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Contribution from the Kenan Laboratories of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27599-3290

Site Dilution of Osmium Polypyridine Complexes in Three Electron-Hopping Conductive Polymer Films on Electrodes by Electrochemical Copolymerization of Osmium with Ruthenium and with Zinc Complexes

Nigel A. Surridge, F. Richard Keene,[†] Brent A. White,[‡] John S. Facci,[§] Marvin Silver,[∥]
and Royce W. Murray*

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The electrochemical copolymerization of three pairs of metal complexes was investigated for utility of the copolymers for electron-transport studies. The ligands within each pair are the same, in order that polymer sites for the electron-transport-active osmium metal complexes can be isostructurally diluted with the other complex, which is based on Ru or Zn centers. The ligands include the electropolymerizable groups *N*-(4-pyridyl)cinnamamide, 4-vinylpyridine, and 4-methyl-4′-vinyl-2,2′-bipyridine. A kinetic analysis was used to estimate the degree of random copolymer formation properties of the three metal complex pairs. The pairs $[Os(bpy)_2(p\text{-cinn})_2]^{2+}/[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$ and $[Os(vbpy)_3]^{2+}/[Zn(vbpy)_3]^{2+}$ formed ideal and near-ideal random copolymers, while the behavior of the $[Os(bpy)_2(vpy)_2]^{2+}/[Ru(bpy)_2(vpy)_2]^{2+}$ pair indicated a greater relative reactivity of the osmium monomer. A preliminary sandwich electrode measurement of electron transport in a $[Os(vbpy)_3]^{2+}/[Zn(vbpy)_3]^{2+}$ copolymer is given.

Polymer films that contain electron-transfer-active metal complexes affixed to the polymeric lattice exhibit changes in oxidation states[1] in electrochemical reactions when (a) the electron-hopping reactions between metal complex sites are reasonably rapid on the experimental time scale and (b) the films contain diffusively mobile charge-compensating counterions. The electrochemical behavior provides a convenient avenue to study the electron self-exchange dynamics of the immobilized metal complex, which is interesting for its own sake and for its relevance to electrocatalytic applications of the films.[1] The electron self-exchange rate is often (phenomenologically) expressed as the "electron diffusion coefficient", D_e, which is translatable into a bimolecular rate constant k_{ex}.[2]

The electron self-exchange reaction in the polymer phase differs from that familiar in homogeneous solution in that the metal complex sites are diffusively immobile (or only slowly mobile), being affixed to the polymer lattice. The rate constant k_{ex} may, accordingly, depend on the concentration of metal complex sites (donor/acceptor sites) within the polymer film. In particular, the electron-hopping rate constant may decrease as the sites are diluted, because of decreased populations of nearest neighbor D/A pairs, slow polymer-controlled translational modes of the sites, and/or increased distances of electron transfer.[3,4] Detecting and understanding site concentration depedencies of k_{ex} values is crucial to a basic appreciation of electron dynamics in electroactive polymer films.

The literature on the electrochemistry of site-dilutable polymer films[5] and their electron-transport rates[3,6] remains sparse. A difficulty is in the synthesis of polymeric films with the desired properties: (i) a sufficiently large ionic conductivity that the electron-hopping rate is a property of the chemistry of the sites and not of the mobility of the charge-compensating counterion, (ii) metal complexes substitutionally inert in both oxidation states (or stable organic donor/acceptor pair), (iii) a combination of k_{ex} and metal complex site concentration values that gives a readily measurable D_e value (i.e., D_e between 10^{-12} and 10^{-7} cm^2/s), and (iv) an ability to alter the site concentration without changing details of the polymer structure (and thus any polymer-related kinetic factors). As for factor i, theory is evolving that potentially allows accounting for electron hopping driven by bulk potential gradients that are consequences of low ionic mobility;[7,8] other theoretical and experimental approaches[9] rely on negligible ionic motions. Factors ii and iii can be anticipated on the basis of an analogy between solution- and polymer-phase chemistry.[10]

Factor iv is, on the other hand, an important constraint on polymer design. Our approach[3] to the problem has been based on forming polymeric metal polypyridine films by electrochemical *co*polymerization[11] of two metal complexes, having the same coordination shell and polymerization linkages but differing metals. One of the metal complexes has a redox couple suitable for an electron-hopping study, while the other is electrochemically silent (does not form a mixed-valent state) at electrode potentials where the first is active. Because their coordinations are identical, copolymerization from solutions containing the two complexes in different proportions yields copolymers in which electron-transfer-active complexes are controllably diluted by nonactive but *structurally equivalent* sites of the other complex. By change in

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[†] On approved Special Studies Program from the Department of Chemistry and Biochemistry, James Cook University, Townsville, Queensland 4811, Australia.

[‡] Present address: The Upjohn Co., Kalamazoo, MI 49001.

[§] Present address: Xerox Corp., Webster, NY 14580.

[∥] Department of Physics, University of North Carolina, Chapel Hill.

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the copolymer composition, the concentration of the active sites can thus be systematically altered without changing any dynamics of the polymer lattice that might be important in the electron-transfer chemistry. The objective is that site concentration is the sole varied parameter.

This scheme depends on identifying copolymerizable pairs of metal complexes that exhibit easily measured metal ratios in the resulting polymer film. Further, the metal ratios must be relatable to the composition of the feed electropolymerization solution. In particular, if the population of the two metal complexes in the polymer film is equal to that in the feed solution, we have a random copolymerization reaction forming an ideal solid "solution" of one metal complex in the other.

This paper deals with an analysis of the copolymerization characteristics of three pairs of metal polypyridine complexes. An osmium complex serves as the electron-transfer-active metal complex in each case; Ru and Zn complexes serve as the inactive diluents.

The three metal complex pairs are based on the electropolymerizable ligands: *N*-(4-pyridyl)cinnamamide (*p*-cinn), 4-vinylpyridine (vpy), and 4-vinyl-4'-methyl-2,2'-bipyridine (vbpy), bound in the following pairs: $[Os(bpy)_2(p\text{-cinn})_2]^{2+}$ and $[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$, $[Os(bpy)_2(vpy)_2]^{2+}$ and $[Ru(bpy)_2(vpy)_2]^{2+}$, and $[Os(vbpy)_3]^{2+}$ and $[Zn(vbpy)_3]^{2+}$. Polymerization properties of all of these complexes, taken singly, and the ability to form copolymers during electropolymerization have been previously described.[11] Additionally, the electron-hopping properties of the poly-$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$ pair were published earlier.[3]

We will show that copolymerization of $[Os(bpy)_2(p\text{-cinn})_2]^{2+}$ with $[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$, and of $[Os(vbpy)_3]^{2+}$ with $[Zn(vbpy)_3]^{2+}$, are nearly ideal as to randomness of osmium complex sites in the product film. We have previously presented[3] results for D_e in the poly-$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$ pair and present here a preliminary result for electron transfer in the newer poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ pair. The $[Os(vbpy)_3]^{2+}/[Zn(vbpy)_3]^{2+}$ pair is especially promising for solid state electron transfer studies of the kind recently described for 1:1 poly-$[Os(bpy)_2(vpy)_2]^{2+/3+}$ mixed valent films.[9]

Experimental Section

Chemicals. Acetonitrile (CH_3CN, Burdick and Jackson) was stored over molecular sieves. Tetraethylammonium perchlorate (Et_4NClO_4) electrolyte was recrystallized twice from water; tetraethylammonium tetrafluoroborate (Et_4NBF_4, Fluka) was used as received.

Electrochemistry. Experiments were performed with conventional potentiostats in three-electrode cells employing Pt auxiliary and either saturated (sodium chloride) calomel (SSCE), Ag/Ag^+ (0.01 M in CH_3CN) reference, or Ag-wire quasi-reference electrodes. Potentials are corrected to and reported vs SSCE. The copolymerizations were performed under N_2, either in an inert (dry N_2) atmosphere enclosure or in cells under N_2 purge. The former technique is more reliable.

Ligand. Preparation of the vbpy ligand was based on a literature method, where α,4-dichloroanisole was substituted for (chloromethyl) methyl ether.[12]

Monomers. Preparations of $[(Os\text{ or }Ru)(bpy)_2(vpy)_2]^{2+}$, $[Os(vbpy)_3]^{2+}$, $[Zn(vbpy)_3]^{2+}$, and $[(Os\text{ or }Ru)(bpy)_2(p\text{-cinn})_2]^{2+}$, were as reported in the literature.[11]

Copolymerizations of Films. Copolymeric films composed of the poly-$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$ and poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ monomer pairs were prepared from 0.1 M Et_4NClO_4/CH_3CN solutions of the complexes at concentrations in the 1–2 mM range, by cycling the Pt electrode potential at 100 mV/s between −1.0 and −1.75 V vs SSCE for the first pair[11] and between −1.0 and −1.70 V vs SSCE for the latter pair.[11] The total surface coverage of metal centers (Os plus Ru) varied between 2×10^{-9} and 9×10^{-9} mol cm^{-2} as determined by integrations of the charges under the Os(III/II) and Ru(III/II) cyclic voltammograms.

Copolymeric films containing poly-$[Os(vbpy)_3]^{2+}$ and poly-$[Zn(vbpy)_3]^{2+}$ were deposited on Pt electrodes (0.002 cm^2 for electrochemical measurements and 0.19 cm^2 for XPS experiments) by cycling the electrode potential between −1.0 and ≈−1.75 V vs SSCE at 150 or 200 mV/s

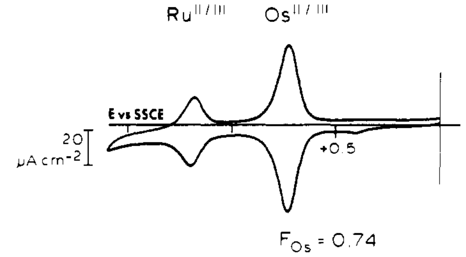

Figure 1. Cyclic voltammogram of poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ copolymer in 0.1 M Et_4NClO_4/CH_3CN. Scan rate = 20 mV/s, $\Gamma_{TOTAL} \sim 8.6 \times 10^{-9}$ mol/cm^2, $f_{Os} \sim 0.4$, $F_{Os} \sim 0.74$.

in 0.1 M Et_4NBF_4/CH_3CN. The typical concentration of Os plus Zn complexes in the polymerizing feed solution was 0.2–0.5 mM. The surface coverage of poly-$[Os(vbpy)_3]^{2+}$ sites was determined by Os(III/II) cyclic voltammetry, with that of the poly-$[Zn(vbpy)_3]^{2+}$ sites determined by replacement of the metal with Fe as described in the following section.

Substitution of Zn by Fe in $[Os(vbpy)_3]^{2+}/[Zn(vbpy)_3]^{2+}$ Copolymer Films. The copolymer-coated electrode was soaked in a degassed solution of $FeCl_2$ (≈50 mM, recrystallized from CH_3CN) in 0.1 M Et_4NBF_4/CH_3CN for 1 h (overnight gave equivalent results),[11c] rinsed with CH_3CN, and transferred to an electrochemical cell. The film was "conditioned"[11] by potential cycling at 200 mV/s between +1.5 V and the initial rising current for the first bipyridine reduction (usually ca. −1.4 V) until there was no further change in the voltammogram. The film surface coverage was then assessed by 5–10 mV/s potential scans between 0 and +1.5 V vs SSCE to observe voltammograms for the poly-$[Os(vbpy)_3]^{2+/3+}$ and poly-$[Fe(vbpy)_3]^{2+/3+}$ couples. The Os/Fe ratio thus derived has error estimated at ca. ±20% owing to the overlap of the two voltammetric waves ($E°_{Fe(II/III)} \approx 0.92$ V, $E°_{Os(II/III)} \approx 0.74$ V). The Os/Fe ratio is taken as the same as the original Os/Zn ratio, assuming complete replacement of Zn by Fe. This assumption is investigated as described in the text.

Removing Copolymer Films from Electrodes. The copolymer films were lifted off the Pt electrode by overcasting of a film of poly(vinyl alcohol).[13] A casting solution was prepared by adding 0.5 g of Aldrich Low MW PVA (average MW = 14 000; 99% hydrolyzed) to 15 mL of Nanopure water, heating (50 °C) with stirring until the solution cleared, and adding a further 0.5 g of PVA with stirring again until clear. Two or three drops of the warm solution were cast carefully onto the copolymer film surface so as to give a high-profile droplet spreading somewhat onto the Teflon shroud surrounding the Pt-disk electrode. The solution was allowed to dry for 6 h and the PVA film peeled from the electrode surface with tweezers, in most cases taking the electropolymerized film nearly quantitatively with it (vide infra). Drying the PVA film for longer periods results in a brittle film, not easily removed.

XPS Analysis of Films. Survey (BE = 0–1000 eV) and higher resolution spectra for Os, Zn, Fe, C, F, and N were obtained for the exterior surfaces of copolymer films by placing the entire electrode/film assembly in a Perkin-Elmer Physical Electronics Model 5400 XPS instrument. Mg Kα X-rays, anode energy 1253.6 eV, 300 W, were typically used with collection from an area of ≈1 mm^2 on the film surface. Binding energies are charge corrected to C 1s at 284.6 eV. The interior copolymer film surface (the side originally next to the electrode surface) was analyzed, with similar results, by observing the underside of peeled-off PVA films or, on occasion, the remnants of copolymer that sometimes remained on the Pt electrode after PVA peeling.

***D* Measurements.** A preliminary measurement of electron transport in a poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymer film was performed with a "sandwich" cell, made by growing the copolymer on a Pt wire tip electrode (glass shrouded, 0.002 cm^2) and overcoating with a porous Au (ca. 300 Å) film as previously described.[9] Immersing the "sandwich" in 0.1 M Et_4NBF_4/CH_2Cl_2 and applying 0.0 V to the Au side and +1.2 V vs SSCE to the Pt side gave a limiting current for hopping electron transport via the Os(III/II) couple. The Zn(II) couple is electrochemically inactive and acts only as a diluent of osmium sites.

Results

Copolymer Films Based on *p*-cinn and vpy Ligands. As objects of electron-exchange dynamics studies, it is desirable that the active metal sites be randomly dispersed within the copolymer film. Criteria for randomness are available from comparing the composition of a two-monomer polymerization feed solution to that

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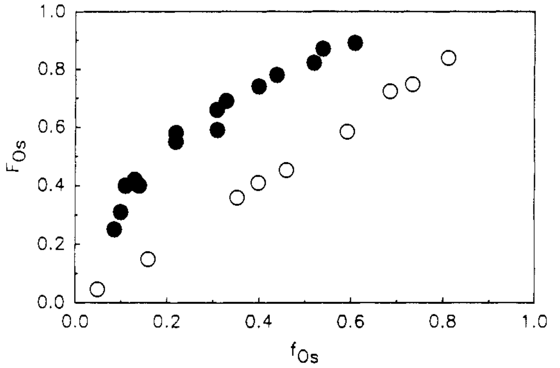

Figure 2. Plot of mole fraction of osmium in the copolymer, F_{Os}, vs that in the feed solution, f_{Os}, for copolymers containing poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ (●), and poly-$[Os(bpy)_2(p\text{-}cinn)_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-}cinn)_2]^{2+}$ (○).

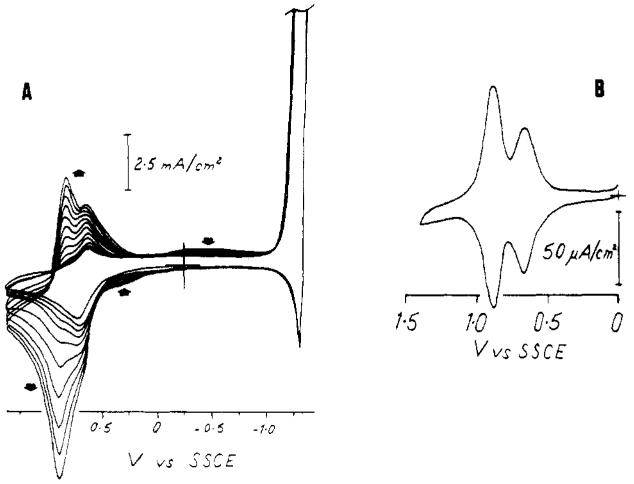

Figure 3. (A) Electrochemical conditioning of poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymer, in 0.1 M Et_4NBF_4/CH_3CN after exposure to a ~50 mM solution of $FeCl_2$ for ca. 1 h. Scan rate = 200 mV/s. (B) Cyclic voltammogram in 0.1 M Et_4NBF_4, scan rate 10 mV/s, of the copolymer in part A after substitution of the Zn with Fe. f_{Os} = 0.5; F_{Os} ~ 0.46.

of the resulting copolymer.[14] Figure 1 exemplifies cyclic voltammetry of a poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ copolymer film; that for a poly-$[Os(bpy)_2(p\text{-}cinn)_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-}cinn)_2]^{2+}$ copolymer has nearly the same appearance. The mole fraction f_{Os} of the $[Os(bpy)_2(vpy)_2]^{2+}$ complex in the feed solution producing the film of Figure 1 was 0.4; that (F_{Os}) in the film, measured from the voltammogram charges, was 0.74. Repeating the analysis of Figure 1 for a series of f_{Os} values in the feed solution produced the results for F_{Os} vs f_{Os} shown in Figure 2. It is clear that F_{Os} vs f_{Os} is linear for the poly-$[Os(bpy)_2(p\text{-}cinn)_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-}cinn)_2]^{2+}$ copolymers but decidedly nonlinear for those based on copolymerization of $[Os(bpy)_2(vpy)_2]^{2+}$ with $[Ru(bpy)_2(vpy)_2]^{2+}$. The latter result shows that the poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ copolymer film contains a greater proportion of $[Os(bpy)_2(vpy)_2]^{2+}$ sites than does the feed solution; the polymerization is more selective for the Os monomer.

Copolymer Films Based on vbpy Ligands. In the previous description[11c] of $[Zn(vbpy)_3]^{2+}$ copolymerization, it was observed that the substitution of Fe for Zn by soaking in $FeCl_2$ solution required a subsequent "electrochemical cycling period of 10–20 min" to develop the redox response of the poly-$[Fe(vbpy)_3]^{2+/3+}$ couple.[11c] The voltammetric behavior during this "conditioning", conducted as in the Experimental Section, is shown in Figure 3A; initially, only the Os(III/II) response is observed (at the left), but with time peaks for the more positive Fe(III/II) couple grow in. The current at the right is for the reduction of bipyridine rings in copolymer sites; partial reduction of the bipyridine rings is essential for obtaining maximum incorporation of electroactive $[Fe(vbpy)_3]^{2+}$ into the copolymer.

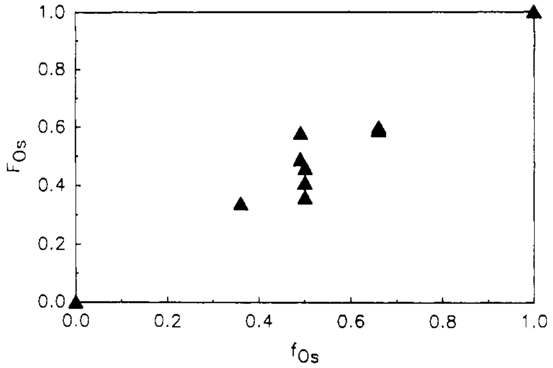

Figure 4. Plot of F_{Os} vs f_{Os} for poly-$[Os(bpy)_3]^{2+}$/poly-$[Zn(bpy)_3]^{2+}$ copolymer.

Figure 3B shows the voltammetry of the copolymer film prepared in Figure 3A. The Os(III/II) and Fe(III/II) voltammetric waves are not well separated at the relatively fast potential scan rate used in Figure 3A, but are well-defined at the slow potential scan rates in Figure 3B. However, the moderate overlap of the Os(III/II) and Fe(III/II) waves is still troublesome during determination of the electrochemical charges under the two waves: this was done by assuming the Os wave to be symmetric about its $E_{p,a}$, reflecting the negative side of the wave about $E_{p,a}$, and using the resultant wave as the background current to be subtracted in order to measure the charge under the Fe(III/II) wave. Cyclic voltammograms of an undiluted poly-$[Os(vbpy)_3]^{2+}$ film are slightly asymmetric with the wave being slightly broader on the positive side,[15] so if this asymmetry occurs also in the copolymer the above procedure slightly underestimates the mole fraction F_{Os} of Os complex in the film.

For the film undergoing Zn/Fe replacement in Figure 3A, the Os mole fraction f_{Os} was 0.50 in the $[Os(vbpy)_3]^{2+}/[Zn(vbpy)_3]^{2+}$ feed solution producing the film, whereas the mole fraction F_{Os} of Os sites measured from the voltammogram of Figure 3B was 0.46. Repeating this procedure for a series of films produced the F_{Os} vs. f_{Os} results of Figure 4. The data are mainly in the middle range; although poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymers are readily made at large and small f_{Os} feed ratios, the analysis of F_{Os} outside the range 0.3–0.7 is difficult owing to the Os(III/II)–Fe(III/II) wave overlap noted above. It should be stressed, however, that the points at f_{Os} = 0 and f_{Os} = 1 are known limits of the plot. The scatter in the F_{Os} results obtained for the five films grown at f_{Os} ~ 0.5 is suspected more to reflect variability in the Zn/Fe replacement and in quantifying the overlapping Os/Fe voltammetry of Figure 3B, rather than variability in the actual F_{Os}.

Analysis of the Copolymerization. Plots analogous to Figures 2 and 4 are commonly used in kinetic studies of monomer addition to growing polymer chains in free-radical polymerizations of two monomers.[14] Applying this theory to the present circumstance (an approximation since cross-linking may also occur), we define four propagation rate constants (where M = Os or Ru, or Os or Zn, and $-M-M-Os^{\bullet-}$ indicates a chain terminating in an activated Os complex site):

$$-M-M-Os^{\bullet-} + Os \xrightarrow{k_{11}} -M-M-Os-Os^{\bullet-}$$

$$-M-M-Os^{\bullet-} + Ru \xrightarrow{k_{12}} -M-M-Os-Ru^{\bullet-}$$

$$-M-M-Ru^{\bullet-} + Os \xrightarrow{k_{21}} -M-M-Ru-Os^{\bullet-}$$

$$-M-M-Ru^{\bullet-} + Ru \xrightarrow{k_{22}} -M-M-Ru-Ru^{\bullet-}$$

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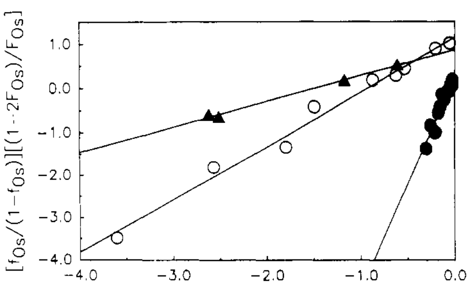

Figure 5. Analysis of data in Figures 2 and 4 according to eq 3, showing linear fits to the data. Copolymer: poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ (●); poly-$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$ (○); poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ (▲).

Writing kinetic equations for the ratio of the rate of incorporation of the two monomers M_1 and M_2, applying steady-state approximations for the concentrations of radical species during polymerization, and defining the reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, gives

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])} = \frac{1 + r_1[M_1]/[M_2]}{1 + r_2[M_2]/[M_1]} \quad (1)$$

Accordingly, the mole fraction F_1 of M_1 (the Os complex) incorporated into the polymer can be expressed in terms of the mole fraction in the solution f_1 and of the reactivity ratios r_1 and r_2:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (2)$$

We see that if the reactivity ratios are equal, i.e., $r_1 = r_2 = 1$, then $F_1 = f_1$; i.e., the polymer and feed solution compositions are equal. This satisfies the criterion $r_1 r_2 \approx 1$ required for forming a *random copolymer*;[14] i.e., the reactivities of Os and Ru (or Zn) monomers are identical whether they encounter an activated Os or a Ru site on the polymer chain (film surface). On the other hand, if r_1 and r_2 are both <1, then Os and Ru monomers are (relatively) unreactive toward Os and Ru polymer sites, respectively, which is the condition for an *alternating copolymer*. If r_1 and r_2 are $>$ 1, then Os and Ru monomers prefer to react with Os and Ru polymer sites, respectively, which indicates a tendency for the monomers to homopolymerize. When $r_1 r_2 > 1$ with $r_1 > 1$ r_2, the formation of a *block copolymer* is indicated.

Equation 2 can be rearranged to a form suitable for analysis of F_1 vs f_1 data

$$\frac{f_1}{1-f_1}\,\frac{1-2F_1}{F_1} = r_2 + \left(\frac{f_1}{1-f_1}\right)^2 \frac{F_1 - 1}{F_1}\, r_1 \quad (3)$$

where a plot of the expression on the left-hand side vs the coefficient of r_1 should be linear and give r_2 and r_1 from the intercept and slope.

Figure 5 shows such plots and regression lines for the three copolymer systems. The results for the poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymer (▲) at $f_{Os} \approx 0.5$ in Figure 4 are averaged as a single point in Figure 5. This does not distort the obtained values of r_1 and r_2; a separate nonlinear least-squares fit of the raw unaveraged data in Figure 4 gave the same results.

Figure 5 shows that all three copolymers follow the form of eq 3, producing linear plots. The results for r_1 and r_2, and their interpretation, are as follows.

(1) For the poly-$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$ copolymer, $r_1 = 1.01$ and $r_2 = 1.04$ ($r_1 r_2 = 1.06$). The poly-$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$/poly-$[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$ pair appears to form ideal random copolymers, i.e., $r_1 r_2 = 1$. The electrochemical polymerization relies on reduction of the ligand system and activation of the reactivity of the vinyl-containing ligand (*p*-cinn) as a pseudo-radical anion, in head-to-head hydrodimerization-type couplings that would produce a linear polymer[5] and/or in the recently described[16] "living polymerization" metal complex chain reaction, which would allow for cross-linking steps. The ideal behavior of the $[Os(bpy)_2(p\text{-cinn})_2]^{2+}$/$[Ru(bpy)_2(p\text{-cinn})_2]^{2+}$ metal complex pair demonstrates the absence of any significant metal-related difference in the coupling reactivity of the *p*-cinn ligand complexes or in their lifetimes as end-units on active polymer chains.

Table I. Fraction of Os Sites Occurring in Blocks of ν Sites for the $Os(vbpy)_3$:$Zn(vbpy)_3$ System[a]

	fraction of sites				
f_{Os}	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$	$\nu = 5$
0.00	0.00	0.00	0.00	0.00	0.00
0.10	0.94	0.06	0.00	0.00	0.00
0.20	0.87	0.11	0.01	0.00	0.00
0.30	0.80	0.16	0.03	0.01	0.00
0.40	0.72	0.20	0.06	0.02	0.00
0.50	0.63	0.23	0.09	0.03	0.01
0.60	0.53	0.25	0.12	0.05	0.03
0.70	0.42	0.24	0.14	0.08	0.05
0.80	0.30	0.21	0.15	0.10	0.07
0.90	0.16	0.13	0.11	0.10	0.08
1.00	0.00	0.00	0.00	0.00	0.00

[a] Fraction of sites for each value of ν calculated by using values for $r_1 \sim 0.58$ and $r_2 \sim 0.87$, obtained from fit in Figure 5.

(2) For the poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymer, $r_1 = 0.58 \pm 0.04$ and $r_2 = 0.87 \pm 0.06$ ($r_1 r_2 = 0.51$). These results, while not far from the ideal $r_1 r_2 \approx 1$, suggest a tendency toward forming an alternating copolymer, or preferred heterocoupling. Given the uncertainties in the assay of copolymer composition (noted above, Figures 3–5), and results from XPS (vide infra), we are inclined to accept the $[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymerization as "near-ideal", and as suitable for site dilution purposes in electron transport studies.

(3) For the poly-$[Os(bpy)_2(vpy)_2]^{2+}$/poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ copolymer, $r_1 = 4.84 \pm 0.36$ and $r_2 = 0.26 \pm 0.05$ ($r_1 r_2 = 1.28$). By examination of the definitions of r_1 and r_2, this somewhat nonideal result suggests that the $[Os(bpy)_2(vpy)_2]^{2+}$ monomer has a greater reactivity toward electropolymerization than does the $[Ru(bpy)_2(vpy)_2]^{2+}$ monomer. This is surprising given the ideal and near-ideal copolymerization behavior of the two structurally related metal complex pairs based on *p*-cinn and vbpy ligands. The possible reasons for this variance in behavior are as follows: (i) There may be a difference in coupling reactivity of a vpy ligand attached to Os vs Ru metals or in its lifetime as an end-unit on active polymer chains. It is potentially significant that, of the three vinyl-substituted ligands, the least ideally behaved (vpy) is also the least extensive aromatic system, whose electronic structure can be expected to be most sensitive to the influence of coordinated metal.[17] Note that the most ideally behaved (*p*-cinn) involves a coupling unit more electronically remote from the metal. (ii) To some extent, films grow by precipitation of polymer formed in the diffusion layer around the electrode (as opposed to direct grafting of monomers to the polymer film surface). Thus, differing solubility properties of Os- vs Ru-containing oligomers could alter the apparent values of r_1 and r_2 by promoting incorporation of less-soluble oligomer into the film. (iii) A related factor influencing the $[Os(bpy)_2(vpy)_2]^{2+}$/$[Ru(bpy)_2(vpy)_2]^{2+}$ copolymerization may be the presence, in the particular samples of $[Os(bpy)_2(vpy)_2]^{2+}$ employed, of oligomeric poly-$[Os(bpy)_2(vpy)_2]^{2+}$ impurities (preblocks) arising from the relatively harsh reaction conditions of the $[Os(bpy)_2(vpy)_2]^{2+}$ synthesis. We have independent evidence[18] that solutions of oligomeric forms of poly-$[Os(bpy)_2$-

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[16] (a) A recent study[16b] showed that the related complex $[Fe(4\text{-methyl-}4'\text{-vinyl-}2,2'\text{-bipyridine})_3]^{2+}$ undergoes efficient electropolymerization and produces films containing average coupled ligand chain lengths of seven. (b) Elliott, C. M.; Baldy, C. J.; Nuwaysir, L. M.; Wilkins, C. L. *Inorg. Chem.* **1990**, *29*, 389.

[17] (a) Kober, E. M. Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1982. (b) In the $[Os(bpy)_2(vpy)_2]^{2+}$/$[Ru(bpy)_2(vpy)_2]^{2+}$ metal complex pair, a greater degree of spin–orbit coupling in the Os monomer may yield greater stability of its reduced and or chain end-unit form and preferential incorporation of Os.

$(vpy)_2]^{2+}$ form polymer films more efficiently during electropolymerization, but no attempt was made in the present study to further elucidate this problem.

The reactivity ratios r_1 and r_2 can be used, with a probability analysis,[14] to calculate the expected distribution of site neighbors, i.e., the fraction of Os sites (on a chain) that exist in a block length of one Os (i.e. are isolated Os sites, in the chain) or that exist in a block length of two or three or four Os sites etc. Table I shows such calculations using the r_1 and r_2 values for the nonideal $[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ pair, where, for example, in a polymer made from a growth solution with $f_{Os} = 0.5$, ca. 63% of the Os sites in a chain are bounded by Zn sites whereas ca. 23% are bounded by one Os and one Zn.

The r_1 and r_2 determinations and Table I calculations are instructive, but it is important to realize that they refer to the pattern of site distributions *on a given polymer chain*. In the context of electron-hopping events in a polymer film assembled from Os complexes, the chains of metal complexes are quite concentrated (total metal complex concentration >1 M). Electron self-exchanges undoubtedly occur between Os(III) and Os(II) sites on the same chain (*intrachain* exchange), but they will also occur between sites that are ***adjacent but are on different polymer chains*** (*interchain*). The literature of electron transport in redox polymers as yet offers no experimental way to distinguish between interchain and intrachain electron hopping in concentrated polymers. The analysis in Table I, strictly speaking, best applies to a dilute, *soluble* copolymer chain. As a consequence, it is possible that the effects of compositional irregularities in copolymer formation (i.e., blocking or alternation of sites) may be diminished by randomness in how adjacent chains pack together and thus randomness in the identity of nearest neighbors on adjacent chains. That is, interchain electron hops should relax to some extent the requirement that $r_1r_2 = 1$ for a useful, dilutable copolymer electron-transfer system. In the absence of a way to estimate the importance of interchain electron transfers and the randomness of interchain packing (potentially oligomer solubility-sensitive), the selection of copolymer systems with r_1 and r_2 near unity is, at present, the least ambiguous course.

XPS Experiments. The analysis of r_1 and r_2 for the poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymer depends on the efficacy of replacing poly-$[Zn(vbpy)_3]^{2+}$ sites with voltammetrically active poly-$[Fe(vbpy)_3]^{2+}$ sites. Sullivan et al.[11c] indicate >95% site replacement in this chemistry; we explored this question further with XPS measurements of the exterior and interior surfaces of copolymer films deposited on Pt electrodes.[19] A PVA overcasting/peeling technique was employed to expose the film interior surface (see Experimental Section). The metal complex surface coverages (poly-$[Os(vbpy)_3]^{2+}$ plus poly-$[Zn(vbpy)_3]^{2+}$) in the films used for XPS studies, measured as in Figure 3, were typically between 5×10^{-9} and 2×10^{-8} mol/cm^2.

XPS Spectra of poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ Copolymers. Survey spectra of typical poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymers (Figure 6A, $f_{Os} = 0.5$) exhibit the expected peaks for Os 4f ($4f_{7/2}$, $4f_{5/2}$ doublet, ≈52 eV), Zn 3p (≈86 eV), Zn 3s (≈136 eV), Zn Auger (≈263 eV), N 1s (≈397 eV), C 1s (≈284 eV), F 1s (≈682 eV), and F Auger (≈596 eV). The observed F 1s peak is consistent[20] with the BF_4^- counterion becoming incorporated into the film during electropolymerization. A peak at ca. 196 eV appears with highly variable intensity; this may be a Cl 2p impurity that could have arisen from the CH_2Cl_2 rinse of the films prior to XPS analysis. Peaks associated with the Pt substrate were never observed, which means that the 50–200 nm thick films were free of macroscopic pinhole defects.

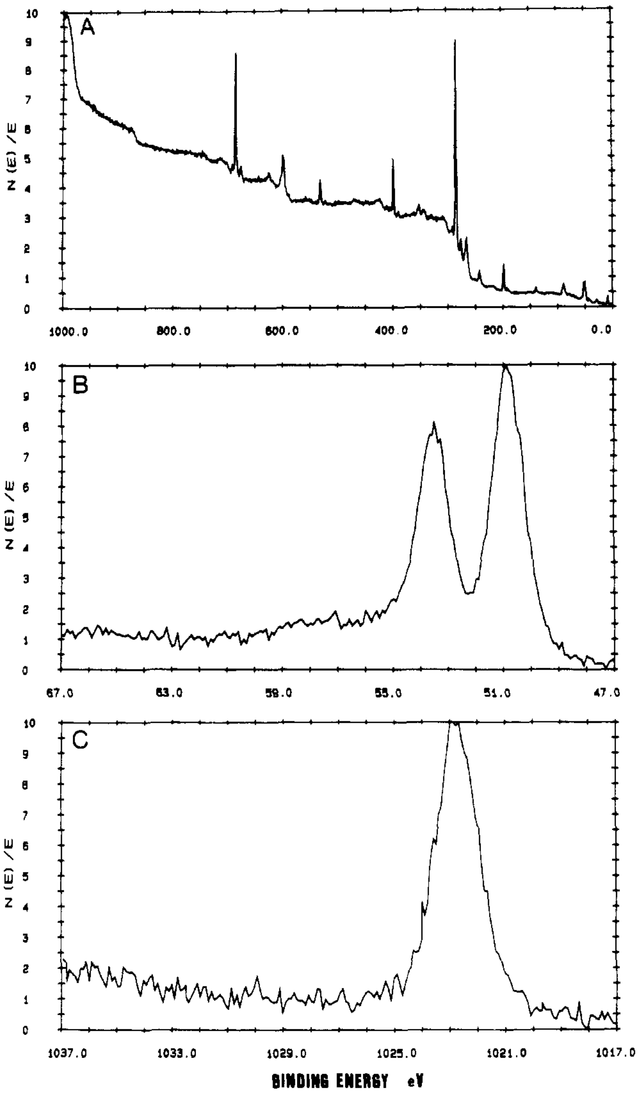

Figure 6. XPS spectra of the exterior surface of a poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymer grown on a Pt electrode from a solution where $f_{Os} \approx 0.5$: (A) survey spectra; (B) Os 4f region; (C) Zn 2p region.

Spectral expansions showing the Os $4f_{7/2}$, $4f_{5/2}$ and Zn 2p regions (Figure 6B,C) reveal only one chemical form of the two elements, as expected.

XPS Spectra of poly-$[Os(vbpy)_3]^{2+}$/poly-$[Fe(vbpy)_3]^{2+}$ Copolymers. Survey spectra of films like that in Figure 6, using $f_{Os} = 0.5$ in the feed solution, and following exposure to $FeCl_2$ solutions, "conditioning" (vide supra), and rinsing, are completely free of Zn peaks and exhibit Fe 2p, 3p, and Auger peaks. Qualitatively, the signals for C, N, O, and F were unchanged.

Similar results were obtained in spectra of exterior and interior surfaces of the film. Figure 7 compares spectra of the film exterior (Figure 7A) and interior (Figure 7B) surfaces in the Os 4f/Fe 3p region. The two lower BE bands represent Os 4f and the solid lines are Gaussian fits using a linear baseline correction. Again there is no obvious multiplicity of Os and Fe chemical forms. Figure 7C shows for the same film the Zn 2p region for the interior surface; the exterior spectrum is the same. Exposure to $FeCl_2$ solution and electrochemical "conditioning" clearly completely removes Zn from the interior surface and thus presumably throughout the film. On the other hand, if the film is exposed to $FeCl_2$ but *not* conditioned, residual Zn is found at the interior film/electrode interface, as shown by Figure 7D. This demonstrates that the conditioning potential cycling *is* required for complete removal of Zn and presumably its substitution by Fe. The reduction of bipyridine rings in the films may facilitate Zn/Fe substitution both by labilizing the Zn^{2+} and by facilitating Fe^{2+}

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(18) McCarley, R. L.; Thomas, R. E.; Irene, E. A.; Murray, R. W. *J. Electrochem. Soc.* **1990**, *137*, 1485.

(19) The initial experiments used copolymer films grown on Au-coated Si wafers. This procedure was satisfactory for XPS examination of the exterior film surface, but subsequent peeling of the copolymer with overcast PVA films stripped off the Au layer as well. The PVA stripping of copolymer is successful for non X-ray irradiated films, so X-ray irradiation apparently improves adhesion at the copolymer–Au interface.

(20) *Handbook of X-ray Photoelectron Spectroscopy*; G. E. Muilenburg, G. E., Ed.: Perkin-Elmer: Minneapolis, MN, 1979.

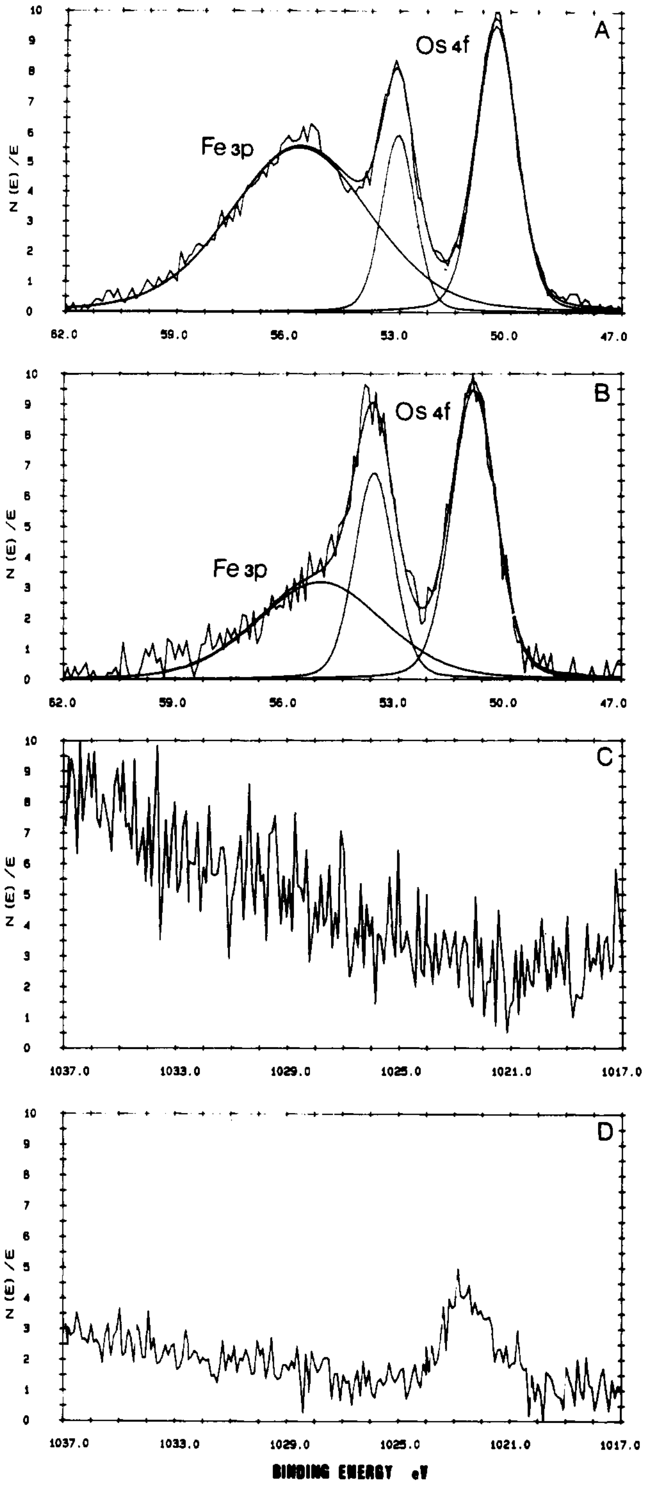

Figure 7. XPS spectra of poly-$[Os(vbpy)_3]^{2+}$/poly-$[Fe(vbpy)_3]^{2+}$ copolymer grown from a $[Os(vbpy)_3]^{2+}/[Zn(vbpy)_3]^{2+}$ solution where $f_{Os} \approx 0.5$. (A) Exterior surface of film, supported on Pt electrode, after exposure to a $FeCl_2$ solution and electrochemically "conditioned". Also shown is a least-squares fit using three Gaussian curves of the Os 4f and Fe 3p peaks. (B) Interior surface of the film in part A after removal from Pt, supported on PVA. (C and D) Zn 2p region of interior surface of PVA-supported film similar to that in part A where $f_{Os} \sim 0.5$, which was then exposed to a $FeCl_2$ solution and (C) electrochemically conditioned or (D) not electrochemically conditioned.

diffusion in the less positively charged film. Also, XPS (not shown) of the exterior surface of a $[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymer film that has been soaked in Fe(II) solution but *not* conditioned, reveals a very large Fe 3p signal (obscuring that due to Os 4f). This observation shows that a large residue of uncoordinated Fe remains on the film surface, and probably within it, prior to the conditioning potential cycling. Presumably this Fe serves as a reservoir for incorporation into the Zn sites that remain after soaking and are labilized by the bipyridine reduction part of the electrochemical conditioning. The ultimate fate of any excess Fe following conditioning is unknown.

The relative areas of the Os 4f and Fe 3p bands in spectra like Figure 7A,B, accounting for elemental sensitivities,[21] yield the mole fractions of Fe on the film exterior and interior surfaces. For the example of Figure 7A,B, the XPS result for F_{Fe} was 0.54 and 0.35 for the exterior and interior, respectively. While this suggests that Fe incorporation at the film's interior may not be quantitative, we note that the reliability of the XPS quantitation is actually not very good. For example, determinations of the relative Fe and Os band intensities on a series of films polymerized in a single run from the same feed solution, which gave similar values of F_1 based on the Os(III/II)–Fe(III/II) voltammetry, unfortunately varied as much as 3×. The XPS results therefore are qualitatively consistent with the voltammetric results, but the latter are quantitatively more reliable.

Determination of *D* in an Os–Zn Copolymer. To preliminarily test electron transport in the poly-$[Os(vbpy)_3]^{2+}$/poly-$[Zn(vbpy)_3]^{2+}$ copolymer, two copolymer films were grown under identical conditions on the polished tips of two Pt wire electrodes set in an insulating shroud from a solution of $[Os(vbpy)_3]^{2+}$ and $[Zn(vbpy)_3]^{2+}$ in 0.1 M Et_4NBF_4/CH_3CN where $f_{Os} = 0.61$. One of the films was assayed for F_{Os} by Fe replacement and "conditioning"; the voltammetric results were similar to those shown in Figure 3, and values of $\Gamma_{Os+Zn} = 9.2 \times 10^{-9}$ mol/cm² and $F_{Os} = 0.69$ were obtained. These values correspond to an approximate film thickness of 71 nm and an osmium complex site concentration of 0.9×10^{-3} mol/cm³, taking total film concentration as 1.3 M.

A thin, porous Au film was evaporated over the other copolymer film, forming a "sandwich" electrode.[9] Application of 0.0 V to the Au electrode and +1.2 V vs SSCE to the Pt electrode, in a Et_4NBF_4/CH_2Cl_2 solution, gave a limiting current of 0.88 mA/cm². Assuming that the films were identical, this current corresponds to a value of $D_e = 5 \times 10^{-11}$ cm²/s. If this result is compared to that[15] for undiluted poly-$[Os(vbpy)_3]^{2+}$ sites, where $D_e = 3.4 \times 10^{-9}$ cm²/s, a substantially attenuated rate of electron transport through the film is indicated. The main value of the preliminary result is in showing that sandwich electrodes can be fashioned from copolymers based on these monomers for use in conductivity studies, which are on-going.

One further consideration in choosing a system for electron-transport measurements is potential interference by the diluent through its own electron self-exchange. The Zn complex used above is completely silent in terms of electron transport at potentials near that of the Os complex. The potentials of the Ru complexes are ca. 600 mV away from the Os potential, which in most circumstances ensures that Ru–Ru or Os–Ru electron-hopping activity will not contribute to the electron transport of Os(III/II) mixed-valent films. On the other hand, if the ratio of Os(III)/Os(II) sites is made quite large, and large ΔG driving energy is applied (as with a large dE/dX),[9] participation by the diluent Ru sites might become noticeable. That is, under particular circumstances, there will be constraints in Ru–Os pairs, such as in doping the Os polymer to large Os(III)/Os(II) mixed valent ratios, whereas Os–Zn pairs have no such constraints. In the present experiments, this is not a major limitation since working with large Os(III)/Os(II) ratios is experimentally difficult on other grounds, namely their large oxidizing potential.

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(21) The atom fraction, C_x, of a species x can be expressed by: $C_x = n_x/\sum n_i = (I_x/S_x)/(\sum I_i/S_i)$, where n is the number of atoms per cubic centimeter, S is the instrument-dependent atomic sensitivity factor, and I is the signal intensity.