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Poly(pyridyl)ruthenium(II) Complexes of Poly(4-vinylpyridine). Synthesis, Characterization, and Investigation of Optical and Electrochemical Properties

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A series of metallopolymers have been prepared by the reaction between poly(4-vinylpyridine) ($M_n \approx 3900$) and $[Ru(trpy)(bpy)(OH_2)]^{2+}$ (trpy is 2,2′,2″-terpyridine and bpy is 2,2′-bipyridine). The synthetic procedure allows for the degree of metalation of the polymer to be controlled in a systematic and reproducible way. The degree of metalation in a series of samples was determined by ^1H NMR, UV-vis spectroscopy, elemental analysis, and ESCA. The redox properties of materials as thin films on electrode surfaces were investigated electrochemically. The results of UV-visible absorption and emission studies in solution suggest that, in samples where the degree of metalation is low, the optical properties of the polymer-bound sites are essentially those of the related monomer $Ru(trpy)(bpy)py^{2+}$, but at high degrees of metalation, evidence for interactions between sites has been obtained.

Introduction

In the search for new chemical materials, one of the most attractive areas in chemistry is the development of metallopolymers. This relatively new class of materials has promise for applications in a number of diverse areas including heterogeneous catalysis[1] and electrode modifications,[2] in biomimetic chemistry[3] and possibly for device applications.

Our interest in the area originated with the idea of combining the potential advantages offered by polymeric materials with the extensive ground- and excited-state chemistry which has been established for poly(pyridyl) complexes of ruthenium. Similar monomeric and dimeric ruthenium complexes have proven to be of value in the development of redox catalysts,[4] for the existence of exploitable excited states,[5,6a] and as model compounds for the study of electron-transfer processes.[6]

Metallopolymers in which ruthenium-bipyridyl complexes are chemically bound to poly(4-vinylpyridine) (4-PVP) have been reported whose preparations are based on the substitutional chemistry of $Ru(bpy)_2Cl_2$.[7] In this paper we report our results on the attachment of the group $(trpy)(bpy)Ru^{II}$ (trpy is 2,2′,2″-terpyridine and bpy is 2,2′-bipyridine) to 4-PVP. The metallopolymers prepared in this manner are of interest because of the synthetic control and reproducibility available in the preparations and the high degree of definition which results from their characterization. However, the most important feature of these materials is the carryover of properties from the monomer to polymers, in terms of both electrochemical redox properties in thin films on electrode surfaces and excited-state properties of the bound chromophoric sites. Ultimately, both properties may be exploitable in a number of applications.

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Experimental Section

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) and tetraethylammonium perchlorate (TEAP) were prepared with the use of previously published procedures,[8] recrystallized from hot ethanol–water three times, dried at 70 °C for 10 h, and stored in a desiccator. Water was deionized and then distilled from alkaline permanganate. CD_2Cl_2 (99%) was purchased from Merck and CD_3CN (99%) from Aldrich Chemical Co. Acetonitrile (MCB Spectrograde), CH_2Cl_2, and 1,2-dimethoxyethane were stored over Davison 3-Å molecular sieves. All other materials were obtained commercially and were used as received.

Measurements. Elemental analyses were performed by Integral Microlabs, Raleigh, N.C. ^1H NMR spectra were determined with a 100-MHz Varian Fourier-transform spectrometer with Me_4Si as an internal standard. Ultraviolet and visible spectra were recorded by using a Bausch and Lomb Model 210 spectrophotometer. Infrared spectra were obtained by using a Beckman 4250 spectrophotometer with samples either as KBr pellets or as thin films deposited from CH_2Cl_2. ESCA measurements were made by using a Du Pont Instruments 650B electron spectrometer. Samples were prepared by attaching double-sided tape to the surface of a gold probe and pressing the sticky surface against the solid complex. Emission spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter using quartz spectral cells polished on four sides. Solutions were degassed with solvent-saturated argon for 20 min with use of stainless steel needles. The cells were then closed with rubber serum caps and the needle holes sealed by applying a layer of Dow Corning high-vacuum silicone grease. Electrochemical measurements were recorded vs. the saturated sodium chloride (SSCE) electrode at 25 ± 2 °C and are uncorrected for junction potential effects. No IR compensation was employed. The electrochemical instrumentation included a Princeton Applied Research Model 174A Polarographic Analyzer and a home-built waveform generator as described in the literature.[9] The electrodes used were Pt disks surrounded by a heat-shrinkable Teflon shroud and were pretreated according to previously published procedures.[10] Laser-lifetime measurements were made by using a Molectron IL200 tunable dye laser pumped by a Molectron UV400 nitrogen laser. The beam from the nitrogen laser was passed through an ethanol solution of Coumarin 480 dye (Exciton Co.) and tuned with a J-Y H20 monochromator to an exciting wavelength of 467 nm. A Hammamatsu R777 photomultiplier tube (time constant = 2.5 μs) was used for detection and amplification of the signal, which was then processed by a Tektronix R7912 transient digitizer interfaced to a PDP 11/34 computer. The results were displayed on a Tektronix 4010-1 terminal.

Preparation of Starting Materials. Poly(4-vinylpyridine) Synthesis. 4-Vinylpyridine was distilled at reduced pressure (77 °C (31 torr)). The purity of the distillate was checked by gas chromatography. The monomer was polymerized in a manner similar to published procedures.[11] In a Pyrex tube adapted for attachment to a high-vacuum line were placed 15.4 mL of freshly distilled monomer, 44.7 mL of absolute ethanol, and 75.5 mg of 2,2′-azobis(isobutyronitrile) (AIBN). The mixture was freeze–pump–thaw degassed three times. The tube was then sealed off and immersed for 5 days in a mineral oil bath maintained at 70 °C. The resulting viscous, yellow liquid was dropped into a large beaker of water, yielding a white coagulated solid. The solid was dissolved in ~600 mL of ethanol and filtered through a medium-porosity sintered-glass funnel containing infusorial earth. The alcoholic filtrate was concentrated by rotary evaporation and then precipitated by addition to ether. The resulting solid was again dissolved in ethanol and reprecipitated from water. It was collected and dried in vacuo at 55 °C for 2 h, yielding a hard, brittle clump of white solid which was ground to a fine powder by use of a mortar and pestle; yield about 5 g of PVP.

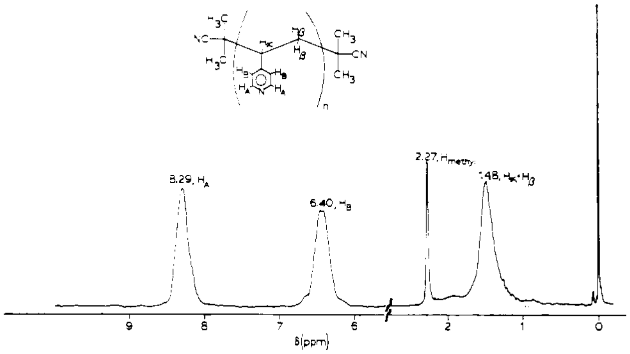

Figure 1. ^1H NMR spectrum of poly(4-vinylpyridine) with isobutyronitrile end groups in CD_2Cl_2, referenced to Me_4Si. Note break in horizontal scale.

Characterization of PVP. On a qualitative basis, the infrared[12] and ^1H NMR[13] spectra of PVP were found to match those in the literature. The NMR spectrum shows three broad resonances due to the main chain of the polymer (H_A, H_B, and $H_\alpha + H_\beta$) and a sharp singlet from the terminal isobutyronitrile ($-C(CN)(CH_3)_2$ (IBN)) groups.[14] (See Figure 1.) The fact that the resonance from the IBN groups is observable reflects the short-chain nature of the polymer, but even more importantly, it functions as an internal standard and, as such, offers a sensitive probe for determination of the number-average molecular weight (M_n) of the PVP. The degree of polymerization ($\overline{DP}$), or number of vinylpyridine units in the polymer chain, and M_n were determined as follows. The ratio of the number of 4-vinylpyridine protons to IBN protons, *R*, is given by

$$R = \frac{\text{area } H_A + \text{area } H_B + \text{area } (H_\alpha + H_\beta)}{\text{area } H_{IBN}} \tag{1}$$

With the assumption that the polymer is terminated at both ends by a $-C(CH_3)_2(CN)$ unit, the number of IBN protons in the molecule is fixed at 12. The total number of vinylpyridine protons, *n*, can then be expressed as

$$n = 12 \times R \tag{2}$$

Each vinylpyridine unit contains 7 protons so the number of monomer units in the chain, $\overline{DP}$, is

$$\overline{DP} = n/7 \tag{3}$$

and making the appropriate substitutions

$$\overline{DP} = \frac{12}{7}\,\frac{\text{area } H_A + \text{area } H_B + \text{area } (H_\alpha + H_\beta)}{\text{area } H_{IBN}} \tag{4}$$

M_n is then easily calculated by using the formula weights of a vinylpyridine monomer (105) and two isobutyronitrile groups (136)

$$M_n = 105\overline{DP} + 136 \tag{5}$$

Elemental analyses for PVP were somewhat variable due to the hygroscopic nature of the polymer and the tenacity which it exhibits toward retention of solvent. However, analytical data from dried and undried PVP samples yield the result that undried PVP contains approximately 6% water by weight, a result noted previously.[15] Samples dried in vacuo still retain 2.1–2.5% H_2O.

Analytical results for PVP: $\overline{DP}$ = 36, 2 IBN end groups, and 2.3% H_2O. Anal. Calcd for $C_{260}H_{274}N_{38}O_5$: C, 77.84; H, 6.89; N, 13.28. Found: C, 77.94; H, 7.22; N, 12.88.

Preparation of the Polymer–Metal Complexes. Ruthenium(II) complexes were coordinated to PVP at varying degrees of metalation by allowing the appropriate stoichiometric amounts of $[(trpy)(bpy)Ru(OH_2)]^{2+}$[16] and PVP to react in ethanol for at least 12 h at

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reflux. More specific preparative information is given in the next section. Formulas for complexes prepared in this way can be written as $[(trpy)(bpy)Ru(VP)_x]^{2+}$, where VP represents a coordinated vinylpyridine unit of the polymer and x is the ratio of total to Ru-bound pyridyl sites on the polymer. For example, if all possible pyridyl groups were metal bound, the formula for the resulting polymeric complex would be $[(trpy)(bpy)Ru(VP)_1]^{2+}$, and if one out of every five possible sites were Ru bound, the formula would be $[(trpy)(bpy)Ru(VP)_5]^{2+}$.

Complexes with x values less than about 7 tend to precipitate from the reaction mixture as yellow films on the wall of the reaction vessel. Complexes with x values greater than about 10 more closely resemble the original polymer in their solubility properties and remain in solution. They were isolated by rotary evaporation of the mixture to dryness followed by extraction of the polymer–metal complex with acetonitrile. Examples of two typical preparations are given below.

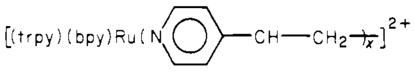
Preparation of $[(trpy)(bpy)Ru(VP)_x]^{2+}$, $x \lesssim 7$. A 70-mg sample (0.1 mmol) of $[(trpy)(bpy)Ru(OH_2)](ClO_4)_2$ was completely dissolved in a round-bottom flask containing 50 mL of hot ethanol. A 32-mg sample (0.3 mmol) of poly(4-vinylpyridine), which had previously been dried in vacuo at 80 °C, was dissolved separately in 25 mL of ethanol. The solutions were combined, the volume was brought to 100 mL, and the mixture was heated at reflux for 2 days. The red, ethanolic solution of unreacted starting material was decanted, and the yellow film coating the surface of the flask was rinsed with ethanol until the wash solution was colorless. The film was extracted with acetonitrile, evaporated to a small volume, and added dropwise to ~125 mL of stirring diethyl ether. The powdery, red-brown precipitate which formed was cooled at 0 °C and then collected by suction filtration; yield 50 mg.

Preparation of $[(trpy)(bpy)Ru(VP)_x]^{2+}$, $x \gtrsim 10$. A 21-mg sample (0.03 mmol) of $[(trpy)(bpy)Ru(OH_2)](ClO_4)_2$ was dissolved in a round-bottom flask containing 50 mL of hot ethanol, and 32 mg (0.3 mmol) of previously dried poly(4-vinylpyridine) was added to a separate flask with 25 mL of ethanol. The two solutions were combined and heated at reflux for 2 days. The resultant homogeneous mixture was rotary evaporated to dryness, and the unreacted starting material was removed by rinsing the flask copiously with acetone until a red color was no longer apparent. The remaining yellow solid was extracted with acetonitrile and precipitated from ether. The flocculent brown solid was cooled and then collected by filtration. The isolated solid had a much gummier and more rubbery appearance than the more highly metalated samples, presumably due to its greater resemblance to the polymer itself with respect to its mechanical and physical properties. To put these observations into perspective, it should be noted that when x equals 7, the contribution to the total molecular weight of the metallopolymer is approximately evenly distributed between the organic and inorganic components. Therefore, at the extreme of high metalation, the bulk of the compound, in terms of both mass and molecular volume occupied, consists of the attached ruthenium complex, and one can probably account for the changes in macroscopic properties as the degree of metalation changes on this basis.

Preparation of Films from the Polymer–Metal Complexes. Thin and thick films of the metallopolymers can be deposited on silica glass cover slides, quartz spectral cells, or platinum and glassy carbon electrodes by dip-coating from homogeneous acetone or acetonitrile solutions which contain a polymer complex, followed by air evaporation of the solvent. A study of the adsorption isotherms for the various polymers has not been undertaken, but it seems apparent that approximate thicknesses of the films can be controlled simply by varying the concentration of the complex in the solution from which the films are deposited. A problem which seems to be inherent in the dip-coating approach is the formation of visibly nonuniform films when attempts are made to cover surfaces with areas larger than a standard disk electrode (~0.2 cm²). This severely limits quantitative studies involving absorption or emission measurements. The use of complexes of lower degree of metalation results in a trade-off between enhanced film-forming ability and attenuated sensitivity due to the decreased population of metal sites.

Results

Characterization of the Metallopolymers. The characterization of the series of polymer-bound complexes was accomplished by applying several analytical techniques to each sample. The critical issues were first to establish the ratio of bound ruthenium to pyridyl sites and then to reproduce complexes of a specific ratio in a systematic manner with our synthetic procedures. The rationale behind the multifaceted approach was twofold: first, we believed that comparisons between results obtained by using various techniques would reinforce the validity of the results acquired by any one method and hence provide the most accurate possible identification; second, by applying several methods initially, we could then choose the most convenient one for use on a regular basis. We have used mass balance, elemental analyses, ¹H NMR, ESCA, and UV–vis spectroscopy to characterize the polymer complexes. The results obtained in the determination of the degree of metalation, x, of the complexes



are summarized below for the different techniques.

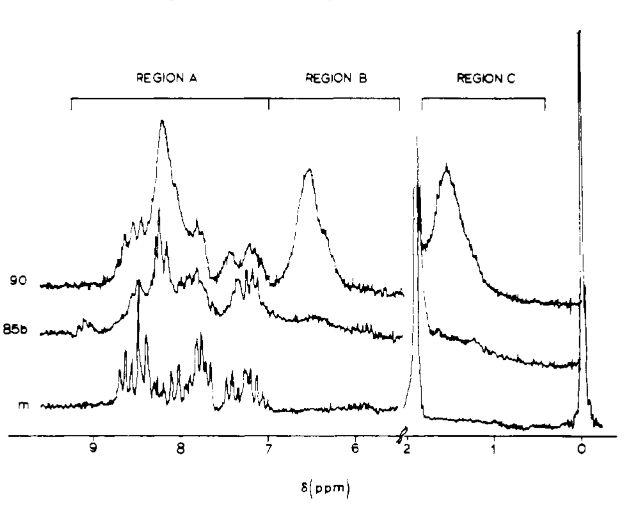


Figure 2. ¹H NMR spectra of $[(trpy)(bpy)Ru(py)]^{2+}$ and metallopolymers of high and low degrees of metalation (labeled m, 85b, and 90, respectively) in CD_3CN, referenced to Me_4Si. Note break in horizontal scale. Most of the solvent peak at 2 ppm is omitted for clarity.

¹H NMR. Representative ¹H NMR spectra of metallopolymer complexes having low and high x values are shown in Figure 2. A spectrum of the analogous monomer $[(trpy)(bpy)Ru(py)]^{2+}$[17] (py is pyridine) is included for comparison. By analogy to the spectrum of PVP itself (Figure 1), the resonances from the metallopolymer assignable to the protons of the PVP backbone, designated in Figure 1 as H_A, H_B, and $H_\alpha + H_\beta$, will occur in the regions designated as A, B, and C, respectively, in Figure 2. Spectra of the monomeric series of complexes $[(trpy)(bpy)Ru(L)]^{n+}$ (L = py, 1,2-bis(4-pyridyl)ethane, CH_3CN, $n = 2$; L = Cl^-, NO_2^-, CN^-, $n = 1$) show that the resonances due to the 2,2′,2″-terpyridyl and 2,2′-bipyridyl protons of the attached ruthenium complex are found only at δ values downfield from 7 ppm, or in other words, solely in the region designated in Figure 2 as A. The same protons in the metallopolymer complexes are also expected to appear in region A. A method for determining the extent of metalation can be derived by taking into account only the integrated areas of regions A and B.

The origins of the total areas in regions A and B are given algebraically by

$$\text{area A} = H_A(\text{py-bound}) + H_A(\text{py-unbound}) + H(\text{bpy}) + H(\text{trpy}) \quad (6)$$

$$\text{area B} = H_B(\text{py-bound}) + H_B(\text{py-unbound}) \quad (7)$$

Since there will always be identical numbers of H_A and H_B

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[17] Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.

on each pyridine ring, it follows that

$$H_A(\text{py-bound}) = H_B(\text{py-bound}) \quad (8)$$

$$H_A(\text{py-unbound}) = H_B(\text{py-unbound}) \quad (9)$$

In a ruthenium-bound pyridyl unit there are 19 (bpy + trpy) protons per 2 H_A protons, so the term H(bpy) + H(trpy) in eq 7 can be replaced by (19/2)[H_A(py-bound)].

$$H(\text{bpy}) + H(\text{trpy}) = (19/2)[H_A(\text{py-bound})] \quad (10)$$

Using the above relationship, it is possible to solve eq 6 and 7 simultaneously for the ratio of unbound to bound pyridyl protons in terms of the areas of the A and B regions of the spectrum.

$$\frac{H_A(\text{py-unbound})}{H_A(\text{py-bound})} = \frac{19(\text{area A})}{2(\text{area A} - \text{area B})} - 1 \quad (11)$$

The numerical value for x, the number of pyridyl groups per Ru, is then given by

$$x = \frac{19(\text{area B})}{2(\text{area A} - \text{area B})} \quad (12)$$

The accuracy of the determination of x is limited when the extreme of high metalation is approached. As x nears unity, the area of the peak containing H_B(py-unbound) protons approaches zero and eq 12 loses experimental meaning.

UV–Vis Spectroscopy. The qualitative appearances of the UV–vis spectra for all of the $[(\text{trpy})(\text{bpy})\text{Ru}(\text{VP})_x]^{2+}$ complexes are similar, although subtle differences between samples can be distinguished. In general, the most notable feature of the visible spectrum is a broad band whose maximum absorbance occurs at 468 nm. Two shoulders appear on the high-energy side of the band. The visible absorption bands are metal to ligand charge transfer (MLCT) in nature and encompass a manifold of $\pi^*(\text{trpy}) \leftarrow d\pi(\text{Ru})$ and $\pi^*(\text{bpy}) \leftarrow d\pi(\text{Ru})$ transitions. The visible spectra also exhibit two smaller peaks (~10–15% of the intensity of the main absorption band) at approximately 535 and 595 nm, which appear to be characteristic of the $\pi^*(\text{trpy}) \leftarrow d\pi(\text{Ru})$ chromophore and do not appear in analogous bipyridine complexes. The slight differences between the visible spectra of various metallopolymers become apparent when a series of complexes with varying x values are compared (see Figure 3). Polymer complexes having x greater than about 3 give superimposable spectra and are characterized by having a distinct second shoulder on the high-energy side of the main MLCT band at about 415 nm. The complexes with x less than 3 show the second shoulder to be red-shifted by about 5–20 nm into the main body of the MLCT band and, in addition, the two relatively weak low-energy transitions are even less intense and almost disappear into the tail of the main transition.

The UV spectra exhibit three main bands and four discernible shoulders whose intensities are 25–30% greater than the main visible transition. The most intense near-UV peak (313 nm) is a characteristic trpy $\pi^* \leftarrow \pi$ transition and the remainder of the absorption features are assignable to a variety of trpy and bpy intraligand transitions. Once again, there are small variations within the UV spectra for metallopolymers having different metal content, but these are ascribable to changes in the number of free pyridine sites on the polymer chain.

The estimation of x from visible spectra was carried out in the following manner. The assumption was made that the total absorbance of each metallopolymer molecule was the sum of the absorbance of each of the ruthenium chromophores on the polymer chain. A second assumption used was that the extinction coefficients of the monomeric analogue, $[(\text{trpy})(\text{bpy})\text{Ru}(\text{py})]^{2+}$, in the same medium could be used for the polymer-bound ruthenium sites.

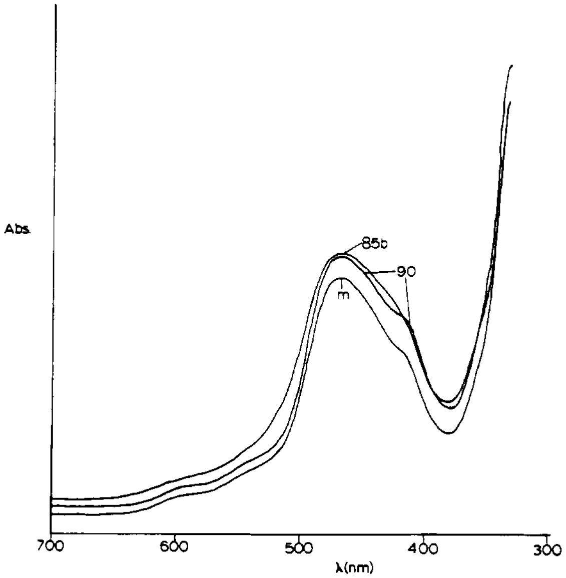

Figure 3. Electronic absorption spectra of $[(\text{trpy})(\text{bpy})\text{Ru}(\text{py})]^{2+}$ and metallopolymers of high and low degrees of metalation (labeled m, 85b, and 90, respectively) in CH_3CN. $[\text{Ru}^{2+}]$ in all samples is ~1 × 10^{-4} M (1-cm path length).

Using these assumptions, it is possible to calculate the number of moles of attached ruthenium sites n (and hence the number of bound vinylpyridine groups) in the sample, with the use of Beer's law in the form (1-cm path length)

$$n = lA/\epsilon \quad (13)$$

where A is the measured absorbance at a given wavelength, ϵ is the molar extinction coefficient for the monomeric complex at that wavelength, and l is the solution volume in liters. The wavelength chosen was the MLCT maximum $\lambda_{max} = 468$ nm, where $\epsilon = 8.11 \times 10^3$ M^{-1} cm^{-1} for $[(\text{trpy})(\text{bpy})\text{Ru}(\text{py})]^{2+}$ in acetonitrile.

From n, the mass contributed by the ruthenium-attached VP units to the total sample mass, M_s, can be obtained by multiplying n by the formula weight of a single Ru–VP unit (794 for $[(\text{trpy})(\text{bpy})\text{Ru}(C_7H_7N)](ClO_4)_2$). When this mass is subtracted from the measured sample mass and the result is divided by the formula weight of an unbound vinylpyridine unit (105/unit), the number of moles of unbound VP is obtained, and x is given by

$$x = (\epsilon M_s/105lA) - Z \quad (14)$$

The value of Z in eq 14 is 6.56 for ClO_4^- as the counterion and 7.43 for PF_6^-.

Elemental Analyses. Elemental analyses were obtained for different samples after they were dried in vacuo at 80 °C for 24 h. The results indicated that the samples still retained 2.0–2.5% water by weight after the drying procedure. The analytical data were then manipulated in order to obtain the VP/Ru ratio which would best fit the data. Calculations were carried out by using the previously determined value of $\overline{DP}$ = 36 as the length of the polymer chain and also including two IBN groups in the molecular weight.

Mass Balance. The percent ruthenium uptake in the synthetic reactions was determined by difference. The initial concentration of the solvento complex was known precisely, and the absorbance of an aliquot of the solution after appropriate dilution was recorded at the absorption maximum for the complex at 477 nm. After the reaction had gone to completion and the precipitated polymer had been removed, the absorbance due to the remaining starting complex was measured and the ratio of the two absorbance values was used to calculate the amount of ruthenium uptake by the polymer.

Table I. Ratios of Available to Bound Pyridyl Sites As Determined by Various Techniques

sample no.	reaction stoichiometry[a]	mass balance	elemental analyses	UV-vis spectrometry	^{1}H NMR	ESCA
54	4.7:1	6.6	5.76	4.87	6.39	2.2
64a	1.9:1	2.8	3.05	3.18	2.38	
94	10:1			13.5	11.9	
97	3.1:1		5.25	5.85	5.60	

[a] Ratio of available pyridyl sites on PVP backbone to $[(trpy)(bpy)Ru(OH_2)]^{2+}$ added.

ESCA. Peaks attributable to the following elements were observed in the X-ray photoelectron spectrum (BE = binding energy).

element (orbital)	BE, eV	element (orbital)	BE, eV
C (1s), Ru ($3d_{5/2}$)	~284.5[18]	F (1s)	685.4
Ru ($3P_{3/2}$)	401.6	P ($2P_{1/2}$)	135.2
N (1s)	398.4		

The integrated areas for the nitrogen, fluorine, and phosphorus peaks were normalized with respect to number of scans and corrected to account for differences in scattering cross section, mean free path,[19] and orbital angular distribution.[20] The ratios of F/P, F/N, and N/P were then calculated; the F/P ratio was used as an internal standard and adjusted to a value of 6.00. The remaining values were fit to the optimum VP/Ru ratio.

Evaluation of the Characterization Techniques. Of the techniques chosen for the characterization experiments, the one expected to be the least accurate for the determination of the extent of ruthenium binding is ESCA. It is extremely matrix dependent, subject to oxide and carbon contamination, and relies heavily on correction factors and calibration standards. The fact that ESCA is a surface-sampling technique can be detrimental because there is no guarantee that the surface observed in the experiment is representative of the bulk sample. In fact, the single value of x obtained by ESCA is only within a factor of 3 of values obtained with the use of other techniques. Our experience clearly demonstrates the limitations of the ESCA experiment in obtaining reliable quantitative data. However, the magnitude of the error is small enough to distinguish between samples of high and low degrees of metalation, and our results are encouraging in terms of the possible use of ESCA to characterize thin films of the polymer-metal complexes on electrodes or other materials.

The use of the mass-balance approach is also of questionable quantitative validity because the spectrophotometric analysis is performed on a solution which in actuality contains unreacted polymer, metallopolymer which is not sufficiently metalated to precipitate from solution, and the actual unreacted starting complex, $[(trpy)(bpy)Ru(OH_2)]^{2+}$.

The remaining three techniques—^{1}H NMR, UV-vis spectrometry, and elemental analysis—all appear to offer valid estimates for the degree of metalation. Of these three, the UV-vis approach is clearly dependent upon the assumption that the extinction coefficients for the polymer-bound and monomer chromophores are identical. Long experience with complexes of this type suggests that the assumption is a reasonably accurate one.

The other two techniques suffer from the drawback that as the extent of metalation approaches the 1:1 upper limit and the molecular weight fraction due to the polymer backbone becomes only a small part of the total, minor inaccuracies in sample weighing can cause significant errors in the calculation of x.

The inherently most sensitive method for determining the extent of metalation should be NMR. It is a purely counting technique and is limited only by the accuracy with which the integrated areas can be evaluated and the intrinsic limitation of eq 12 at high degrees of metalation.

Results of the Characterization Studies. The analytical results for a series of selected metallopolymer samples are summarized in Table I.

There are three important points to be made with regard to the data in Table I. (1) In almost all cases, the experimentally determined value of x was greater than that which would have been expected solely on the basis of the reaction stoichiometry. This is a realistic result since unreacted $[(trpy)(bpy)Ru(OH_2)]^{2+}$ was present in solution after completion of the syntheses. (2) Considering the assumptions made and the variety of techniques, the agreement between x values in Table I is striking and suggests that we are able to achieve a high degree of definition in terms of controlling the extent of metalation. (3) The chemistry of related monomeric complexes is extensive and well-defined. The data presented suggest that a great deal of that chemistry can be extended to polymer-attached groups and that the chemical composition of the resulting materials, with regard to the extent of metalation, can be established in detail.

In the following sections, the value of x which will be used to describe the metallopolymers will be the average of the ^{1}H NMR and UV-vis results.

Redox Properties of the Metallopolymers. The redox properties of the PVP complexes were investigated electrochemically as films on platinum electrodes. Formal potential values ($E^{\circ\prime}$), as determined by cyclic voltammetry, of the various members of the $[(trpy)(bpy)Ru(VP)_x]^{2+}$ series and the monomeric analogue, $[(trpy)(bpy)Ru(py)]^{2+}$, were found to be similar, regardless of the thickness of the film or of the degree of metalation.[21] However, the wave shapes and ΔE_p values (ΔE_p is the peak potential difference between the oxidative and reductive sweeps) varied considerably with film thickness, degree of metalation, solvent, and scan rate (v).

Cyclic Voltammetry Studies. The electrodes were dipped into homogeneous acetone or acetonitrile solutions containing the polymer complexes, and the solvent was allowed to evaporate. Electrochemistry was then performed in a solvent (dichloromethane or 1,2-dimethoxyethane (DME)) which would not dissolve the polymer film off the electrode. The "effective surface coverages", Γ, of the polymers on the electrodes with known surface areas were determined by measuring the areas under cyclic voltammetric waves to es-

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[18] The peak due to Ru ($3d_{5/2}$) appears in the spectrum as a shoulder on the low-energy side of the C(1s) peak. The value of the binding energy listed is for the main carbon peak.

[19] Penn, D. R. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *9*, 29.

[20] Reilman, R. F.; Msezane, A.; Manson, S. T. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 389.

[21] The definition of "thin" and "thick" films as used here is somewhat arbitrary, but a distinction can be made based on the surface coverages, Γ,[22] and from the physical appearance of the electrode surfaces after coating. "Thick" films wave formed by evaporation of solutions $\sim 10^{-4}$ M in polymer complex yielding opaque, gold-colored electrodes with coverage values of $(10-40) \times 10^{-10}$ mol/cm^2. "Thin" films, which do not visibly affect the mirror-polished appearance of the electrode surface, were formed by dipping and evaporation from solutions which were $\sim 10^{-5}$ M in metallopolymer. Coverages were generally in the range $(2-10) \times \sim 10^{-10}$ mol of Ru^{2+}/cm^2.

[22] (a) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *52*, 395. (b) Brown, A. P.; Anson, F. C. *Anal. Chem.* **1977**, *49*, 1589.

Table II. Cyclic Voltammetry Data for the Polymer Films on Platinum and for Related Complexes in Solution[a]

complex	$E°'$ (Ox),[b] V	ΔE_p, mV	$E°'(1)$ (Red),[c] V	ΔE_p, mV	$E°'(2)$ (Red),[d] V	ΔE_p, mV	$10^{10}\Gamma$,[e] mol/cm²
$[(trpy)(bpy)Ru(py)]^{2+}$ [f]	1.21	60	−1.26	60	−1.55	160	
$[(trpy)(bpy)Ru(VP)_{2.1}]^{2+}$ [g]	1.21	50	−1.24	40	~−1.5		4.6
$[(trpy)(bpy)Ru(VP)_{3.4}]^{2+}$ [h]	1.30	70					2.1
$[(trpy)(bpy)Ru(VP)_{3.4}]^{2+}$ [h]	1.29	80					4.1
$[(trpy)(bpy)Ru(VP)_{3.4}]^{2+}$ [h]	1.21	200					15.0
$[(trpy)(bpy)Ru(VP)_{12.7}]^{2+}$ [h]	1.20	160					3.4
$[Ru(bpy)_3]^{2+}$ [f]	1.29	60	−1.33	60	−1.52	60	

[a] All data were obtained with platinum-disk electrodes and are referenced to the saturated sodium chloride electrode (SSCE). Results for the polymeric complexes were obtained as films coated onto the electrode surface. The scan rate for all experiments was 200 mV/s.
[b] $Ru^{3+/2+}$ couple. [c] $Ru^{2+/+}$ couple; ligand reduction. [d] $Ru^{+/0}$ couple; ligand reduction. [e] Γ is the surface coverage of redox sites determined by cyclic voltammetry and not a direct measure of surface coverage. [f] In CH_3CN, with 0.1 M $[NEt_4](ClO_4)$ as electrolyte. [g] In 1,2-dimethoxyethane, with 0.2 M $[N(n\text{-}Bu)_4](PF_6)$ (TBAH) as electrolyte. [h] In CH_2Cl_2, with 0.2 M TBAH as electrolyte. Salmon, D. J. Ph.D. Dissertation, The University of North Carolina.

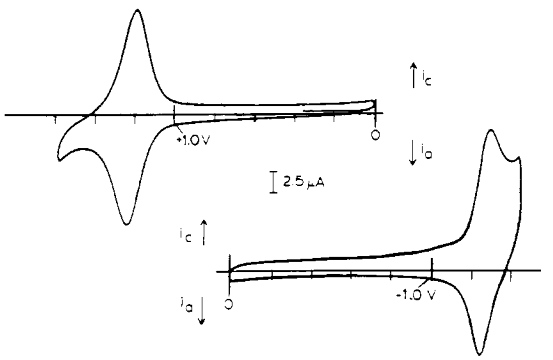

Figure 4. Cyclic voltammograms of a thin film of $[(trpy)(bpy)Ru(VP)_{2.1}]^{2+}$ on a platinum-disk electrode. The supporting electrolyte is 0.2 M $[N(n\text{-}Bu)_4]PF_6$ (TBAH) and the solvent is CH_2Cl_2. The scan rate is 200 mV/s. The effective surface coverage is calculated to be 4.6 × 10^{-10} mol/cm². Reductive data were obtained in a nitrogen-purged cell.

tablish total charge passed. It should be realized that this approach to defining surface coverages gives an effective surface concentration of redox sites. Because of variations in the degree of metalation in our samples, Γ is not directly related to the extent of surface covered by the metallopolymer.

The coated electrodes are stable for indefinite periods of time with ruthenium in the 2+ state and exhibit a slow decay of electrochemical activity when exposed to one-electron oxidation. For example, in a sample where $x = 5.4$ and $\Gamma = 5.4 \times 10^{-10}$ mol/cm², a 45% decay of the redox couple was observed after 2600 cycles through the $Ru^{2+/3+}$ wave, as shown by the extent of the decrease in area under the wave. A 60% decay was found when the metallopolymer film was held at 8.75 h at a potential sufficient to keep the attached complex in the 3+ oxidation state. The passivation of the surface is not due to loss of the polymeric material from the electrode surface because, in the cases involving films which are thick enough to be observed visually, the gold color of the surface persists after the electrochemical response has disappeared.

In contrast to the stability of the surface-bound metallopolymer when oxidized, one-electron reduction, which is based on electron transfer to the π^* levels of the poly(pyridyl) ligands, led to a more rapid rate of passivation of the electroactive species on the electrode. Complete disappearance of the redox couple from the electrode typically occurred following ~100 scans through the wave for the attached $[(trpy)(bpy)Ru(VP)]^{2+/+}$ couple. Reduction by a second electron leads to a completely unstable surface, as shown by cyclic voltammetry. An initial reductive sweep past the wave for the bound $[(trpy)(bpy)Ru(VP)]^{+/0}$ couple led to nearly a complete loss of the electrochemical response on the following oxidative sweep, even though visual inspection indicated that the polymeric film remained on the electrode.

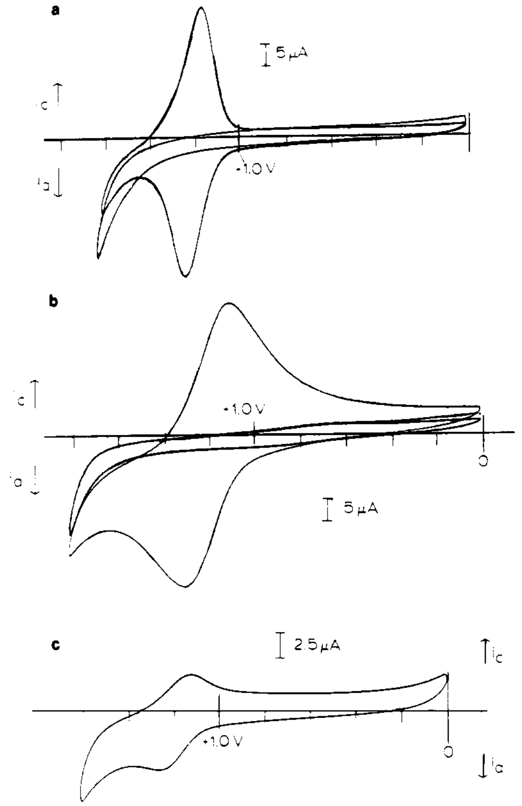

Figure 5. Oxidative cyclic voltammograms of metallopolymer films on Pt electrodes, using 0.2 M TBAH in CH_2Cl_2 as the supporting electrolyte. The scan rate was 200 mV/s in all cases. Degree of metalation (x) and effective surface coverage (Γ) for the samples are as follows: (a) 3.4, 9.4 × 10^{-10} mol/cm²; (b) 3.4, 15 × 10^{-10} mol/cm²; (c) 12.7, 3.4 × 10^{-10} mol/cm².

The similarity in the chemical environments at the ruthenium sites in the monomeric and polymeric compounds is reflected by the similarity in $E°'$ values shown in Table II. It is interesting to note that the potentials are affected only slightly by the choice of solvent and show essentially no dependence on the nature of the film or scan rate used in the experiment.

A result of potentially greater importance is the apparent dependence of ΔE_p on the degree of metalation (x), the surface coverage (Γ), and the scan rate. Some of our initial results are summarized in Table II. Although we have no intention of discussing the results in detail at this point, there are some features in the data which are worth noting.

Thin films of highly metalated polymer show peak splittings for both the oxidative and reductive processes which approach zero, as predicted by theory for a noninteracting, reversible, surface-immobilized redox couple undergoing rapid electron

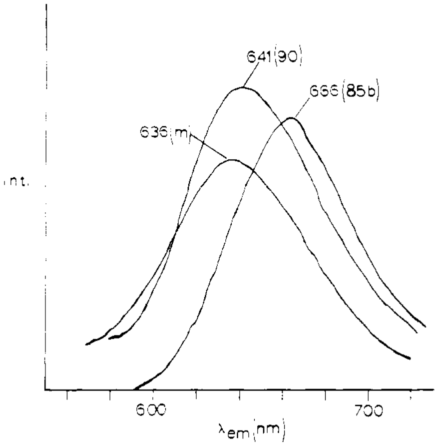

Figure 6. Emission spectra of $[(trpy)(bpy)Ru(py)]^{2+}$ and metallopolymers of high and low degrees of metalation (labeled in parentheses as m, 85b, and 90, respectively) in CH_3CN. λ_{max} values for emission are given. Relative intensities of the peaks are not drawn to scale. Excitation wavelength was 468 nm.

transfer (Figures 4, 5a).[22] If the film thickness for the same metallopolymer sample is increased by a factor of 5–10, peak splittings of 200 mV or greater can result (Figure 5). Making direct comparisons between samples with different degrees of metalation is difficult and requires assumptions to be made about molecular sizes and orientations. As mentioned above, Γ values determined electrochemically are a measure of the surface concentration of redox sites and not directly of film thickness. For two samples where Γ is about the same but x is significantly different, the actual film thicknesses of the samples are also different.

Wave shapes are symmetrical for samples of high ruthenium content applied as "thin" films.[21] For other cases, as the coverage increases or the metal content of the film becomes more dilute, the waves take on a more diffusional-like shape with distinct tailing edges, even though the electroactive species is still confined to the electrode surface. A related observation is that plots of i_p vs. $v^{1/2}$ (v = scan rate) are linear for the diffusional-shaped cases, and the symmetrical ones yield linear plots of i_p vs. v.

Optical Properties: **Emission Spectra.** In contrast to the obvious luminescence from the MLCT excited state of $[Ru(bpy)_3]^{2+}$, the metallopolymer samples irradiated at their MLCT λ_{max} values show a broad, relatively much less intense peak in their emission spectra. The intrinsically lower efficiency for luminescence is essentially a consequence of the nature of the chromophore since $[Ru(trpy)(bpy)(py)]^{2+}$ is also only weakly luminescent at room temperature in fluid solution or in the solid state. For polymer samples where the degree of metalation is less than approximately 3, the emission maxima of the monomer and polymeric complexes are similar (637 and 641 nm, respectively). However, as x becomes smaller, necessarily forcing the average distance between metal centers to decrease, the emission becomes red-shifted by 20–25 nm and increases significantly in intensity (see Figure 6). The effect is reproducible between samples as shown by the properties of five independently prepared samples where x was greater than 3 and three where x was less than 3.

Transient absorbance measurements currently in progress show that excited-state lifetimes for the monomeric and metallopolymeric trpy complexes are short (a few nanoseconds)[23] and are in the same time range as estimated previously for $Ru(trpy)_2^{2+}$.[24] By comparison with $Os(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$, the experiments also suggest that the origin of the shortened lifetimes and weakened emission for the trpy complexes is probably an intervening radiationless decay process following absorption which competes effectively with population of the lowest CT state.

The dependence of excited-state emission on the degree of metalation is a fascinating result which suggests the presence of excited-state communication between neighboring metal centers when they are held by the polymer backbone in close proximity. As the degree of metalation increases, there may also be ground-state electronic interactions as shown by the shifts in absorbance noted earlier for the cases where x was greater than 3. Given the evidence for "outer-sphere" electronic interactions provided by the appearance of charge-transfer bands in ion pairs like $Ru(NH_3)_5py^{3+}$, $Fe(CN)_6^{4-}$, $[Ru^{III}(NH_3)_5py, Fe^{II}(CN)_6]^- \xrightarrow{h\nu} [Ru^{II}(NH_3)_5py, Fe^{III}(CN)_6]^-$,[25] the origin of the electronic interaction may be outer sphere in nature rather than along the polymer backbone.

Conclusions and Final Comments

Our primary goal in this paper was to describe our results on the preparation of polymeric materials containing varying amounts of poly(pyridyl)ruthenium sites. The preparations are reproducible, and the degree of definition in terms of the extent of metalation of the materials is high. Our initial results are encouraging because they suggest the possibility of further experiments where the primary issues will be exploitation of the redox and excited-state properties of these or related polymeric materials. The utility of the materials may arise from their ability to be deposited on various surfaces as films, their reasonably high stability to one-electron oxidation and reduction, and the availability of an experimentally observable excited state.

The data already in hand suggest that the metallopolymers are not merely synthetic novelties but have the potential to elucidate fundamental questions regarding such diverse phenomena as the mechanism of charge transfer through polymeric matrices, intramolecular energy and electron transfer, and the effects of multiple excitation within polymer strands. Our ultimate hope is that the materials may have properties which are exploitable in such practical ends as electrocatalysis and solar energy conversion.

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Registry No. $[(trpy)(bpy)Ru(OH_2)](ClO_4)_2$, 16389-43-8; PVP, 25232-41-1; $[(trpy)(bpy)Ru(py)]^{2+}$, 75102-49-7; $[Ru(bpy)_3]^{2+}$, 18955-01-6.

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