Novel approach to the study of the ion and solvent content of thin polymer films

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The admittance response of $[Os(bpy)_2(PVP_x)_{10}Cl]^+$ crystal coatings, where x signifies the percentage of poly(4-vinylpyridine) (PVP) in PVP : styrene copolymers, is probed as a function of both the styrene content of the polymer backbone and the $HClO_4$ bathing electrolyte concentration. Analysis of the admittance response of these coated crystals provides information about solvent uptake when the coatings are immersed in water and also about the changes in layer mass accompanying protonation of the unbound pyridine units in acidic solution. With increasing styrene content of the polymer backbone the requirement for anion and solvent ingress is proportionally reduced. For the polymers investigated, there is good correlation between the mass change observed in 0.5 M $HClO_4$ and the mass change anticipated, assuming complete protonation of the polymer backbone. The apparent acid dissociation constant of the protonated pyridine units, pK_a^{app}, for these polymers is 2.66 ± 0.06, and is independent of the styrene content of the polymer backbone.

In recent years we have been involved in the study of $[Os(bpy)_2(PVP)_{10}Cl]^+$ polymer film coated electrodes, where PVP signifies poly(4-vinylpyridine).[1–15] These studies have investigated the rate and mechanism of homogeneous and heterogeneous charge transport and, more recently, the associated mass transport processes; processes that are strongly dependent on both the type and concentration of the contacting electrolyte.[1–17] These observations emphasise the important interplay that exists between the polymer morphology and the nature of the bathing electrolyte. In this publication we investigate how the rigidity and the ion content of these metallopolymer coatings depends on the nature of the polymer backbone. This study is based on the analysis of the admittance response of the polymer coated quartz crystals which enables both the rigidity and resident layer mass of the attached layer to be probed. Firstly, the shape of the crystal resonance may be used as a probe of layer rigidity. A decrease in admittance and a broadening of the resonance (as characterised by the peak width at half height) is a qualitative reflection of a decrease in layer rigidity, which may be equated with structural changes occurring within the polymer.[7–11,17–23] Secondly, the shift in resonant frequency, determined from the frequency of maximum admittance, when corrected for the viscous load of the contacting electrolyte, may be used to probe the layer mass, once layer rigidity has been established.

The interaction of $[Os(bpy)_2(PVP_x)_{10}Cl]Cl$ polymer coatings, where x signifies the percentage of PVP in PVP : styrene copolymer backbones, with water and perchloric acid is investigated. The results obtained in this study illustrate that admittance analysis can provide detailed information about the interaction between polymer layers and contacting liquids. Although the results obtained are specific for the material investigated, we believe that the methods described can be applied to many other polymer/liquid interfaces.

Experimental

Apparatus

10 MHz AT-cut laboratory monitor crystals were used as supplied from International Crystal Manufacturing Company Inc., Oklahoma City, USA. The crystals had a 90 nm thick layer of gold sputter coated onto each side. The calibrated mass sensitivity of the crystals was $0.232\ Hz\ cm^2\ ng^{-1}$ and the electrochemically active area was $0.23\ cm^2$. Crystal admittance measurements were made using a Hewlett-Packard 8753A network analyser as outlined previously.[9]

Materials

Polymers. Poly(4-vinylpyridine) was prepared as described previously.[24] The molecular mass of the polymer, as determined by viscometry in absolute ethanol using the Mark–Houwink equation, $[\eta] = 2.5 \times 10^{-4}\ M_v^{0.68}$, was found to be *ca.* 325 000 $g\ mol^{-1}$. The poly(4-vinylpyridine) : styrene copolymers, PVP_{75}, PVP_{67} and PVP_{33} were prepared and characterised by Dr. D. Leech.[24] These polymers are identified in terms of the percentage of poly(4-vinylpyridine) in the copolymer backbone, *i.e.* PVP_{33} signifies a copolymer of 33% 4-vinylpyridine and 67% styrene.

$[Os(bpy)_2(PVP_x)_{10}Cl]Cl$. The metallopolymers were prepared as described previously.[25] In a typical synthesis of $[Os(bpy)_2(PVP_{100})_{10}Cl]Cl$, 40 mg of $[Os(bpy)_2Cl_2]$ were dissolved in 30 cm^3 of ethanol and refluxed for 30 min. A total of 73 mg of PVP in 10 cm^3 of ethanol were then added and refluxing continued for *ca.* 72 h. The reaction was continually monitored using UV–VIS spectroscopy and cyclic voltammetry. The metallopolymer was isolated by precipitation into diethyl ether and purified by repeated precipitation (2×) in diethyl ether from ethanol.

Metallopolymers of the PVP : styrene copolymers were prepared in a similar manner. Reaction times typically increased with increasing styrene content and varied from 3–11 days. A constant 1 in 10 metal to polymer-unit loading was prepared in each case. These metallopolymers are identified as $OsPVP_{100}$, $OsPVP_{75}$, $OsPVP_{67}$ and $OsPVP_{33}$, in order of increasing styrene content of the polymer backbone. The general structure of these metallopolymers is illustrated in Fig. 1.

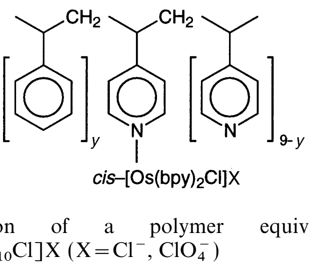

Fig. 1 Composition of a polymer equivalent of *cis*-$[Os(bpy)_2(PVP_x)_{10}Cl]X$ ($X = Cl^-$, ClO_4^-)

Procedures

Polymer coatings were prepared by droplet evaporation from 0.25% (m/v) ethanolic solutions of the individual polymers as was described previously.[8–11] Gravimetric surface coverages (Γ_g) were estimated from the shift in resonant frequency of the quartz crystals upon deposition of the polymer layers.

The equilibrium solvent and ion populations within $OsPVP_{100}$, $OsPVP_{75}$, $OsPVP_{67}$ and $OsPVP_{33}$ crystal coatings were measured at open circuit (Os^{II} oxidation state) as a function of the $HClO_4$ electrolyte concentration. The polymer coated crystals were first exposed to pure Milli-Q water that did not contain any deliberately added electrolyte and the level of solvent imbibition was determined from the shift in resonant frequency. The change in rigidity and layer mass of the crystal coating were then probed as a function of increasing $HClO_4$ electrolyte concentration. In a typical experiment the admittance spectra of the modified crystals were recorded in a series of $HClO_4$ electrolyte concentrations, as the concentration was increased from zero to 1.0 M $HClO_4$. The cell was cleaned with Milli-Q water between each electrolyte concentration. No voltammetry was performed at this stage of the experiment and equilibration time, *i.e.* the time required to achieve a stable frequency reading, varied from 2 to 3 h depending on the particular polymer under investigation. The higher styrene content copolymers, *i.e.* $OsPVP_{67}$ and $OsPVP_{33}$, typically required 3 h equilibration compared with 2 h for the $OsPVP_{100}$ and $OsPVP_{75}$ polymers. This behaviour most likely reflects the greater difficulty in attaining equilibrium solvent and ion populations within the more hydrophobic $OsPVP_{67}$ and $OsPVP_{33}$ polymers. Admittance spectra were also recorded as a function of decreasing electrolyte concentration. In these experiments, the polymer layers were voltammetrically scanned at each concentration for two hours; intermittently changing from 1 to 50 mV s^{-1} scan rates, prior to the recording of the open circuit (Os^{II} oxidation state) admittance spectra.

All experiments were carried out at 20 ± 2 °C. The duration of the experiments was such that temperature fluctuations were negligible. A constant volume of solution was used for all experiments so that the height of liquid above the crystal was kept approximately constant. All solutions were purged with argon to remove oxygen, while the Ar stream was directed over the solution during data acquisition to maintain quiescent solution conditions.

Results and Discussion

Solvent imbibition

In the first set of experiments, the coated crystals were immersed in pure water and the uptake of this solvent by the $OsPVP_{100}$–$OsPVP_{33}$ series of metallopolymers was studied. For all polymers studied, the chloride salt form of the polymer was used. On immersion of these polymer coated crystals in deoxygenated Milli-Q water, the resonant frequency of the coated crystal decreased slowly with time, reflecting the slow imbibition of solvent. As mass changes occurring within these polymers can only be quantitatively evaluated when layer rigidity has been established,[26] the shape of the crystal resonance of these coated crystals is considered first. Table 1 summarises characteristic features of the admittance response of these coated crystals in H_2O, *i.e.* the admittance maximum and the peak width at half maximum admittance (PWHM).

Table 1 Admittance response for bare, and $OsPVP_{75}$, $OsPVP_{67}$ and $OsPVP_{33}$ coated crystals in Milli-Q H_2O. Gravimetric surface coverage $= (1–2) \times 10^{-8}$ mol cm^{-2}

	admittance/$10^{-2}\Omega^{-1}$	PWHM/Hz
bare	0.352	5510
$OsPVP_{75}$	0.271	6947
$OsPVP_{67}$	0.307	6056
$OsPVP_{33}$	0.342	5391

Comparison of the three polymer coated crystals with the bare crystal illustrates that the crystal resonance shape of these crystal coatings is sharpest for the highest styrene content polymer, *i.e.* $OsPVP_{33}$. This behaviour clearly indicates that these layers become more compact with increasing styrene content of the polymer backbone, which is likely a consequence of the more hydrophobic nature of the styrene moiety (see below). For the $OsPVP_{75}$ polymer in H_2O, the PWHM is *ca.* 26% larger than that observed with a bare crystal. The absolute change in PWHM that a polymer must undergo before the rigid layer approximation is compromised is unknown. However, it has been illustrated that more extensive swelling than observed here of similar polymer layers in organic solvents does not invalidate the Sauerbrey equation.[8] We can therefore safely assume the layer to be rigid in water.

Table 2 summarises the level of solvent uptake for each polymer in terms of the number of absorbed water molecules per $[Os(bpy)_2(PVP_x)_{10}Cl]Cl$ polymer unit. In each case the shift in resonant frequency on immersion was corrected for the viscous load of the solvent by subtraction of the frequency shift observed on immersion of an uncoated crystal in this solvent. From Table 2, it is apparent that the level of solvent imbibition is greatly reduced for the styrene copolymers and decreases quite dramatically with increasing styrene content. For the $OsPVP_{33}$ polymer, the uptake of 0.7 ± 0.1 molecules of water per polymer unit is nearly sixty times less than that observed for the $OsPVP_{100}$ polymer. For the series of metallopolymers studied, all parameters such as metal loading, surface coverage *etc.* were similar in each case. It is, therefore, anticipated that the trends observed reflect the changing nature/properties of the polymer backbone on incorporation of the styrene moieties. This decrease in the level of polymer solvation likely reflects the more hydrophobic nature of the styrene moieties and emphasises the importance of the chemical properties of the polymer backbone on the overall layer properties of these materials.

Effect of $HClO_4$ concentration on layer rigidity

In a series of studies we have investigated the charge and mass transport properties of these redox active polymers.[1–17] It was noted that the ion and solvent content of the polymer films was strongly dependent on the nature and concentration of the electrolyte used.[1–17] Here we investigate the interaction of the copolymer film with different concentrations of $HClO_4$. The results obtained are compared with those reported earlier for the $OsPVP_{100}$ polymer.[9] Admittance spectra were recorded for $OsPVP_{75}$, $OsPVP_{67}$ and $OsPVP_{33}$ crystal coatings as a function of the $HClO_4$ bathing electrolyte concentration. To simplify the expected mass changes (see below), the polymer layers were first voltammetrically cycled over the $Os^{II/III}$ redox couple in 0.1 M $HClO_4$ to exchange the polymer counter ions, yielding the material $[Os(bpy)_2(PVP_x)_{10}Cl]ClO_4$. Upon immersion and voltammetric cycling of solvent saturated coat-

Table 2 Solvent uptake by $OsPVP_{100}$–$OsPVP_{33}$ metallopolymers, on immersion in Milli-Q H_2O. Gravimetric surface coverage $= (1–2) \times 10^{-8}$ mol cm^{-2}

polymer	ΔM per mol. equiv[a,b]/ g (pol. equiv)$^{-1}$	solvent content[a,b]/ mol (pol. equiv)$^{-1}$
$OsPVP_{100}$	756	42
$OsPVP_{75}$	162	9
$OsPVP_{67}$	54	3
$OsPVP_{33}$	13	0.7

[a] Estimated from the shift in resonant frequency (corrected for solution viscosity). [b] The variations between individual coatings are ±10%

ings in 0.1 M HClO$_4$, a mass change of 71 ± 6 g (polymer equiv.)$^{-1}$, corresponding to this exchange process, was noted in each case. This mass change was corrected for the mass influx associated with protonation of the layer at this electrolyte concentration (see below) and is in addition to the initially imbibed solvent.

The reported hydration numbers for chloride and perchlorate ions in aqueous solution are 3.9 and 2.6 respectively.[27] If it is assumed that completely solvated Cl$^-$ and ClO$_4^-$ ions are exchanged, then a mass change of 41 g (pol. equiv.)$^{-1}$ is anticipated. However, if it is assumed that completely unsolvated ions are exchanged, then a mass change of 64 g (pol. equiv.)$^{-1}$ is anticipated. Although the observed mass changes suggest that all the polymer counter ions are exchanged and that this exchange process occurs between unhydrated counter ions, the lack of detailed information regarding the hydration of ionic species in polymer networks precludes a more detailed discussion of these points.

Table 3 summarises the characteristic features of the admittance spectra recorded for bare, and OsPVP$_{75}$, OsPVP$_{67}$ and OsPVP$_{33}$ coated crystals as a function of the HClO$_4$ bathing electrolyte concentration. Firstly, the change in crystal resonance of these crystals was examined as a function of increasing electrolyte concentration. No voltammetry was performed at this stage of the experiment and all spectra were recorded at open circuit (Os$^{\text{II}}$ oxidation state). Columns A of Table 3 summarise the characteristic features of these spectra. Admittance spectra were then recorded as a function of decreasing electrolyte concentration. The layer was voltammetrically cycled at each concentration prior to the recording of the open circuit crystal resonance (Os$^{\text{II}}$ oxidation state). The characteristic features of these spectra are summarised in columns B of Table 3.

Compared with the uncoated crystal, there is little variation in the shape of the crystal resonance of the three polymer coated crystals as the bathing electrolyte concentration is varied, *i.e.* $<5\%$ change in the PWHM. Similar behaviour has been observed previously for the OsPVP$_{100}$ polymer and is likely a consequence of the crosslinking properties of the perchlorate anion.[28,29] Under these conditions, the polymer coatings are sufficiently rigid for accurate quantitation of the changes in layer mass using the Sauerbrey equation.[8,9]

Change in resident layer mass with increasing HClO$_4$ concentration

Having demonstrated that these polymers are essentially rigid in all HClO$_4$ electrolyte concentrations it is now possible to give a quantitative assessment of the changes in layer mass. Fig. 2 and Table 4 illustrate the change in layer mass, with increasing electrolyte pH, for these OsPVP$_{75}$, OsPVP$_{67}$ and OsPVP$_{33}$ polymer layers. At each concentration, the shift in resonant frequency (taken from the shift in the admittance peak) resulting from the change in viscous load of the electrolyte was corrected for by subtraction of the frequency shift observed for an uncoated crystal. All mass changes were calculated using a mass sensitivity of 0.232 Hz cm^2 ng^{-1}.[9] It is anticipated that these mass changes result primarily from the influx of perchlorate anions, in response to the electroneutrality constraints imposed by protonation of the polymer backbone.

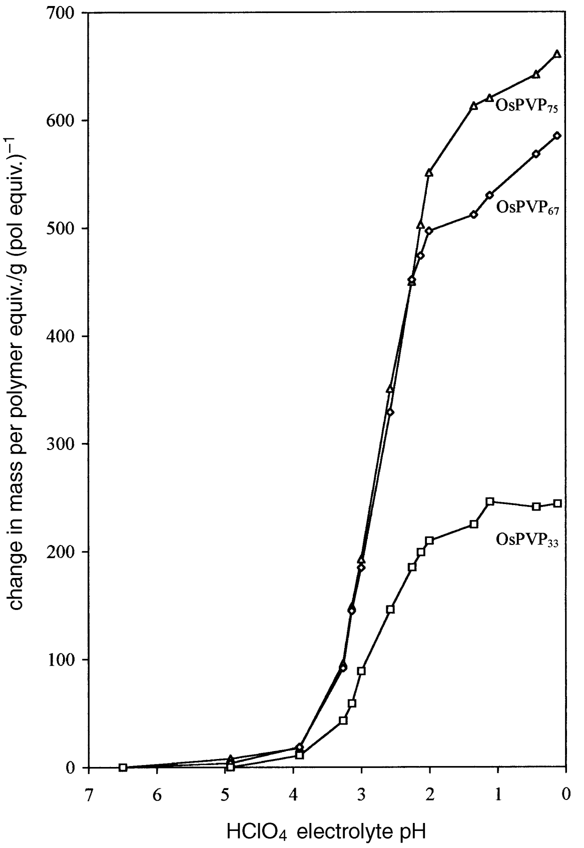

Fig. 2 Change in layer mass as a function of HClO$_4$ electrolyte pH for OsPVP$_{75}$, OsPVP$_{67}$ and OsPVP$_{33}$ crystal coatings

A central assumption of these calculations is that the shift in resonant frequency, on immersion of an uncoated crystal in electrolyte, may be used to compensate for the corresponding shift in frequency of a coated crystal in the same electrolyte. The greater surface roughness of the polymer layer will likely result in greater trapping of electrolyte in pores at the polymer/ solvent interface compared with the uncoated crystal/ solution interface.[30–32] Compensation for the frequency shift due to the viscous load of the electrolyte using an uncoated crystal may

Table 3 Admittance response for bare, and OsPVP$_{75}$, OsPVP$_{67}$ and OsPVP$_{33}$ coated crystals in HClO$_4$ electrolytes. Gravimetric surface coverage = $(1\text{–}2)\times10^{-8}$ mol cm^{-2}

HClO$_4$ conc./M	bare		OsPVP$_{75}$				OsPVP$_{67}$				OsPVP$_{33}$			
	admittance/ $10^{-2}\,\Omega^{-1}$	PWHM/ Hz	admittance/ $10^{-2}\,\Omega^{-1}$		PWHM/ Hz		admittance/ $10^{-2}\,\Omega^{-1}$		PWHM/ Hz		admittance/ $10^{-2}\,\Omega^{-1}$		PWHM/ Hz	
			A	B	A	B	A	B	A	B	A	B	A	B
0	0.352	5510	0.271	0.259	6947	7303	0.307	0.300	6056	6215	0.342	0.337	5391	5504
1×10^{-5}	0.352	5542	0.270	0.256	6975	7396	0.307	0.301	6084	6187	0.341	0.335	5446	5541
1×10^{-4}	0.353	5531	0.268	0.258	7050	7312	0.308	0.299	6046	6233	0.345	0.330	5372	5606
5×10^{-4}	0.350	5576	0.267	0.258	7069	7398	0.308	0.299	6102	6234	0.339	0.330	5456	5578
1×10^{-3}	0.349	5658	0.267	0.257	7097	7398	0.306	0.298	6169	6253	0.338	0.326	5542	5681
5×10^{-3}	0.348	5662	0.264	0.256	7238	7500	0.310	0.302	6093	6243	0.343	0.333	5512	5652
0.01	0.345	5691	0.262	0.256	7312	7500	0.311	0.304	6093	6188	0.343	0.335	5502	5365
0.1	0.342	5749	0.263	0.258	7294	7444	0.312	0.307	6019	6131	0.346	0.338	5457	5587
1.0	0.341	5821	0.259	0.256	7350	7529	0.304	0.302	6196	6206	0.338	0.333	5606	5700

Table 4 Change in layer mass on immersion of $OsPVP_{75}$, $OsPVP_{67}$ and $OsPVP_{33}$ coated crystals in $HClO_4$ electrolytes. Gravimetric surface coverage = (1–2) × 10^{-8} mol cm^{-2}

	$OsPVP_{75}$			$OsPVP_{67}$			$OsPVP_{33}$		
$HClO_4$ pH	mass per polymer unit/ g (pol. equiv)$^{-1}$	ClO_4^- content/ mol (pol. equiv)$^{-1}$		mass per polymer unit/ g (pol. equiv)$^{-1}$	ClO_4^- content/ mol (pol. equiv)$^{-1}$		mass per polymer unit/ g (pol. equiv)$^{-1}$	ClO_4^- content/ mol (pol. equiv)$^{-1}$	
		A	B		A	B		A	B
6.5	0	0.0	0.0	0	0.0	0.0	0	0.0	0.0
3.91	18	0.2	0.1	19	0.2	0.2	11	0.1	0.1
3.14	149	1.5	1.0	145	1.4	1.0	59	0.6	0.4
2.12	503	5.0	3.4	474	4.7	3.2	199	2.0	1.4
1.11	620	6.2	4.2	530	5.3	3.6	246	2.4	1.7
0.43	642	6.4	4.4	568	5.7	3.9	241	2.4	1.6
0.12	661	6.6	4.5	585	5.8	4.0	244	2.4	1.7

therefore be incomplete. Consequently, the data in Table 4 may slightly overestimate the level of anion ingress, *i.e.* these values may be viewed as the upper limit for anion ingress into these polymer layers.

Columns A and B in Table 4 are estimates of the number of perchlorates required for electroneutrality, assuming the influx of (A) unhydrated perchlorate ($H^+ClO_4^-$) and (B) hydrated perchlorate ($H^+ClO_4^-\cdot 2.6H_2O$). Assuming the influx of hydrated perchlorate anions, the level of anion influx is less than that anticipated for protonation of the backbone. This suggests incomplete protonation of the backbone, which is unlikely considering the pK_a of PVP ($pK_a = 3.3$[33]). However, the values given in columns A of Table 4 suggest total protonation of the free pyridine groups when one assumes the influx of unhydrated ions. Taking the $OsPVP_{33}$ polymer as an example, the $OsPVP_{33}$ polymer unit $[Os(bpy)_2(PVP_{33})_{10}Cl]^+$ comprises 3.3 pyridine units, one of which is bound to the osmium redox centre. There are, therefore, 2.3 free pyridine units available for protonation. The influx of 2.4 perchlorate anions (see Table 3) is close to the anticipated influx of 2.3 perchlorates, on complete protonation of the polymer. Similarly, for the $OsPVP_{75}$ and $OsPVP_{67}$ polymers, the data illustrate the influx of 6.6. and 5.8 perchlorate anions, respectively; close to the anticipated influx of 6.5 and 5.7 perchlorates. An influx of 9 perchlorate anions was reported for the $OsPVP_{100}$ polymer under similar experimental conditions.[9] This behaviour suggests that all three copolymers are completely protonated in 0.5 M $HClO_4$ and that the observed mass changes are associated solely with the protonation process and the consequent anion uptake. Furthermore, it suggests that the styrene moieties act merely as diluents and do not inhibit protonation of the neighbouring pyridine units. The data in columns A of Table 4 suggest that for each individual metallopolymer, all the pyridine units of the polymer backbone are protonated.

For the $OsPVP_{100}$ polymer, the mass of the layer continues to increase with increasing $HClO_4$ concentration in excess of 0.5 M $HClO_4$ and is, therefore, in excess of that anticipated for the protonation process.[9] This behaviour reflects the breakdown in permselectivity of this layer and the accompanying ingress of acid ($H^+ClO_4^-$).[9] This behaviour is also observed for the $OsPVP_{75}$ and $OsPVP_{67}$ polymers reported here. However, for the $OsPVP_{33}$ polymer, there is little variation in the resident layer mass at concentrations in excess of 0.5 M $HClO_4$, suggesting that this polymer layer behaves permselectively, even at these high electrolyte concentrations. This also suggests that the mass influx is associated solely with the protonation process and that this process is complete in 0.5 M $HClO_4$. The primary effect of this behaviour is the absence of free electrolyte in this polymer network in all $HClO_4$ concentrations. In comparison, the failure of permselectivity in the $OsPVP_{75}$ and $OsPVP_{67}$ polymers in higher electrolyte concentrations likely reflects the less hydrophobic and compact nature of these polymers.

Estimation of the pK_a^{app} of the free pyridine units

The change in layer mass with increasing electrolyte pH may be viewed as a titration of the unbound pyridine units of the polymer backbone and may therefore be used to estimate the apparent pK_a of the protonated pyridine units, pK_a^{app}. The relationship between the solution pH and the pK_a^{app} is given by:[9]

$$pH = pK_a^{app} + \log\,[(\Delta M_{total}/\Delta M) - 1] \qquad (1)$$

ΔM_{total} is the total mass change observed on increasing the pH from 5.0 to *ca.* pH 0.0. ΔM is the individual mass change observed at each intermediate pH.

Fig. 3 illustrates plots of $\log\,[(\Delta M_{total}/\Delta M) - 1]$ *vs.* pH for the three polymers under investigation. Eqn. (1) predicts a linear plot of slope unity with an intercept with the x axis (*i.e.* the pH at which this term goes to zero) corresponding to the pK_a^{app} of the pyridine units of the polymer backbone. The relevant data from these plots are given in Table 5.

Linear plots with slopes approaching unity were obtained in all cases. The near unity slopes for each plot suggest that protonation proceeds as dictated by the pH of the bathing solution. The pK_a^{app} values, evaluated for each polymer, are

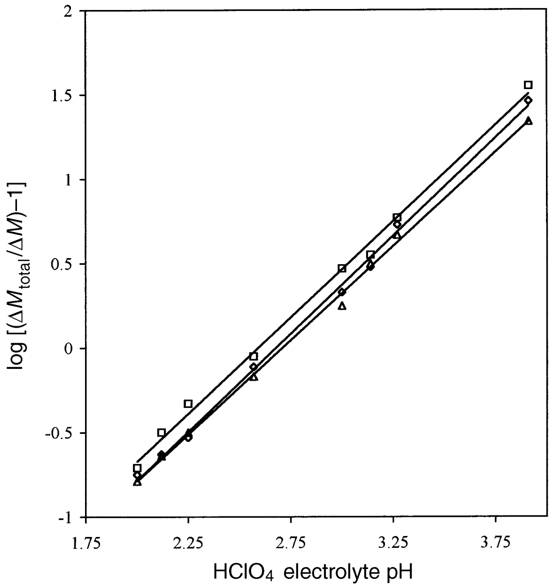

Fig. 3 Plots of $\log\,[(\Delta M_{total}/\Delta M) - 1]$ *vs.* electrolyte pH for $OsPVP_{75}$ (□), $OsPVP_{67}$ (◇) and $OsPVP_{33}$ (△) crystal coatings

Table 5 Change in pK_a^{app} of the unbound pyridine units with increasing styrene content of the copolymer backbone

polymer	slope	intercept: pK_a^{app}
OsPVP$_{75}$	1.14 (0.03)	2.59 (0.05)
OsPVP$_{67}$	1.16 (0.02)	2.68 (0.04)
OsPVP$_{33}$	1.11 (0.02)	2.71 (0.04)

almost identical in each case, which suggests that the presence of the styrene moieties in the polymer backbone does not adversely affect the protonation of the pyridine units and reiterates what was stated above. The pK_a of the PVP backbone of these metallopolymers is clearly more acidic than the pK_a of the PVP homopolymer in solution, *i.e.* 2.66 ± 0.06, compared with 3.30.[33] This likely reflects the compact and dehydrated nature of these copolymers and the resulting difficulty in protonation of the PVP units due to the electroneutrality requirement for anion insertion. This observation is supported by the protonation behaviour of the OsPVP$_{100}$ polymer in toluene-*p*-sulfonic acid (*p*-TSA).[10] In this electrolyte, the polymer is extensively swollen as a result of the large volume of the bulky anion.[10] The ingress of this species is anticipated to occur more easily into the swollen polymer network that exists in this electrolyte. This point is indicated by the observed pK_a^{app} of 3.0, which is closer to the reported pK_a of the homopolymer.

The general behaviour of the OsPVP$_{100}$ polymer is decidedly different from that observed for the copolymers. In $HClO_4$ and *p*-TSA electrolytes, dual sloped pK_a^{app} plots were observed, with two distinct regions of differing behaviour.[9,10] In $HClO_4$, this transition occurred at pH 2.5 and is related to slight changes in the polymer morphology at this pH. At pH above 2.50 a slope of 0.60 was observed, whilst at pH more acidic than this, a slope of 1.20 was noted.[9] A pK_a of 2.54 for the protonated pyridine units was reported.[9] The slope of less than unity suggests that protonation of the pyridine units is hindered and does not proceed as dictated by the pH of the external solution.[9] The styrene polymers under these conditions behave more 'ideally' than the less compact OsPVP$_{100}$ polymer and would appear to provide a less hindered path for anion influx. This behaviour is quite surprising and may reflect the reduced requirement for compensating counter ions within the lower PVP content polymers. At pH >2.5, the behaviour of the OsPVP$_{100}$ polymer is comparable with that observed for the copolymers.[9]

Conclusions

Characterisation of the crystal impedance of polymer coated quartz crystals provides a novel approach to the study of the membrane properties of polymer films. Here, we have investigated the influence of the interaction between the polymer layer and the contacting solution on the morphology of the polymer films. In $HClO_4$ electrolyte concentrations up to and including 1.0 M $HClO_4$, $[Os(bpy)_2(PVP_x)_{10}Cl]^+$ layers are compact and rigid. This behaviour is a direct consequence of the chemical nature of both the electrolyte anion and the polymer backbone. In these electrolytes, protonation of the pyridine units of the polymer backbone provides the driving force for anion ingress. For the OsPVP$_{75}$–OsPVP$_{33}$ polymers investigated, there is a good correlation between the number of free protonable pyridine units and the quantity of anion ingress, assuming the uptake of a single unhydrated anion per protonated site. The ingress of this species is not apparently accompanied by the ingress of solvent, assuming of course that mass transfer occurs in one direction only. Furthermore, there is a slight increase in polymer rigidity with increasing styrene content of the polymer backbone. This behaviour reflects the reduced ion and solvent content of the higher styrene content polymers, which is a consequence of the more hydrophobic nature of the styrene moieties. Protonation of the pyridine moieties of the copolymer backbone occurs under more acidic conditions than that observed for the homopolymer and likely reflects the compact nature of these structures. In summary, characterisation of the admittance response of polymer coated quartz crystals provides detailed information about the solvent and ion content of polymer coatings and enables the pK_a^{app} of the polymer units to be ascertained. Although the results obtained are specific for the polymers investigated, we believe that the methods described can be applied to other materials.

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