4-dione and the fraction boiling at 115-116°C at 24 mmHg was collected to give 13.5 g (136 mmol; 68%) of the desired product, m.p. 40-42°C (lit. 151 43°C).

IV Preparation of 2-amino-3-benzylpent-2-en-4-one

3-Benzylpentane-2,4-dione (3.80 g; 20 mmol) was stirred with concentrated aqueous ammonia (3 ml) in a stoppered flask for 24 h. The reaction mixture was extracted with ether (2x25 ml), dried and concentrated. The residue was distilled in a Kugelrohr apparatus to give 2-amino-3-benzylpent-2-
en-4-one (1.17 g; 31%) b.p. 150°C at 0.45 mmHg, m.p. 73-73.5°C. (Found: C, 76.4; H, 8.0; N, 7.2. C_{12}H_{15}NO requires C, 76.2; H, 8.0; N, 7.4%). δ_H (CDCl_3): 1.87 (s, 3H, CH_3), 1.96 (s, 2H, 2NH_2), 2.02 (s, 3H, CH_3), 3.64 (s, 2H, CH_2), 7.14 (s, 5H, ArH). m/e 189 (M^+, 100%), 174 (54), 146 (27), 129 (30), 91 (36). ν_{max} (nujol mull) 3340, 3190, 2920, 2860, 1597, 1562 (sh), 1400, 1356, 1292, 948 cm^{-1}.

F. Preparation of polymer supported reagents

I. Preparation of polymer bound 6-diketones

The polymer used in the preparation of these resins was macroporous, crosslinked polystyrene beads (20-50 mesh) as available from Aldrich which were firstly chloromethylated by the method of Relles and Schluenz. Thus the resin (25 g) was allowed to swell in chloromethylmethyl ether (100 ml) and the mixture saturated with boron trifluoride. The reaction mixture was stirred for 3 h at 25°C, the product filtered off on a Buchner funnel and washed thoroughly with methylene chloride:methanol (2:3, 3:1, 9:1, 500 ml of each) and finally with pure methylene chloride (750 ml). The product was dried at 50°C at 0.3 mmHg for 16 h, yielding 36.5 g. Its chlorine content was found to be 6.4 mmol g^{-1}.

i) Polymer bound pentane-2,4-dione

Chloromethylated resin (15.0 g; 96 mmol) chloromethyl residues), pentane-2,4-dione (10.12 g; 100 mmol), anhydrous
potassium carbonate (13.27 g; 96 mmol) and dry acetone (150 ml) were heated under reflux with the exclusion of moisture for 72 h. The reaction mixture was allowed to cool to room temperature, and the solids filtered off on a Buchner funnel. These were washed thoroughly with acetone, water (to remove the potassium carbonate), acetone and ether prior to drying for 16 h at 30°C at 1 mmHg. This yielded 15.8 g of a pale yellow polymer containing 3.5 mmol Cl·g⁻¹, indicating a functional yield of ~55%. In an attempt to improve on this functional yield, the experiment was repeated under the same conditions using the partially reacted product from the first attempt. In the course of this second reaction, the polymer beads disintegrated and, after work-up as previously, 13.8 g of a fine powder containing 3.35 mmol Cl·g⁻¹ was obtained.

The infra-red spectrum of the polymer showed two carbonyl absorptions at 1585 cm⁻¹ and 1690 cm⁻¹ due to the keto and enol forms of the structure.

ii) Polymer bound dipivaloylmethane

Sodium hydride (5.43 g; 113 mmol; 50% dispersion in mineral oil) was suspended in dry dimethoxyethane (60 ml). To this was added dropwise a solution of dipivaloylmethane (17.69 g; 96 mmol) in dry dimethoxyethane (60 ml) and the resulting mixture heated, with stirring, under reflux for 2 h with the exclusion of moisture. Chloromethylated resin (15.0 g; 96 mmol chloromethyl residues) was added and reflux continued for a further 5 days. The solid products were filtered off on a Buchner funnel and washed thoroughly with ether and acetone. The resulting fine powder was dried at
40°C at 0.4 mmHg for 18 h, yielding 19.3 g. Its chlorine content was found to be 4.1 mmol g⁻¹, indicating a functional yield of ∼36%.

The infra-red spectrum of the polymer showed two carbonyl absorptions at 1705 cm⁻¹ and 1725 cm⁻¹.

II. Preparation of resin impregnated tetraphenylporphyrin

meso-Tetraphenylporphyrin was prepared by the method of Adler and co-workers.  

Thus, pyrrole (28 ml; 0.4 mol) and benzaldehyde (40 ml; 0.4 mol) were added to refluxing propionic acid (1.5 l) and the mixture refluxed for a further 30 min. The reaction mixture was cooled to room temperature and the product filtered off on a sintered funnel. The purple crystals were washed thoroughly with methanol, then once with hot water and dried at 20°C at 1 mmHg for 16 h to yield 6.22 g (10%) of purple-blue crystals. A further crop of the desired product was obtained by concentration of the mother liquors to give a total yield of 8.96 g (14%). \[\delta H (CDCl_3) \text{-}2.9 (2H, s), 7.80 (12H, m), 8.30 (8H, m), 8.90 (8H, s)\]  

The porphyrin as prepared by this method is known to contain a significant amount of tetraphenyl chlorin as impurity. However, the porphyrin may be obtained in the pure form by the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone following the method of Rousseau and Dolphin.  

Crude tetraphenylporphyrin (2 g; 3.2 mmol) was dissolved in refluxing toluene (1 l) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.5 g; 2.2 mmol) added in one portion. After refluxing for a further 30 min, the reaction mixture was
cooled to room temperature and extracted with a 1% aqueous sodium hydroxide solution (1%) containing sodium dithionite (1 g). The organic layer was washed with water (3x150 ml) and dried over anhydrous sodium sulphate. The desiccant was filtered off and the solvent removed in vacuo. The product was recrystallised from a mixture of dichloromethane and methanol to yield 1.82 g (91%). The purity of the product was checked by recording its visible spectrum which indicated that there was still about 2% of the chlorin present. This was, however, considered to be sufficiently pure for further use.

The impregnated resin was prepared by dissolving tetraphenylporphyrin (4.6 g; 7.5 mmol) in dichloromethane (25 ml). To this was added Amberlite resin XAD-2 (10.0 g). The mixture was stirred at room temperature for 7 days after which time the polymer was filtered off on a sinter and dried at 50°C at 1 mmHg for 8 h to yield 14.4 g of purple polymer beads.

III. Preparation of polymer bound poly(maleic anhydride)

This was prepared as a graft polymer of maleic anhydride onto polystyryl(diphenylphosphine), polystyryl(ethyl pyridine), or poly(4-vinyl pyridine-co-styrene).

i) Preparation of polystyryl(diphenylphosphine)

This was prepared from brominated polystyrene by the method of Farrall and Frechet. The brominated polymer was obtained by the methods of Card and Neckers and Farrall and Frechet.

Amberlite XAD-2 resin (50 g) was allowed to swell in dry
chloroform (500 ml) for 30 min prior to the addition of aluminium chloride (1 g; 7.5 mmol) and bromine (12 ml; 234 mmol). The resulting mixture was stirred at room temperature for 48 h, the polymer filtered off on a sinter and washed thoroughly with benzene, acetone, water, acetone, n-hexane and ether. The product was firstly air dried and then at 40°C at 0.5 mmHg overnight to yield 59.1 g of pale yellow polymer which was found to contain 21.6% bromine. This corresponds to a functional loading of 2.7 mmol.g⁻¹.

An alternative method of bromination giving a higher functional loading involved the use of a thallium(III) salt in a catalytic amount.

Macroporous polystyrene (20 g) as available from Aldrich was suspended in dry carbon tetrachloride (300 ml). Thallic chloride (1.21 g; 3.2 mmol) was added, the reaction mixture stirred in the dark for 30 min and bromine (32 g; 200 mmol) in dry carbon tetrachloride (50 ml) added dropwise. After being stirred in the dark at room temperature for a further hour, the reaction mixture was heated under reflux for 1½ h. The product was filtered off on a Buchner funnel and washed thoroughly with carbon tetrachloride, acetone, acetone-water (2:1), acetone, benzene and methanol. The polymer was dried at 40°C at 0.5 mmHg for 18 h to yield 32 g of resin containing 41.1% bromine. The functional loading of 5.1 mmol of bromine per gram indicates that bromination has occurred at every available phenyl residue.

Brominated Amberlite XAD-2 (25 g; 67.5 mmol bromine residues) was added to "superdry" tetrahydrofuran (300 ml) in a 3-neck round bottom flask fitted with a dry nitrogen inlet
and rubber septum. To this was added n-butyl lithium (70 ml of 1.4M solution in n-hexane, 98 mmol) and the reaction mixture stirred at room temperature for 1½ h. The liquid phase was decanted off in a dry nitrogen atmosphere and "super-dry" tetrahydrofuran (300 ml) added to the flask. A further portion of n-butyl lithium (70 ml of 1.4M solution in n-hexane, 98 mmol) was added and the mixture stirred under dry nitrogen for a further 1½ h at room temperature. The liquid phase was again decanted off in a dry nitrogen atmosphere and "super-dry" tetrahydrofuran (200 ml) added.

Chlorodiphenylphosphine (50 ml; 270 mmol) was added dropwise with stirring and the mixture stirred under dry nitrogen for 18 h. The polymer was filtered off on a Buchner funnel and washed with tetrahydrofuran, ether, tetrahydrofuran-water (2:1), water and tetrahydrofuran.

It was observed during the course of these reactions that the polymeric beads were disintegrating to a fine powder which was considered to be unsuitable for further use.

The complete reaction sequence was repeated using a 3% cross-linked macroporous polystyrene as available from Aldrich with a shorter reaction time at each step during lithiation.

Bromination with aluminium chloride as above resulted in a polymer containing 8.5% bromine, which corresponds to a functional loading of 1.1 mmol g⁻¹.

The brominated polymer (20 g; 22 mmol bromine residues) was added to "super-dry" tetrahydrofuran (150 ml). n-Butyl lithium (22 ml of 1.4M solution in n-hexane, 30.8 mmol) was added slowly and the mixture stirred under dry nitrogen for 1 h. The liquid phase was decanted off as previously and
the lithiation step repeated. After stirring for a further hour, the liquid phase was decanted off and "super-dry" tetrahydrofuran (150 ml) added. Chlorodiphenylphosphine (16 ml; 88 mmol) was added slowly with stirring and once the addition was complete the reaction mixture was stirred at room temperature for 2 h. The polymer was filtered off on a Buchner funnel and washed with tetrahydrofuran, ether, tetrahydrofuran-water (2:1), water, tetrahydrofuran and methanol. It was dried at 30°C at 1 mmHg for 16 h.

Elemental analysis of the polymer showed it to contain 1.6% phosphorus and 0.3% bromine, indicating a functional yield of ~60%.

ii) Polymerisation of maleic anhydride initiated by polystyryl(diphenylphosphine)

Polystyryl(diphenylphosphine) (15 g; 7.8 mmol diphenyl phosphine residues) was added to a stirred melt of maleic anhydride (100 g; 1.02 mol) at 120°C under dry nitrogen. Heating and stirring were continued for a further 3 h, during which time it was observed that the reaction mixture became dark brown in colour. The reaction mixture was allowed to cool to ca.50°C and acetone (200 ml) was added to dissolve any unreacted maleic anhydride. The polymer was filtered off on a Buchner funnel and washed thoroughly with acetone, water and acetone before drying at 40°C at 0.6 mmHg for 16 h to yield 18.7 g of brown polymer beads.

Assuming that complete decarboxylation of the poly-(maleic anhydride) has taken place, the weight increase of 3.7 g corresponds to 68.5 mmol of monomer units, indicating an average chain length of 4.1 units.
Scheme 16

NaNH₂ / benzene
\[ \nu_{\text{max}}: 3410 (\text{OH}), 2918, 1729 (\text{C=O}), 1599, 1185, 1110 \text{ cm}^{-1}. \]

**iii) Preparation of polystyryl(ethyl pyridine)**

This polymer was prepared by a modification of the method of Kyte *et al.*\(^{159}\) as shown in Scheme 16.

a) **Reaction in the absence of solvent**

Dry 4-picoline (29.8 g; 310 mmol) and powdered sodamide (3.12 g; 80 mmol) were stirred at room temperature under dry nitrogen for 30 min. To this was added chloromethylated Amberlite XAD-2 (5 g; 8 mmol chloromethyl residues) and the mixture stirred for a further 18 h, after which time the reaction mixture, which had turned black, was cautiously poured into ice-cold water (100 ml) to destroy excess sodamide. The polymer was filtered off on a Buchner funnel and washed thoroughly with water, acetone, benzene, and methanol prior to drying at 40°C at 0.6 mmHg for 16 h to yield 5.6 g of fawn coloured polymer beads. Elemental analysis of the polymer showed it to have a total chlorine content of 0.72 mmol g\(^{-1}\), of which 0.71 mmol g\(^{-1}\) could be identified as being ionic. This represents a functional yield of \(\sim 56\%\).

b) **Reaction using benzene as solvent**

Powdered sodamide (3.12 g; 80 mmol) was added to dry 4-picoline (298 g; 320 mmol) in dry benzene (75 ml). The mixture was stirred at room temperature under dry nitrogen for 30 min and chloromethylated Amberlite XAD-2 (5 g; 8 mmol chloromethyl residues) added. The reaction mixture was stirred for a further 18 h and then poured slowly into ice-cold water (100 ml). The polymer was filtered off on a Buchner funnel and washed and dried as previously to yield 5.4 g of fawn coloured polymer of which 3.8 g was still in the form of the original beads, the remainder having disinte-
grated to a fine powder. The polymer contained a total of 0.41 mmol Cl g\(^{-1}\) of which 0.27 mmol g\(^{-1}\) was ionic; a functional yield of 74%.

This method was used for all further preparations of polystyryl(ethyl pyridine).

iv) **Polymerisation of maleic anhydride initiated by polystyryl(ethyl pyridine)**

Polystyryl(ethyl pyridine) (20 g; 22 mmol pyridine residues) was added to a stirred melt of maleic anhydride (150 g; 1.53 mol) at 120°C under dry nitrogen. An immediate orange coloration of the reaction mixture was observed, this coloration darkening with time until after a reaction time of 5 h, it was dark brown. The reaction mixture was cooled to ca. 50°C and acetone (250 ml) added. The polymer was filtered off on a Buchner funnel and extracted with firstly acetone and next water in a Soxhlet apparatus. It was further washed with acetone and dried at 35°C at 0.8 mmHg to yield 25.6 g of dark polymer beads.

If complete decarboxylation has occurred, the weight increase of 5.6 g corresponds to 104 mmol of monomer units, indicating an average chain length of 4.7 units.

\[ \nu_{\text{max}} 3430 (\text{OH}), 2920, 1725 (\text{C=O}), 1602, 1210 \text{ cm}^{-1} \]

v) **Polymerisation of maleic anhydride initiated by poly(4-vinyl pyridine-co-styrene)**

Poly(4-vinyl pyridine-co-styrene) (2 g; 8.6 mmol pyridine residues) as available from Aldrich was added to a stirred melt of maleic anhydride (15 g; 0.153 mol) at 120°C under dry nitrogen and the mixture allowed to stir for a further 2 h. The reaction mixture was allowed to
cool to ca. 50°C and acetone (75 ml) added. The polymer was filtered off on a Buchner funnel, washed with acetone, water and acetone and dried at 40°C at 1 mmHg for 15 h to yield 4.1 g of brittle brown polymer.

IV Preparation of polymer bound resorcinol

This polymer was prepared by a modification of the method of Eliseeva and Savvin\textsuperscript{81} as outlined in Scheme 17.

i) Nitration of polystyrene\textsuperscript{160}

Styrene-2\% divinyl benzene copolymer (15.7 g), 200-400 mesh beads as available from Fluka was added, with stirring, to fuming nitric acid (180 ml). The reaction mixture was heated to 80°C for 14 h. After cooling to room temperature, the mixture was poured slowly onto an ice-water mixture (494 and the pale yellow polymer filtered off on a Buchner funnel. Impurities were removed by continuous extraction with benzene in a Soxhlet apparatus. The polymer was dried at 60°C at 0.6 mmHg to yield 20.9 g of nitrated resin. (Found: C, 60.0; H, 4.2; N, 10.7. 100\% nitration C, 64.9; H, 4.8; N, 9.2. 122\% nitration requires C, 60.5; H, 4.3; N, 10.7\%). This indicates a functional loading of 7.6 mmol.g\textsuperscript{-1}.

A lower degree of nitration may be obtained by the method of Seliger\textsuperscript{161}.

Styrene-2\% divinylbenzene copolymer (15 g) was suspended in a mixture of carbon tetrachloride (105 ml) and acetic anhydride (3.75 ml). To the stirred mixture was added, at room temperature, a nitrating mixture consisting of fuming nitric acid (3.75 ml) and acetic anhydride (7.5 ml) in carbon tetrachloride (45 ml) at a rate such that the temperature of
Scheme 17
the reaction did not rise above 13°C throughout the addition. The mixture was stirred at room temperature for a further 16 h, the polymer filtered off on a sintered funnel and washed with water, carbon tetrachloride and benzene. It was dried at 60°C at 0.5 mmHg for 16 h to yield 16.5 g of yellow polymer beads. (Found: N, 3.8; 32% nitration requires N, 3.8%). This polymer has a functional loading of 2.7 mmol.g\(^{-1}\).

ii) Reduction of poly(p-nitrostyrene)\(^{161}\)

Nitratred polystyrene (15.0 g; 36.4 mmol nitro residues) was added to phenylhydrazine (100 g; 925 mmol) and the mixture heated under reflux under dry nitrogen for 8 h. After cooling to room temperature, the polymer was filtered off on a sintered funnel and washed with benzene. Any remaining phenylhydrazine was removed by continuous extraction with benzene in a Soxhlet apparatus. The product was dried at 50°C at 0.6 mm for 16 h to yield 12.5 g. (Found: C, 85.6; H, 7.3; N, 3.8. 100% reduction of nitro groups requires C, 88.2; H, 7.7; N, 4.1%).

iii) Diazotisation of poly(p-aminostyrene) and coupling to resorcinol)

Amino-polystyrene (12.1 g; 19.6 mmol amino residues) was allowed to swell overnight in 1M hydrochloric acid (190 ml). The mixture was cooled on a salt-ice bath and a chilled solution of sodium nitrite (17 g) in water (40 ml) added at a rate such that the temperature did not rise above 0°C. The mixture was stirred for 3 h on a salt-ice bath and then poured into an ice-cold coupling mixture prepared from resorcinol (6.7 g; 61 mmol) in 2M aqueous sodium hydroxide
The reaction mixture was left to stand at 0-5°C for 2 h, and then stirred vigorously for 1 h at the same temperature. The polymer was filtered off on a Buchner funnel, washed with water, and then stirred with 1M hydrochloric acid (100 ml) for 4 h. The product was filtered off on a Buchner funnel and washed with water until acid-free and then with acetone. It was dried in vacuo over phosphorus pentoxide to yield 10.2 g of brown powder.

Preparation of polymer bound 2,2'-bipyridine

This was prepared by the method of Card and Neckers as outlined in Scheme 18.

Brominated polystyrene (10.0 g; 41 mmol bromine residues) was added to "super-dry" tetrahydrofuran (100 ml) through which dry nitrogen was bubbled throughout the reaction. The mixture was cooled to 0°C and n-butyl lithium (61 ml of 1.6M solution in n-hexane; 89 mmol) added slowly. The reaction mixture was stirred at 0°C for 30 min and then allowed to warm to room temperature and stirred for a further hour prior to the addition of 2,2'-bipyridyl (15.5 g; 99.3 mmol). The mixture was refluxed under dry nitrogen for 3 h and then cooled to room temperature. Air was bubbled through the reaction mixture until both the solution and the polymer had changed in colour from red-purple to golden yellow. The polymer was filtered off on a Buchner funnel and purified by Soxhlet extraction with each of tetrahydrofuran, benzene and ethyl acetate. It was dried at 60°C at 0.8 mmHg for 16 h to yield 11.6 g of yellow polymer. (Found: C, 78.8; H, 6.2; N, 5.3%, corresponding to 1.9 mmol bipyridyl residues per gram of resin).
G. Standard Procedure for the Determination of Metal Adsorption by Polymers.

I. Flow System

An accurately weighed sample (~1g) of polymer was packed into a 13mm i.d. glass column by a slurry method using water. The water was allowed to drain completely from the column. A reservoir was attached to the top of the column and plastic tubing leading to a fraction.
collector to the bottom. The reservoir was filled with an aqueous solution of the metal ion under investigation, the pH of the solution having been adjusted with buffer solution as required. The rate of flow of the solution through the column was controlled by a gate clip round the plastic tubing. Typically, the flow rate was 75 ml h\(^{-1}\). The effluent from the column was collected in either 10 ml or 25 ml fractions and analysed for metal concentration, usually by atomic absorption spectrometry.

II. Static System

An accurately weighed sample (~200 mg) of polymer was added to a flask containing an aqueous solution of the metal ion under investigation. The flask was sealed and left at room temperature for 48 h, after which time the polymer was filtered off and washed thoroughly with de-ionised water. The combined washings and filtrate were then analysed for metal ion concentration.
RESULTS AND DISCUSSION

A. Polymer bound \( \beta \)-diketones and related compounds

The chelate compounds of several \( \beta \)-diketones with a variety of metal ions, and in particular Cu(II), are well known$^{163}$. They are formed by the loss of a proton from the enol tautomer (7) to form a six-membered chelate ring (8).

This group of molecules appeared to be suitable for an investigation into the preparation and use of their polymer
bound forms.

One of the major reactions of \( \beta \)-diketones is their mono- or di-alkylation at the \( \alpha \) carbon atom via the carbanion (9) which can be represented as a resonance hybrid. It is

\[
-C-CH-C- \quad \leftrightarrow \quad -C=CH-C- \quad \leftrightarrow \quad -C-CH=C-
\]

(9)

thus possible for these species to attack a saturated carbon atom with either their carbon atom (leading to \( C \)-alkylation) or with their oxygen atom (leading to a mono enol ether) as shown in Scheme 19.
Alkyl halides, dialkyl sulphides and alkyl toluene-p-sulphonates have all been used in these reactions with a variety of bases such as potassium carbonate and alkali metal alkoxides or hydroxides. Dialkylation may occur if one or more than one equivalent of base is used.

These reactions indicated that a possible route for the preparation of polymer supported β-diketones would be by the C-alkylation of the desired β-diketone with chloromethylated polystyrene.

I Pentane-2,4-dione (Acetyl acetone)

An initial study of the benzylation of acetyl acetone was carried out using either benzyl bromide or benzyl chloride as a model for chloromethylated polystyrene. This enabled easier analysis of the reaction products, making it possible to determine the most suitable reaction conditions. It was shown that, under the reaction conditions used, both the mono- and di-benzylated products were obtained in good yield. The use of chloromethylated polystyrene as the alkylating agent would most likely not give rise to any significant amount of dialkylation due to the isolation of the chloromethyl residues in the polymer infrastructure. The model reactions indicated that there was good potential for the reaction of acetyl acetone with a highly functionalised chloromethylated polystyrene to yield a heavily loaded chelating system.

Of the three base-solvent systems used in the trial experiments, that utilising potassium carbonate in acetone gave
the highest total conversion to benzylated products, and also involved a simple work-up procedure. It was thus this method that was chosen for the preparation of polystyrene bound acetyl acetone. The functional yield of \( \approx 55\% \) for the prepared polymer indicates that approximately half of the available phenyl residues carry the chelating moiety.

The efficacy of the polymer in adsorbing metal ions was examined by flow and static experiments, the results of which are presented in Table 3.

In both flow experiments, analysis of the fractions of column effluent by atomic absorption spectrophotometry indicated that the metal ion concentration did not deviate significantly from that of the feedstock, indicating that no metal ions were being adsorbed onto the polymer.

Other metal ions were selected for the static investigation. From the results of these experiments it was seen that there was no detectable uptake of metal ion.

It should be noted that, for the reasons given earlier, divalent metal ions were used in all these experiments. The formation of the acetyl acetonates of divalent metal ions necessitates the involvement of two acetyl acetone moieties to produce a neutral species, as illustrated in Scheme 20.

When it is taken into account that only about half of the available phenyl residues of the polymer have an acetyl acetone residue attached, it is probable that the acetyl acetone residues are too far apart within the polymer structure for chelation to occur.
<table>
<thead>
<tr>
<th>Metal ion</th>
<th>System type</th>
<th>Concentration/ppm</th>
<th>pH</th>
<th>Quantity adsorbed/mmol metal per gram of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$^{2+}$</td>
<td>flow</td>
<td>250</td>
<td>0.58</td>
<td>nil</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>flow</td>
<td>200</td>
<td>3.37</td>
<td>nil</td>
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<tr>
<td>Cu$^{2+}$</td>
<td>static</td>
<td>5000</td>
<td>4.4</td>
<td>nil</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>static</td>
<td>5000</td>
<td>6.0</td>
<td>nil</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>static</td>
<td>5000</td>
<td>3.9</td>
<td>nil</td>
</tr>
</tbody>
</table>

Table 3

Metal ion uptake by polymer bound acetylacetone
As in the case of acetyl acetone, it was thought beneficial to undertake an investigation of the benzylation of dipivaloylmethane with model alkylating agents. Use of the potassium carbonate-acetone system in this instance led to the recovery of the starting materials after an extended reaction time of 20 hours. Although a suitable preparation of the polymer bound species, utilising sodium hydride as base, was found, the functional yield of \( \sim 36\% \) was poor, and could not be improved upon either by increasing reaction time or by further reaction of a partially converted product.

The use of the polymer in removing metal ions from aqueous solutions was investigated by static experiments, the
results of which are shown in Table 4.

The investigation was again limited to divalent metal ions and the lack of any adsorption of the ions by the polymer may again be attributed to the isolation of the chelating groups.

III 4-Amino-pent-3-en-2-one

Experiments using 3-benzylacetylacetone indicated that it was possible to prepare the benzylated derivative of the title compound. It was thus intended to prepare the polymer bound analogue by further reaction of the polystyrene bound acetyl acetone.

2-Amino-3-benzylpent-2-en-4-one was found to be hydrolytically unstable, losing ammonia to form 3-benzylacetylacetone, and it was thus considered to be of little value to prepare the polymer supported version as the intention would have been to investigate its capability of adsorbing metal ions from aqueous solution.
<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Concentration/ppm</th>
<th>pH</th>
<th>Quantity adsorbed/mmol metal per gram of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>5000</td>
<td>4.4</td>
<td>nil</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>5000</td>
<td>6.0</td>
<td>nil</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>5000</td>
<td>3.9</td>
<td>nil</td>
</tr>
</tbody>
</table>

Table 4

Metal ion uptake by polymer bound dipivaloylmethane
B. Tetraphenylporphin impregnated resin

The tetrapyrrole nucleus (10) has unique chelating properties. In the naturally-occurring metal-porphin compounds, modifications to the nucleus lead to a wide range of specific biological activities as found in the complexes of iron (the haemproteins), of magnesium (chlorophyll: 11) and of cobalt (Vitamin B$_{12}$).

The preparation of polymer bound tetraarylporphins has been reported$^{165,166}$, but there has been no investigation made into metal chelating ability. The synthesis of King and Sweet is multi-staged and yields are not quoted for every step. It seemed that this would be a suitable system in which to impregnate a suitable resin with the porphin rather than attempt an involved synthesis.
The prepared resin was tested for its ability to adsorb metal ions in static experiments. In the course of these experiments it was observed that difficulty was being experienced in "wetting" the polymer beads, which remained in a layer on the surface of the aqueous solution. This hydrophobic character is a well-known problem with polymers prepared by this method. Vernon and Eccles 70 have noted that this may frequently be overcome by soaking the polymer in a very dilute (ca.0.01%) solution of sodium lauryl sulphate prior to use. This method was used in a re-run of the static experiments, the results of which are given in Table 5. Although there was a slight improvement in the
degree of wetting it was not sufficient to provide good contact between the polymer beads and the metal ion solution. The inability of the polymer to adsorb metal ions may be attributed to this phenomenon.
<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Concentration/ppm</th>
<th>pH</th>
<th>Quantity adsorbed/mmol metal per gram of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>5000</td>
<td>4.4</td>
<td>nil</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>5000</td>
<td>6.0</td>
<td>nil</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>5000</td>
<td>3.9</td>
<td>nil</td>
</tr>
</tbody>
</table>

Table 5

Metal ion uptake by tetraphenylporphin impregnated resin
C. Polymer bound resorcinol

The exchange capacity of this resin (12) was determined by static experiments, the results of which are given in Table 6.

This resin had previously been prepared by Eliseeva and Savvin\(^8\), who tested its efficacy with copper, uranium, niobium and lanthanum. Their results for the uptake of copper (Table 7) are in contrast with those obtained in this work.

<table>
<thead>
<tr>
<th>pH</th>
<th>Exchange capacity/ mmol.g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
</tr>
<tr>
<td>10</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 7

Cu\(^{2+}\) uptake by polymer bound resorcinol\(^8\)
<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Concentration/ppm</th>
<th>pH</th>
<th>Quantity adsorbed/mmol metal per gram polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{3+})</td>
<td>5000</td>
<td>4.1</td>
<td>nil</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>5000</td>
<td>4.4</td>
<td>nil</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>5000</td>
<td>4.3</td>
<td>nil</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>5000</td>
<td>4.4</td>
<td>nil</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>5000</td>
<td>6.0</td>
<td>nil</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>5000</td>
<td>3.9</td>
<td>nil</td>
</tr>
</tbody>
</table>

Table 6

Metal ion uptake by polymer bound resorcinol
Although the methods of analysis differ in the two investigations: Eliseeva and Savvin measured the copper content of the polymer by ashing and complexometric determination, this does not provide any reason for the variation in results.

The major difference in the preparation of the two resins is the original polymer used. Eliseeva and Savvin used a low molecular weight (ca.1000) polystyrene as the backbone of their resin, in the form of a very fine powder, which was separated from the aqueous solutions by centrifugation. In the work described herein a 200-400 mesh cross-linked polystyrene-divinyl benzene resin of higher molecular weight was used, and it must be presumed that it is this difference which is causing the variation in results.
D. Polymer bound 2,2'-bipyridine

A study of the reaction of poly(styryl) bipyridine (12a) with a variety of transition metal salts has been reported by Card and Neckers\textsuperscript{56}. Their results indicated that the extent of metal incorporation was dependent upon the reaction solvent, the metal ion under investigation and its concentration.

The results of the present investigation of metal uptake from aqueous solution by the polymer are shown in Table 8.

These results show the polymer to be ineffective for these metals in aqueous systems whereas, in the case of tetrahydrofuran as solvent, Card and Neckers found an uptake of 0.34 mequiv Cu\textsuperscript{2+}/g polymer. They also determined that greater than 99% of the bipyridyl residues were located within the pore structure of the polymer. It is thus possible to attribute the lack of uptake in aqueous systems to the inability of the water molecules to penetrate the pore structure.
<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Concentration/ppm</th>
<th>pH</th>
<th>Quantity adsorbed/mmol metal per gram polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>5000</td>
<td>4.4</td>
<td>nil</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>5000</td>
<td>6.0</td>
<td>nil</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>5000</td>
<td>3.9</td>
<td>nil</td>
</tr>
</tbody>
</table>

Table 8

Metal ion uptake by polymer bound 2,2'-bipyridine
E. Polymer bound poly(maleic anhydride)

I. Preparation of initiators

The reaction of maleic anhydride with either tertiary amines or tertiary phosphines will, as previously discussed, yield a polymer with structure based on vinyleneketoanhydride or succinic anhydride units. Pyridine and triphenylphosphine have frequently been used as the polymerisation initiators, and it was decided to investigate the use of these species bound to a polystyrene support.

The preparation of polystyryl diphenylphosphine has previously been reported by Parrall and Frechet and it was found convenient to follow this procedure. There was no evidence in the literature of a suitable polymer bound pyridine moiety having been prepared. However, the preparation of 4-alkyl pyridines by the C-alkylation of 4-picoline with alkyl halides has been reported by Vogel et al. Alkyl chlorides are the preferred alkylating agents in the reaction. Thus it seemed possible that chloromethylated polystyrene might prove a suitable alkylating agent in the preparation of polymer bound pyridine.

The attempted preparation of the polymer by reaction of chloromethylated polystyrene with pure 4-picoline as reagent and solvent gave a good overall functional yield of ~100%. Analysis of the resulting polymer indicated that the 4-picoline had been N-alkylated, as well as C-alkylated, to produce a quaternary ammonium salt which would be of no
further use for the intended polymerisation of maleic anhydride. The functional yield of the C-alkylated product was only ~56%.

It was thus necessary to find alternative reaction conditions under which the extent of the undesired N-alkylation was minimised and the functional yield of C-alkylated product could be improved.

One possibility for this was not to use 4-picoline as both reagent and solvent but to introduce another, less polar, solvent to the system as this would, hopefully, make the quaternisation reaction less favourable.

Repetition of the experiment using benzene as solvent gave an overall functional yield of ~87% for the reaction, which was slightly lower than that obtained by the first method. The functional yield of the desired C-alkylated product (13) was increased to 74%. Hence the use of the less polar solvent in the reaction has had the desired effect of reducing the degree of N-alkylation such that at only about one in every eight functionalised residues is there a quaternary ammonium moiety.

This final procedure was chosen for all further preparations of polystyryl(ethyl pyridine).
II Functional Group Analysis

In the past, much weight has been placed on the nuclear magnetic resonance and infra-red spectroscopic analysis of poly(maleic anhydride), although there is still a lack of consensus between the various groups of workers.

Poly(maleic anhydride) bound to a polystyrene support is insoluble in both organic solvents and water, thus an n.m.r. structural investigation was not possible. It has been reported\textsuperscript{168} that it is possible to obtain n.m.r. spectra of insoluble polymers by the use of a suitable organic solvent
which will swell the polymer. This technique was attempted, but did not prove successful due to the polymer not swelling sufficiently, if at all. The difficulty of obtaining n.m.r. spectra of insoluble materials has been partially overcome by such techniques as 'magic angle' spinning, but it was not possible to carry out such experiments with the available facilities.

The infra-red spectra of poly(maleic anhydride) as a graft on polystyrene prove to be difficult to interpret because of the very broad absorption bands produced by the overlap of individual absorptions due to similar functional groups experiencing non-identical chemical environments.

From the broad absorption bands at 1220, 1730 and 3420 cm\(^{-1}\) in these spectra, Figures 2 and 3, it was postulated that the structure may contain carbonyl and carboxylic acid functional groups.

The most favourable approach to an analysis of the type and quantity of the various functional groups present in the structure thus appeared to be by the adaptation of the chemical methods used by Schnitzer and Khan\(^89\) in the determination of oxygen-containing functional groups in soil humic substances.

Their first determination is for the "total acidity" of the sample which they then compare with the value obtained for the "carboxyl content." In the case of the humates, the difference between these two values is taken to represent the phenolic residues present in the structure. In the case
Polystyryl (diphenylphosphine) initiated polymer

![Graph](image1)

Figure 2

Polystyryl (ethyl pyridine) initiated polymer

![Graph](image2)

Figure 3
of poly(maleic anhydride), it is most unlikely that there will be any phenolic residues present and so it would be anticipated that the "total acidity" and "carboxylic content" values would be identical.

Examination of the results obtained for these determinations (Table 9) show that these two values do differ in every case, and that it is always the value obtained for "total acidity" which is the greater. This may well be due to the fact that the conditions for the determination of "total acidity" are sufficient to hydrolyse any anhydride residues present in the structure whereas the hydrolysis does not occur under the conditions for the determination of "carboxyl content". This hypothesis was tested by the analysis of a previously hydrolysed sample of polymer. The results of these determinations are shown in the final line of Table 9 and, although there is a slight increase in the value obtained for "carboxyl content", the results are not consistent with the hypothesis.

It is possible that the method used for the "carboxyl" determination, although suitable in the case of humic substances, is not applicable to the situation under investigation in this work and hence the value obtained for "total acidity" is representative of the carboxyl groups present in the polymer structure.

It is also apparent from the results in Table 9 that the ratio of "total acidity" to "carboxyl content" is different for the poly(maleic anhydrides) produced by the two different
<table>
<thead>
<tr>
<th>Polymer type</th>
<th>Total acidity</th>
<th>Carboxyl content</th>
<th>Carbonyl content</th>
</tr>
</thead>
<tbody>
<tr>
<td>phosphine initiated(^a)</td>
<td>7.1±0.3</td>
<td>2.9±0.3</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td>phosphine initiated(^b)</td>
<td>4.0±0.2</td>
<td>1.1±0.1</td>
<td>0.7±0.1</td>
</tr>
<tr>
<td>pyridine initiated(^c)</td>
<td>13.0±1.0</td>
<td>9.0±0.5</td>
<td>*</td>
</tr>
<tr>
<td>pyridine initiated(^d)</td>
<td>4.6±0.6</td>
<td>1.5±0.1</td>
<td>0.6±0.1</td>
</tr>
<tr>
<td>hydrolysed</td>
<td>4.7±0.4</td>
<td>1.7±0.1</td>
<td></td>
</tr>
</tbody>
</table>

Values expressed as mequiv.g\(^{-1}\)

Polymers prepared from a, 2.8 mmol Br.g\(^{-1}\); b, 1.1 mmol Br.g\(^{-1}\); c, 2.6 mmol Cl.g\(^{-1}\);
d, 1.6 mmol Cl.g\(^{-1}\)

* not determined.

Table 9

Functional group determination for various poly(maleic anhydrides)
III Uptake of Metal Ions from Aqueous Solution

(a) Phosphine initiated polymer

The results of the experiments to determine the capacity of the phosphine initiated polymer for a variety of metal ions are given in Table 10. Several trends can be seen in these results; notably the increase in uptake with increasing pH and metal ion concentration of the feedstock. This observation suggested that there may be an ion-exchange mechanism involved in the adsorption process. This hypothesis was further investigated in the system involving the pyridine initiated polymer.

It is also worth noting, when comparing polymers A and B, that although there is a 2.6-times increase in the degree of functionality of the initiating polymer, the increase in the corresponding uptake capacity is much less in proportion. The ratios for lead, mercury and cadmium are shown in Table 11.

The chains of poly(maleic anhydride) will be attached to the polystyrene backbone both on the external surface of the bead and within its pore structure. There are thus two distinct areas where chelation of the metal ions may occur.

It would not be expected that an increase in the degree of functionality of the polymer would greatly affect the initiating polymers. This may well be an indication that there are indeed subtle differences in the structure of the products depending on the initiator used.
<table>
<thead>
<tr>
<th>POLYMER</th>
<th>Metal</th>
<th>Concentration</th>
<th>pH</th>
<th>POLYMER CAPACITY (mmol.g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Fe³⁺</td>
<td>15 ppm</td>
<td>2.6</td>
<td>0.014</td>
</tr>
<tr>
<td>A</td>
<td>Fe³⁺</td>
<td>100 ppm</td>
<td>3.0</td>
<td>0.051</td>
</tr>
<tr>
<td>A</td>
<td>Pb²⁺</td>
<td>15 ppm</td>
<td>2.2</td>
<td>Nil</td>
</tr>
<tr>
<td>A</td>
<td>Pb²⁺</td>
<td>15 ppm</td>
<td>4.8</td>
<td>&gt;0.019</td>
</tr>
<tr>
<td>A</td>
<td>Pb²⁺</td>
<td>75 ppm</td>
<td>4.8</td>
<td>0.150</td>
</tr>
<tr>
<td>A</td>
<td>Pb²⁺</td>
<td>500 ppm</td>
<td>5.0</td>
<td>0.269</td>
</tr>
<tr>
<td>A</td>
<td>Cd²⁺</td>
<td>500 ppm</td>
<td>4.0</td>
<td>0.074</td>
</tr>
<tr>
<td>A</td>
<td>Hg²⁺</td>
<td>500 ppm</td>
<td>4.4</td>
<td>0.059</td>
</tr>
<tr>
<td>A</td>
<td>Zn²⁺</td>
<td>500 ppm</td>
<td>5.1</td>
<td>0.018</td>
</tr>
<tr>
<td>A</td>
<td>Pb²⁺</td>
<td>75 ppm</td>
<td>4.8</td>
<td>0.142</td>
</tr>
<tr>
<td>B</td>
<td>Hg²⁺</td>
<td>500 ppm</td>
<td>4.4</td>
<td>0.152</td>
</tr>
<tr>
<td>B</td>
<td>Cd²⁺</td>
<td>500 ppm</td>
<td>4.1</td>
<td>0.124</td>
</tr>
<tr>
<td>Static A</td>
<td>Pb²⁺</td>
<td>50 000 ppm</td>
<td>3.6</td>
<td>0.521</td>
</tr>
<tr>
<td>Static B</td>
<td>Pb²⁺</td>
<td>50 000 ppm</td>
<td>3.6</td>
<td>0.563</td>
</tr>
</tbody>
</table>

Table 10

Metal ion uptake by polymer bound phosphine initiated poly(maleic anhydride)

Polymers prepared from A 1.1 mmol Br.g⁻¹; B 2.8 mmol Br.g⁻¹
ability of the ions to approach the chelating sites.

<table>
<thead>
<tr>
<th>ION</th>
<th>POLYMER A:B UPTAKE RATIO</th>
<th>IONIC RADIUS Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb²⁺</td>
<td>1.08</td>
<td>1.20</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>1.10</td>
<td>1.10</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>1.68</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 11

However, in the case of the sites located within the pore structure, it is very likely that in the case of the more highly loaded polymer the pores have become too congested with the grafted poly(maleic anhydride) and hence the entry of the metal cations to the chelating sites is restricted. This is in accordance with the observation that the increase in adsorbed cations is in indirect proportion to the size of the cation.

(b) - Pyridine initiated polymer

In the investigation of the properties of this polymer, both static and flow systems were used. From the results of the flow experiments shown in Table 12 it will be seen that there is dependence of the uptake on the pH and cation concentration of the feedstock solution.
<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>Metal</th>
<th>Concentration</th>
<th>pH</th>
<th>POLYMER CAPACITY (mmol.g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>Pb(^{2+})</td>
<td>500 ppm</td>
<td>5.0</td>
<td>0.42</td>
</tr>
<tr>
<td>Flow</td>
<td>Hg(^{2+})</td>
<td>500 ppm</td>
<td>4.4</td>
<td>0.07</td>
</tr>
<tr>
<td>Flow</td>
<td>Zn(^{2+})</td>
<td>500 ppm</td>
<td>5.1</td>
<td>0.09</td>
</tr>
<tr>
<td>Flow</td>
<td>Cd(^{2+})</td>
<td>500 ppm</td>
<td>4.0</td>
<td>0.08</td>
</tr>
<tr>
<td>Flow</td>
<td>Cu(^{2+})</td>
<td>500 ppm</td>
<td>4.2</td>
<td>nil</td>
</tr>
<tr>
<td>Static</td>
<td>Cd(^{2+})</td>
<td>3 600 ppm</td>
<td>2.0</td>
<td>4.4</td>
</tr>
<tr>
<td>Static</td>
<td>Cd(^{2+})</td>
<td>3 600 ppm</td>
<td>2.45</td>
<td>12.3</td>
</tr>
<tr>
<td>Static</td>
<td>Cd(^{2+})</td>
<td>3 600 ppm</td>
<td>3.3</td>
<td>49.1</td>
</tr>
<tr>
<td>Static</td>
<td>Hg(^{2+})</td>
<td>3 600 ppm</td>
<td>2.0</td>
<td>44.0</td>
</tr>
<tr>
<td>Static</td>
<td>Hg(^{2+})</td>
<td>3 600 ppm</td>
<td>2.5</td>
<td>42.4</td>
</tr>
<tr>
<td>Static</td>
<td>Pb(^{2+})</td>
<td>3 600 ppm</td>
<td>1.85</td>
<td>41.7</td>
</tr>
<tr>
<td>Static</td>
<td>Pb(^{2+})</td>
<td>3 600 ppm</td>
<td>2.5</td>
<td>86.4</td>
</tr>
<tr>
<td>Static</td>
<td>Pb(^{2+})</td>
<td>3 600 ppm</td>
<td>3.5</td>
<td>132.4</td>
</tr>
<tr>
<td>Static</td>
<td>Pb(^{2+})</td>
<td>500 ppm</td>
<td>4.05</td>
<td>97.0</td>
</tr>
<tr>
<td>Static</td>
<td>Pb(^{2+})</td>
<td>1 000 ppm</td>
<td>3.95</td>
<td>99.1</td>
</tr>
<tr>
<td>Static</td>
<td>Pb(^{2+})</td>
<td>1 500 ppm</td>
<td>3.9</td>
<td>99.7</td>
</tr>
<tr>
<td>Static</td>
<td>Pb(^{2+})</td>
<td>2 000 ppm</td>
<td>3.75</td>
<td>103.4</td>
</tr>
<tr>
<td>Static</td>
<td>Pb(^{2+})</td>
<td>2 500 ppm</td>
<td>3.7</td>
<td>109.3</td>
</tr>
</tbody>
</table>

Table 12

Metal ion uptake by polymer bound pyridine initiated poly(maleic anhydride)
(i) **Effect of pH**

In several experiments, the pH of the column effluent was monitored in addition to the usual determination of metal ion concentration. Graphic representation of these results (Figure 4) shows that the lower the pH of the effluent the greater the quantity of metal ion removed from the feedstock, that is the lower the concentration of metal ion in the effluent.

This observation, together with the previously noted fact that more metal ions were adsorbed at higher pH suggests that there is an ion-exchange mechanism in operation. If this is the case, it should therefore be possible to remove the adsorbed metal ions from the chelating sites by treatment of the polymer with an acid solution of very low pH.

Initial experiments were carried out in which the metal saturated polymer was treated with deionised water in a flow system. Metal ions were not detected in the analysis of the column effluent, indicating that it was not possible to remove the cations at neutral pH. It was thus possible to wash down the polymer after loading experiments to remove any free metal ions without affecting the polymer in any way.

Analysis of the effluent from washing the column with dilute nitric acid showed complete and rapid removal of the adsorbed metal ions from the polymer (Figure 5). The polymer sample under investigation could be used in this adsorption-stripping cycle several times with no apparent deterioration in either physical or chemical properties.
Figure 4

Fraction number

Concentration of Pb²⁺ in fraction/ppm

pH of fraction
Line A represents total lead adsorbed by polymer.

Figure 5
This system showed promise as being a suitable method for the pre-concentration of selected metal ions, prior to chemical analysis, and further research in this area has shown this to be the case.169

(ii) **Effect of feedstock concentration**

An investigation into the dependence of uptake capacity on the metal ion concentration in the feedstock was most suitably carried out using buffered solutions in a static situation.

The results of these experiments are shown in Table 13, from which it can be seen that the uptake capacity of the polymer increases with an increase in the concentration of the feedstock. This is also in agreement with the idea of an ion-exchange equilibrium.

As part of this investigation it was thought important to ascertain whether, once the polymer was saturated, with metal ions, the cations were firmly chelated or they were undergoing a continuous exchange with the cations in the feedstock as in a chromatography type situation.

A sample of polymer was saturated with lead and washed free of any unbound lead with deionised water. The polymer was then used in a flow system in which the feedstock was spiked with labelled lead. If the lead initially bound to the polymer undergoes continuous exchange with that of the feedstock a loss of label would be expected in the column
FEEDSTOCK CONCENTRATION $\text{Pb}^{2+}$  |  pH  |  UPTAKE CAPACITY (mg)
---|---|---
500  | 4.05  | 97.0±1.6  
1000 | 3.95  | 99.1±1.4  
1500 | 3.9   | 99.6±0.3  
2000 | 3.75  | 103.4±0.4 
2500 | 3.7   | 109.3±4.2 

Table 13

Effect of feedstock concentration on $\text{Pb}^{2+}$ uptake.

If, however, the bound lead remains so there should be no loss of label in the effluent. The $^{210}\text{Pb}$ counts for the fractions of effluent (Table 14), would suggest that once the lead is bound to the chelating group, it does remain bound, and that there is no exchange with the feedstock. The lower count for the first two fractions can be attributed to a slight variation in the pH of the solution used to saturate the polymer and that used in the 'spiking' experiment.
<table>
<thead>
<tr>
<th>FRACTION</th>
<th>210(^{\text{Pb}}) COUNT (cph)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>670±21</td>
</tr>
<tr>
<td>2</td>
<td>833±15</td>
</tr>
<tr>
<td>3</td>
<td>1097±27</td>
</tr>
<tr>
<td>4</td>
<td>1210±28</td>
</tr>
<tr>
<td>5</td>
<td>1144±17</td>
</tr>
<tr>
<td>6</td>
<td>1023±16</td>
</tr>
<tr>
<td>7</td>
<td>1016±26</td>
</tr>
<tr>
<td>8</td>
<td>1022±16</td>
</tr>
<tr>
<td>9</td>
<td>1232±29</td>
</tr>
<tr>
<td>10</td>
<td>1154±17</td>
</tr>
<tr>
<td>11</td>
<td>1139±28</td>
</tr>
<tr>
<td>12</td>
<td>1159±28</td>
</tr>
<tr>
<td>13</td>
<td>1174±17</td>
</tr>
<tr>
<td>14</td>
<td>1101±17</td>
</tr>
<tr>
<td>15</td>
<td>1132±27</td>
</tr>
<tr>
<td>16</td>
<td>1127±17</td>
</tr>
<tr>
<td>17</td>
<td>1109±17</td>
</tr>
<tr>
<td>18</td>
<td>1153±28</td>
</tr>
<tr>
<td>19</td>
<td>1128±17</td>
</tr>
<tr>
<td>Standard</td>
<td>1081±16</td>
</tr>
</tbody>
</table>

Table 14

210\(^{\text{Pb}}\) counts of column effluent.
REFERENCES

77 B. Strong, R.P. Henry, Hydrometallurgy, 1976, 1, 311.
84 D.J. Linehan, H. Shepherd, Plant Soil, 1979, 52, 281.
93 Macaulay Institute for Soil Research, Annual Reports, 1975-76, 46, 55.
97 Macaulay Institute for Soil Research, Annual Reports, 1977-78, 48, 49.


146 A saturated aqueous solution of ferric ammonium sulphate should be used.
APPENDIX

I. 

II. 
Polystyrene-bound poly(maleic anhydride): a new type of lead-adsorbing polymer for water clean-up

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Maleic anhydride can be polymerised in the presence of either tertiary phosphines or tertiary amines. Although the detailed structures of the resulting polymers are not well defined, it has been pointed out that the polymer produced by initiation with pyridine is very similar both spectroscopically and in many of its properties to 'fulvic acid', one of the humic components of soils.

Fulvic acid is important as a natural chelator of metal ions and as such is implicated in the mobilisation of metals in soils and in natural waters. Both fulvic acid and polystyrene-bound poly(maleic anhydride) are water-soluble and hence are unsuitable as adsorbents for the removal of toxic metals from water but here, the preparation and study of polystyrene-bound poly(maleic anhydride) which has been insolubilised through being chemically bonded to a polystyrene support is reported.

The polymerisation of maleic anhydride (150g), at 120°C, was initiated by treatment with 20g of polystyrene-bound pyridine (22mmol pyridine). After 5h the cooled mixture was washed free of monomer and of unbound poly(maleic anhydride) to yield, after drying, 25.6g of a brown polymer.

The capacity of this material to adsorb metals was determined by slurry-packing samples (1g) into a 13mm i.d. glass column and passing through them aqueous solutions of the metal ion under study (normally 500mg l⁻¹, as nitrate, at pH 5) at a flow rate of 75cm³ h⁻¹. Aliquots of effluent were collected for analysis (normally by atomic absorption) until it became apparent, from the effluent composition, that the column of polymer was saturated. The capacities of the polymer for uptake of various metals, in mmol of X⁻² g⁻¹ of polymer, were: Pb²⁺, 0.42; Mg²⁺, 0.07; Zn²⁺, 0.09; Cd²⁺, 0.08, and it can be seen that the capacity of the material for lead adsorption is particularly noteworthy.

Similar experiments with a polymer produced by polymerisation of maleic anhydride initiated by polystyryl(diphenylphosphine) gave a material of broadly similar properties and performance.

The adsorption is pH dependent, being ca 0.1mmol Pb g⁻¹ at pH 2, and rising with increasing pH until problems of metal-ion insolubility prevent reliable analysis.

The adsorbent can easily be regenerated for re-use. Treatment of the metal saturated polymer with 2M nitric acid (25cm³ g⁻¹ of polymer) removed all the adsorbed metal ions and restored the polymer to its original capacity. There was no evidence to indicate deterioration of the material over repeated saturation-regeneration cycles.

Given the potential of the material as a lead scavenger, and current concern about lead toxicity, its use has been examined for the removal of lead from very dilute solutions as would be required, for example, in the treatment of drinking water.

In column experiments similar to those already described, polymer (1g) was fed with a 15ppm aqueous solution of lead (II) at a flow rate of 75cm³ h⁻¹. The initial effluent contained no lead (<0.04ppm) and after 5h the level had risen to only 0.1ppm. In a similar experiment with a 5.0ppm lead (II) solution at pH 5.5, and a flow rate of 150cm³ h⁻¹, after 13.5h the lead (II) level in the column effluent was still <0.05ppm.

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It is believed, therefore, that the polymers which have been described are of potential value for the removal of lead from water and, being easily made from cheap precursors and apparently indefinitely regenerable, that they may be economically useable on a large scale. Currently, the structure of the materials is being studied and a report will be made at a later date.

The SERC is thanked for a studentship for Mrs F. M. Husband and for an equipment grant.

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References


REMOVAL OF TOXIC METALS FROM AQUEOUS SOLUTION

This invention relates to the removal of heavy metals, in particular mercury, zinc, cadmium and especially lead, from aqueous, e.g. effluent, media.

The presence of heavy, generally toxic metals, e.g. as the result of industrial pollution, in surface water and water supply is an increasing problem. Previous attempts to remove dissolved heavy metals, e.g. from industrial effluent, have involved the use of metal absorbing polymers. Thus for example conventional cation exchange resins can be used for metal absorption under some circumstances but their use is limited by pH and by the fact that they are relatively indiscriminate as regards cation absorption. Thus they are of little value where effluents containing substantial concentrations of relatively innocuous metals, e.g. alkali and alkaline earth metals, are being treated since the resin will rapidly become saturated with these innocuous metal ions. In addition polymeric absorbents bearing relatively selective metal chelating groups are available, such as Chelex 100, which is a polystyrene based ion exchange resin the active groups being paired iminodiacetate ions. However, these materials are inevitably expensive to manufacture and are suited to small scale use, for example in a laboratory, rather than in large scale water clean-up. In addition these materials are often difficult to regenerate effectively and economically.

It has been found that heavy metals, e.g. mercury, zinc, cadmium, and in particular, lead, can be absorbed from aqueous media using insolubilized poly(maleic anhydride). The invention accordingly provides a method of removing a heavy metal from an aqueous medium using such material.

The insolubilizing agent may suitably be a polymer such as polystyrene to which the poly(maleic anhydride) compound is bound.

The invention also provides, as novel material, insolubilised poly(maleic anhydride).
The poly(maleic anhydride) may be insolubilised by cross-linking; or by copolymerisation of poly(maleic anhydride) or monomeric maleic anhydride with a hydrophobic polymer or comonomer, preferably by copolymerisation of monomeric maleic anhydride with a hydrophobic polymer which may itself be cross-linked; for example, a substituted or unsubstituted polystyrene.

The structure of poly(maleic anhydride) has not yet been fully elucidated but the preferred polymers of this invention are water-soluble polyelectrolytes which have IR absorption maxima at 3,480 to 3,500 cm\(^{-1}\), 1,670 to 1,690 cm\(^{-1}\) and 1,190 to 1,210 cm\(^{-1}\). It is postulated that the polymer obtained by polymerisation of maleic anhydride according to this invention has a structure similar to that of fulvic acid, a constituent of the humic components of soils (Nature, H.A. Anderson and J.D. Russell, Vol. 260, 1976, 597). The humic components of soils represent the product decay of organic detritus and are involved in the transporting of metals ions through soil. These humic components comprise humic acid and fulvic acid, which is that fraction of the humic materials soluble in mineral acid. These components are found both in the soil and in surface water. Fulvic acid is particularly important as a natural chelating agent and has been found to have a specific affinity for heavy metals. However neither fulvic acid, nor poly(maleic anhydride), are useful chelating agents for effluent clean-up since they, and their chelates, are water-soluble.

Suitable insolubilised poly(maleic anhydride) according to the invention includes poly(maleic anhydride) bound to polystyrene, which renders it insoluble in water. The polystyrene acts as a non-polar support of the poly(maleic anhydride). The poly(maleic anhydride) bound to polystyrene is relatively cheap to prepare and can easily be regenerated for reuse. Also the material has a good selectivity for heavy metals, especially mercury, zinc, cadmium and in particular lead, and accordingly in use does not become saturated by innocuous metals which may be present in the effluent being treated. Thus the material can effectively be used for large scale clean-up.
This invention also provides a process comprising cross-linking poly(maleic anhydride) or copolymerising poly(maleic anhydride) or monomeric maleic anhydride with a hydrophobic polymer or comonomer, preferably wherein monomeric maleic anhydride is copolymerised with a hydrophobic polymer which may itself be cross-linked; for example a substituted or unsubstituted polystyrene. In a particularly preferred embodiment of this invention the polymerisation of the monomeric maleic anhydride is initiated by a Lewis base, especially a compound of the formula:

$$R_n R_1 R_2 M$$

for example wherein $R_n$ represents a polystyryl group; wherein at least one of $R_1$ and $R_2$ represents a phenyl group; wherein $M$ represents nitrogen or phosphorus; or wherein $R_1 R_2$ and $M$ represent pyridine and $R_n$ is a ring substituent.

The insolubilized poly(maleic anhydride) according to the invention may be prepared by polymerising maleic anhydride, under anhydrous conditions, in the presence of a polymer having bound thereto an initiator for the maleic anhydride polymerisation reaction. Examples of polymer bound initiators include polystyrene bound phosphines and tertiary amines e.g. polystyryl (diphenyl phosphine) and polystyrene bound pyridine. The polymerisation of maleic anhydride in the presence of tertiary amines and phosphines is known (H. Zweifel, T. Loliger and T. Volker, Makromol. Chem. 1972, 153, 125, and 1973, 170, 141, and D. Braun and J. Pomakis, Makromol. Chem. 1974, 175, 1411).

Polystyrene bound phosphine initiators may be prepared by reaction of a chlorophosphine with a lithiated polystyrene obtained by reacting brominated polystyrene with an excess of n-butyl lithium. The preparation of lithiated polystyrenes and their subsequent reaction with phosphines is described in M.J. Farrall and J.M.J. Frechet, J. Org. Chem. 1976, 41, 3877. Thus the polystyrene is first brominated using bromine in the presence of catalytic amounts of thallium (III) salt and then lithiated with an excess of n-butyl lithium in benzene. The
resulting lithiated polystyrene is then reacted with e.g. chlorodiphenylphosphine in, suitably, tetrahydrofuran solvent to give the desired polystyryl phosphine product. The degree of substitution of the polystyrene may be controlled by the degree of bromination achieved in the first step, all subsequent steps being substantially quantitative. The degree of bromination can be varied by varying the ratio of bromine to polystyrene used in the first step. Generally satisfactory results can be achieved with material containing diphenylphosphine substituents at 30 to 40% of the polystyrene rings. Introduction of too many diphenylphosphine substituent groups may result in physical breakdown of the polymer structure. On the other hand of course an insufficient number of diphenylphosphine substituents may lead to a commercially insufficiently active polymer.

Polystyrene bound pyridine groups according to the invention may be obtained by reacting chloromethyl polystyrene with 4-picoline in the presence of sodamide using benzene as solvent.

Chloromethyl polystyrene is a known material which can for example be prepared by the chloromethylation of polystyrene using chloromethyl methyl ether in the presence of anhydrous tin (IV) chloride (R.B. Merrifield, J. Am. Chem. Soc., 1963, 85, 2149). Chloromethylated polystyrene is an intermediate in the manufacture of conventional ion exchange resins. Further its use in the present invention has the added advantage that there are obtained polymer beads substantially the same size as the starting polystyrene.

The degree of chloromethylation determines the final functional loading of the polymer as again subsequent steps are substantially quantitative. The degree of chloromethylation used is generally such as to give 1 to 2 mM Cl per g.

The chloromethylated polystyrene is reacted with 4-picoline in the presence of e.g. sodamide using benzene as solvent. This method is essentially a modification of the method of Vogel et al, J. Chem. Soc., 1960, 4454 for the C-alkylation of picolines. Vogel et al carried out the reaction using the picoline in vast excess as solvent. We have found if these
conditions are used with the materials used according to the present invention, substantial quaternisation of the nitrogen occurs as an undesirable side reaction. However if there is used as solvent, benzene, successful reaction of the polymer is achieved.

The reaction with 4-picoline according to the invention proceeds according to the following route:

\[
\begin{align*}
\text{CH}_3 & \quad \text{NH}_2^- \\
& \quad \text{P}\text{CH}_2\text{Cl} \\
& \quad \text{CH}_2^- \\
\end{align*}
\]

wherein P represents the polystyrene backbone.

This route represents a substantially cheaper method of obtaining initiator bound to polystyrene using relatively cheap reactants than the route involving the more expensive bromination and lithiation steps.

As mentioned above, the polymers according to the present invention are efficient in selectively absorbing from aqueous media heavy metal ions, in particular mercury, zinc and cadmium and especially lead. The polymers are suitable for use as absorbent beds and in columns for water treatment. The polymers may be used in the treatment of effluents and they are also suitable for use in the removal of lead from tap water and indeed other applications in which toxic metal pollution is a problem. The metal capacity of the polymers tends to be pH dependent with the capacity increasing with pH from acid to neutral.

Further the metals can readily be recovered from the polymers according to the invention after use for example by passing a strong acid, such as nitric acid through the polymer column or by stripping the absorbent bed with a strong acid, such as nitric acid. In this way the polymer is also easily and completely regenerated for re-use.
The invention is further illustrated by reference to the following Examples.

Example 1
Preparation of polystyrene bound initiators.

A. Polystyryl (diphenylphosphine).

This known material was prepared by the routine outlined below and detailed in M.J. Farrall and J.M.J. Frechet, J. Org. Chem. 1976, 41, 3877.

Amberlite XAD-2 resin (a polystyrene resin) was brominated with bromine in the presence of thallium (III) chloride in carbon tetrachloride.

The resulting resin was then treated with n-butyl lithium in benzene followed by chlorodiphenyl phosphine in tetrahydrofuran (THF) to give the desired product.

B. Polystyrene bound pyridine.

Dry 4-picoline (22ml; 224 mmol) and powdered sodamide (2.2g; 56 mmol) were stirred for 30 min. at 20°C in dry benzene (50 ml) under dry nitrogen. To this was added chloromethylated polystyrene (5g; 5.6 mmol Cl residues) and the mixture stirred for a further 18 hours, after which time the reaction mixture, which had turned black, was poured into water (250 ml) to destroy excess sodamide.

The polymer was filtered off, washed thoroughly with water, acetone, benzene and methanol prior to drying at 40°C/0.6 mm for 16 hours.

Yield: 5.1g of fawn coloured polymer.

Example 2
Polymerisation of Maleic Anhydride.

A. Polystyryl (diphenylphosphine) initiated polymerisation - Preparation of Polymer 1

To maleic anhydride (100g; 1.02 mol) at 120°C under dry nitrogen was added, with stirring, polystyryl (diphenylphosphine) (45g; 16.5 mmol - PPh₂ residues; Ph = phenyl). After 3 hours the reaction mixture was allowed to cool to ca. 50°C and acetone (200 ml) added to dissolve unreacted maleic anhydride. Polymer was
filtered off on a sinter and washed with acetone, water, and finally acetone, before drying at 40°C/0.6 mm for 16 hours to yield 18.7g of brown polymer beads.

B. Polystyrene bound pyridine initiated polymerisation - Preparation of Polymer 3

The procedure was as described above for the polystyrene (diphenylphosphine)initiated polymerisation except that reaction time was 5 hours.

20g of polymer bound pyridine (22 mmol pyridine residues) obtained in Example 1B above and 150g maleic acid yielded 25.6g of a brown polymer.

Example 3

Measurement of the capacity of the Polymers to absorb metals, general method.

The capacity of the polymers obtained as in Example 2 above as metal adsorbents by the use of a simple flow system was as follows:

1g of beads of the polymer to be tested were slurry packed in 100 ml deionised water into a 13 mm (internal diameter) glass column. The water was drained and a test metal ion solution allowed to flow through the column at 75 ml. hour⁻¹. The column effluent was collected in 25 ml fractions analysed by atomic absorption, or, in the case of zinc, by titration with ethylenediaminetetraacetic acid (EDTA).

The results of these experiments for three different polymers are shown in the following Table. In addition the Figures 1 and 2 of the accompanying drawings show typical elution curves for the uptake of lead by a column containing Polymer 1 and one containing Polymer 3 respectively using the same method. The capacities quoted in the following Table are determined from such curves.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Metal</th>
<th>Column Feed Concentration</th>
<th>pH</th>
<th>Capacity of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe$^{3+}$</td>
<td>100 ppm</td>
<td>3.0</td>
<td>0.051 mmol g$^{-1}$</td>
</tr>
<tr>
<td>1</td>
<td>Pb$^{2+}$</td>
<td>15 ppm</td>
<td>2.2</td>
<td>nil</td>
</tr>
<tr>
<td>1</td>
<td>Pb$^{2+}$</td>
<td>500 ppm</td>
<td>5.0</td>
<td>&gt; 0.27 mmol g$^{-1}$</td>
</tr>
<tr>
<td>1</td>
<td>Zn$^{2+}$</td>
<td>500 ppm</td>
<td>5.1</td>
<td>0.07 mmol g$^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>Hg$^{2+}$</td>
<td>500 ppm</td>
<td>4.4</td>
<td>0.02 mmol g$^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>Cd$^{2+}$</td>
<td>500 ppm</td>
<td>4.0</td>
<td>0.16 mmol g$^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>Pb$^{2+}$</td>
<td>500 ppm</td>
<td>5.0</td>
<td>0.12 mmol g$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>Pb$^{2+}$</td>
<td>500 ppm</td>
<td>5.0</td>
<td>&gt; 0.35 mmol g$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>Hg$^{2+}$</td>
<td>500 ppm</td>
<td>4.4</td>
<td>~ 0.42 mmol g$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>Zn$^{2+}$</td>
<td>500 ppm</td>
<td>5.1</td>
<td>0.07 mmol g$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>Cd$^{2+}$</td>
<td>500 ppm</td>
<td>4.0</td>
<td>0.09 mmol g$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>Cu$^{2+}$</td>
<td>500 ppm</td>
<td>4.2</td>
<td>nil</td>
</tr>
<tr>
<td>3</td>
<td>Pb$^{2+}$</td>
<td>15 ppm</td>
<td>5.5</td>
<td>&lt; 0.04 ppm after 550 ml passed through column</td>
</tr>
</tbody>
</table>

20 Polymer 1 - from polystyryl (diphenylphosphine) prepared from bromopolystyrene with 1.1 mmol Br g$^{-1}$ (obtained in Example 2A above).

Polymer 2 - obtained as for polymer 1 but from polystyryl(diphenylphosphine) prepared from bromo-polystyrene with 2.9 mmol Br g$^{-1}$ as initiator.

25 Polymer 3 - from polymer bound pyridine from chloromethylpolystyrene with 1.1 mmol Cl g$^{-1}$ (obtained in Example 2B above).

Discussion of Results

- Saturation of the polymer was not reached in these experiments.

Comparison of the capacities for Polymers 1 and 2, which are of the same type but with different maleic anhydride loadings, shows that the capacity for metals is not directly proportional to the functional group loading and that high loadings are not necessarily beneficial.
Polymer 3 is quite satisfactory for lead adsorption although inferior to Polymer 2 for mercury and cadmium adsorption.

Example 4

The metals were completely stripped from the polymers of Example 3 using 2M nitric acid (25 ml g\(^{-1}\) polymer). The regenerated polymer exhibited exactly the performance of the newly prepared material. There was no evidence that the performance deteriorated over repeated saturation regeneration cycles.
1. Insolubilised poly(maleic anhydride).
2. Poly(maleic anhydride) according to claim 1 which has been
insolubilised by cross-linking; or by copolymerisation of
poly(maleic anhydride) or monomeric maleic anhydride with a
hydrophobic polymer or comonomer.
3. Poly(maleic anhydride) according to claim 2 wherein the
hydrophobic polymer comprises a substituted or unsubstituted
copolymer.
4. Poly(maleic anhydride) according to any preceding claim which
has IR absorption maxima at 3,480 to 3,500 cm⁻¹, 1,670 to 1,690 cm⁻¹
and 1,190 to 1,210 cm⁻¹.
5. Poly(maleic anhydride) according to any preceding claim wherein the
polymerisation of the maleic anhydride has been initiated by a Lewis
base.
6. A process for the preparation of insolubilised poly(maleic
anhydride), which process comprises cross-linking poly(maleic
anhydride) or copolymerising poly(maleic anhydride) or monomeric
maleic anhydride with a hydrophobic polymer or comonomer.
7. A process according to claim 6 wherein monomeric maleic anhydride
is copolymerised with a hydrophobic polymer.
8. A process according to claim 6 or 7 wherein the hydrophobic
polymer comprises a substituted or unsubstituted polystyrene.
9. A process according to any of claims 6 to 8 wherein the
polymerisation of the monomeric maleic anhydride is initiated by
a Lewis base.
10. A process according to claim 9 effected under anhydrous
conditions.
11. A process according to claim 9 or 10 wherein the Lewis
base comprises a compound of the formula:
\[ R_n R_1 R_2 M \]
wherein:
- \( R_n \) represents a monovalent hydrophobic polymeric group;
- \( R_1 \) and \( R_2 \), which may be the same or different, each represent
  a substituted or unsubstituted hydrocarbyl group or, together with
  \( M \), represent a heterocyclic moiety; and
- \( M \) represents an element of Group VB of the Periodic Table.
12. A process according to claim 11 wherein R represents a polystyryl group.
13. A process according to claim 11 or 12 wherein at least one of R₁ and R₂ represents a phenyl group.
14. A process according to any of claims 11 to 13 wherein M represents nitrogen or phosphorus.
15. A process according to claim 11, 12 or 14 wherein R₁R₂ and M represent pyridine and Rₙ is a ring substituent.
16. Insolubilised poly(maleic anhydride) whenever prepared by the process of any of claims 6 to 15.
17. A method of removing a heavy metal from an aqueous media, which method comprises contacting the medium with insolubilised poly(maleic anhydride) according to any of claims 1 to 5 or 16.
18. A method according to claim 17 wherein the insolubilised poly(maleic anhydride) is contained in an absorbent bed or column through which the medium is passed.
19. A method according to claim 17 or 18 wherein the heavy metal comprises one or more of lead, mercury, zinc or cadmium.
20. A method according to claim 19 wherein the heavy metal comprises lead.
21. A method of recovering a heavy metal from an aqueous medium according to any of claims 17 to 20, which method additionally comprises treating the insolubilised poly(maleic anhydride) contacted with the medium with a strong acid.
22. A method according to claim 21 wherein the strong acid comprises nitric acid.
23. Heavy metal whenever recovered by the method of any of claims 21 or 22.
ABSTRACT

Insolubilised poly(maleic anhydride) is disclosed for use in a method of removing heavy metals, particularly lead, from aqueous media.