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Synthesis and Characterization of Redox Polymers of $[M(4\text{-vinyl-4}'\text{-methyl-2,2}'\text{-bipyridine})_3](PF_6)_2$ (M = Ru, Os)

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We have prepared polymers of $[M(vbpy)_3(PF_6)_2]$ (M = Ru, Os) (vbpy = 4-vinyl-4′-methyl-2,2′-bipyridine) in solution via free-radical polymerization and fractionated them according to molecular weight using size exclusion chromatography. Different fractions have been characterized by electrochemical and spectroscopic means. We find that whereas for the osmium containing polymers the relative polymer size varies in proportion to the number of vinyl groups consumed during the polymerization reaction, the same is not true for the analogous ruthenium polymers. In addition, the emission energy of both the ruthenium and osmium polymers is also related to the concentration of residual vinyl groups in the polymer. Upon polymerization, there is a shift in the emission toward higher energies. Electrochemically determined diffusion coefficients are consistent with the relative size of the various fractions.

Introduction

There has been considerable interest in the synthesis and characterization of electroactive polymers and in their application in polymer-modified electrodes,[1] to areas such as catalysis,[2] electronic devices,[3] electroanalysis,[4] and others. Although these areas have received much attention, advances in the understanding and characterization of electroactive polymers have been slow. This is due, in part, to the lack of materials that will allow the preparation of polymers that are chemically well-defined and that can be prepared as adherent films and soluble polymers.

Because of their versatility in terms of how their spectroscopic and redox properties can be tuned via synthetic variations, polymerizable transition-metal complexes of vinyl derivatives of bipyridine and related ligands are very attractive for the study of physicochemical properties of redox polymers. Transition-metal complexes of such ligands are chemically stable and can be readily purified and fully characterized, and more importantly, they can be polymerized to give materials of well-defined repeating units. Most of the work on these materials has been on insoluble polymer films prepared by electroreductive polymerization. In order to increase the number of techniques that can be applied in their characterization, we have prepared soluble polymers by solution polymerization.

Specifically, we have prepared polymers of tris(vinylbipyridine) complexes of ruthenium and osmium in solution and fractionated them according to molecular weight. In this work we have sought to emphasize variations in their physicochemical properties as a function of their relative molecular weight. In addition, we were also interested in the effect of the metal center on the polymer's structure and properties.

Experimental Section

(a) Chemicals and Solvents. Ammonium hexachloroosmate (Alfa Products), ammonium hexafluorophosphate (Aldrich Chemical Co.) and ruthenium(III) chloride (Strem Chemicals, Inc.) were used as received. AIBN (AIBN = azobisisobutyronitrile) (Aldrich) was recrystallized from diethyl ether. 4-Vinyl-4′-methyl-2,2′-bipyridine was prepared by the method reported by Abruña et al.[5]

Electrochemical and spectroscopic experiments were performed in acetonitrile (Burdick & Jackson distilled in glass) dried over 4-Å molecular sieves. Tetrabutylammonium perchlorate (TBAP) (G. F. Smith), which had been recrystallized three times from ethyl acetate and dried under vacuum for 72 h, was used as the supporting electrolyte.

Luminescence experiments were performed in a 4:1 ethanol/methanol solvent mixture. Ethanol (Quantum Chemical Corporation) was dried over 4-Å molecular sieves and distilled from anhydrous calcium sulfate under nitrogen. Methanol (Burdick & Jackson) was dried over 4-Å molecular sieves and used without further purification.

Sepharose CL-6B (Pharmacia) was used in polymer fractionation. The as received material was placed in acetone for at least 3 days to allow for appropriate swelling.

(b) Instrumentation. Cyclic voltammetric experiments were performed on either an IBM EC 225 voltammetric analyzer or a Princeton Applied Research Model 173 potentiostat/galvanostat in conjunction with a Model 175 universal programmer or a Pine Instrument Co. electrochemical analyzer, Model RDE4. Double-potential step chronocoulometric experiments performed on a BAS 100 electrochemical analyzer were used for determining surface diffusion coefficients. In these experiments the potential was stepped at least 400 mV past the redox potential of the process under study and a 25-ms pulse width was employed. A Pine Instrument Co. analytical rotator, Model MSR, was used for rotated disk electrode experiments. Data were recorded on either a Soltec Model VP-6423S or a Hewlett-Packard Model 7045B X-Y recorder.

The working electrode for cyclic voltammetric and chronocoulometric experiments consisted of a platinum disk (0.0072 cm^2) sealed in soft glass. A commercial platinum disk electrode (Pine Instruments) was used for the rotated disk electrode experiments. Platinum electrodes were cleaned by polishing them with 1-μm diamond paste (Buehler) followed by rinsing with deionized water and acetone. A coiled platinum wire was used as the counter electrode. All potentials are referenced to the sodium saturated calomel electrode (SSCE) without regards to the liquid-junction potential. Electrochemical cells were of conventional design.

Ultraviolet–visible spectra were obtained with a Hewlett Packard Model 8451A diode array spectrophotometer, and a Spex Fluorolog 2 Series spectrofluorometer was used for the luminescence experiments.

Free-radical polymerization reactions were run in an Allied Fisher Scientific Model 800 constant-temperature bath.

(c) Spectral Characterization. Ultraviolet–visible spectra were obtained in spectrochemical grade acetonitrile at room temperature. Quartz cuvettes of 1.0 cm path length were used. Luminescence spectra were obtained in 4:1 ethanol/methanol. The samples were degassed by at least three freeze–pump–thaw cycles and sealed in 7 mm path length quartz cells under vacuum. Low-temperature experiments were performed by submerging the samples in a quartz cold finger dewar filled with liquid

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Table I. Reaction Conditions for the Synthesis of (A) the [$Os(vbpy)_3(PF_6)_2$] and (B) the [$Ru(vbpy)_3(PF_6)_2$] Homopolymers

polymerization, reacn no.	amt of AIBN, mg	amt of monomer, mmol	vol. of acetone, mL	time of reacn, h
		A. [$Os(vbpy)_3(PF_6)_2$]		
1	5.0	0.0852	5.0	120
2	15.4	0.0741	5.0	72
3	6.2	0.0886	6.0	72
4	7.7	0.0936	4.0	72
		B. [$Ru(vbpy)_3(PF_6)_2$]		
1	5.6	0.102	5.0	72
2	15.0	0.103	5.0	72
3	9.6	0.0617	5.0	48
4	9.9	0.102	5.0	72
5	10.4	0.102	5.0	72
6	16.8	0.102	3.0	96
7	10.6	0.0763	3.0	168

nitrogen. The entrance and exit slits for both the excitation and emission monochromators were 1.25 mm and the bandpasses were 4.6 and 2.25 nm, respectively (the emission monochromator had a double diffraction grating).

(d) Synthesis. 1. Tris(4-vinyl-4′-methyl-2,2′-bipyridyl)ruthenium(II) Bis(hexafluorophosphate). To a solution of ruthenium trichloride (0.1060 g, 0.511 mmol) in 1:1 ethanol/water (8 mL) was added vbpy (0.3161 g, 1.613 mmol). The reaction mixture was purged with prepurified nitrogen for 20 min, heated at reflux, and stirred for 3 h under nitrogen. The bright orange complex was isolated as the hexafluorophosphate salt by adding aqueous saturated ammonium hexafluorophosphate solution and filtering. The crude product was chromatographed on neutral alumina with acetone as eluant and recrystallized from acetone/diethyl ether.

2. Tris(4-vinyl-4′-methyl-2,2′-bipyridyl)osmium(II) Bis(hexafluorophosphate). Ammonium hexachloroosmate(IV) $(NH_4)_2[OsCl_6]$ (0.2063 g, 0.449 mmol) was added to a solution of vbpy (vbpy is 4-vinyl-4′-methyl-2,2′-bipyridine) (0.2773 g, 1.415 mmol) in ethylene glycol (8 mL). The solution was purged with prepurified nitrogen for 20 min, heated at reflux and stirred for 3 h under nitrogen. After the resulting black reaction mixture was allowed to cool to room temperature, an equivalent volume of distilled water was added and the solution filtered. The product was isolated and purified by the method used for the analogous ruthenium complex.

3. Homopolymers of Tris(4-vinyl-4′-methyl-2,2′-bipyridyl)osmium(II) Bis(hexafluorophosphate). The [$Os(vbpy)_3(PF_6)_2$] homopolymers were prepared via free-radical polymerization in acetone solution using AIBN as initiator.

To a solution of the monomer complex (100 mg, 0.094 mmol) in acetone (4 mL) was added the desired amount of AIBN (see Table IA). The reaction mixture was transferred to a Pyrex ampule, which was evacuated by three freeze–pump–thaw cycles and sealed under vacuum. The reaction was run at 60 °C for a prescribed amount of time in a controlled-temperature bath. The soluble polymer was precipitated by the addition of diethyl ether. After being redissolved in acetone and reprecipitated in diethyl ether, the polymer was filtered, rinsed several times with ether, and dried under vacuum at room temperature.

In order to obtain homopolymers with different molecular weight distributions, the amount of initiator was varied for a given concentration of monomer in acetone. Table IA summarizes the reaction conditions for the synthesis of the [$Os(vbpy)_3(PF_6)_2$] homopolymers.

4. Homopolymers of Tris(4-vinyl-4′-methyl-2,2′-bipyridyl)ruthenium(II) Bis(hexafluorophosphate). The [$Ru(vbpy)_3(PF_6)_2$] homopolymers were prepared by the same method used for the analogous osmium polymers. However, larger amounts of AIBN had to be used to avoid the formation of very high molecular weight polymers, which were insoluble in all of the solvents or solvent mixtures generally employed in electrochemical, as well as in spectroscopic experiments (Table IB). Nevertheless, in most reactions, an insoluble polymer fraction remained on the walls of the polymerization ampule.

(e) Polymer Fractionation. Homopolymers of the osmium and ruthenium complex monomers were fractionated according to molecular weight using a size exclusion chromatography (SEC) column of cross-linked Sepharose CL-6B (Pharmacia Biotechnology Products) with acetone as eluant.

Results and Discussion

(a) Polymer Fractionation. The homopolymers were fractionated according to molecular weight using size exclusion chromatography (SEC). Although some adsorption was observed, electrochemical measurement of the diffusion coefficients of polymer fractions separated in the same column confirmed that the dominant separation process was size exclusion. In the cases where more than one fraction was recovered in a polymerization reaction, a smaller diffusion coefficient was obtained for the first band that eluted from the column, consistent with the size exclusion process. Furthermore, samples of the monomers were run through the SEC column and they could not be recovered, even after the polarity of the eluant was increased significantly, again consistent with the assertion that the size exclusion was the dominant factor in the separation.

Table II. Redox Potentials and Diffusion Coefficients for the $Ru^{III/II}$ Couple in the $Ru(vbpy)_3(PF_6)_2$ Polymers and Related Metal Complexes

polymer reacn no.	$E^{\circ\prime}$ (solution),[a] V	$E^{\circ\prime}$ (surface),[a] V	diffusion coeff,[b] cm^2/s
$Ru(vbpy)_3(PF_6)_2$	1.14		5.2×10^{-6}
7-2	1.11	1.11	3.1×10^{-6}
2-2	1.14	1.14	3.0×10^{-6}
6-1	1.14	1.14	2.1×10^{-7}
$Ru(dmbpy)_3(PF_6)_2$	1.11		5.3×10^{-6}

[a] Measured in 0.1 M TBAP in acetonitrile; ±0.01 V. [b] Diffusion coefficients were measured in homogeneous solution, using a rotated disk electrode.

Table III. Redox Potentials and Diffusion Coefficients for the $Os^{III/II}$ Couple in the $Os(vbpy)_3(PF_6)_2$ Polymers and Related Metal Complexes

polymer reacn no.	$E^{\circ\prime}$ (soltuion),[a] V	$E^{\circ\prime}$ (surface),[a] V	diffusion coeff,[b] cm^2/s
$Os(vbpy)_3(PF_6)_2$	0.71	0.69	4.7×10^{-6}
3-1	0.71	0.70	3.1×10^{-6}
1-1	0.69	0.68	2.6×10^{-6}
2-2	0.70	0.68	7.0×10^{-7}
2-1	0.70	0.69	2.3×10^{-8}
$Os(dmbpy)_3(PF_6)_2$	0.68		4.8×10^{-6}

[a] Measured in 0.1 M TBAP in acetonitrile; ±0.01 V. [b] Diffusion coefficients were measured in homogeneous solution, using the rotated disk electrode.

In a number of cases, an insoluble polymer fraction remained adhered to the walls of the polymerization ampule. Only the polymer in solution was run through the SEC column. In several cases, some bands remained on the column, and therefore, the numbers reported refer to the number of fractions that actually eluted from the column. However, on the basis of the yield, the amount of material that remained on the column was typically less than 10%. Within the text, the polymer fractions will be referred to by the polymerization reaction number and the order of elution, e.g. 4-1 (fourth reaction; first fraction).

(b) Electrochemical Characterization. The formal potentials for the ruthenium and osmium polymer fractions, both in solution and on the electrode surface, are presented in Tables II and III, respectively. Formal potentials for the $M^{III/II}$ couple in these types of complexes are known to be sensitive to the relative energetic location of the bipyridyl ligands (in the metal complex) due to mixing of the t_{2g} and π orbitals. For example, in Table II it can be seen that the formal potential for the $Ru^{III/II}$ couple in $Ru(vbpy)_3(PF_6)_2$ is more positive than in $Ru(dmbpy)_3(PF_6)_2$ (dmbpy is 4,4′-dimethyl-2,2′-bipyridine) since the π orbitals in vbpy are lower in energy. In this context, the $Ru(dmbpy)_2(PF_6)_2$ complex would represent a fully polymerized material. The difference in formal potentials is only 34 mV, and although the values for the $M^{III/II}$ couple in the polymer fractions should be sensitive to changes in the degree of polymerization, the uncertainty in the measurements makes such a comparison difficult.

The solution diffusion coefficients for the polymer fractions were measured using the rotated disk electrode technique[6] in 0.1 M TBAP/acetonitrile. Tables II and III present the diffusion

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(6) Bard, A. T.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 8.

coefficient data for the ruthenium and osmium polymers, respectively. Since the molecular weights of the polymer fractions are unknown, the concentration of electroactive centers was calculated using the molecular weight of the respective monomer, assuming that the contribution of the end groups to the total molecular weight of the polymer was negligible. (The molecular weight of the end group C_4H_6N (MW = 68) is 6.9% of the molecular weight for the $Ru(vbpy)_3(PF_6)_2$ monomer unit and 6.4% for $Os(vbpy)_3(PF_6)_2$.) Concentrations determined in this way were used in the determination of the diffusion coefficients.

Again, since the molecular weights are unknown, values of the diffusion coefficient in solution can be employed as a measure of the relative size of the different polymer fractions. In some cases, a difference of more than 1 order of magnitude was observed. Assuming, as has been previously done[7] for other redox active polymers, that there is an $M^{1/3}$ (M = molecular weight) dependency on the diffusion coefficient (such a dependency is, in essence, derived from the Stokes–Einstein equation), the ratio of the molecular weights for the corresponding polymer fractions would equal 1000.

(c) Transport Studies. There has been much attention given to the study of the mechanisms of charge propagation in electroactive polymer films. One of the mechanisms that can dominate charge propagation in redox polymers is electron hopping between adjacent redox centers.[8] An alternative mechanism is that of physical diffusion of the electroactive species. Depending on the specific system, there can be contributions from both mechanisms.[9]

The theory of Dahms–Ruff[10] for electron conduction states that an electrochemically measured diffusion coefficient has contributions from both physical movement of the species and electron self-exchange. The expression for the experimentally measured diffusion coefficient (D_{exp}) is

$$D_{exp} = D_0 + (k_{ex}\delta^2 C)/6 \qquad (1)$$

where D_0 is the contribution due to physical movement, k_{ex} is the second-order rate constant ($M^{-1}\ s^{-1}$) for the self-exchange reaction, C is the total concentration of the co-reactant with which the diffusing molecule exchanges electrons, and δ is the distance between the redox centers when the electron exchange occurs. The term $(\pi k_{ex}\delta^2 C)/6$ represents the contribution of the self-exchange reaction to the experimentally measured diffusion coefficient and will be referred to as D_{ct}.

In homogeneous solution, the contribution of self-exchange to the experimentally measured diffusion coefficient is typically very small since D_0 values are of the order of 5×10^{-6} cm^2/s so that even assuming that reactions are at their diffusion-controlled limit, the contribution would be no more than a few percent. Because in redox polymers the physical mobility of species can be significantly decreased, D_0 values may drop by orders of magnitude relative to solution so that the contribution from D_{ct} can be significant.

For the polymers studied here, it would be anticipated that D_0 would dictate the magnitude of D_{exp} since D_{ct} would be essentially identical for the same family of polymers for a given concentration of electroactive centers, assuming that the packing density (effective volume concentration) of the polymer is not a function of its molecular weight. However, in the limiting case of very high molecular weight, D_{exp} would be expected to asymptotically approach a limiting value.

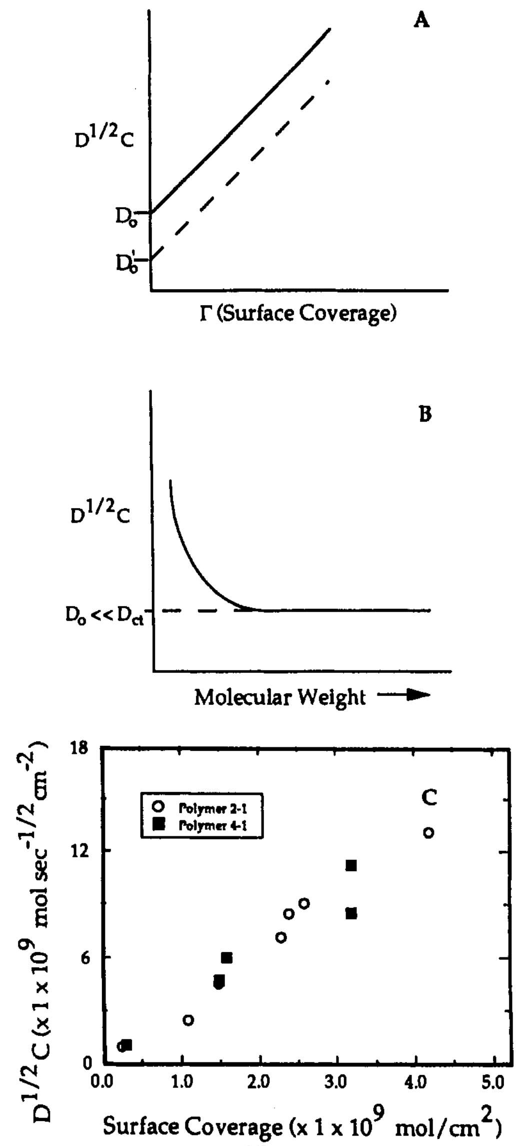

Figure 1. (A) Idealized plot of $D^{1/2}C$ vs Γ for polymers that only differ in their relative molecular weight. (B) Idealized plot of the expected behavior of $D^{1/2}C$ vs molecular weight. (C) Plot of $D^{1/2}C$ (surface diffusion coefficient) versus the surface coverage for osmium polymers 2-1 and 4-1.

An idealized plot of $D^{1/2}C$ versus the surface coverage (Γ) for polymers that only differ in their relative molecular weight is shown in Figure 1A. A difference in D_0 between polymers would be reflected by a shift in the y intercept. As the molecular weight of the polymer increases, D_0 decreases so that its contribution to the charge-transport process decreases significantly. As mentioned above, in the limit of high molecular weight, D_{exp} would become independent of molecular weight since the charge-transport process would be controlled by self-exchange and not physical diffusion. Figure 1B shows an idealized plot of the anticipated behavior of D_{exp} as a function of molecular weight.

Both osmium and ruthenium polymers adsorb from solution onto platinum electrodes. A coverage equivalent to a monolayer could be readily obtained after potential cycling (2–3 times) over the metal-localized oxidation for the respective material in a polymer solution in acetonitrile containing 0.1 M TBAP. In order to obtain a coverage of about 5×10^{-9} mol/cm^2 or higher, the scanning had to be carried out for about 24 h. This procedure, however, only worked for the osmium polymers 2-1 and 4-1. It was also found that, at higher coverages, the polymer films tended to flake off the electrode surface. A coverage of no more than

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(8) Kaufman, F. B.; Engler, E. M. *J. Am. Chem. Soc.* **1979**, *101*, 544. See also ref 1a,b,d and references therein.

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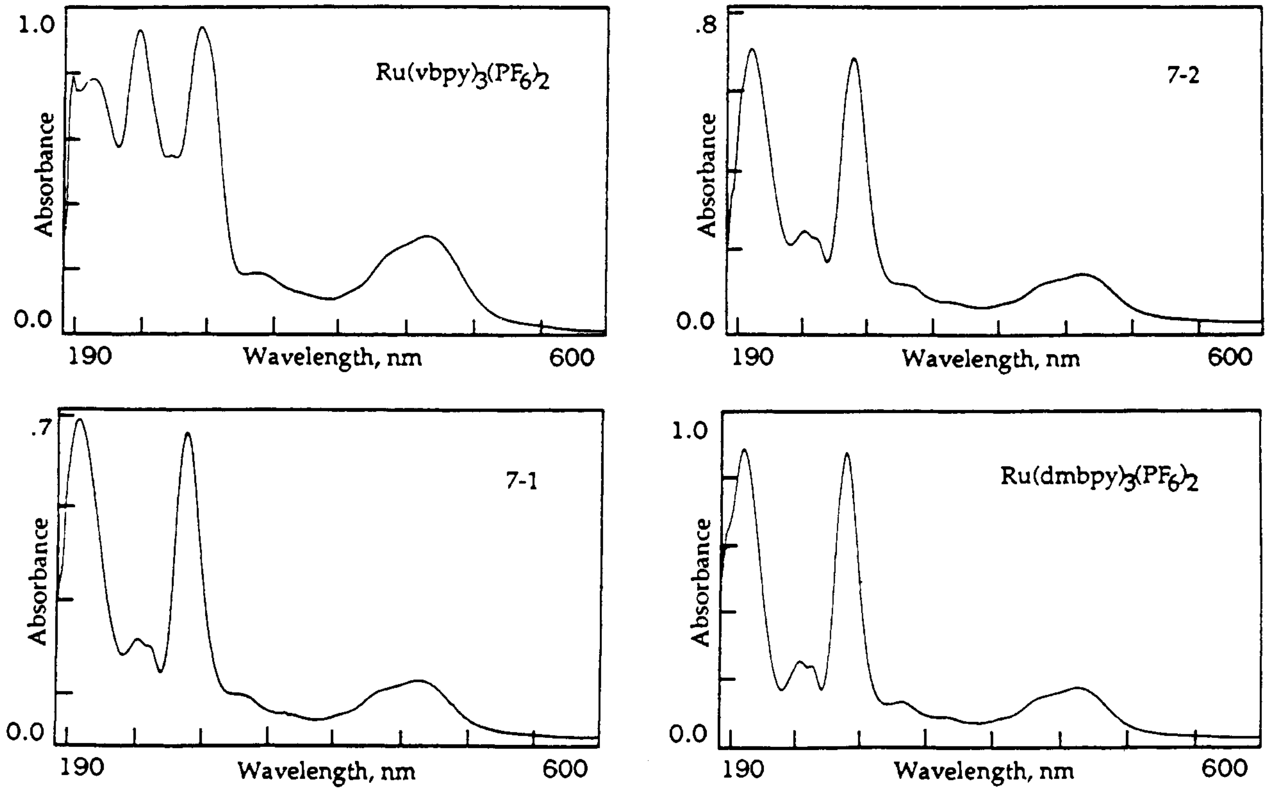

Figure 2. UV–vis absorption spectra of some of the $Ru(vbpy)_3(PF_6)_2$ polymers and related complexes in acetonitrile at room temperature.

a few monolayers could be obtained for the remaining osmium polymers. Deposition of the polymers by cycling in the negative region (ligand-based reductions) was not attempted in order to avoid structural changes in the polymers due to possible polymerization of residual vinyl groups.

Diffusion coefficients for the adsorbed polymer were measured using double-potential step chronocoulometry as described in the Experimental Section. However, only for the osmium polymer fractions 2-1 and 4-1 were we able to measure the diffusion coefficients of the adsorbed polymer. Figure 1C shows a plot of the square root of the diffusion coefficient times the concentration ($D^{1/2}C$) versus the surface coverage, for both polymer fractions. For these two polymers, D_{exp} was constant within experimental error. Although the diffusion coefficient in solution could not be determined for polymer fraction 4-1, the large difference in solubility relative to poymer 2-1 indicated that it had a higher molecular weight. Thus, for both of these polymer fractions the contribution from D_0 appears to be negligible when compared to D_{ct}.

The ruthenium polymers of higher molecular weight could not be deposited on the electrode surface due to their low solubility and thus could not be studied.

(d) UV–Vis Spectral Properties. UV–vis spectra of some of the ruthenium and osmium polymers and related complexes are presented in Figures 2 and 3, respectively. Energies for the principal intraligand and charge transfer bands for the ruthenium polymers are summarized in Table IV where the relative size of a given fraction, as determined from the value of the diffusion coefficient in solution, decreases going down the row.

We were able to measure the diffusion coefficients for all the osmium polymers, except for fraction 4-1. However, since this polymer showed the lowest solubility when compared to all the other polymer fractions, it was assumed that it had the highest molecular weight. In general, the ruthenium polymers exhibited lower solubility than their osmium counterparts prepared under similar polymerization conditions. From all the ruthenium polymer fractions, only six were soluble enough to allow spectroscopic characterization, and from these, only three afforded sufficiently concentrated solutions so that solution diffusion coefficients could be reliably measured with the rotated disk electrode technique.

Table IV. UV–Vis Absorption Data and Ratios of the Intraligand Transition Bands for $Ru(vbpy)_3(PF_6)_2$ Polymers and Related Compounds in Acetonitrile at Room Temperature[a]

polymer reacn no.	λ, nm				π-π*(2): π-π*(1),
	π-π*(3)	π-π*(2)	π-π*(1)	d-π*(1)	%
$Ru(vbpy)_3(PF_6)_2$	216	248	296	466	96
7-2	212	252	292	464	37
2-2	210	248	294	466	86
6-1	212	250	292	462	36
5-1	206	246	294	464	66
2-1	210	248	292	464	62
7-1	210	250	290	462	34
$Ru(dmbpy)_3(PF_6)_2$	208	250	288	458	29
$Ru(bpy)_3(PF_6)_2$	b	246	288	452	31

[a] Error in λ is ±2 nm. [b] Band cannot be resolved from the solvent cutoff.

Relatively concentrated solutions were required for the diffusion coefficient measurements so as to enhance the response from the polymers in solution since, as mentioned above, the polymers tended to adsorb on the electrode surface. Since the diffusion coefficients could not be obtained for the ruthenium polymers 5-1, 2-1, and 7-1, their relative molecular weights are unknown. Thus, their order in Table IV is based on solubility differences.

In general, we found that the energies for the intraligand and charge-transfer transitions were not very sensitive to molecular weight changes. Although a blue shift was observed for some of the ruthenium polymers, it did not correlate with relative molecular weights.

The visible spectra of the osmium polymers consisted of two broad plateaus, rather than well-resolved bands. Therefore, it was difficult to assign a λ_{max} and thus to determine the shifts in the charge-transfer transition energies. However, when the spectra were superimposed, a slight blue shift could be observed. Unlike what we found for the ruthenium polymers, for the osmium polymers this blue shift appeared to vary according to the relative molecular weight of the fraction.

Absorption in the ultraviolet region was found to be very sensitive to changes in the vinyl group concentration within the polymer. As can be clearly seen in Figures 2 and 3, the intraligand band at ~250 nm in the vbpy monomer complexes has a sig-

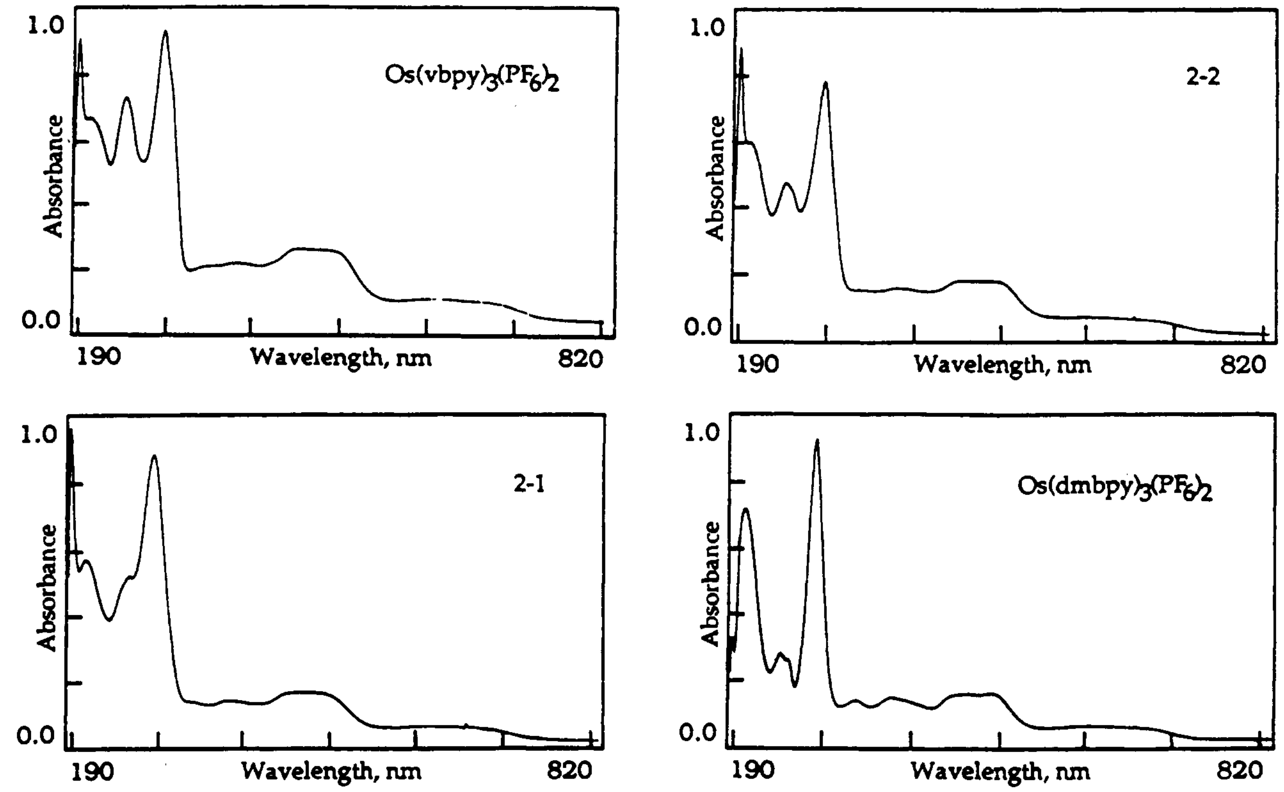

Figure 3. UV–vis absorption spectra of some of the Os(vbpy)$_3$(PF$_6$)$_2$ polymers and related complexes in acetonitrile at room temperature.

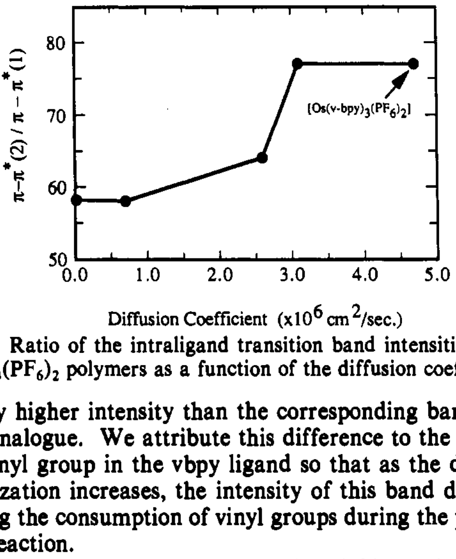

Figure 4. Ratio of the intraligand transition band intensities for the Os(vbpy)$_3$(PF$_6$)$_2$ polymers as a function of the diffusion coefficient.

nificantly higher intensity than the corresponding band in the dmbpy analogue. We attribute this difference to the presence of the vinyl group in the vbpy ligand so that as the degree of polymerization increases, the intensity of this band decreases, indicating the consumption of vinyl groups during the polymerization reaction.

For the osmium polymers, the intensity of this band decreased as the relative size of the polymer increased. However, this trend was not observed for the ruthenium polymers as the intensity of the π–π^*(2) band did not vary in a way consistent with the relative size of the polymer. In addition, the UV spectra of most of the ruthenium polymer fractions resembled the spectrum of Ru(dmbpy)$_3$(PF6)$_2$, suggesting that most of the vinyl groups were consumed during the polymerization. This would imply a higher extent of polymerization and/or cross-linking consistent with the low solubility previously alluded to.

These results appear to indicate that for the osmium polymers, the relative polymer size varies proportionally with the degree of polymerization or, in other words, the consumption of the vinyl groups during the polymerization reaction. In Figure 4 is plotted the ratio of the intensities of the intraligand transitions at about 250 and 290 nm, respectively (π–π^*(2):π–π^*(1)) as a function of the diffusion coefficient of the polymer fractions. This ratio was used instead of the absorptivity of the π–π^*(2) band since the exact concentration of the polymers is unknown. The intensity of the intraligand π–π^*(2) band was normalized to that of the π–π^*(1) band, assuming that the absorptivity of the latter is not affected by the degree of polymerization. It can be seen (Figure 4) that this ratio tends to an upper limit in the high diffusion coefficient region and decreases asymptotically to a lower limit in the low diffusion coefficient region. The upper limit in this ratio is determined by the value for the Os(vbpy)$_3$(PF6)$_2$ monomer (see Figure 4) whereas the low limit would correspond to the ratio in the Os(dmbpy)$_3$(PF6)$_2$ complex where there clearly are no residual vinyl groups. Tables IV and V show the ratios of the intraligand transition band intensities for the osmium and ruthenium polymers, respectively.

Table V. Ratios of the Intraligand Transition Band Intensities for the Os(vbpy)$_3$(PF$_6$)$_2$ Polymers

polymer reacn no.	π-π^*(2): π-π^*(1), %	polymer reacn no.	π-π^*(2): π-π^*(1), %
Os(vbpy)$_3$(PF$_6$)$_2$	77	2-1	58
3-1	77	4-1	47
1-1	64	Os(dmbpy)$_3$(PF$_6$)$_2$	28
2-2	58	Os(bpy)$_3$(PF$_6$)$_2$	29

The blue shift in the MLCT transition in these materials is also attributed to the degree of polymerization. Due to the increased resonance stabilization of the ligand's π^* orbitals in the vinyl-substituted monomers, the MLCT energy will be lower relative to that of the dmbpy complex. Thus in the polymers, the MLCT energy should vary within the limits dictated by the vbpy and dmbpy complexes, according to the concentration of remaining vinyl groups within the polymer, provided that there are no additional electronic interactions between the metal complexes in the polymer.

As mentioned above for the osmium complexes, there was a slight blue shift in the MLCT energy as the polymer size increased. Although these shifts were relatively small, they were consistent with the arguments presented above. Also recall that the ratio of the intraligand bands for the osmium polymers also varied with the degree of polymerization. On the other hand, noticeable blue shifts in the visible spectra were observed for the ruthenium polymers. However, these shifts did not correlate with the relative

Table VI. Luminescence Data for $Ru(vbpy)_3(PF_6)_2$ Polymers in 4:1 EtOH/MeOH

polymer reacn no.	$\lambda_{298\ K}$, nm	emission energy at 298 K, 10^{-4} cm^{-1}	$\lambda_{77\ K}$, nm	emission energy at 77 K, 10^{-4} cm^{-1}
$Ru(vbpy)_3(PF_6)_2$	631	1.585	602	1.661
7-2	622	1.608	610	1.639
			665	1.503
2-2	631	1.585	607	1.647
			653	1.531
6-1	611	1.637	593	1.686
			646	1.548
5-1	617	1.621	598	1.672
			648	1.543
2-1	620	1.613	600	1.667
			648	1.543
$Ru(dmbpy)_3(PF_6)_2$	612	1.636	591	1.692
			639	
			710	
$Ru(bpy)_3(PF_6)_2$	603	1.658	581	1.721
			626	1.597
			693	1.443

Table VII. Luminescence Data for $Os(vbpy)_3(PF_6)_2$ Polymers in 4:1 EtOH/MeOH

polymer reacn no.	$\lambda_{298\ K}$, nm	emission energy at 298 K, 10^{-4} cm^{-1}	$\lambda_{77\ K}$, nm	emission energy at 77 K, 10^{-4} cm^{-1}
$Os(vbpy)_3(PF_6)_2$	744	1.344	738	1.355
3-1	743	1.346	737	1.357
1-1	741	1.350	736	1.358
2-2	736	1.359	731	1.368
2-1	733	1.364		1.357
4-1	738	1.355	755	1.325
$Os(dmbpy)_3(PF_6)_2$	725	1.379	723	1.383
$Os(bpy)_3(PF_6)_2$	710	1.408	704	1.420

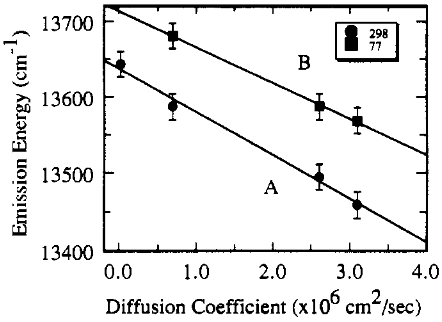

Figure 5. Emission energies at (A) 298 and (B) 77 K for the $Os(vbpy)_3(PF_6)_2$ polymers in EtOH/MeOH 4:1 as a function of the relative size as determined from diffusion coefficient measurements.

polymer size, as was also the case with the UV spectra as discussed above. For example, ruthenium polymers 7-2 and 6-1 showed a blue shift in the MLCT band as well as a low intensity band at 250 nm. However, the spectrum of polymer 2-2 had a high intensity π–π^*(2) band and did not show a blue shift in the MLCT energy.

From the data presented above, it appears that for the osmium polymers, the relative size of the polymers varies proportionally with the degree of polymerization. However, such a trend was not observed for the ruthenium polymers. These results appear to indicate that the metal center can strongly influence the reactivity of the vinyl group in the vbpy ligand. Because osmium is a third-row transition element, it can have stronger π-backbonding stabilization. The π^* orbitals of the vinylbipyridine in the osmium monomer are likely to be at a lower energy than in the ruthenium complex, and therefore, the osmium monomer would be expected to exhibit lower reactivity.

It is worth noting that, in general, the three vinyl groups in the ruthenium complex monomer were polymerized whereas most of the osmium polymers exhibited a relatively high concentration of unreacted vinyl groups. This is a rather surprising observation since, due to steric hindrance, one would expect that perhaps two but not all three vinyl groups would react. Thus, the ruthenium polymers are likely highly cross-linked, consistent with their lower solubility when compared to osmium polymers of similar size.

On the basis of these observations, the UV–vis spectra can be used to infer structural differences, such as the relative concentration of unreacted vinyl groups within the polymers, which reflects the degree of cross-linking. For example, although ruthenium polymers 7-2 and 2-2 have similar diffusion coefficients, they must be structurally different since polymer 7-2 shows a much higher degree of polymerization.

(e) Emission Spectroscopy. The emission spectra for the osmium and ruthenium polymers were obtained at room temperature and at 77 K in a 4:1 EtOH/MeOH solvent mixture, and data are summarized in Tables VI and VII for the ruthenium and osmium polymers, respectively.

In the tris(vinylbipyridyl) metal complexes of osmium and ruthenium, luminescence originates from a MLCT excited state. Since as mentioned before, there is a blue shift in the energy of the MLCT transition as the degree of polymerization increases, one would also anticipate a blue shift in the emission energy as well. Significant blue shifts are observed in the emission energy of the ruthenium polymers, and the trends are in agreement with the results from absorption spectroscopy. For instance, the ruthenium polymer fraction 2-2, which had a high-intensity absorption band at 250 nm and a MLCT band at 466 nm, had a small blue shift in the emission energy, indicating a high concentration of residual vinyl groups. For the osmium polymers, the emission energy decreased as the relative polymer size increased. Figure 5A shows a plot of the emission energy at room temperature for the osmium polymers as a function of the diffusion coefficient, and as can be seen, an excellent correlation ($r = 0.98$) is obtained.

As would be anticipated, at low temperature, the emission of these complexes shifts toward higher energy. This is because, in the ethanol/methanol glass, the solvent dipoles cannot reorient within the lifetime of the excited state to solvate the highly polar excited state. As a result, in this low-temperature glass, the excited state is at a higher energy, relative to the ground state, than the same excited state is when solvated in fluid media. This effect has been previously documented and is referred to as rigidochromism.[11]

The emission energy at low temperature also showed a decrease as the relative polymer size increased. Figure 5B shows a plot of the emission energy at 77 K for the osmium polymers as a function of the diffusion coefficient. Again, an excellent correlation ($r = 0.99$) is obtained. (Note: there is one less data point in this plot due to excessive noise in one of the spectra at low temperature due to scattering.) In general, similar trends were observed for the ruthenium polymers.

We also found that polymerization of the monomer complexes could be light induced. Upon excitation, the promoted electron resides largely on a vbpy π^* orbital, producing an excited state reactive toward free-radical polymerization. Thus, polymerization could be effected in the absence of any initiator. The advantage of this procedure is the elimination of any matrix effects between samples and, also, the absence of the nonchromophoric end group from the initiator in the free-radical polymerization reaction. Such a procedure was employed in order to study the luminescent properties of the ruthenium polymers as the molecular weight increased, by preparing a ruthenium monomer sample (without AIBN) in a luminescence cell. The emission spectrum was obtained immediately after the sample was prepared. The monomer solution was exposed to ambient laboratory light for 24 h, and the emission spectrum was obtained again. This procedure was repeated until no further changes in the emission energy, as well

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(11) (a) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Barigelletti, F.; von Zelwsky, A.; Juris, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3680. (c) Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 5307.

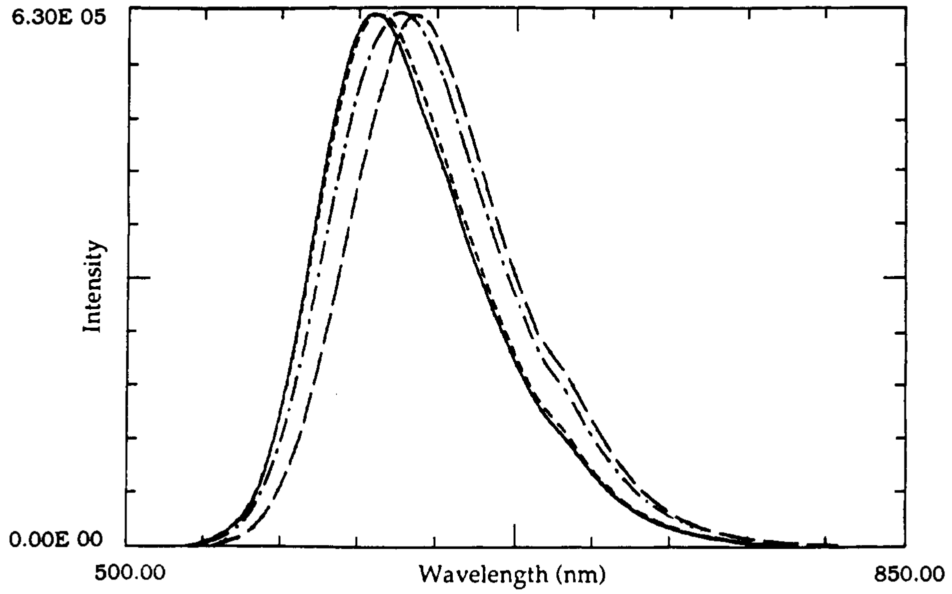

Figure 6. Emission spectra at room temperature at different times during the light-induced polymerization of $Ru(vbpy)_3(PF_6)_2$ in 4:1 EtOH/MeOH: (a) spectrum before light-induced polymerization (– –); (b) spectrum after 24 h (– -); (c) spectrum after 48 h (- - -); (d) spectrum of $Ru(dmbpy)_3(PF_6)_2$ (—).

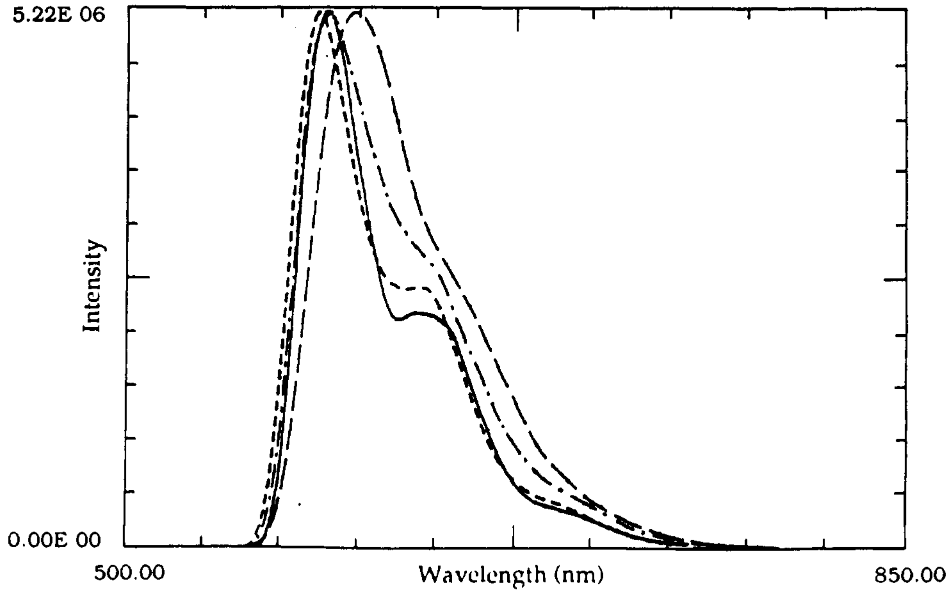

Figure 7. Emission spectra at 77 K at different times during the light-induced polymerization of $Ru(vbpy)_3(PF_6)_2$ in 4:1 EtOH/MeOH: (a) spectrum before light-induced polymerization (– –); (b) spectrum after 24 h (– -); (c) spectrum after 48 h (- - -); (d) spectrum of $Ru(dmbpy)_3(PF_6)_2$ (—).

as in the overall spectra, were observed.

As the polymerization reaction proceeded, a blue shift in the emission energy was observed at both room temperature and 77 K (Figures 6 and 7). At room temperature, the emission spectrum of the "completely" polymerized sample was very similar to that of the $Ru(dmbpy)_3(PF_6)_2$ complex. However, at low temperature, the emission energy of the polymerized sample was higher than the emission energy of the dmbpy monomer. A similar effect was also observed for the osmium polymers.

As mentioned before most of the osmium polymers had a relatively high concentration of unreacted vinyl groups. While performing the luminescence experiments on the osmium polymers, we noticed that if the low-temperature spectrum was obtained after the room-temperature one, the composition of the polymers was altered. In this case, a higher emission energy than that corresponding to that particular polymer fraction would be obtained. However, if the low-temperature experiment was performed first, no changes in the emission energy at room temperature were observed. Since most of the osmium polymer fractions contained a significant number of unreacted vinyl groups, they could be further polymerized in the luminescence cells. Thus, they were exposed to light until no further shifts in the emission energy were observed. At room temperature, the emission energy for the osmium polymers corresponded to that for $Os(dmbpy)_3(PF_6)_2$, which would represent the limiting case of having all vinyl groups reacted. However, at 77 K, the emission energy was shifted to an energy higher than that of the dmbpy monomer. This effect was observed for all the osmium polymers fractions, and regardless of the original molecular weight of each polymer fraction, the

Table VIII. Emission Energies for the Light-Induced Polymerization Fractions

polymer sample	$\lambda_{298\,K}$, nm	emission energy at 298 K, 10^{-4} cm^{-1}	$\lambda_{77\,K}$, nm	emission energy at 77 K, 10^{-4} cm^{-1}	ΔE,[a] cm^{-1}
$Ru(dmbpy)_3(PF_6)_2$	611	1.637	591	1.692	
Ru polymer	611	1.637	588	1.700	80
$Os(dmbpy)_3(PF_6)_2$	725	1.379	723	1.383	
Os polymers	725	1.379	719	1.390	70

[a] $\Delta E = E^{77K}(M(vbpy)_3(PF_6)_2 \text{ polymer}) - E^{77K}(M(dmbpy)_3(PF_6)_2)$.

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 $[M(vbpy)_3]^{2+}$ (M = Ru, 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.

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Registry No. $[Ru(vbpy)_3(PF_6)_2]$, 81315-17-5; $[Os(vbpy)_3(PF_6)_2]$, 130728-19-7; $[Os(vbpy)_3(PF_6)_2]$ (homopolymer), 97056-94-5; $[Ru(vbpy)_3(PF_6)_2]$ (homopolymer), 81315-14-2.

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

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Copolymers of $[Ru(vbpy)_3(PF_6)_2]$ and $[Os(vbpy)_3(PF_6)_2]$ (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 paper[1] 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.

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

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