Polymer-bound Ligands and Metal Complexes *via* Catalysed Reactions of Polybutadienes

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Polybutadiene functionalised with chlorosilyl groups *via* homogeneous catalytic reactions can be treated with picolyl- or bipyridyl-lithium reagents to give polymer-bound ligands, which will bind metal centres chemically or electrochemically; alternatively, zinc porphyrin units can be bound to the polymer *via* phenolysis of the Si–Cl bonds.

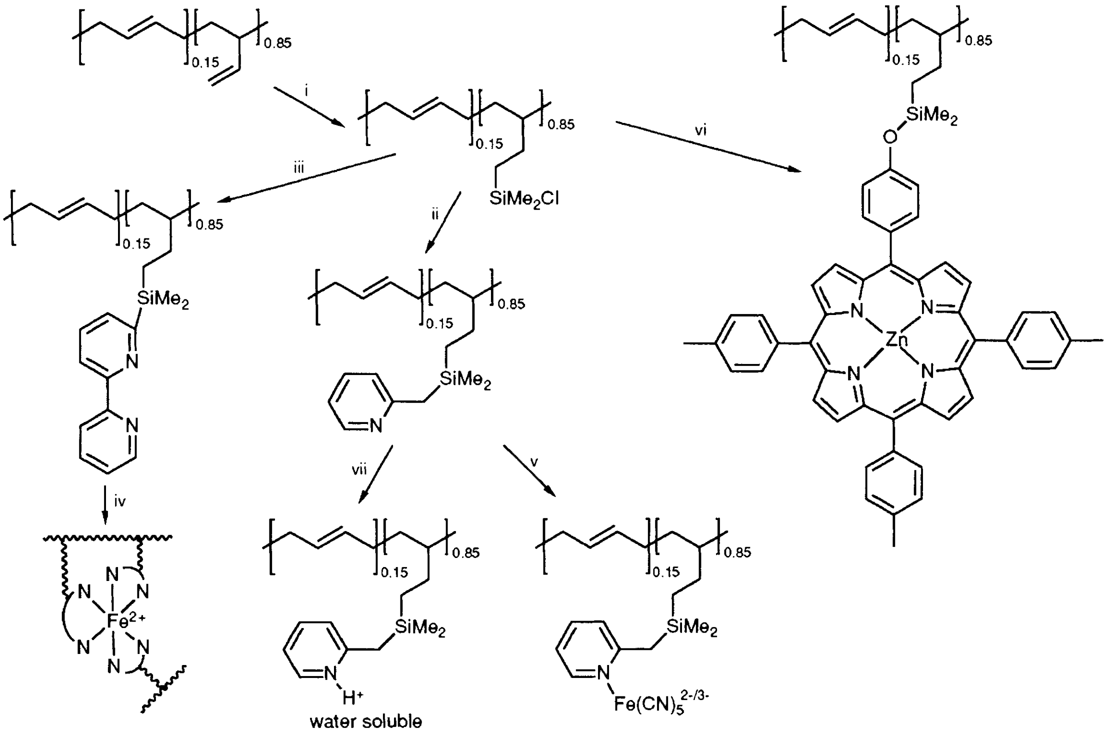
There is considerable interest in the binding of metal complexes to polymers because of their potential electrochemical, photochemical or conductive properties.[1] Many of the reported polymer-bound metal complexes are formed by direct polymerisation of vinyl-substituted ligands or intact metal complexes. This often leads to insoluble complexes that are difficult to characterise fully and the metal complex is usually attached close to the backbone of the polymer so that its mobility within the polymer is restricted. Some examples of soluble polymeric metal complexes have been reported[2] and Meyer has described complexes that are separated from the main polymer chain by a flexible spacer group.[2]

We are interested in the synthesis of soluble polymers in which metal complexes can be bound with variable spacing from the main chain and now report a versatile method for the synthesis of a range of different polymer-bound ligands and metal complexes.

Polybutadienes are available with a wide variety of microstructures and molecular weight ranges. The different microstructures arise because the butadiene units entering during the growing process can add either in a 1,4- or a 1,2-fashion so that the residual double bonds can be either in the main chain (1,4-addition *cis* or *trans*) or pendant from the main chain (1,2-addition). We have been examining[3–7] homogeneous catalysis as a means of functionalising polybutadienes and find that selectivity towards functionalisation of the various double bonds can be achieved using different reactions or reaction conditions.

In particular, hydrosilation of polybutadienes using H_2PtCl_6 as a catalyst gives selective functionalisation at the terminal C atoms of the pendant double bonds.[7] A small amount of reactivity of *cis* backbone double bonds is observed if an excess of silylating agent is used. Polymers functionalised in this way react smoothly with 2-lithiomethylpyridine or 6-lithio-2,2′-bipyridyl to give polymer-bound pyridine or bipyridyl functions (see Scheme 1). These polymers are soluble in common organic solvents of medium polarity and, at least in the case of the polymer bound pyridine, dissolve in dilute acid, presumably on account of protonation to give ionic pyridinium polymers. The microstructures of the polymers are readily analysed by ^1H and ^{13}C NMR spectroscopy and high loadings are obtained.

Scheme 1 also illustrates ways in which these polymers can be used to bind metal ions. Thus, reaction of the bipyridyl



Scheme 1 Methods for forming metal containing polymers. (*i*) $HSiMe_2Cl$, H_2PtCl_6, 80 °C, 18 h; (*ii*) 2-lithiomethylpyridine, −20 °C, 1 h, then 18 °C, 12 h; (*iii*) 6-lithio-2,2′-bipyridyl, −30 °C, 1 h, then 18 °C, 12 h; (*iv*) Ammonium iron(II) sulfate, H_2O/CH_2Cl_2 (5% loading) or $Fe(ClO_4)_2$, CH_2Cl_2 (80% loading) both 18 °C, 1 h; (*v*) $[Fe(CN)_5(H_2O)]^{2-}$, H_2O (monitored by electrochemical cycling); (*vi*) 5-*p*-hydroxyphenyl-10,15,20-tris-*p*-tolylporphinatozinc(II), CH_2Cl_2, 18 °C, 1 h; (*vii*) HCl (1 mol dm^{-3}).

containing polymer with aqueous ammonium iron(II) sulfate gives a red polymer, which is still soluble in *e.g.* CH_2Cl_2. Atomic absorption analysis indicates that *ca.* 5% of the bipyridyl groups are bound to the polymer and UV–VIS studies (λ_{max} 493sh, 525 cm^{-1}, *cf.* 488sh, 523 cm^{-1} for $[Fe(bipy)_3]^{2+}$)[8] show that each iron atom is surrounded by three bipyridyl ligands. Evidently the cross-linking in this case is not sufficient to render the polymer insoluble. However, addition of iron(II) perchlorate in CH_2Cl_2 gives an insoluble red polymer for which atomic absorption analysis suggests that 80% of the bipyridyl groups are bound to iron.

Electrochemical studies in water of the polymer with 5% loading of Fe^{2+} cast as a film from CH_2Cl_2 onto an indium tin oxide (ITO) electrode show [Fig. 1(*a*)] a clear response from a surface immobilised Fe^{III}/Fe^{II} couple at E^0 = 0.86 V (ref. saturated calomel electrode, SCE) (*cf.* 0.74 for $[Fe(bipy)_3]^{2+}$).[9]† The small separation of the oxidation and reduction maxima (20 mV at 100 mV s^{-1}) for the polymer-based complex indicates fast electron transfer even at quite rapid scan rates (100–500 mV s^{-1}). The area under the peaks measured at low scan rates suggests that the electrons can penetrate to a depth equivalent to *ca.* 20 monolayers indicating that fast redox conduction occurs through the polymer, even though the iron centres are well separated. Interestingly, this electrochemical response is only observed at low pH in the presence of *e.g.* toluene-*p*-sulfonic acid (*p*-TsOH). The origin of this effect is currently under investigation, but it is possible that it arises from partial protodesilylation, although it does not happen if HCl is used. Whatever the mechanism, the redox centres clearly remain surface confined throughout the electrochemical experiment since the separation of the oxidation and reduction maxima is $\ll$59 mV and the height of the waves, at least in the range 10–200 mV s^{-1} is linearly dependent upon the scan rate. This latter observation also suggests fast kinetics for the redox process.

Potential cycling (−0.6 to 1.6 V *vs.* SCE) of the pyridine functionalised polymer modified electrode in a solution containing $Na_2[Fe(CN)_5(H_2O)]$ (10^{-3} mol dm^{-3}) in aqueous sodium acetate (1 mol dm^{-3}, pH 9) monitors the complexation of the $[Fe(CN)_5]^{n-}$, n = 2 or 3, to the pyridine groups (*cf.* binding of the same complex to polyvinylpyrazine).[11] The binding is manifested by the rapid growth of a redox couple at +0.45 V *vs.* SCE [Fig. 1(*b*)], corresponding to the reversible oxidation and reduction of polymer bound $[\text{-}C_5H_4NFe(CN)_5]^{2-}$. No redox couple is observed when an uncoated electrode is used. The area under the curve corresponds to an apparent molar coverage of 20 nmol cm^{-2} or about 200 monolayers. The redox wave has a large peak separation (180 mV at a scan rate of 50 mV s^{-1}) reflecting the slow rate of charge propagation. Since this separation is even greater at lower coverages, it presumably reflects the wide spacing between the redox sites in the polymer. Potential cycling of the $[\text{-}Fe(CN)_5]^{2-}$ loaded polymer in fresh sodium acetate (1 mol dm^{-3}) solution leads to gradual loss of $[Fe(CN)_5]^{2-}$ from the polymer.

The final illustration of how metal complexes may be bound to the hydrosilated polybutadiene involves the direct reaction of a suitably functionalised metal complex with the polymer. The Si–Cl units are susceptible to reactions with molecules containing acidic protons *e.g.* water or alcohols.[7] Usually, the formed Si–OR bonds are susceptible to hydrolysis so that the R groups are readily lost and cross-linking occurs.[7] We find, however, that the hydrosilated polymers react with *e.g.* phenol to give phenoxy-substituted polymers which are less susceptible to hydrolysis. We have used this as a means of preparing a polymer containing bound zinc porphyrin units. Thus, reaction of 5-*p*-hydroxyphenyl-10,15,20-tris-*p*-tolylporphyrinatozinc(II)[12] with a polymer containing pendant $\text{-}SiMe_2Cl$ units in the presence of triethylamine gives the

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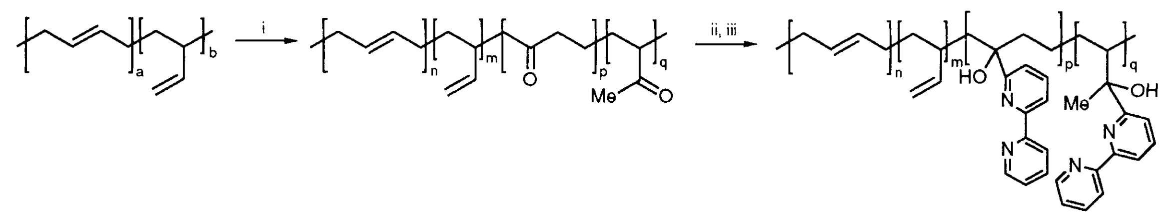
† Immobilisation of $[Fe(bipy)_3]^{2+}$ in *e.g.* montmorillonite clay has been shown to shift this redox potential to *ca.* 0.86 V.[10]



Scheme 2 Binding of 2,2′-bipyridyl units *via* reaction of polyketones. (*i*) Bu^{t}OOH, [$PtCF_3(Ph_2PCH{=}CHPPh_2)(CH_2Cl_2)$]$BF_4$, 80 °C, 70 h; (*ii*) 6-lithio-2,2′-bipyridyl, −78 °C, 1 h, then 18 °C for 12 h; (*iii*) H_2O, 18 °C; backbone double bonds can be *cis* or *trans*, only *trans* are shown.

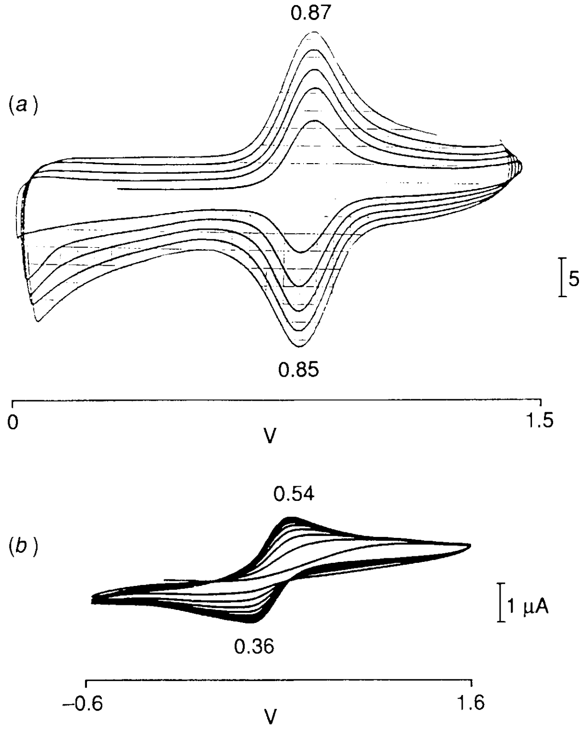


Fig. 1 Electrochemical responses for (*a*) indium tin oxide electrode (0.5 cm^2) coated with polymer bound [$Fe(bipy)_3$]$^{2+}$ (5% loading) at different scan rates [100 mV s^{-1} (smallest wave) → 500 mV s^{-1}, (largest wave)] in aqueous *p*-TsOH (0.1 mol dm^{-3}); (*b*) Pt disk electrode coated with polymer-bound pyridine in aqueous $Na_2[Fe(CN)_5(H_2O)]$ (2 mmol dm^{-3}) containing NaOAc (1.0 mol dm^{-3}), pH 7. Successive scans, smallest wave is first scan.

polymer bound zinc porphyrin with *ca.* 70% of the Si–Cl bonds functionalised (see Scheme 1). Evidence for binding of the porphyrin to the polymer is provided by shifts of certain resonances of the porphyrin in the ^1H NMR spectrum. In particular, the resonances from the protons on the phenoxo ring are shifted to higher field (δ 8.01 br d, 7.1 br s) and broadened in the polymer *cf.* the free porphyrin (8.08 d, 7.18 d). Characteristic shifts‡ are also observed for the protons of the polymer. This polymer is soluble in CH_2Cl_2, $CHCl_3$ or THF, and stable for several hours, although on standing in THF for two weeks, the peaks for polymer-bound porphyrin are replaced by those from the free zinc porphyrin and the resonances from the polymer protons are both shifted and reduced in intensity. These changes indicate that the Si–O linkage does undergo slow hydrolysis.

These preliminary experiments indicate that soluble polymers loaded with metal complexes are available by rather simple means from polybutadienes. Since we have found that polyketones, which can be obtained from oxidation of polybutadienes with Bu^{t}OOH in the presence of [$PtCF_3(Ph_2PCH{=}CHPPh_2)(CH_2Cl_2)$]$BF_4$, also react smoothly with 6-lithio-2,2′-bipyridyl to give bipyridyl functionalised polymers with the bipyridyl group attached directly to the main chain and/or on carbon atoms next to the main chain (Scheme 2), a very wide variety of different metal containing polymers with varying spacings from the main chain will be available.

We thank the SERC for a Fellowship (A. I.), Dr L. Milgrom (Brunel University) for a sample of the zinc porphyrin, the Japanese Soda Company for generous gifts of polybutadienes with a high proportion of pendant double bonds, and Johnson Matthey PLC for generous loans of platinum salts.

Received, 27th August 1991; Com. 1/04479F

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‡ Shifts (δ) for the free polymer, the polymer bound to the porphyrin and the hydrolysed polymer in the presence of the free porphyrin are respectively: vinyl protons (5.3; 5.35; 5.7); aliphatic protons on C not attached to Si (1.87, 1.3; 1.92, 1.25; 2.0, 1.3); $SiCH_2$(0.6, 0.4, 0.45); $SiMe_2$(0.3, 0.0, 0.05).

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