The Structure of Iron(III) Tetra(4-*N*-methylpyridyl)porphyrin Species Bound to Synthetic Water-soluble Anionic Polymers and their Reactions with *tert*-Butyl Hydroperoxide in Aqueous Solution

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This paper describes studies carried out to investigate the nature of the species that are formed when the cationic iron(III) tetra(4-*N*-methylpyridyl)porphyrin (Fe^{III}T4MPyP) is bound to three water-soluble anionic polymers, namely, poly(styrene-4-sulfonate), poly(vinylsulfonate) and poly(acrylate), in water at pH 9.2. GPC studies with Fe^{III}T4MPyP and its free base, H_2T4MPyP, show that the iron porphyrin is bound by electrostatic interactions and by ligation to the metal. UV–VIS spectroscopy reveals that the polymers induce a broadening and a blue-shift of the metalloporphyrin Soret band and for poly(styrene-4-sulfonate) the extent to which this occurs depends on the method of preparation of the polymer-bound porphyrin. Resonance Raman spectroscopy shows that with poly(styrene-4-sulfonate) the iron porphyrin is bound as a low spin iron species whilst with poly(acrylate) it is a mixture of high and low spin species.

The rates of reactions of polymer-bound Fe^{III}T4MPyP with imidazole and with Bu^tO_2H in the presence of 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) are found to be dependent on the nature of the polymer and, for poly(styrene-4-sulfonate), on the method of preparation of the bound catalyst. Products from the polymer–Fe^{III}T4MPyP-catalysed decomposition of *tert*-butyl hydroperoxide in the presence and absence of ABTS have been determined and the oxidant accountability is excellent. Evidence for the formation of polymer-bound oxoiron(IV) tetra(4-*N*-methylpyridyl)porphyrin in the reactions with Bu^tO_2H is presented.

Possible structures for the polymer-bound Fe^{III}T4MPyP are discussed and it is concluded that the metalloporphyrin is extensively aggregated on the polymer chains as μ-oxo x-mers.

Metalloporphyrins are catalysts for many classes of organic oxidations including oxygenation (mimics of the cytochrome P450 monooxygenases),[1] electron and hydrogen atom transfer (models for peroxidase),[2] autoxidation,[3] and photooxidation.[4] Recent years have seen an increased interest in these reactions and the potential of metalloporphyrin catalysts is being actively studied with a particular emphasis on developing new clean oxidation processes. Metalloporphyrins should, through control of the metal centre, the axial ligands, the structure of the macrocycle and oxidant provide a versatile range of oxidation catalysts.[1]

The performance/potential of metalloporphyrin catalysts in most oxidations should be improved if they can be heterogenised by binding them to the surface of a solid. The beneficial effects of the resulting materials would include increased stability, ease of separation from products, recovery and reuse. Five methods have been employed to attach these catalysts to solids, namely, electrostatic binding of charged porphyrins to counter-charged supports,[5] intercalation of charged porphyrins between the layers of clay,[6] entrapment within the pores or matrices of solids,[7] covalent binding of the support to the porphyrin ring[8] and axial ligation to surface bonded ligands.[9] The potential utility of each method is determined by a number of factors, including its general applicability to a wide range of metallophorphyrins, the ease of preparation and the catalyst's stability and activity.

Our interest in the development of supported metalloporphyrin catalysts has led us to investigate the nature of the binding of charged metalloporphyrins to counter-charged supports. In a previous paper[5f] we concluded, from epoxidations with iodosylbenzene catalysed by iron(III) tetra(*N*-methylpyridyl)porphyrins supported on sulfonated organic polymers, that the charged porphyrins are not rigidly fixed to, but rather free to aggregate on, the polymer surface. The difficulty in studying the metalloporphyrin species on a heterogeneous surface has led us to investigate the binding of cationic iron(III) tetra(4-*N*-methylpyridyl)porphyrin (Fe^{III}T4MPyP) to soluble anionic polymers, since the resulting homogeneous systems are amenable to spectroscopic analysis. The results from this study are reported here.

Results

This study employed three water-soluble linear polymers, namely the sodium salts of poly(styrene-4-sulfonic acid) (PSS; M.w. 12 200), poly(vinylsulfonic acid) (PVS; M.w. 5700) and poly(acrylic acid) (PAA; M.w. 454 000) with Fe^{III}T4MPyP and its free base H_2T4MPyP (Fig. 1). A limited number of experiments were also carried out with iron(III) tetra(2-*N*-methylpyridyl)porphyrin (Fe^{III}T2MPyP). The pH of the solutions was maintained at 9.2 to ensure the polymers were fully ionised. Since at this pH Fe^{III}T4MPyP is known to form dimers in free solution at concentrations $> 10^{-5}$ mol dm^{-3},[10] the porphyrin concentration was maintained at 5×10^{-6} mol dm^{-3} for all the spectroscopic studies to minimise this complication, although for GPC it was 5×10^{-5} mol dm^{-3} to aid observation of the porphyrins by eye.

The Fe^{III}T4MPyP polymer solutions were prepared in two different ways to give 250 equivalents of polymer side-chain units over porphyrin. Either all the polymer was added to the solution of iron(III) porphyrin in one aliquot (single addition) or it was added gradually in a series of smaller quantities (multiple addition).

Gel Permeation Chromatography.—The GPC studies used columns packed with Sephadex G-25M which has a fractionation range of M.w. 100–5000 for globular proteins. The ionic strength of the solutions was maintained at 0.05 mol dm^{-3} using

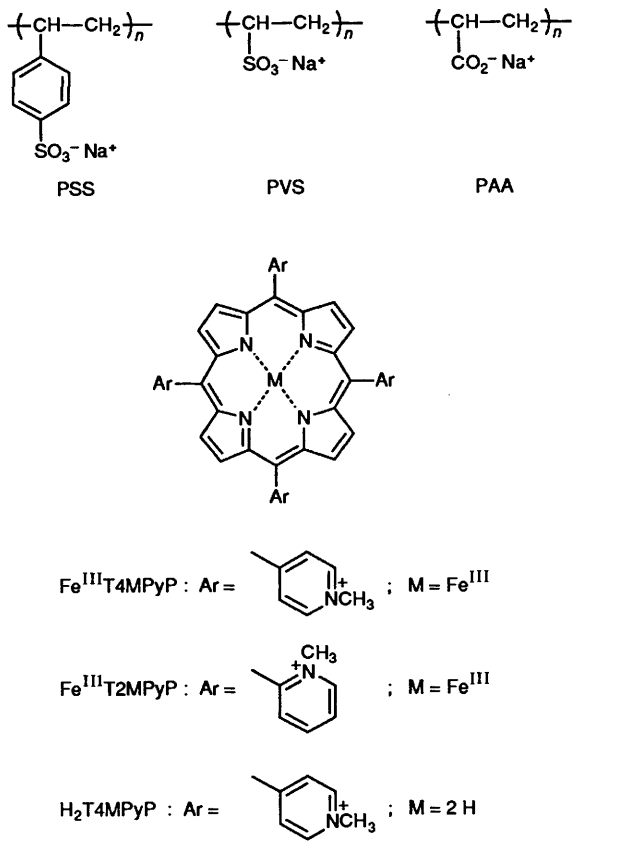

Fig. 1 Structure of polymers and porphyrins used in this study

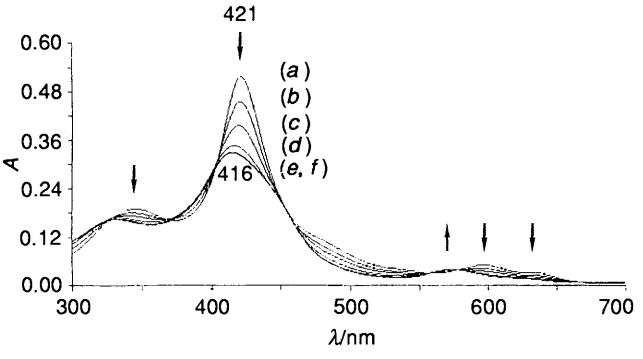

Fig. 2 UV–VIS spectrum of Fe^{III}T4MPyP in the presence of the following equivalents of PAA side-chain units: (*a*) 0, (*b*) 1, (*c*) 2, (*d*) 3, (*e*) 4, (*f*) 5. Fe^{III}T4MPyP, 5.0×10^{-6} mol dm^{-3}; borate buffer, 0.01 mol dm^{-3}, pH 9.2; μ = 0.005 mol dm^{-3}.

Table 1 The elution of Fe^{III}T4MPyP and H$_2$T4MPyP by GPC on Sephadex G-25M in the presence and absence of PSS, PVS and PAA using aqueous borate buffer as eluent[a]

	GPC observations	
Polymer (equivalents)[b]	Fe^{III}T4MPyP	H$_2$T4MPyP
—	binds to Sephadex	binds to Sephadex
PSS (250)	100% elutes rapidly	100% elutes rapidly
PVS (250)	100% elutes rapidly	*ca.* 50% elutes rapidly
PAA (250	100% elutes rapidly	binds to Sephadex
PAA (250)[c]	—	*ca.* 80% elutes rapidly
PSS (8)[d]	100% elutes rapidly	—

[a] Porphyrin 5×10^{-5} mol dm^{-3}; borate buffer 0.1 mol dm^{-3}, pH = 9.2; μ = 0.05 mol dm^{-3}. [b] Equivalents of polymer side-chain units over porphyrin. [c] Borate buffer 0.01 mol dm^{-3}, pH = 9.2; μ = 0.005 mol dm^{-3}. [d] Borate buffer 0.1 mol dm^{-3}, pH = 9.2; μ = 0.2 mol dm^{-3} (with $NaNO_3$).

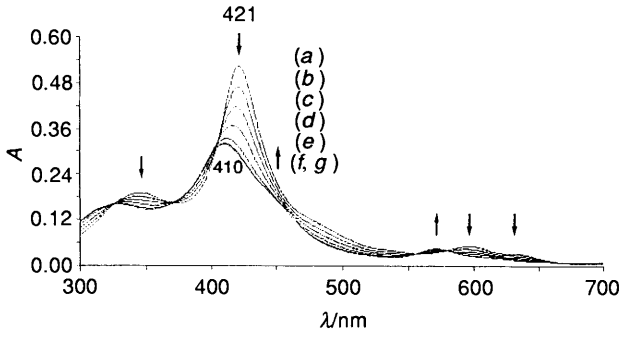

Fig. 3 UV–VIS spectrum of Fe^{III}T4MPyP in the presence of the following equivalents of PVS side-chain units: (*a*) 0, (*b*) 1, (*c*) 2, (*d*) 3, (*e*) 4, (*f*) 5, (*g*) 10. Conditions as in Fig. 2.

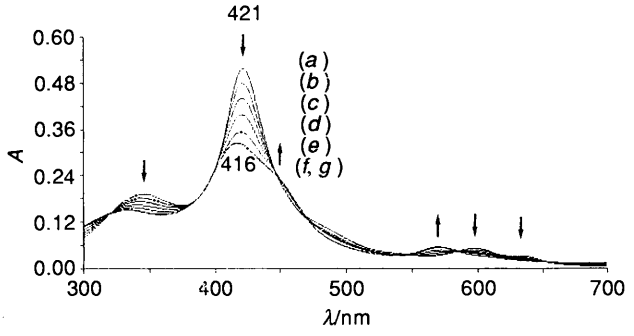

Fig. 4 UV–VIS spectrum of Fe^{III}T4MPyP in the presence of the following equivalents of PSS side-chain units: (*a*) 0, (*b*) 1, (*c*) 2, (*d*) 3, (*e*) 4, (*f*) 5, (*g*) 10. Conditions as given in Fig. 2.

0.1 mol dm^{-3} borate buffer, unless otherwise stated. The solutions of the polymer-bound porphyrins were added to the column and eluted with aqueous borate buffer.

Table 1 shows that in the absence of polymer both Fe^{III}T4MPyP and H$_2$T4MPyP bound to the top of the columns and were not eluted with borate buffer. However, the presence of any of the three polymers caused all the Fe^{III}T4MPyP to be eluted rapidly, irrespective of whether the polymer-bound porphyrin was prepared by the single or multiple addition procedure. Even in the presence of only eight equivalents of PSS side-chain units, all of the Fe^{III}T4MPyP was rapidly eluted from the column. The metal-free porphyrin in the presence of PSS also passed quickly through the column whereas, in contrast, with PAA it bound to the top of the column and with PVS approximately half was eluted quickly. With PAA at a lower ionic strength (0.005 mol dm^{-3}) approximately 80% of the H$_2$T4MPyP was eluted rapidly.

UV–VIS Spectroscopy.—The UV–VIS spectra of Fe^{III}T4MPyP in the presence and absence of PAA, PVS and PSS were recorded at pH 9.2 (Figs. 2–4, respectively). Each polymer results in the porphyrin Soret absorption band being blue-shifted and broadened. A shoulder was also observed at 445–448 nm with each polymer. Furthermore, the two Q bands at 598 and 630 were replaced by a single band at a shorter wavelength with each polymer (569–573 nm). The change to the new species was complete after adding five equivalents of polymer side-chains over iron(III) porphyrin molecules at an ionic strength of 0.005 mol dm^{-3}. Higher concentrations of polymers were required to produce the same changes in the UV–VIS spectrum of Fe^{III}T4MPyP at higher ionic strengths. In fact, at ionic strengths above 0.15 mol dm^{-3} the UV–VIS spectrum of Fe^{III}T4MPyP was unaltered on adding 250 equivalents of PAA. The same occurred for PVS at ionic strengths above 0.25 mol dm^{-3}. In contrast, the multiple

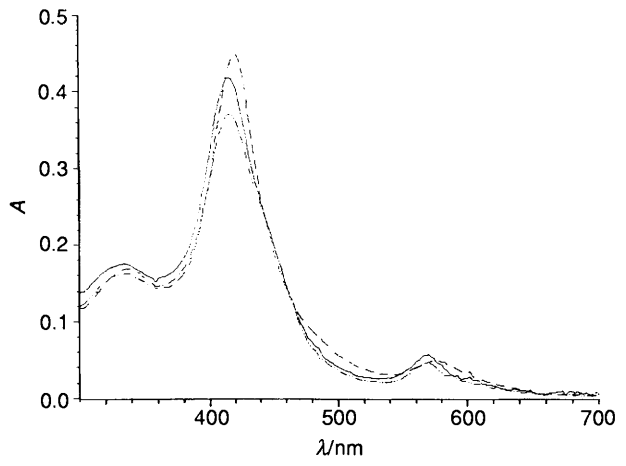

Fig. 5 UV–VIS spectrum of single addition PSS–Fe^{III}T4MPyP (– – –, Soret λ_{max} 419 nm), multiple addition PSS–Fe^{III}T4MPyP (— · · — · · —, Soret λ_{max} 414 nm) and equilibrated PSS–Fe^{III}-T4MPyP (——, Soret λ_{max} 412 nm). Fe^{III}T4MPyP, 5.0×10^{-6} mol dm^{-3}; PSS side-chain units, 1.25×10^{-3} mol dm^{-3}; borate buffer 0.01 mol dm^{-3}, pH 9.2; μ = 0.005 mol dm^{-3}.

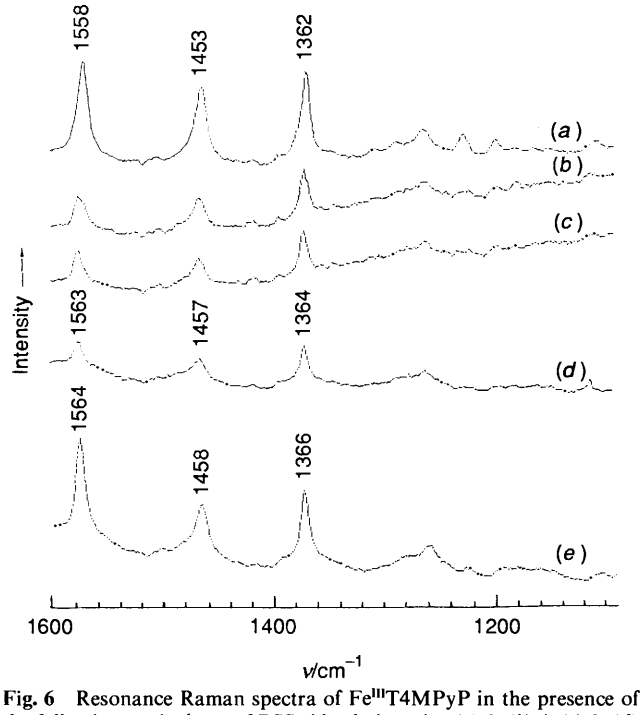

Fig. 6 Resonance Raman spectra of Fe^{III}T4MPyP in the presence of the following equivalents of PSS side-chain units: (*a*) 0, (*b*) 4, (*c*) 8, (*d*) 250 (multiple addition) and (*e*) 250 (single addition). Fe^{III}T4MPyP, 5.0×10^{-6} mol dm^{-3}; borate buffer, 0.1 mol dm^{-3}, pH 9.2; μ = 0.2 mol dm^{-3} (with $NaNO_3$).

addition of a total of 250 equivalents of PSS to solutions of Fe^{III}T4MPyP produced similar UV–VIS spectral changes at ionic strengths of 0.005 and 1.5 mol dm^{-3}.

Fig. 5 shows that the UV–VIS spectrum of Fe^{III}T4MPyP in the presence of 250 equivalents of PSS is dependent upon the manner in which the polymer was added to the iron(III) porphyrin. The spectrum of single addition PSS–Fe^{III}T4MPyP (Soret λ_{max} 419 nm) more closely resembles that of Fe^{III}-T4MPyP in free solution (Soret λ_{max} 421 nm) than that when PSS had been added by multiple additions (Soret λ_{max} 414 nm). However, allowing the two polymer–porphyrin solutions to equilibrate over 48 h gave rise to spectra which were identical to each other (Soret λ_{max} 412 nm). This spectrum is more similar to that of the non-equilibrated, multiple addition PSS–Fe^{III}T4MPyP than that of non-equilibrated, single addition

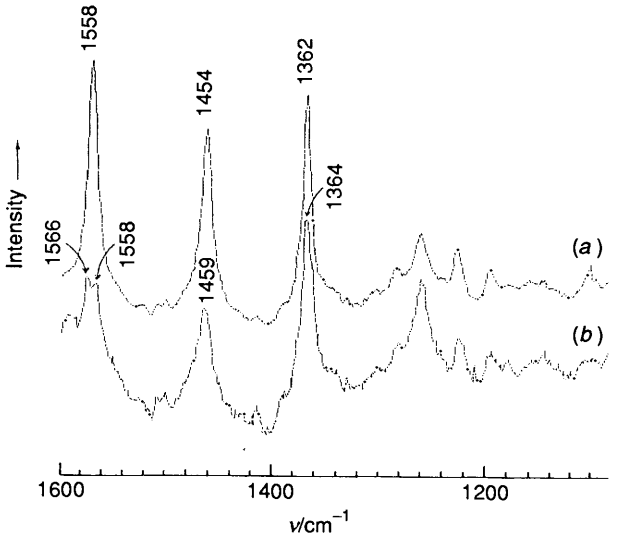

Fig. 7 Resonance Raman spectra of Fe^{III}T4MPyP in the absence (*a*) and in the presence of 250 equivalents of PAA side-chain units (*b*). Fe^{III}T4MPyP, 5.0×10^{-6} mol dm^{-3}; PA side chain units, 1.25×10^{-3} mol dm^{-3}; borate buffer, 0.1 mol dm^{-3}, pH 9.2; μ = 0.05 mol dm^{-3}.

PSS–Fe^{III}T4MPyP. In contrast, the UV–VIS spectra of Fe^{III}-T4MPPyP in the presence of PAA or PVS were not dependent upon the method in which the polymer was added to the solution of iron(III) porphyrin and did not change on standing.

The UV–VIS spectrum of Fe^{III}T4MPyP was found to be unchanged by the addition of 250 equivalents of the sodium salts of 4-methylbenzenesulfonate, acetate or hexane-1,6-dioate. Furthermore, the UV–VIS spectrum of the more sterically hindered Fe^{III}T2MPyP was found to be unaltered on adding 250 equivalents of PAA or PVS. In contrast, when 250 equivalents of PSS were gradually added to the solution of Fe^{III}T2MPyP, the Soret band became broader, even though the position of its peak did not change.

Resonance Raman Spectroscopy.—The resonance Raman spectrum of Fe^{III}T4MPyP was recorded at pH 9.2 in the presence and absence of PSS and PA (Figs. 6 and 7). The gradual addition of 250 equivalents of PSS side-chain units to Fe^{III}T4MPyP generated a new metalloporphyrin species, as indicated by the shift of the iron(III) spin state marker bands from 1362 and 1558 cm^{-1} to 1364 and 1563 cm^{-1}, respectively. Indeed, the change was complete with only eight equivalents. With four equivalents both the original and the new porphyrin species were present in the solutions (Fig. 6). The mixtures from the single addition of 250 equivalents gave very similar resonance Raman spectra to those from the slow multiple additions.

The spectra from Fe^{III}T4MPyP in the presence of a 250-fold excess of PAA have a split marker band at 1558 and 1566, suggesting the mixtures may contain two kinds of iron(III) species bound to the polymer (Fig. 7).

The Influence of Imidazole on Solutions of Polymer-bound Fe^{III}T4MPyP.—The relative rates of reaction of imidazole with the polymer-bound and free Fe^{III}T4MPyP at 30 °C in 0.1 mol dm^{-3} borate buffer at pH 9.2 with a 3×10^4 fold excess of imidazole over Fe^{III}T4MPyP (5×10^{-6} mol dm^{-3}) were measured. With free Fe^{III}T4MPyP reaction occurred on mixing (< 10 s). In contrast, however, the reactions of PVS- and PAA-bound Fe^{III}T4MPyP, whether prepared by the single or multiple addition method, took *ca.* 7 and *ca.* 3 min, respectively, to go to completion (Fig. 8).

The reaction of imidazole with single addition-PSS–Fe^{III}-T4MPyP was biphasic. The first phase was very rapid and took

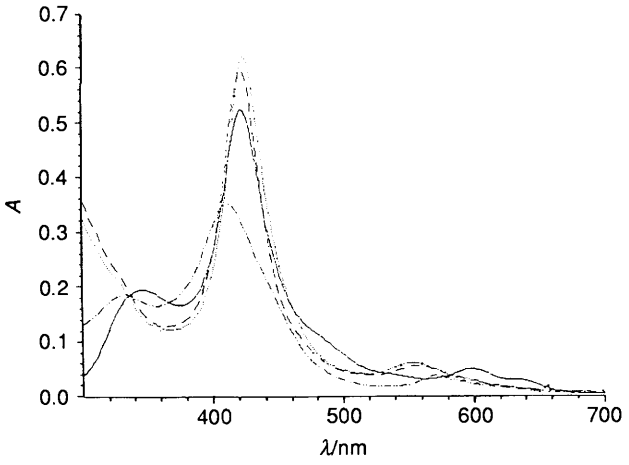

Fig. 8 UV–VIS spectrum of $Fe^{III}T4MPyP$ (——, Soret λ_{max} 421 nm) and with imidazole after 1 min (· · ·, Soret λ_{max} 423 nm), PVS–$Fe^{III}T4MPyP$ (— · · — · · —, Soret λ_{max} 410 nm) and with imidazole after 7 min (– – –, Soret λ_{max} 421 nm). $Fe^{III}T4MPyP$, 5.0×10^{-6} mol dm^{-3}; PVS side-chain units, 1.25×10^{-3} mol dm^{-3}; imidazole 0.15 mol dm^{-3}; borate buffer, 0.1 mol dm^{-3}, pH 9.2; μ = 0.05 mol dm^{-3} at 30 °C.

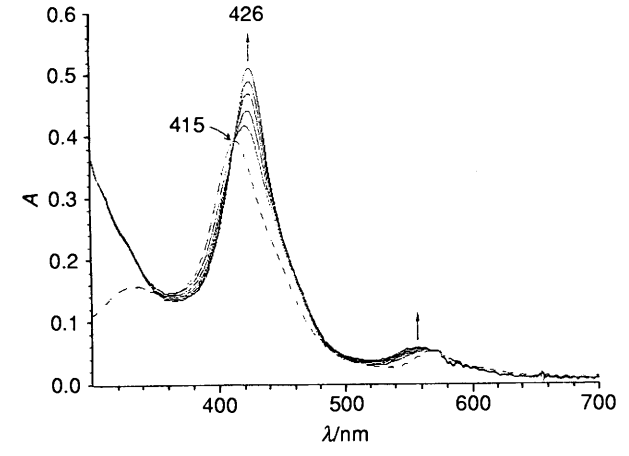

Fig. 9 UV–VIS spectrum of multiple addition PSS–$Fe^{III}T4MPyP$ (– – – –) and with imidazole after 12, 24, 36, 48 and 60 h (——). Conditions as given for Fig. 8.

place during the mixing time (< 10 s) whilst the second occurred over a period of 3 days. The latter part of the reaction was characterised by a broadening of the Soret band. In contrast, the reactions of multiple addition-PSS– and equilibrated-PSS–$Fe^{III}T4MPyP$ were not biphasic and occurred extremely slowly, requiring approximately 5 days to reach completion (Fig. 9).

It is noteworthy that all the final spectra of mixtures involving the reactions of imidazole with free or bound $Fe^{III}T4MPyP$ are very similar, although not identical.

GPC experiments were also carried out on Sephadex G-25M columns with the imidazole-containing solution of equilibrated-PSS–$Fe^{III}T4MPyP$ and also with a solution of the bis-imidazole complex of $Fe^{III}T4MPyP$ [$Fe^{III}T4MPyP$ (5.0×10^{-6} mol dm^{-3}): imidazole, 1 : 30 000] in the absence of polymer to act as a blank. Both solutions were loaded onto the columns, and eluted with 0.1 mol dm^{-3} borate buffer containing 0.15 mol dm^{-3} imidazole. Whereas 100% of the polymer–porphyrin was rapidly eluted, the bis-imidazole–$Fe^{III}T4MPyP$ complex remained bound to the top of the column.

Kinetic Studies of the Reactions of Equilibrated PSS–Fe^{III}-T4MPyP *with* tert-*Butyl Hydroperoxide.*—The kinetics were investigated in 0.1 mol dm^{-3} aqueous borate buffer solution (pH 9.16) at 30 °C at constant ionic strength [μ = 0.20 mol dm^{-3} with $NaNO_3$ using the one-electron trap diammonium 2,2′-azinobis(3-ethylbenzthiazoline-6-sulfonate), ABTS].[11] These conditions have been used previously for kinetic studies in the absence of polymer.[12] Control experiments showed that the iron(III) porphyrin was not removed from the PSS by ABTS and that ABTS was not oxidised by Bu^tO_2H in the absence of the $Fe^{III}T4MPyP$. The kinetic studies used 5×10^{-6} mol dm^{-3} $Fe^{III}T4MPyP$, 1.25×10^{-3} mol dm^{-3} of PSS side-chain units with (1.0–10) $\times 10^{-5}$ mol dm^{-3} Bu^tO_2H and 7.5×10^{-3} mol dm^{-3} ABTS. Under these conditions the formation of $ABTS^{\bullet+}$ (λ_{max} 660 nm) was triphasic; an initial lag phase was followed by a first-order growth and a decay. The length of the lag phase, which was not very reproducible (Fig. 10 shows the initial part of a typical kinetic study), decreased with higher concentrations of Bu^tO_2H. The maximum yield and the rate of the first-order build-up of $ABTS^{\bullet+}$ were significantly less than those from corresponding reactions in the absence of PSS.[12]

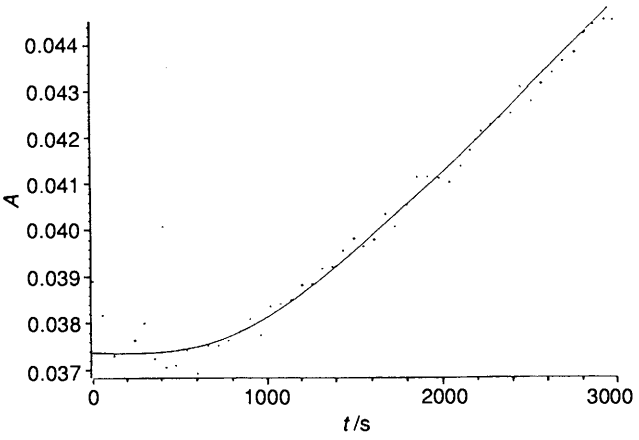

Fig. 10 The lag phase and the initial part of the first-order growth of $ABTS^{\bullet+}$ absorbance in the reaction of Bu^tO_2H with equilibrated PSS–$Fe^{III}T4MPyP$ in the presence of ABTS. $Fe^{III}T4MPyP$, 5.0×10^{-6} mol dm^{-3}; PSS side-chain units, 1.25×10^{-3} mol dm^{-3}; Bu^tO_2H, 1×10^{-5} mol dm^{-3}; ABTS 7.5×10^{-3} mol dm^{-3}; borate buffer 0.1 mol dm^{-3}, pH 9.2; μ = 0.2 mol dm^{-3} with $NaNO_3$ at 30 °C.

The data were analysed by measuring the maximum rate of formation of $ABTS^{\bullet+}$ following the induction period, a quasi-initial rate method. Repeat experiments showed that the quasi-initial rates of reaction with PSS-bound catalyst were less reproducible (±30%) than the first-order rate constants obtained from $Fe^{III}T4MPyP$ in free solution (±10%).[12] Although this analysis of the rate is not rigorous it does enable trends in the rates to be established. Increasing the initial concentration of Bu^tO_2H increased the maximum yield and the quasi-initial rates of formation of $ABTS^{\bullet+}$. Fig. 11 shows the quasi-initial rates are linearly related to the initial [Bu^tO_2H]. The variation of the quasi-initial rates of reaction with [$Fe^{III}T4MPyP$] was not examined.

The quasi-initial rate of formation of $ABTS^{\bullet+}$ and the length of the initial lag phase were both dependent on the mode of preparation of PSS–$Fe^{III}T4MPyP$ (Fig. 12). They decreased in the order single addition, multiple addition and equilibrated PSS–$Fe^{III}T4MPyP$.

Product Studies on the Reactions of Equilibrated PSS–$Fe^{III}T4MPyP$ *with* Bu^tO_2H.—The product yields from these reactions were examined under the four regimes used previously.[12] These are: (i) unstirred reactions in the presence of ABTS in air; (ii) stirred reactions in the absence of ABTS in air; (iii) unstirred reactions in the absence of ABTS in air; (iv) unstirred reactions in the absence of ABTS under nitrogen.

The reaction with ABTS present was finished in 24 h whilst those in its absence required 10 days to go to completion. The product yields, recorded in Table 2, show that oxidant account-

Table 2 Percentage yields of products from the reaction of Bu^tO_2H with equilibrated PSS–Fe^{III}T4MPyP (and Fe^{III}T4MPyP in free solution).[a] Fe^{III}T4MPyP, 5×10^{-6} mol dm^{-3}; PSS side-chain units, 1.25×10^{-3} mol dm^{-3}; Bu^tO_2H, 2.5×10^{-3} mol dm^{-3}; ABTS, 3.0×10^{-2} mol dm^{-3}; borate buffer, 0.1 mol dm^{-3}, pH = 9.2; μ = 0.20 mol dm^{-3} with $NaNO_3$ at 30 °C

Reaction conditions	Yields of products (%)[b]					Carbon balance (%)	
	Bu^tOH	Me_2CO	MeOH	HCHO	Bu^tO_2Me	$(C_3 + C_4)$[c]	$(C_1 + C_4)$[c]
ABTS in air, unstirred	97(98)	2(4)	—(3)	n.d.(n.d.)[d]	—(—)	99(102)	—(—)
No ABTS in air, stirred	10(6)	85(79)	13(15)	63(56)	4(12)	99(97)	94(101)
No ABTS in air, unstirred	9(4)	80(77)	11(30)	63(26)	9(19)	98(100)	101(98)
No ABTS under N_2, unstirred	5(1)	64(70)	12(35)	13(3)	32(30)	101(101)	94(99)

[a] Figures in parentheses are percentage yields from reactions without PSS; ref. 12. [b] Based on oxidant. Traces of $Bu^tO_2Bu^t$ also detected. [c] $(C_3 + C_4)$ is the sum of the percentage yields of Bu^tOH, Me_2CO and Bu^tO_2Me; $(C_1 + C_4)$ is the sum of the percentage yields of Bu^tOH, MeOH, HCHO and 2 × Bu^tO_2Me. [d] Interference from $ABTS^{\bullet+}$ made the colorimetric determination of HCHO impossible.

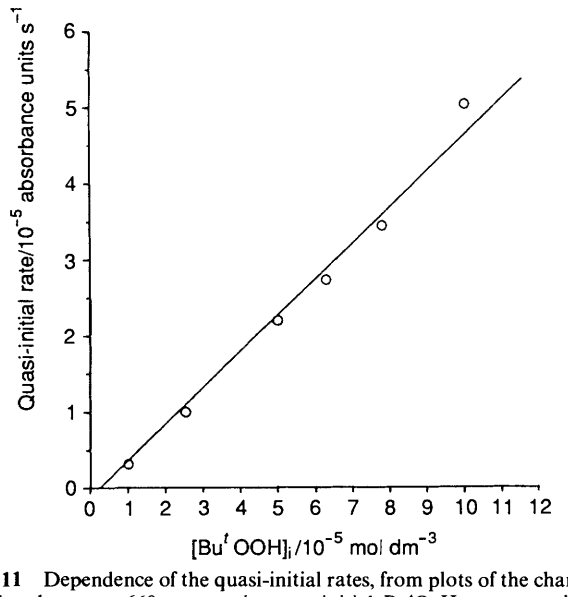

Fig. 11 Dependence of the quasi-initial rates, from plots of the change in absorbance at 660 nm *vs.* time, on initial Bu^tO_2H concentration. Conditions as given for Fig. 10.

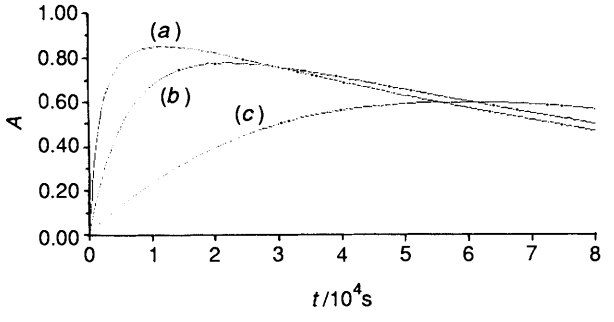

Fig. 12 The growth of $ABTS^{\bullet+}$ absorbance in the reactions of Bu^tO_2H with (*a*) single addition, (*b*) multiple addition and (*c*) equilibrated PSS–Fe^{III}T4MPyP in the presence of ABTS. Conditions as given for Fig. 10.

ability in each oxidation regime was excellent. Furthermore, the product distributions from these reactions are very similar to those from Fe^{III}T4MPyP in free solution except that the yields of formaldehyde are higher and those of methanol are lower with some of the polymer–Fe^{III}T4MPyP-catalysed reactions.

Attempts to Detect Polymer-bound Oxoiron(IV) *Tetra*(4-N-*methylpyridyl*)*porphyrin*.—The UV–VIS spectra of the polymer-bound Fe^{III}T4MPyP species in 0.1 mol dm^{-3} borate buffer solution (pH 9.2) were monitored following the addition of a 10-fold excess of Bu^tO_2H. With multiple addition and equilibrated PSS–Fe^{III}T4MPyP no changes were observed. In contrast, the Soret bands of single addition PSS– and PVS–Fe^{III}T4MPyP

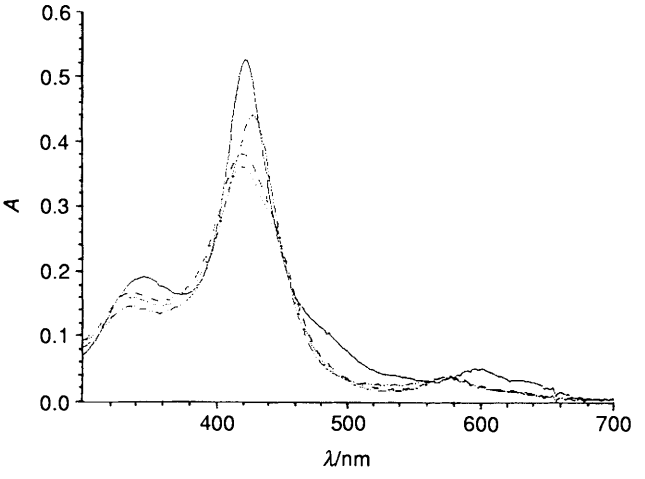

Fig. 13 UV–VIS spectra of Fe^{III}T4MPyP (——, Soret λ_{max} 421 nm), PAA–Fe^{III}T4MPyP (– – –, Soret λ_{max} 419 nm), PAA–Fe^{III}T4MPyP with Bu^tO_2H after 3 min (— · · — · · —, Soret λ_{max} 427 nm) and after 3 h (· · ·, Soret λ_{max} 419 nm). Conditions as given for Fig. 10.

showed small transient red shifts but, more significantly, in the latter spectrum a shoulder appeared at 430 nm which grew to a maximum during the first 10 min of reaction and then decayed over the next hour. With PAA–Fe^{III}T4MPyP the spectral change was more pronounced; the Soret band shifted to 427 nm in the first 3 min of reaction, increased in intensity before slowly reverting to its original position over the following 3 h (Fig. 13).

Discussion

These studies show that Fe^{III}T4MPyP readily interacts with PSS, PVS and PAA in aqueous solution at pH 9.2. Furthermore, the spectral and GPC changes brought about by these polymers must arise from the collective influence of the anionic groups on the polymer chains, since monomeric models for the polymer repeat units, such as sodium 4-methylbenzenesulfonate, acetate and hexane-1,6-dioate do not give rise to similar effects.

The nature of the binding of the cationic porphyrins to the anionic polymers, the origins of the observed spectral changes and the influence of the polymers on the reactivity of the porphyrins are considered below.

The results from the GPC experiments are very informative about the extent to which Fe^{III}T4MPyP and its free base, H_2T4MPyP, bind to the three ionised polymers at pH 9.2. Sephadex G-25M columns were chosen because they have a molecular weight fractionation range of 100–5000 for globular protein[13] and it was expected that the polymers and polymer-bound porphyrins would be excluded from the pores of the gel

on account of their large size. In contrast, unbound porphyrins would permeate the pore structure of the gel which should result in their being eluted more slowly than the polymeric species. The polymer-bound Fe^{III}T4MPyP did indeed elute rapidly from the columns. However, probably as a consequence of the Sephadex having a small number of surface carboxylate groups,[13] the cationic Fe^{III}T4MPyP and H_2T4MPyP were found to bind to the top of the GPC columns in the absence of the polymers (Table 1) instead of slowly eluting. Furthermore, these experiments show that H_2T4MPyP is less strongly bound to the polymers than Fe^{III}T4MPyP since it becomes detached from PVS and PAA during GPC. In fact the unmetallated porphyrin was not eluted in the presence of PAA and only 50% rapidly eluted in the presence of PVS at an ionic strength of 0.05 mol dm^{-3}. Interestingly, at ten times lower ionic strength the PAA–H_2T4MPyP binding is stronger, with the result that the latter elutes rapidly from the GPC columns.

The difference in behaviour of Fe^{III}T4MPyP and H_2T4MPyP suggests that the former is not bound to the polymers simply by electrostatic interactions between the *N*-methylpyridyl substituent and anionic sulfonate or carboxylate polymer side-chains. The stronger binding of the metalloporphyrin indicates that the iron(III) centres are also ligated to the polymers and/or are linked together by μ-oxobridges. It is noteworthy that sulfonate and carboxylate ions are known to ligate to iron(III) porphyrins.[14] With the H_2T4MPyP, where the dominant interactions are electrostatic, the GPC results show that the porphyrin is not anchored as firmly to PAA and PVS as it is to PSS. The origin of this difference is unclear but it might arise from extra π–π interactions between the styrene units on the polymer and the pyridyl substituents of the porphyrin.

The stoichiometry of the binding of Fe^{III}T4MPyP to PSS is approximately 5–8 polymer side-chain units per porphyrin. Thus, only a small excess of polymer side-chain units over porphyrin is sufficient to ensure a complete change from free to bound species as adjudged by UV–VIS (Fig. 4) and resonance Raman spectroscopy (Fig. 6) and rapid elution from the Sephadex columns. However, consideration of the distances between adjacent sulfonate or carboxylate groups on the polymers compared to the distances between adjacent *N*-methylpyridyl positive charges or between iron(III) and *N*-methylpyridyl groups makes it unlikely that, at these relative concentrations of polymer to porphyrin, each porphyrin is linked to the polymers by one or two axial ligands and four electrostatic interactions. In fact it suggests that, with small excesses of polymer side-chains, some of the binding sites on the porphyrin are not directly associated with the polymers, although indirect binding *via* hydrogen-bonded water molecules might be possible. It is noteworthy that in crystals of hydrated Fe^{III}T4MPyP pentachloride a hydrogen-bonded anionic network of chloride ions and water molecules is interleaved between the cationic porphyrin rings.[15]

The binding of Fe^{III}T4MPyP and H_2T4MPyP to the ionic polymers is sensitive to the ionic strength of the solution. Both UV–VIS spectroscopy and GPC show that larger excesses of polymer side-chains over porphyrin are required to bind the latter at higher ionic strengths. These results indicate that the charged groups are screened by the increased concentration of ions in the solution, thereby reducing the attractive forces between the ionised polymers and porphyrin.[16] Interestingly, UV–VIS spectroscopy shows that binding of Fe^{III}T4MPyP to PSS is less affected by increases in ionic strength than its binding to PVS and PAA which again points to additional binding interactions between the styrene units and the pyridylporphyrin rings. The latter would be less sensitive to changes in ionic strength than ionic interactions.

Aggregation of Fe^{III}T4MPyP *Bound to Polymers.*—The changes in the UV–VIS spectrum of Fe^{III}T4MPyP arising from the addition of PSS, PVS or PAA might arise either from modification of the local solvent relative permittivity by the polymers or from cofacial, or nearly cofacial, aggregation of the porphyrin on the polymers, leading to exciton coupling between these species. Since the evidence presented here points to extensive porphyrin aggregation on the polymers, it seems more likely that the latter gives rise to the observed spectral changes.

Cofacial aggregation of porphyrins is known to result in blue-shifts and broadening of the Soret band relative to that of the monomer, similar to those observed in this study.[17] Exciton coupling[18] is very successful at explaining how the magnitude of the effect is dependent on the inter-porphyrin separation,[17c] the relative orientation of the porphyrin molecules,[17c] the oscillator strengths of the monomer transitions,[17a,19] and the number of porphyrins in the aggregates.[20] The differences in the UV–VIS spectra of Fe^{III}T4MPyP aggregated on PSS, PVS or PAA are then explicable in terms of differences in the orientation and conformational freedom of the porphyrin rings, inter-porphyrin distances and extent of aggregation.

The spectral changes cannot be explained simply by electrostatic binding or axial ligation to porphyrin monomers since monomeric models of the polymer side-chains do not alter the UV–VIS spectrum of Fe^{III}T4MPyP in free solution. Aggregation is further supported by the absence of changes in the UV–VIS spectrum of iron(III) tetra(2-*N*-methylpyridyl)porphyrin (Fe^{III}T2MPyP) on addition of PVS or PAA, since the 2-*N*-methyl group would hinder the close approach of the porphyrin rings and thus prevent exciton coupling.[21] The small changes seen when PSS was added to Fe^{III}T2MPyP might arise from π–π interactions between the polymer and pyridyl groups of the porphyrin, as described above.

It is not surprising that Fe^{III}T4MPyP exists as aggregates on the flexible polymers since its local concentration is markedly higher than in the bulk solution. The concentration dependence of μ-oxo-dimer formation of Fe^{III}T4MPyP in aqueous alkali is well documented and on this basis it seems probable that the iron(III) porphyrin is bound to the polymers as μ-oxo x-mers.[10,22]

UV–VIS spectroscopy and reactions with imidazole and with Bu^tO_2H reveal that the structure of PSS–Fe^{III}T4MPyP depends on its mode of preparation, whereas this is not apparent with the comparable PVS and PAA species (Figs. 2–4). A single addition of 250-equivalents of PSS side-chains to Fe^{III}T4MPyP gives species with a Soret λ_{max} = 419 nm whilst with multiple additions, giving the same final excess of PSS, the λ_{max} value is 414 nm. On standing for 48 h at 30 °C both spectra change to give a Soret band with λ_{max} = 412 nm. The reactivity of these PSS-bound species with imidazole and with Bu^tO_2H also suggests they have different structures. Since the binding of Fe^{III}T4MPyP to PVS and PAA is weaker than that to PSS, the porphyrin can more readily move on the former polymer chains to form porphyrin aggregates. In contrast, with PSS equilibration of bound porphyrin molecules to form aggregates becomes more difficult and takes longer to achieve. Differences between the PSS–Fe^{III}T4MPyP species then arise because, by multiple small additions of PSS, the porphyrin is almost completely bound by a relatively small excess of the polymer early in the addition process, resulting in extensive aggregation. However, with a single addition of a large excess of PSS the porphyrin molecules should be more evenly dispersed over all the polymer chains and consequently will be less aggregated. Indeed, single addition PSS–Fe^{III}T4MPyP may well contain a significant proportion of bound monomeric Fe^{III}T4MPyP species. In agreement with this conclusion, the former has a larger blue-shift (7 nm) of the Soret band than the latter (2 nm). Prolonged equilibration might allow extensive reorganisation

and further aggregation of the Fe^{III}T4MPyP molecules on PSS, resulting in a 9 nm blue-shift of the Soret band. The UV–VIS spectra of these species suggest that the equilibrated material may be closer in structure to the more aggregated species from multiple small additions than that from a single large addition of PSS.

Resonance Raman spectroscopy does not distinguish between the different PSS–Fe^{III}T4MPyP species (Fig. 6). Irrespective of the method of preparation the same spectrum was obtained. Comparison of the spectra of the polymer-bound species with that from Fe^{III}T4MPyP in free solution shows that the two oxidation/spin state marker bands at 1362 and 1558 cm^{-1} are shifted to higher wavenumbers by the addition of PSS (or PAA) whilst the bands associated with the porphyrin structure are unchanged. The absence of changes to the Raman frequencies for the porphyrin ring on addition of the polymer, despite the changes in the UV–VIS spectra, seems to be a general phenomenon since π–π interactions cause only small shifts (< 3 cm^{-1}) in the Raman lines of cofacial metalloporphyrins.[23]

The shifts in the oxidation/spin state marker bands on addition of the polymers is best explained by a change from high spin to low spin iron(III) on binding to the polymers. Thus, both the marker bands for the polymer-bound species lie in the range of values reported for low spin iron(III) porphyrins,[24] although that at 1564 cm^{-1} is somewhat lower than the 1569 cm^{-1} values reported for the low spin bis-cyano complex of Fe^{III}T4MPyP.[25] An alternative possibility is that the bound iron(III) porphyrin is a quantum admixture of $S = \frac{3}{2}$ and $S = \frac{5}{2}$ states. Indeed, Goff and his coworkers[26] reported that this is the spin state of iron(III) tetraphenylporphyrin with the weakly coordinating 4-nitrobenzenesulfonate ligand, which could be considered as a monomeric model of PSS.

The low spin state of the polymer–metalloporphyrin aggregates contrasts with the high spin of the μ-oxo dimer of Fe^{III}-T4MPyP.[22a] However, the iron atom in the latter is pentacoordinated whereas that in the μ-oxo x-mers would be hexacoordinated. In this respect polymer-bound Fe^{III}T4MPyP might more closely resemble the bis-hydroxy complex of Fe^{III}-T4MPyP, which is known to be a low spin species.[22a,b,e,f,25,27] Metalloporphyrin literature cites many examples of cofacial aggregation, some of which have been proposed to be dimers[28] whereas others have been suggested to exist as x-mers.[29] An analogy for the structure of the hexacoordinated μ-oxo x-mers proposed above can be found in the μ-oxo bridged structure of polymeric iron(IV) hemiporphyrazine which has been established by X-ray crystallography.[30]

The split spin marker bands at 1558 and 1566 cm^{-1} for the PAA–Fe^{III}T4MPyP (Fig. 7) suggest that with this polymer both high spin and low spin iron(III) porphyrins are present. The origin of this difference in behaviour between PSS- and PAA-bound Fe^{III}T4MPyP is unclear.

Relevant to this study is the research into the interactions of porphyrins and metalloporphyrins with nucleic acids.[31] The nature of the complex formed depends upon the structure of the metalloporphyrin. H_2T4MPyP and its metal derivatives, which have no axial ligands or weak axial ligands, can intercalate between guanine–cytosine base pairs but not between adenine–thymine pairs.[31] In contrast, metalloT4MPyP derivatives with axial ligands are sterically hindered from intercalating and instead bind externally to the negatively charged phosphate backbone.[31d] It is noteworthy, however, that although it has been suggested that the latter species are stacked on the DNA surface[31c,32] a blue-shifted Soret band is not seen in the UV–VIS spectra of any of these species, indicating that the aggregates on DNA have a different structure to those on the synthetic anionic polymers used in this study.

Reactivity and Reactions of Polymer-supported Fe^{III}T4MPyP.—The conclusions from the spectroscopic and GPC studies are supported by the studies on the reactions of polymer–Fe^{III}T4MPyP with Bu^tO_2H and with imidazole.

In the presence of a large excess of ABTS, the kinetic behaviour of the polymer–Fe^{III}T4MPyP-catalysed decomposition of Bu^tO_2H is markedly different from that of the analogous reaction with Fe^{III}T4MPyP in free solution.[12] The former is slow and triphasic whereas the latter is relatively fast and shows pseudo-first-order kinetics. However, a closer examination of the two reactions reveals that apart from the induction period the differences between them can be rationalised in terms of their reaction rates; the former is slower by a factor of approximately 10. Thus the second phase in the polymer–porphyrin-catalysed reactions shows first-order kinetics and in this respect resembles the reactions in the absence of polymer. The final phase arises from the slow decay of the 660 nm absorbance resulting from the addition of hydroxide ion to $ABTS^{\bullet+}$ in the basic solution (pH 9.2).[11] This is unimportant in the kinetic studies of the faster reactions of the free iron(III) porphyrin. However, it is more evident in the slow polymer–porphyrin-catalysed reactions, especially towards the end of the second phase when the oxidant concentration is low and the $ABTS^{\bullet+}$ concentration is maximal.

The origin of the induction period and the rate retardation can be attributed to the aggregation of the porphyrin on the PSS. The known low reactivity, towards Bu^tO_2H, of iron(III) μ-oxo dimers relative to the corresponding monomers[6b,33] suggests that aggregation of Fe^{III}T4MPyP would lead to a dramatic decrease in the rate of reaction. This effect might also be enhanced by steric hindrance of the polymer chains around the Fe^{III}T4MPyP restricting access of the oxidant to the iron(III) centres. The induction period might then arise from some reorganisation of the Fe^{III}T4MPyP species on the polymers, in the presence of Bu^tO_2H, generating a low concentration of catalytically active sites. In agreement with these conclusions, the induction period increases and the rate decreases in the order, single addition, multiple addition, equilibrated PSS–Fe^{III}T4MPyP-catalysed reactions: the order of increasing aggregation of the porphyrin on the polymers. It is noteworthy that although the UV–VIS spectrum of PSS–Fe^{III}T4MPyP did not change after 24 h equilibration (the standard time used for equilibration) the catalyst's activity continued to decrease with age; presumably owing to further time-dependent organisation of the polymer–porphyrin.

The order of reactivity above was also observed with the reactions of the three PSS–Fe^{III}T4MPyP species with imidazole. The very rapid first phase of reaction observed with single addition-PSS–Fe^{III}T4MPyP, but not the other species, is probably due to the reaction of some bound monomeric Fe^{III}T4MPyP that is present in this preparation of polymer catalyst. The slower second phase and the slow reactions with the other PSS–Fe^{III}T4MPyP would then arise from reaction with the bound aggregated porphyrin.

Since iron(III) porphyrins readily form bis-imidazole complexes with excess of imidazole,[34] it is likely that the bis-adduct is formed from free and polymer-bound Fe^{III}T4MPyP. This is borne out by the similarity of their respective UV–VIS spectra. That the bis-imidazole adduct remains bound to the polymers is confirmed by GPC which shows that the adduct was only eluted rapidly in the presence of PSS. Presumably the bis-imidazole adduct is bound to PSS by electrostatic interactions.

The greater reactivity of excess imidazole with PVS– and PAA–Fe^{III}T4MPyP than with PSS–Fe^{III}T4MPyP suggests that the iron(III) porphyrin is less tightly anchored to the former polymers than to PSS and as a result the aggregates are more readily broken up. These conclusions are supported by the rapid equilibration of Fe^{III}T4MPyP on PVS or PAA.

$$Fe^{III}P + Bu^tO_2H \longrightarrow \left[\begin{array}{c} HO\text{–}OBu^t \\ | \\ Fe^{III}P \end{array}\right] \begin{array}{l} \nearrow OFe^{IV}P + Bu^tO^{\bullet} \quad (1) \\ \searrow OFe^{IV}P^{\bullet+} + Bu^tOH \quad (2) \end{array}$$

The product distributions from the PSS–Fe^{III}T4MPyP-catalysed decompositions of Bu^tO_2H are very similar to those from the analogous reactions of the iron(III) porphyrin in free solution.[12] In all cases the oxidant accountability is excellent. For these reasons we conclude, as previously, that the cleavage of the peroxy bond is homolytic [reaction (1)] rather than heterolytic [reaction (2)].

The major difference between polymer–porphyrin- and free porphyrin-catalysed reactions lies in the yields of formaldehyde and methanol in the absence of ABTS. With PSS–Fe^{III}T4MPyP, the yields of the former are higher whereas those of the latter are lower. The origin of these differences, which are particularly apparent for the unstirred reactions in air or under nitrogen, may be the much longer times required to consume the oxidant with the polymer-bound catalyst (10 days) as compared to those with the free Fe^{III}T4MPyP ($1\frac{1}{2}$ h). These products arise from the competitive oxidation of methyl radicals [reactions (3)–(5)] and as a consequence an increase in the yield of one leads to a decrease in the other and *vice versa*.[12] We conclude that, in the very slow reactions with the polymer-bound catalyst in dioxygen, stirring the reaction becomes unimportant since replacement of consumed dioxygen by diffusion is no longer critical. In agreement with this, the product distributions from stirred and unstirred reactions with PSS–Fe^{III}T4MPyP in air are identical. The increase in the yield of formaldehyde from the reaction under nitrogen, compared with the corresponding reaction of free Fe^{III}T4MPyP, might have arisen from a small leakage of dioxygen into the system over the long reaction time.

$$Me^{\bullet} + Fe^{III}P \xrightarrow{H_2O} MeOH + Fe^{II}P \quad (3)$$

$$Me^{\bullet} + OFe^{IV}P \xrightarrow{H_2O} MeOH + Fe^{III}P \quad (4)$$

$$Me^{\bullet} + O_2 + Fe^{II}P \xrightarrow{H_2O} MeO_2Fe^{III}P \longrightarrow HCHO + Fe^{III}P \quad (5)$$

The reaction of Bu^tO_2H with Fe^{III}T4MPyP in aqueous buffer (pH 9.2) generates the relatively stable oxoiron(IV) tetra(4-*N*-methylpyridyl)porphyrin (OFe^{IV}T4MPyP). UV–VIS spectroscopy shows that this change is accompanied by a shift and increase of the Soret band from 421 nm (ε_{max} 10 200 m^2 mol^{-1}) to 427 nm (ε_{max} 12 500 m^2 mol^{-1}).[35] Comparable experiments with the three PSS–Fe^{III}T4MPyP species gave little or no evidence for the formation of polymer-bound OFe^{IV}T4MPyP. Only the single addition PSS–Fe^{III}T4MPyP, the least aggregated of the three, showed a small red-shift of the Soret band. Since most of the Fe^{III}T4MPyP is tightly bound to PSS as aggregates, relatively little would have been or become available to form PSS–OFe^{IV}T4MPyP and consequently not unexpectedly the UV–VIS spectra showed little change on addition of Bu^tO_2H.

With PVS–Fe^{III}T4MPyP and to a greater extent PAA–Fe^{III}T4MPyP, the addition of Bu^tO_2H showed UV–VIS spectral changes which we attribute to polymer-bound OFe^{IV}-T4MPyP with a Soret band λ_{max} at 430 nm on PVS and 427 nm on PAA (Fig. 13). As in free solution, UV–VIS spectroscopy shows that these oxoiron(IV) species decay back with time to give the original polymer-bound Fe^{III}T4MPyP. The difference in the behaviour of Fe^{III}T4MPyP bound to PAA and PVS compared with the PSS analogues has been discussed above. All the evidence suggests that the cationic porphyrin is more aggregated and more firmly anchored to the PSS than it is to the other polymers. For these reasons more monomeric species are present or can become available through dynamic equilibria on the PVS and PAA polymer chains. It is noteworthy that in the reaction of Bu^tO_2H with a mixture of the monomer and μ-oxo dimer of Fe^{III}T4MPyP in free solution both species are consumed to give OFe^{IV}T4MPyP.[35] Furthermore, when the oxoiron(IV) species decays back to iron(III) it regenerates the same proportion of monomer and μ-oxo dimer. These results were interpreted in terms of oxidation of the monomer to OFe^{IV}T4MPyP and a rapid equilibrium of monomer and μ-oxo dimer.

In summary, Fe^{III}T4MPyP binds to the water soluble polymers PSS, PVS and PAA by electrostatic interactions between the anionic side-chains and the cationic porphyrins, and by coordination to the iron(III) centres. Additional, possibly π–π interactions, between the pyridylporphyrin and the styrene units result in a stronger binding of the porphyrin to polymer and a slower equilibration between bound porphyrin species with PSS than with PVS or PAA.

Spectroscopic GPC and reactivity studies suggest that Fe^{III}-T4MPyP is extensively aggregated on the anionic polymer chains, probably as μ-oxo x-mers. Product yields from the reaction of Bu^tO_2H with polymer–Fe^{III}T4MPyP are very similar to those from the analogous reactions with free Fe^{III}-T4MPyP although the rate of the former reaction is markedly reduced by aggregation on the polymer chains. UV–VIS spectroscopy reveals the formation of polymer-bound oxoiron(IV) species in the reaction of Bu^tO_2H with PAA– and PVS–Fe^{III}T4MPyP.

Experimental

Materials.—The sodium salt of poly(styrene-4-sulfonic acid) was obtained from Polysciences Inc. The reported M.w. was 70 000, however, the measured value was 12 200.* The sodium salts of poly(vinylsulfonic acid) and poly(acrylic acid) were from Aldrich Chemical Co. Ltd. The reported M.w. of the former was not available and that for the latter was 90 000; the measured values were 5700 and 454 000, respectively.*

The PSS used in the kinetic investigation was purified of iron salts by passing a solution of the polymer through a column of AnalaR Amberlite IRC-50 (Na^+ form). The concentration of PSS in the eluate was determined by comparing its absorbance at 262 nm with that of the non-purified sample of known concentration.[36] Atomic absorption spectroscopy showed the iron content was 9 ppb in a solution containing 1.5×10^{-2} mol dm^{-3} of PSS sidechains.

The preparations of the iron(III) tetra(*N*-methylpyridyl)-porphyrin pentachlorides have been reported previously.[5c] The metal free porphyrin, H_2T4MPyP, was obtained from Strem Chemicals Inc. as the tetraiodide.

All the other chemicals were obtained from Aldrich Chemical Co. Ltd. or Fisons Scientific Apparatus Ltd.

Methods.—UV–VIS spectra were recorded on a Perkin-Elmer Lambda 15 scanning spectrometer and on a Hewlett-Packard 8425A diode array spectrometer. The GC and GC–MS methods and the procedures used for kinetic and product studies in this investigation have been described previously.[12]

Resonance Raman spectra were recorded with a Jobin-Yvon HR64D single spectrograph and a Wright Instruments liquid nitrogen-cooled CCD camera. Indene and 1,4-dioxane were

* The values were obtained by GPC measurements at Unilever Research, Port Sunlight.

used for routine calibration. The peak positions of well defined bands are ± 2 cm^{-1}. The excitation wavelength was 413.1 nm from a Spectra-Physics 170 Kr^+ ion laser. Samples were contained in a spinning quartz cell at room temperature. The sample for resonance Raman spectroscopy typically contained Fe^{III}T4MPyP (5×10^{-6} mol dm^{-3}) and polymer side-chain units (1.25×10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} borate buffer (1.5 cm^3, pH 9.2). Spectra were acquired over a 5 min period.

GPC used prepacked disposable Pharmacia PD-10 columns containing Sephadex G-25M. The bed volume was 9.1 cm^3 and bed height 5 cm. The columns were conditioned for use by equilibrating the gel with 25 cm^3 of the buffer solution. This solution consisted of the same mixture of borate buffer ($\pm$ sodium nitrate) in which the reaction mixture had been made up. The sample for GPC, typically porphyrins (5×10^{-5} mol dm^{-3}), polymer side-chain units (1.25×10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} borate buffer (2.5 cm^3, pH 9.2), was loaded on the column and eluted with the same mixture used to make up the reaction sample. The first 2.5 cm^3 of eluent were discarded and the next 10 cm^3 were collected in ten 1 cm^3 fractions. The amount of polymer–porphyrin eluting in each of these fractions was measured by UV–VIS spectroscopy. Rapidly eluting eluate was defined as that which came off in the first four 1 cm^3 fractions, as specified for high molecular weight components on Pharmacia PD-10 columns.[37]

The single addition polymer–Fe^{III}T4MPyP (polymer side-chains: metalloporphyrin, 250:1) were prepared by adding 0.05 cm^3 of a solution containing 0.075 mol dm^{-3} of polymer side-chains in 0.1 mol dm^{-3} borate buffer to 2.95 cm^3 of a solution of Fe^{III}T4MPyP (5.1×10^{-6} mol dm^{-3}) also in 0.1 mol dm^{-3} borate buffer. This was shaken a few times. The Fe^{III}T4MPyP binds immediately to the polymer.

Multiple addition polymer–Fe^{III}T4MPyP was prepared by adding 10×0.01 cm^3 aliquots of 3×10^{-3} mol dm^{-3} polymer side-chains in aqueous borate buffer to a solution of Fe^{III}-T4MPyP (2.854 cm^3) followed by 1 aliquot of 0.006 cm^3 of 0.075 mol dm^{-3} and a further 4 aliquots of 0.01 cm^3 polymer solution in aqueous borate buffer. The mixtures were shaken between each addition. This gave a final solution of polymer–Fe^{III}T4MPyP (3 cm^3; polymer side-chain: Fe^{III}T4MPyP, 250:1).

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