

emission energy of the resulting polymer was the same. Table VIII shows the emission energies for the light-induced polymerized fractions.

The emission energy differences at low temperature between the various polymers and the corresponding dmbpy metal complexes indicate that there is some interaction between the metal complexes incorporated in the polymer. It is unlikely that this is due to electronic coupling between the metal centers through the hydrocarbon polymer backbone. However, in the absence of electronic coupling, the emission energy should correspond to that for the dmbpy metal complex. Furthermore, the fact that the emission energy of the further polymerized fractions was the same regardless of the original molecular weight of the osmium polymer fractions indicates that any interaction between the metal complexes is independent of the number of chromophores in the polymer chain (assuming that all the polymer fractions did not have similar molecular weights once all the vinyl groups had reacted). Therefore, it does not seem reasonable that electronic coupling between the metal complexes can account for the observed effects. Instead, we attribute the difference in the emission energies to electrostatic repulsions between the positively charged metal complexes incorporated in the polymer. At room temperature, the polymer chains can rotate and move freely in the fluid media so as to minimize repulsions, whereas at 77 K, the solvent mixture is a glass and the motion of the polymer chains is severely restricted by the very high viscosity of the medium. As a result, the metal complexes cannot easily achieve configurations that minimize repulsions.

Conclusions

Polymers of $[M(\text{vbpy})_3]^{2+}$ ($M = \text{Ru}, \text{Os}$) have been prepared in solution via free-radical polymerization using AIBN as initiator. These polymers were fractionated according to molecular weight, using SEC. The relative size of the different polymer fractions was determined by measurement of their diffusion coefficients in solution.

We have found that, in the UV region of the spectrum, the intensity of the intraligand band at ~ 250 nm decreases proportionally with the number of vinyl groups consumed during the polymerization reaction. For osmium polymers the relative polymer size varies in proportion to the number of vinyl groups consumed during the polymerization reaction whereas the same is not true for the ruthenium polymers. In most cases, the three vinyl groups in the ruthenium complex were polymerized, whereas most of the osmium polymers exhibited a relatively high concentration of residual unreacted vinyl groups, pointing to a significant effect on the nature of the metal center.

Similarly, the emission energies of the ruthenium and osmium polymers were also related to the concentration of residual vinyl groups in the polymers. Upon polymerization, the emission energy is blue-shifted (the higher the degree of polymerization, the larger the blue shift). For the osmium polymers, the emission energy varied directly with the relative polymer size, but again such was not the case for the ruthenium polymers.

These results indicate that the metal center can strongly influence the reactivity of the vinyl groups in the bpy ligand and, also, point out significant structural differences between the osmium and ruthenium polymers.

We have also found that the emission energies at 77 K of polymers with ostensibly no residual vinyl groups were higher than those of the corresponding dmbpy metal complexes (the fully polymerized analogues) for both ruthenium and osmium polymers. These differences have been attributed to electrostatic repulsion between the positively charged metal complexes incorporated in the polymer.

Acknowledgment. S.L.B. gratefully acknowledges a MARC from the NIH. H.D.A. is an A. P. Sloan Foundation Fellow (1987-1991) and a Presidential Young Investigator (1984-1989).

Registry No. $[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2]$, 81315-17-5; $[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2]$, 130728-19-7; $[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2]$ (homopolymer), 97056-94-5; $[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2]$ (homopolymer), 81315-14-2.

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Synthesis and Characterization of Redox Copolymers of $[\text{Ru}(4\text{-vinyl-4'-methyl-2,2'-bipyridine})_3]^{2+}$ and $[\text{Os}(4\text{-vinyl-4'-methyl-2,2'-bipyridine})_3]^{2+}$: Unusual Energy-Transfer Dynamics

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Received May 1, 1991

Copolymers of $[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2]$ and $[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2]$ (vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine) have been prepared in solution and by electropolymerization. The ruthenium and osmium monomers were incorporated in the copolymers in different ratios depending on the polymerization method. These results point to fundamental differences between solution polymerization and electropolymerization. In addition, luminescence experiments at liquid-nitrogen temperature and room temperature point to a significant degree of energy transfer from ruthenium to osmium states in the polymer.

Introduction

In the preceding paper¹ we reported on the synthesis, fractionation (by size-exclusion chromatography), and characterization of homopolymers of polypyridyl metal complexes of ruthenium and osmium. In that manuscript we presented data that indicated differences in the reactivity of the monomer complexes as well as of the physicochemical properties of the resulting polymers, depending on the metal center. In order to further explore these effects we have also prepared copolymers of the above-mentioned monomers. Polymerization was carried out by free-radical polymerization of solutions containing the monomer complexes of

osmium and ruthenium in different ratios. The ratios of the monomer complexes employed were 5:1, 1:1, and 1:5 (Ru:Os). The ruthenium monomer appears to have a higher reactivity for polymerization relative to that of the osmium monomer, so that the ratio of Ru/Os monomers incorporated in the polymers was not necessarily that in which they were mixed.

These polymers have been characterized spectroscopically and electrochemically. One of the aims of this work was to ascertain whether the physicochemical properties of the individual metal complexes change upon copolymerization or whether the complexes behave as isolated units.

Copolymers were also prepared by electropolymerization of the same solutions, and the Ru:Os ratios obtained differed from those mentioned above, pointing to fundamental differences between solution polymerization and electropolymerization.

(1) Bommarito, S. L.; Lowery-Bretz, S. P.; Abruña, H. D. *Inorg. Chem.*, preceding paper in this issue.

Table I. Copolymer Deposition Experiments on a Platinum Disk Electrode from a 1:1 Osmium:Ruthenium Monomer Ratio ($[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2] = [\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2] = 0.5 \text{ mM}$) in a 0.1 M TBAP in Acetonitrile Solution

$\Gamma_{\text{Os}}, 10^9$ mol/cm ²	$\Gamma_{\text{Ru}}, 10^9$ mol/cm ²	$\Gamma_{\text{Ru}}/\Gamma_{\text{Os}}$	$\Gamma_{\text{Os}}, 10^9$ mol/cm ²	$\Gamma_{\text{Ru}}, 10^9$ mol/cm ²	$\Gamma_{\text{Ru}}/\Gamma_{\text{Os}}$
Deposition Potential 0 to -1.4 V					
1.2	2.6	2.1	1.3	3.2	2.4
1.2	2.5	2.1	1.5	3.7	2.4
0.10	0.22	2.2	1.4	3.5	2.5
0.95	2.0	2.1	1.3	3.2	2.4
1.4	3.4	2.4			
Deposition Potential 0 to -1.7 V					
3.9	8.6	2.2	5.8	17	2.9
4.1	7.8	1.9	4.8	14	2.9
4.9	10	2.0	6.8	18	2.6
5.4	11	2.0	7.3	18	2.4

Experimental Section

Except as state here, all experimental procedures, chemicals, and instrumentation were as previously described.¹

Synthesis of Copolymers of $[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2]/[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2]$. The $[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2]/[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2]$ copolymers were prepared via free-radical polymerization in acetone solution using AIBN (AIBN is azobis(isobutyronitrile)) as free-radical initiator. The monomers (typically 100 mg total) were mixed in the desired ratio (1:1, 5:1, and 5:1) and dissolved in acetone (4ml) to which 15 mg of AIBN were added as initiator. The reaction mixture was transferred to a Pyrex ampole, which was evacuated by three freeze-pump-thaw cycles and sealed under vacuum. The reaction was run at 60 °C for 72 h in a controlled-temperature bath. The resulting copolymer was precipitated by the addition of diethyl ether. After being redissolved in acetone and reprecipitated in a diethyl ether, the copolymer was filtered, rinsed several times with ether, and dried under vacuum at room temperature.

Polymer Purification. $[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2]/[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2]$ copolymers were purified using a size-exclusion chromatography (SEC) column of cross-linked Sepharose CL-6B (Pharmacia Biotechnology Products) with acetone as eluant. In all cases, only one band (one molecular weight distribution) was recovered from the SEC column.

Electropolymerization. Acetonitrile/0.1 M TBAP (TBAP is tetra-*n*-butylammonium perchlorate) solutions containing the Ru/Os monomer complexes in the same ratios as used in homogeneous polymerization were used in electroreductively initiated polymerization. The solutions were degassed with prepurified nitrogen for at least 20 min, and a constant flow of nitrogen was maintained during polymerization. Electropolymerization was effected by scanning the potential of the electrode between 0 and either -1.4 or -1.7 V depending on the polymerization conditions (vide infra). To assess the relative amounts of the Ru and Os complexes within the polymer films, cyclic voltammograms were run in MeCN containing 0.1 M TBAP in the potential region between 0 and +1.70 V where metal based ($M^{2+/3+}$) redox processes occur for the Os ($E^\circ = +0.74 \text{ V}$) and Ru ($E^\circ = +1.14 \text{ V}$) complexes, respectively.

Results and Discussion

(a) Electrochemical Characterization. In the preceding paper¹ we showed that the tris(vinylbipyridyl) complex of ruthenium appeared to be more reactive toward free-radical polymerization in solution than the osmium analogue. In order to study the relative reactivities of these metal complexes upon electropolymerization and to compare these results to solution polymerization, we prepared electropolymerized films of copolymers of the osmium and ruthenium monomers from solutions containing the same relative concentration (i.e. ratio) of monomers. Table I presents the data for the copolymerization of the ruthenium and osmium monomers (1:1 ratio) by electrochemical reduction at a platinum electrode.

Tris(vinylbipyridyl) complexes of transition metals typically have three one-electron ligand-based reduction waves in the cathodic region with the third typically being at significantly more negative potentials than the first two. For example, $\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2$ exhibits reductions at $E_1^\circ = -1.43 \text{ V}$ and $E_2^\circ = -1.54 \text{ V}$ vs SSCE. Electropolymerization of these complexes can be effected by reduction by either one or two electrons (and ostensibly three). However, polymerization occurs at a significantly faster rate when the potential is scanned past the second reduction wave.

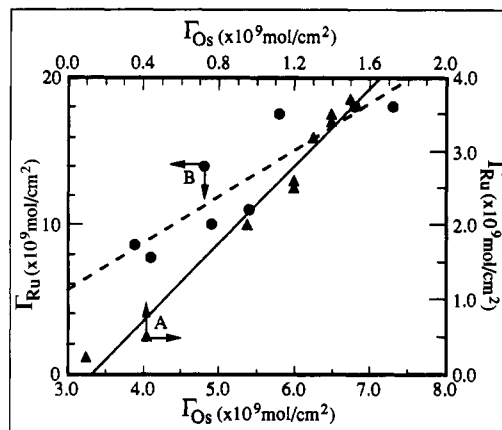


Figure 1. Plot of Γ_{Ru} vs Γ_{Os} for copolymers prepared by electroreduction of a 1:1 $[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2]:[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2]$ solution both at a $5 \times 10^{-4} \text{ M}$ concentration in acetonitrile containing 0.1 M TBAP on a platinum electrode by potential cycling between (A) 0.0 and -1.40 V and between (B) 0.0 and -1.70 V.

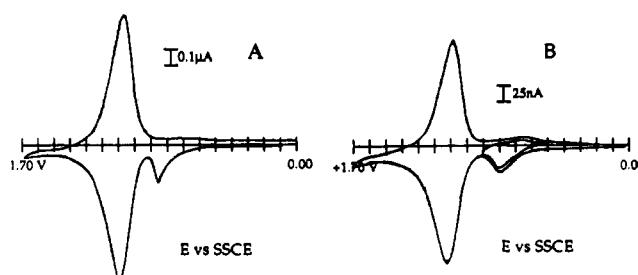


Figure 2. Cyclic voltammograms for a Ru/Os copolymer film deposited on a platinum electrode in 0.1 M TBAP in acetonitrile. The film was prepared by potential reduction ($E = 0.0$ to -1.7 V vs SSCE) of a 5:1 Ru/Os solution ($[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2] = 0.5 \text{ mM}$, $[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2] = 2.5 \text{ mM}$): (A) scan rate 50 mV/s; (B) scan rate 10 mV/s.

Electropolymerization was carried out after both one- and two-electron reduction. When polymerization was performed from 0 to -1.7 V (i.e. after two-electron reduction), the potential was scanned for half the time it was when deposition was obtained between 0 and -1.4 V (i.e., after one-electron reduction). Whereas coverages obtained using deposition potentials between 0 and -1.4 V were about one monolayer (ten scans), coverages 3-7 times larger were obtained upon two-electron reduction (five scans). However, regardless of the deposition conditions, the ratio of ruthenium to osmium centers was about 2:1. (For $E = 0$ to -1.4 V, $\Gamma_{\text{Ru}}/\Gamma_{\text{Os}} = 2.2 \pm 0.1$; for $E = 0$ to -1.7 V, $\Gamma_{\text{Ru}}/\Gamma_{\text{Os}} = 2.3 \pm 0.4$.)

Parts A and B of Figure 1 show plots of Γ_{Ru} as a function of Γ_{Os} for the copolymers prepared by electroreductive polymerization from $E = 0$ to -1.4 V and $E = 0$ to -1.7 V, respectively. In the first case ($E = 0$ to -1.4 V), the correlation factor (r) was 0.98, whereas for the second ($E = 0$ to -1.7 V) it was 0.89. We believe that the larger spread in the results in the second case might be due to differences in the reaction rate during polymerization. At -1.4 V the driving force for the reaction is lower and the polymerization reaction slower, whereas at -1.7 V the reaction rate is much faster and is probably kinetically controlled. Since ruthenium's reactivity appeared to be about twice as large as osmium's, we had expected a larger Ru:Os ratio under kinetically controlled conditions. However, this ratio did not vary as a function of the potential range for electropolymerization.

Electropolymerization of a 5:1 mixture of $\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2$ and $\text{Os}(\text{vbpy})_3(\text{PF}_6)_2$ produced a polymer film that contained both ruthenium and osmium. However, the $\text{Os}(\text{vbpy})_3^{3+/2+}$ redox couple was not readily observed in cyclic voltammograms of the polymer film coated electrodes. In Figure 2 are shown cyclic voltammograms at two different scan rates for an electrode modified with such a copolymer film. At 50 mV/s (Figure 2A), a small prewave which we ascribe to the $\text{Os}^{2+/3+}$ couple is observed

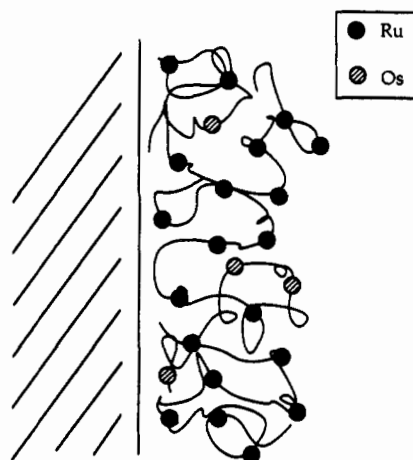


Figure 3. Schematic depiction of the possible distribution of osmium and ruthenium metal centers in the polymer backbone on the platinum electrode surface after electroreductive polymerization of a 5:1 [Ru(vbpy)₃(PF₆)₂]:[Os(vbpy)₃(PF₆)₂] monomer mixture solution.

at +0.92 V. At lower scan rates (e.g. 10 mV/s; see Figure 2B) the prewave shifts to less positive potentials and the presence of a reverse wave is evident.

Prewaves or "charge-trapping spikes" have been previously observed for bilayer films of redox polymers where spatially segregated two-layer films of different monomers were prepared by sequential polymerization of the appropriate monomers.² If the potential of the outer film is less positive than that of the inner film, oxidation of the outer film is mediated by the inner film. This typically occurs as a sharp prewave. Such charge-trapping spikes have also been observed in homopolymer coatings³ and are believed to be due to isolated polymer sites formed during the electropolymerization process. These isolated sites cannot have direct charge transfer with the electrode surface, and therefore, these redox processes occur as mediated electron transfers through the polymer film. If these sites have formal potentials (for oxidation) that are less positive than the first oxidation wave or less negative (for the reduction process) than the first reduction wave of the polymer film, redox events of these sites occur as a prewave.

Anson and Guarr⁴ reported that in electropolymerized films of Ru(vbpy)₃²⁺ and Os(phen)₃²⁺ (phen = 1,10-phenanthroline), the Os(phen)₃^{2+/3+} couple was not observed in cyclic voltammograms of electrodes coated with the copolymer. However, the presence of the osmium complex had been previously confirmed by UV-vis spectrophotometry of the electropolymerized films at a transparent SnO₂ electrode. The presence of charge-trapping spikes was attributed to the oxidation of Os(II) centers by cross-reaction with Ru(III) sites. In order for the [Os(phen)₃]²⁺ to polymerize, it needs to react with reduced vinylbipyridine ligands from [Ru(vbpy)₃]²⁺ since, by itself, the [Os(phen)₃]²⁺ complex will not undergo electropolymerization. As a consequence, the osmium metal centers are isolated, having only ruthenium sites as nearest neighbors. However, since vinylbipyridine ligands can react with each other, the ruthenium centers can have both ruthenium and osmium neighbors.

It is generally believed that charge transport in redox polymers occurs by electron exchange⁵ through nearest neighbors in the polymer matrix. Os(phen)₃²⁺ oxidizes at a less positive potential (by about 350 mV) than the Ru(vbpy)₃²⁺. Therefore at the formal

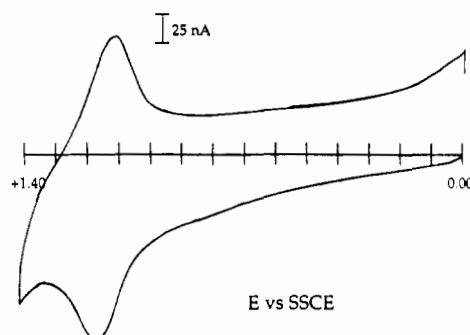


Figure 4. Cyclic voltammogram in 0.1 M TBAP in acetonitrile at 50 mV/s for a 5:1 Ru/Os copolymer (from solution polymerization) deposited on a platinum electrode surface.

potential for the Os^{2+/3+} couple, the ruthenium centers are not oxidized and cannot mediate the oxidation of osmium sites. Since charge transfer can only occur at potentials where ruthenium centers are oxidized, a prewave near the Ru^{2+/3+} couple was attributed to the mediated oxidation of the Os(phen)₃²⁺ sites by the oxidized ruthenium centers.

In the present case, small amounts of Os(vbpy)₃²⁺ (recall that the Ru:Os ratio was 5:1) have been incorporated in the copolymer film and are ostensibly distributed randomly through the polymer.² However, because Os(vbpy)₃²⁺ metal complexes can react with each other, some of the osmium centers will have other osmium complexes as nearest neighbors within the polymer, and electron self-exchange can occur among them. Figure 3 shows a schematic depiction of the possible distribution of osmium and ruthenium metal centers in the polymer backbone on the electrode surface. Although this depiction is clearly speculative, it is consistent with the observed electrochemical behavior. With this picture in mind, we can rationalize the electrochemical behavior of these copolymer films. At relatively fast scan rates, the osmium centers cannot diffuse rapidly enough and are thus oxidized through mediation by the oxidized ruthenium centers. At lower scan rates, the osmium centers have more time to diffuse and can be oxidized (at least in part) by electron self-exchange. Consistent with this, we can see that in Figure 2B the prewave shifts toward the formal potential of the Os(vbpy)₃²⁺ couple and also appears more reversible due to electron transfer via self-exchange.

In copolymer films prepared at a platinum electrode from electropolymerization of a 1:5 mixture of Ru(vbpy)₃²⁺/Os(vbpy)₃²⁺, the Ru(vbpy)₃²⁺ couple is observed as a reversible wave at +1.14 V. As expected, the ruthenium metal complex was incorporated to a much smaller extent than the osmium complex. However, at the formal potential of the Ru(vbpy)₃^{3+/2+} couple, the osmium complex is oxidized, and therefore, oxidation of the Ru(II) centers through the polymer film can take place.

In a recent study, Murray⁶ and co-workers studied copolymers of electropolymerizable metal complexes similar to those studied here in order to assess their reactivity. Specifically, they studied copolymers of [Os(bpy)₂(p-cinn)₂]²⁺/[Ru(bpy)₂(p-cinn)₂]²⁺ (p-cinn is *N*-(4-pyridyl)cinnamamide); and [Os(bpy)₂(vpy)₂]²⁺/[Ru(bpy)₂(vpy)₂]²⁺ (vpy = 4-vinylpyridine). They find that for the p-cinn complexes the Ru and Os complexes exhibit essentially identical reactivities whereas for the vpy complexes the osmium complex appears to be more reactive. This was ascribed, in part, to the fact that the vpy ligand has the least extensive aromatic system and is thus expected to be more sensitive to the metal center. In addition, they alluded to possible effects due to solubility differences.

Given that these differences in the nature of the polymerizable group can give rise to rather large differences in reactivity, it is difficult to make direct comparisons with our results. However, it is to be noted that vbpy is much more extensively conjugated than vpy or p-cinn and in addition, our complexes have three

- (2) Abruña, H. D.; Denisevich, P.; Umaña, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1.
- (3) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153.
- (4) Guarr, T. F.; Anson, F. C. *J. Phys. Chem.* **1987**, *91*, 4037.
- (5) (a) Kaufman, F. B.; Engler, E. M. *J. Am. Chem. Soc.* **1979**, *101*, 544. (b) Murray, R. W. *Electroanal. Chem.* **1984**, *13*, 191. (c) Murray, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 145. (d) Faulkner, L. R. *Chem. Eng. News* **1984**, *62* (Feb. 27), 28. (e) Abruña, H. D. In *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1988; Vol. 1, Chapter p 97.

- (6) Surridge, N. A.; Keene, F. R.; White, B. A.; Facci, J. S.; Silver, M.; Murray, R. W. *Inorg. Chem.* **1990**, *29*, 4950.

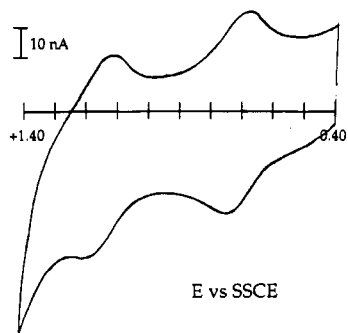


Figure 5. Cyclic voltammogram in 0.1 M TBAP in acetonitrile at 50 mV/s for 1:1 Ru/Os copolymer (from solution polymerization) deposited on a platinum electrode surface.

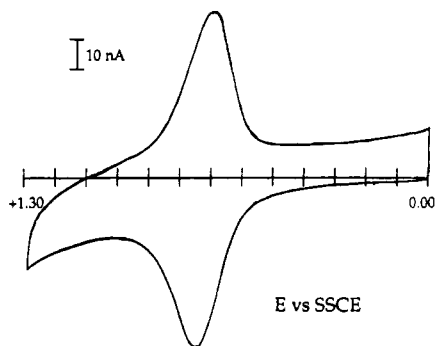


Figure 6. Cyclic voltammogram in 0.1 M TBAP in acetonitrile at 50 mV/s for 1:5 Ru/Os copolymer (from solution polymerization) deposited on a platinum electrode surface.

(rather than two) polymerizable groups.

Copolymers of $\text{Ru}(\text{vbpy})_3^{2+}$ and $\text{Os}(\text{vbpy})_3^{2+}$ were also prepared in solution by free-radical polymerization using the same ratios of monomers (5:1, 1:1, 1:5) as employed in the electropolymerization experiments. The monomers were mixed in the appropriate ratios in a polymerization ampule and purified on a SEC column as described in the Experimental Section.

In Figures 4–6 are shown cyclic voltammograms of the 5:1, 1:1, and 1:5 Ru/Os copolymers prepared by solution polymerization and deposited on a platinum electrode surface by adsorption. The cyclic voltammogram for the 1:1 Ru/Os copolymer (Figure 5) reveals a fundamental difference between solution polymerization and electropolymerization in that both monomers were incorporated in the polymer in the same ratio in which they were mixed in the polymerization reaction. This is rather surprising since as mentioned previously, in films prepared by electropolymerization from 1:1 monomer mixtures, the ruthenium monomer was incorporated in the polymer in a ratio of 2:1 relative to the osmium monomer. In addition, from our studies on the related homopolymers,¹ we had found that, in spite of the large degree of steric hindrance anticipated, in most cases, all the vinyl groups in the ruthenium complexes were consumed during solution polymerization. On the other hand, for osmium homopolymers prepared under similar conditions, a significant concentration of unreactive vinyl groups remained.

Cyclic voltammograms for the Ru/Os 5:1 and 1:5 copolymers deposited on the electrode surface (Figures 4 and 6) only show the $\text{Ru}^{2+/3+}$ couple and the $\text{Os}^{2+/3+}$ couple, respectively. The presence of both monomers in all three copolymers was confirmed by UV–vis spectrophotometry and emission spectroscopy. However, only the monomer incorporated in the largest concentration showed an electrochemical response.

Comparison of the visible spectra of the copolymers prepared by solution polymerization with the corresponding monomer mixtures suggests that the monomers were incorporated in the copolymer in ratios similar to those in which they were mixed in the polymerization reaction. Assuming a Ru:Os ratio of 5:1, the voltammetric response for the $\text{Os}^{2+/3+}$ couple should be about 16% of the peak current of the $\text{Ru}^{2+/3+}$ couple (the same argument

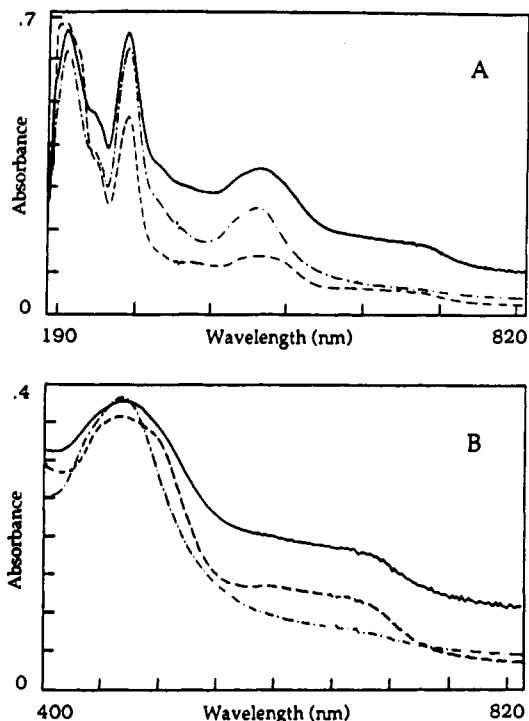


Figure 7. UV–vis (A) and visible (B) absorption spectra for the $\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2/\text{Os}(\text{vbpy})_3(\text{PF}_6)_2$ copolymers in acetonitrile at room temperature: (---) Ru:Os = 1:5; (—) Ru:Os = 1:1; (-·-) Ru:Os = 5:1.

would hold for the $\text{Ru}^{2+/3+}$ couple in the Ru/Os 1:5 copolymer). However, neither couple exhibits a discernible redox response in copolymers where they were present in the smaller amount (Figures 4 and 6). In the case of the Ru/Os 5:1 copolymer, it is possible that the oxidation of $\text{Os}(\text{vbpy})_3^{2+}$ could take place by mediation through the $\text{Ru}(\text{vbpy})_3^{2+/3+}$ couple as described above. If that were the case, however, the charge corresponding to the oxidation of the $\text{Ru}(\text{vbpy})_3^{2+}$ should be larger than that corresponding to the reduction since the former would include the charge associated with the mediated oxidation of the osmium sites whereas $\text{Ru}(\text{vbpy})_3^{2+}$ cannot reduce $\text{Os}(\text{vbpy})_3^{3+}$. This might indicate that the concentration of the osmium monomer is significantly smaller (which disagrees with the spectroscopic data) or that the osmium monomers are incorporated in “isolated sites” within the polymer, which is highly improbable.

What is clear, however, is that there are significant differences in copolymers prepared by electroreductive polymerization versus solution polymerization.

(b) UV–Vis Spectra. The absorption spectra of $\text{Ru}(\text{vbpy})_3^{2+}/\text{Os}(\text{vbpy})_3^{2+}$ copolymers were measured and compared to the spectra of solutions of the monomers mixed in identical ratios. Figure 7A shows the UV–vis spectra for the Ru/Os copolymers. Notice, in particular that the band at 250 nm, associated with the vinyl group in the vinylpyridine, is absent in all three polymers. Figure 7B shows the visible spectra for the same Ru/Os copolymers. In general, we find that the visible spectra of the copolymers resemble a superposition of the individual components mixed in the appropriate ratio. As can be seen in Figure 7B, as the concentration of osmium incorporated in the copolymer increases, the absorption band at 466 nm becomes broader and the ratio of the intensities of the plateau between 600–700 nm to the band at 466 nm increases.

(c) Emission Spectroscopy. The emission spectra of the 5:1, 1:1, and 1:5 Ru/Os copolymers at 298 and 77 K are shown in parts B–D of Figure 8, respectively. For comparison, the emission spectra for a 5:1 solution of the Ru/Os monomers is shown in Figure 8A. The emission data for the mixed monomer solutions and the copolymers are summarized in Tables II and III, respectively.

The emission quantum yield for the ruthenium complex is over an order of magnitude larger than that for the osmium analogue⁷

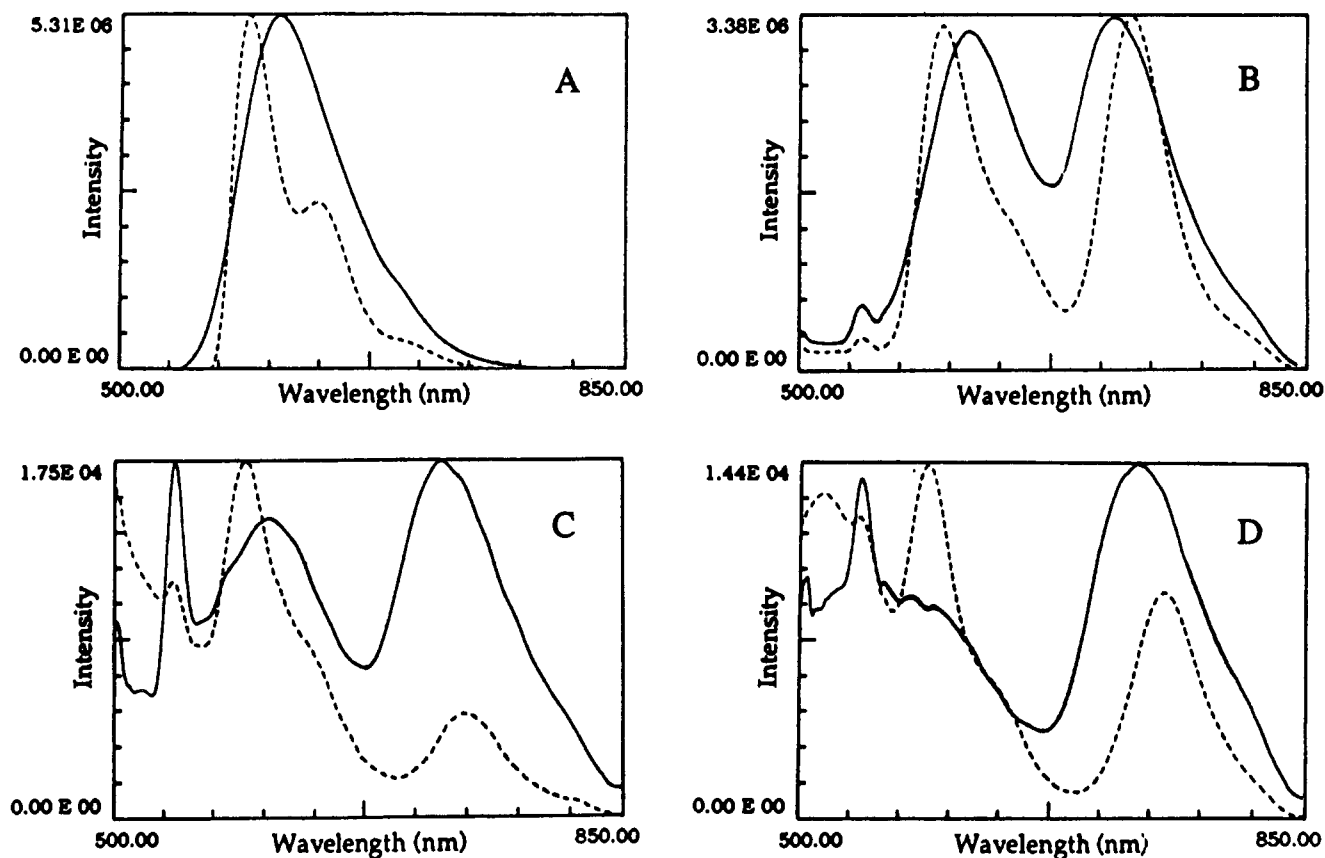


Figure 8. Emission spectra in EtOH/MeOH 4:1 at 298 K (—) and 77 K (---) for a 5:1 Ru(dmbpy)₃(PF₆)₂/Os(dmbpy)₃(PF₆)₂ mixture (A) and copolymers prepared by polymerization of solutions of the monomers with Ru:Os ratios of (B) 5:1, (C) 1:1, and (D) 1:5.

Table II. Luminescence Data (in nm) for Mixtures of Ru(dmbpy)₃(PF₆)₂/Os(dmbpy)₃(PF₆)₂ Metal Complexes in 4:1 Ethanol/Methanol

Ru:OS ratio	λ _{298 K}		Ru:OS ratio	λ _{298 K}		Ru:OS ratio	λ _{77 K}	
	λ _{298 K}	λ _{77 K}		λ _{298 K}	λ _{77 K}		λ _{298 K}	λ _{77 K}
0.80	612	591	5.0	612	591	0.31	612	591
	638			638			638	
		710			710			710

Table III. Luminescence Data (in nm) for Ru(bvpy)₃(PF₆)₂/Os(vbpy)₃(PF₆)₂ Copolymers in 4:1 Ethanol/Methanol

Ru:Os ratio	λ _{298 K}		Ru:Os intensities ratio at 298 K	λ _{77 K}		Ru:Os intensities ratio at 298 K
	Ru	Os		Ru	Os	
1.0	608	729	0.83	592	745	3.3
5.0	619	723	0.96	601	734	0.98
				649		
0.20	586	737	0.61	589	755	1.5
				638		

so that in the absence of any energy-transfer mechanism, the emission from the osmium complex should be largely masked by the ruthenium complex for all the Ru/Os ratios that were used. As expected, in the emission spectra for solutions of the monomer mixtures, only the emission from the ruthenium metal complex was observed, regardless of the Ru/Os ratio. For example, Figure 8A shows the spectra for a solution of the monomers mixed in a 5:1 (Ru/Os) ratio, and as can be seen, only luminescence from the ruthenium centers is detected at 298 K (solid line) or 77 K (dashed line).

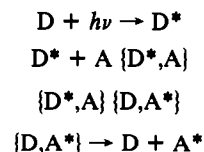
The emission spectra for the Ru/Os copolymers indicate that significant changes occur when the ruthenium and osmium mo-

nomers are copolymerized. The most dramatic feature is the presence of the emission band for the osmium complex at both room and liquid-nitrogen temperatures. In addition, and perhaps even more surprising, is the fact that the osmium emission band has a higher intensity at room temperature than at low temperature (Figure 8B–D). This effect can only be explained by an energy-transfer process from ruthenium to osmium states in the polymer.

Two major mechanisms are typically postulated to account for electronic energy transfer. These are the "trivial" mechanism of radiative transfer and the one involving intermolecular nonradiative energy transfer.⁸ The first one simply involves emission from an excited donor D* and reabsorption by an acceptor A.

In the nonradiative energy-transfer process, the donor and acceptor associate to give a transition-state complex that dissociates into a ground-state donor and an excited acceptor (Scheme I).

Scheme I



Intermolecular nonradiative energy transfer can occur either by resonance energy transfer or exchange ("short-range" or collisional) energy transfer. Resonance or long-range coulombic energy transfer⁹ can occur over intermolecular distances much greater than collisional diameters whereas exchange energy transfer occurs over intermolecular distances in which the electron clouds of the donor and acceptor overlap. As for the "trivial"

(7) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.

(8) (a) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds* Academic Press: London and New York, 1970. (b) Wayne, R. P. *Principles and Applications of Photochemistry* Oxford University Press: Oxford, England, 1988.

(9) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.

mechanism for energy transfer, the resonance process is favored by the overlap between the emission spectrum of D^* and the absorption spectrum of A. Two basic criteria have been identified to differentiate between the two mechanisms and these are that (1) the "trivial" mechanism may occur over extremely large distances, whereas the resonance interaction is effective only over limited distances, and (2) the resonance energy-transfer process occurs before D^* emits.

Since energy transfer is only observed in the copolymers but not in the monomer solutions, the "trivial" radiative energy-transfer mechanism can be ruled out.

Schmehl et al.¹⁰ have reported that in $[(\text{dmbpy})_2\text{Ru}(\text{b-b})\text{Ru}(\text{dmbpy})(\text{CN})_2]^{2+}$ (dmbpy is 4,4'-dimethyl-2,2'-bipyridine; b-b is 1,4-bis[2-(4'-methyl-2,2'-bipyridyl-4-yl)ethyl]benzene) the emission from the $[(\text{dmbpy})_2\text{Ru}(\text{b-b})]$ center is quenched by the $[(\text{b-b})\text{Ru}(\text{dmbpy})(\text{CN})_2]$ chromophore. The temperature dependence (between 200 and 300 K) indicated the existence of more than one energy-transfer path in this bimetallic complex. They postulated that both coulombic and energy-exchange mechanisms were responsible for the overall energy transfer. From emission-quenching studies as a function of temperature, it was apparent that both thermally activated and temperature-independent terms were contributing to the overall energy-transfer process. The observed temperature dependence could be the result of a combination of the energy-exchange and the coulombic energy-transfer paths, with the latter being temperature independent. At high temperature, energy transfer is dominated by energy exchange. As the solution temperature is lowered, the energy-transfer rate constant decreases until it reaches a constant value, attributed to coulombic energy transfer. Energy transfer for other similar binuclear complexes has also been reported by these authors.¹¹

For the 1:1 and 1:5 Ru/Os copolymers (Figure 8C,D), energy transfer decreases at low temperature as evidenced by the relative decrease in the emission intensity from the osmium centers. (Since emission quenching data are not available at this time, the relative differences in energy transfer are based on the relative intensities of the ruthenium and osmium emission bands.) However, energy transfer is still evident at low temperature. Assuming that the osmium and ruthenium monomers are incorporated randomly in the polymer, the copolymers can be envisioned to be composed of Ru-Os "dimeric" units $([\text{-Hvbpy}]_2\text{Ru}(\text{vbpyH-vbpyH})\text{Os}$

$(\text{vbpyH-})_2]$). These would be analogues of the dinuclear complexes studied by Schmehl and co-workers.^{9,10} On the basis of the energy-transfer behavior at room and low temperatures, and in light of the results obtained by them, we believe that energy transfer in these copolymers is taking place by a similar mechanism.

For the 5:1 Ru/Os copolymer (Figure 8B), the ratio of the emission intensities of the ruthenium and osmium chromophores does not change significantly with temperature. In this case, the probability of having a ruthenium chromophore next to an osmium center is much higher than for the 1:1 and 1:5 Ru/Os copolymers. Thus, diffusion of the polymer strands to bring osmium and ruthenium chromophores closer together (in order to allow for energy exchange) will play a relatively minor role. Thus the relative emission intensities would be expected to be insensitive to temperature differences as was indeed observed.

Conclusions

Copolymers of $M(\text{vbpy})_3^{2+}$ ($M = \text{Ru}, \text{Os}$) in varying ratios (1:1, 1:5, 5:1) have been prepared by solution polymerization and purified by SEC. The visible spectra of the copolymers resemble the superposition of the individual components of the polymers mixed in the appropriate ratio. Cyclic voltammograms for the 1:1 Ru/Os copolymer deposited on a Pt electrode show similar currents for the $\text{Os}^{2+/3+}$ and the $\text{Ru}^{2+/3+}$ couples, indicating that the monomers were incorporated in the polymer in the same ratio in which they were mixed. Similar results were obtained by UV-vis spectrophotometry for films deposited onto transparent electrodes. However, cyclic voltammograms for the 5:1 and 1:5 (Ru/Os) copolymers similarly deposited only show the $\text{Ru}^{2+/3+}$ and $\text{Os}^{2+/3+}$ couples, respectively. However, spectrophotometry of films deposited onto transparent electrodes clearly indicated the presence of both metal centers.

In copolymers prepared by electroreductive polymerization of a 1:1 mixture of the monomers, the ratio of Ru/Os in the film was about 2:1, regardless of the electropolymerization conditions.

Finally, on the basis of the emission spectra of the copolymers prepared in solution, there appears to be effective energy transfer from ruthenium to osmium states in the polymer at both room and liquid-nitrogen temperatures.

These results point to fundamental differences between solution polymerization and electropolymerization.

Acknowledgment. S.L.B. gratefully acknowledges a MARC fellowship from the NIH. H.D.A. is an A.P. Sloan Foundation Fellow (1987-1991) and a Presidential Young Investigator (1984-1989).

Registry No. $[\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2]/[\text{Os}(\text{vbpy})_3(\text{PF}_6)_2]$ (copolymer), 137768-23-1.

(10) Ryu, C. K.; Schmehl, R. H. *J. Phys. Chem.* 1989, 93, 7961.

(11) (a) Schmehl, R. H.; Auerbach, R. A.; Wacholtz, W. F.; Elliot, C. M.; Freitag, R. A.; Merkert, J. W. *Inorg. Chem.* 1986, 25, 2440. (b) Schmehl, R. H.; Auerbach, R. A.; Wacholtz, W. F. *J. Phys. Chem.* 1988, 92, 6202.

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Kinetics of the Aqueous Cobalt(II)/Cobalt(III)/EDTA System at Variable Pressure¹

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Received June 21, 1991

The effect of pressure on the rate of the redox exchange reaction of $\text{Co}^{\text{III}}(\text{EDTA})^-$ with $\text{Co}^{\text{II}}(\text{HEDTA})\text{OH}_2^-$ at 85 °C, pH 2.0, and ionic strength 0.5 mol L⁻¹ is described by a volume of activation $\Delta V_{\text{act}}^\ddagger = -3.2 \pm 0.3$ cm³ mol⁻¹ which is apparently constant to within the experimental uncertainty over the range 0.1-228 MPa. This value is consistent with predictions based on Marcus-Hush theory for a nonadiabatic, outer-sphere exchange mechanism in which ring closure and loss of coordinated water occur in $\text{Co}(\text{HEDTA})\text{OH}_2^-$ prior to electron transfer. For the conversion of $\text{Co}^{\text{III}}(\text{EDTA})^-$ to $\text{Co}^{\text{III}}(\text{HEDTA})\text{OH}_2$, $\Delta V_c^\ddagger = +3.5 \pm 0.7$ cm³ mol⁻¹ at 25.0 °C in aqueous HClO₄ (1.0 mol L⁻¹), while for the reverse reaction the corresponding parameter $\Delta V_c^\ddagger = +6.7 \pm 0.7$ cm³ mol⁻¹. It is argued that the transition state for the forward reaction occurs early in the ring-opening step, following closely upon or concurrently with protonation of the carboxyl group.

The EDTA complex of cobalt(II) continues to be of considerable interest as a reductant in mechanistic studies, particularly where

stereochemical information is sought, since the $\text{Co}^{\text{III}}(\text{EDTA})^-$ product is chiral and nonlabile.⁶⁻⁹ The detailed mechanism of