cluding the curvature of the ln k vs P plot, can be accounted for to well within the experimental uncertainty on the basis of a two-sphere, continuous-dielectric, *nonadiabatic* model with a distance scaling factor α of about 19 nm^{-1}. The data are also qualitatively consistent with a mechanism in which electron transfer to Co^{III} occurs adiabatically through the doublet excited state of the Co^{II} complex, in equilibrium with its quartet ground state, but direct adiabatic self-exchange between $Co(en)_3^{3+}(^1A)$ and $Co(en)_3^{2+}(^4T)$ seems to be ruled out.

The extensive experimental work of Endicott and co-workers[40] implies various degrees of nonadiabaticity in the net electron-transfer reactions of a variety of cobalt(III) complexes, more particularly where the electronic structures of the reactant and product are very different; we suggest that it is also important in the symmetrical $Co(en)_3^{3+/2+}$ exchange reaction. For the oxidation of $Co(bpy)_3^{2+}$ by $Co(terpy)_2^{3+}$, which, as noted above, may well involve spin-isomer equilibria but which, because of electron delocalization through the ligand π systems, is also more likely than the $Co(en)_3^{3+/2+}$ exchange to be adiabatic in electron transfer between the ground states of the reactants, ΔV^* is −9.4 $cm^3\ mol^{-1}$,[41] quite close to that predicted from simple SHM theory for, e.g., the $Co(terpy)_2^{3+/2+}$ self-exchange reaction. Comparison of the $Co(bpy)_3^{2+}/Co(terpy)_2^{3+}$ *net* reaction with symmetrical *self-exchange* processes may not be quite legitimate, but it underscores the anomaly of the $Co(en)_3^{3+/2+}$ exchange and suggests that this originates in nonadiabatic electron transfer between the ground states.

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Registry No. $Co(en)_3^{2+}$, 23523-25-3.

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Electrochemical Polymerization of 4-Methyl-4′-vinyl-2,2′-bipyridine-Containing Metal Complexes: Polymer Structure and Mechanism of Formation

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The polymer structure and mechanism of formation of electroreductively polymerized 4-methyl-4′-vinyl-2,2′-bipyridine-containing metal complexes are described. Results from TLC and laser desorption Fourier transform mass spectrometry demonstrate that normal "polyvinyl-type" chains are formed through chain propagation. For electrochemically polymerized poly-$Fe(vbpy)_3^{2+}$ an average chain length of seven repeat monomer units is determined. Separate copolymerization studies of mono- and tris(vinyl)-substituted complexes provide additional information on the nature of the polymerization process.

Introduction

Electrode-bound polymer films formed by the reductive polymerization of metal complexes that contain either 4-methyl-4′-vinyl-2,2′-bipyridine (vbpy) or 4-vinylpyridine have remained a subject of much interest.[2-12] While there has been speculation, the structure and mechanism of formation and these polymers have remained experimentally undetermined. Herein we report studies on the electrochemical polymerization of iron and ruthenium complexes that contain vbpy. Laser desorption Fourier transform mass spectral studies of electrochemically polymerized demetalated poly-$Fe(vbpy)_3^{2+}$ demonstrate that these polymers contain normal "polyvinyl-type" chains. In the case of poly-$Fe(vbpy)^{2+}$, the average polymer chain length is seven repeat monomer units. Additionally, we have reexamined the data that originally led Murray and co-workers[2] to propose a "tail-to-tail" radical-pair coupling path for the formation of these polymers. New electrochemical data allow for a rationalization of these previous results in light of a normal chain propagation mechanism.

Experimental Section

Chemicals and Solvents. Acetonitrile (Burdick & Jackson) for electrochemical measurements was stored under nitrogen and used without further purification. Tetra-*n*-butylammonium hexafluorophosphate ($(TBA)PF_6$) was prepared as previously reported.[13] Electrochemical solutions were all 0.1 M $(TBA)PF_6$ in acetonitrile.

4-Methyl-4′-vinyl-2,2′-bipyridine (vbpy) was prepared from 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) (Strem) by using the method of Guarr and Anson.[14]

Tris(4-methyl-4′-vinyl-2,2′-bipyridine)iron(II), $[Fe(vbpy)_3]^{2+}$. A solution containing 27.7 mg of $FeSO_4\cdot 7H_2O$ (1.0×10^4 mol) dissolved in 30 mL of H_2O was added to 59 mg (3.0×10^4 mol) of vbpy in 50 mL of

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Table I. Relative Incorporation of $[Fe(vbpy)_3]^{2+}$ vs $[Ru(vbpy)(Me_2bpy)_2]^{2+}$

Fe:Ru	% Fe[a]	% Ru[a]	Fe:Ru	% Fe[a]	% Ru[a]
1.0:0.0	100		1.0:1.0	66	34
1.0:0.1	98	2	1.0:3.0	35	65
1.0:0.3	88	12	1.0:7.0	15	85
1.0:0.7	75	25			

[a] Determined by "cutting and weighing" integration of the area under the voltammetric peaks for the copolymer films.

hot acetone. The acetone was first boiled off, and then excess ammonium hexafluorophosphate was added to precipitate $[Fe(vbpy)_3]^{2+}$ as the PF_6^- salt. The dark red product was isolated and washed by repeated centrifugation and vacuum-dried overnight at room temperature.

Bis(4,4′-dimethyl-2,2′-bipyridine)(4-methyl-4′-vinyl-2,2′-bipyridine)ruthenium(II), $[Ru(Me_2bpy)_2(vbpy)]^{2+}$. A 170-mg (2.0 × 10^4 mol) sample of bis(4,4′-dimethyl-2,2′-bipyridine)dichlororuthenium(II) (prepared by the method of Meyer et al.[15]) and 39 mg (2.0 × 10^4 mol) of vbpy were added to 50 mL of methanol, and the solution was refluxed for 3 h. Purification was achieved by elution with methanol on a Sephadex LH-20 column. Addition of NH_4PF_6 and precipitation from H_2O afforded the hexafluorophosphate salt. The rust-orange product was isolated and washed by repeated centrifugation and vacuum-dried overnight at room temperature.

Electrodes and Instrumentation. A 16-cm^2 platinum mesh was used as the working electrode to provide a large surface area upon which the $[Fe(vbpy)_3]^{2+}$ polymer could be formed. Bulk electrolysis was conducted in a 100-mL cell with fritted reference and auxiliary compartments. The reductive polymerization was performed inside a Vacuum/Atmospheres inert-atmosphere box under N_2 to preclude any reaction of the reduced monomer or polymer with O_2. Potentiostatic reduction was conducted with a PAR Model 173 potentiostat and a Model 179 digital coulometer. An Ag/Ag^+ (0.1 M $AgNO_3$ in DMSO) reference electrode was used, although all potentials are corrected and reported relative to a saturated calomel electrode (SCE) unless otherwise stated (0.0 V vs SCE = −0.24 V vs Ag/Ag^+). All potentials are uncorrected for junction potential effects.

Procedure for Electropolymerization. In the inert-atmosphere box, 180 mg (1.9 × 10^{-4} mol) of $[Fe(vbpy)_3](PF_6)_2$ was added to approximately 10 mL of 0.1 M $(TBA)PF_6/CH_3CN$ electrolyte solution. The electropolymerization was carried out by stepping and holding the potential of the platinum working electrode at −1.90 V vs Ag/Ag^+ (−1.66 V vs SCE) for 4 h in a stirred solution. (While the polymer produced from this constant-potential polymerization from relatively concentrated solution is not expected to differ significantly from polymers prepared by potential cycling in more dilute solution, the difference between this and previous reported preparation procedures[2-12] should, nonetheless, be noted.) At the end of this 4-h period, the solution was only slightly purple, indicating that virtually all of the $[Fe(vbpy)_3]^{2+}$ had been incorporated into the polymer on the surface of the electrode. While a very small amount of solid polymer was floating free in solution, the great majority of the polymer adhered tightly to the electrode. The electrode was then potentiostated at 0.00 V followed by addition of excess I_2 to ensure that the polymer was completely reoxidized to the 2+ formal oxidation state. The entire bulk electrolysis setup was then removed from the inert-atmosphere box.

The polymer-coated Pt mesh electrode was removed from solution, rinsed with acetonitrile, and placed in concentrated HCl. After approximately 30 min, with slight heating, all of the polymer had dissolved from the electrode, and the solution had turned slightly brown-yellow, indicating that the iron had been extracted from the tris(bipyridine) complex. A 3-fold excess of cerric ammonium nitrate was then added to this solution to oxidize all of the iron(II) to iron(III). To this solution was added a large excess of Na_2EDTA and the pH increased to >6 through addition of 0.1 M KOH (in the absence of EDTA, upon an increase in pH, a pink color appears, indicating the remetalation of the bipyridines). Upon the increase in pH, a white precipitate of the polymerized vinylbipyridine ligand forms. The ligand polymer was extracted into CH_2Cl_2. This solution was dried over anhydrous $NaCO_3$, filtered, and rotary-evaporated to dryness, yielding a brown, tacky product.

Polymerization of the Copolymer $[Fe(vbpy)_3]^{2+}$-*co*-$[Ru(Me_2bpy)_2(vbpy)]^{2+}$. All copolymer experiments were conducted in the inert-atmosphere box to avoid O_2 oxidation of the polymer-coated electrode during transfer from the monomer-containing solution to clean electrolyte. Solutions of the monomers were prepared in the ratios indicated in Table I by addition of solid $[Ru(Me_2bpy)_2(vbpy)](PF_6)_2$ to a 3-mL solution of 1 mM $[Fe(vbpy)_3]^{2+}$ in 0.1 M $(TBA)PF_6/CH_3CN$. A 0.023-cm^2 Pt disk electrode was scanned between 0.0 and −1.8 V (vs SCE) for ten complete cycles at 100 mV/s resulting in the buildup of a polymer film on the electrode surface. The potential was then held at 0.0 V until no current passed to ensure that all of the polymer was in the 2+ formal oxidation state. The polymer-coated electrode was then rinsed with acetonitrile and transferred to clean electrolyte.

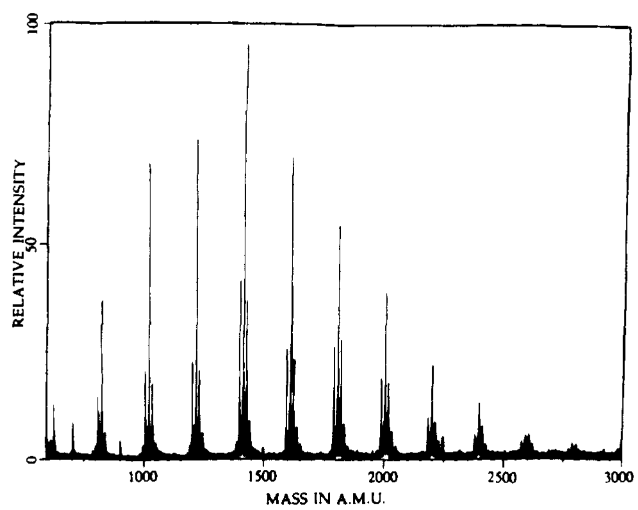

Figure 1. LDFTMS spectrum of poly-vbpy.

To quantitate the approximate amounts of mono- vs tris(vinylbipyridine) complexes incorporated in the films, the relative ratios of the ruthenium(III/II) and iron(III/II) redox waves were compared. In clean electrolyte, the potential of the polymer-coated electrode was scanned between 0.0 V and +1.5 V and recorded on the second scan. Manual integration of the redox waves was afforded by graphical deconvolution of the peaks followed by cutting and weighing.

Laser Desorption Fourier Transform Mass Spectrometry (LDFTMS). Spectra were recorded on a Nicolet FTMS-2000 spectrometer equipped with a 7.0-T superconducting magnet and Tachisto 215 CO_2 laser. The laser beam was focused to about a 1-mm spot size and had a pulse width of 80 ± 40 ns and power density of ca. 10^8 W/cm^2 at the probe tip. Both source and analyzer receive experiments were performed. Delay times between 3 and 10 s (typically 7 s) were employed after desorption and prior to excitation to allow desorbed neutrals to be pumped away. Samples were dissolved in methylene chloride, and the solutions were deposited on a stainless steel probe tip and evaporated to dryness prior to introduction into the vacuum chamber.

Results

Thin-Layer Chromatography (TLC). Results from TLC of the organic brown tacky product (obtained as above) on an alumina plate eluting with 10% acetone/CH_2Cl_2 clearly indicate at least six bipyridine-containing products. Each product has an R_f value less than, or equal to, that of 4-methyl-4′-vinyl-2,2′-bipyridine. The intensity of the spot having the same R_f as that of vbpy indicates that only ca. 5% remains as a monomeric form. Also, cospotting the product with an authentic sample of 1,4-bis(4′-methyl-2,2′-bipyridin-4-yl)butane (the product expected from diradical hydrodimerization) indicates that no more than 10% of the total product is due to tail-to-tail dimer.[16] Three remaining distinguishable spots exist above the origin, with the majority of the product remaining at the origin. An estimated 85–90% of the total bipyridine-containing products have R_f values less than the bis(bipyridin-4-yl)butane, suggesting that these bipyridines

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(16) On the basis of TLC alone, it is not possible to distinguish between bipyridines of similar polarity. Thus, product materials having R_f values indistinguishable from those of vbpy or 1,4-bis(4′-methyl-2,2′-bipyridin-4-yl)butane need not necessarily be these exact compounds. In that sense, the quantitation of the TLC results only provides an estimation of the maximum amount of a given compound that might be present. For example, 4-ethyl-4′-methyl-2,2′-bipyridine (the hydrogenation product of vbpy), which would be indistinguishable from vbpy and 1,3-bis(4′-methyl-2,2′-bipyridin-4-yl)butane (the radical-chain product terminated after dimer formation), would be indistinguishable from the hydrodimerization product, 1,4-bis(4′-methyl-2,2′-bipyridin-4-yl)butane.

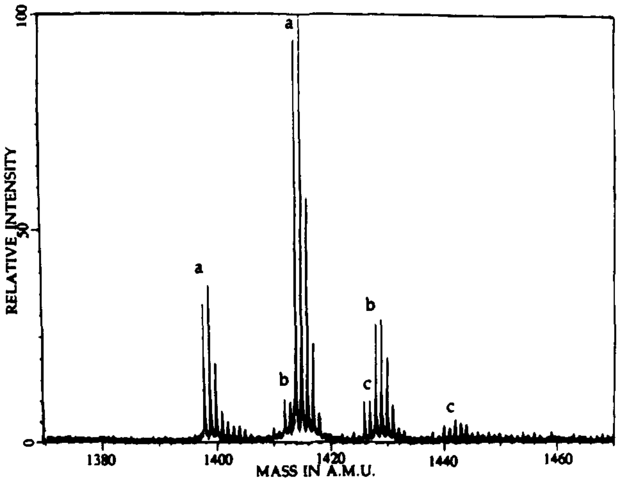

Figure 2. Expanded region of the LDFTMS spectrum of poly-vbpy.

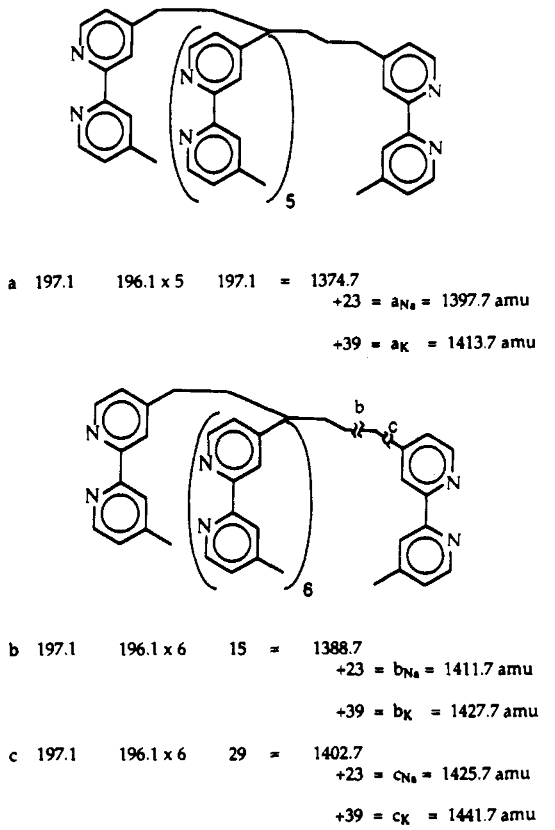

Figure 3. Possible structure for species a. Possible structure for species b and c.

exist as oligomers containing more than two monomer units.

Mass Spectral Analysis of Polymer

Laser Desorption Fourier Transfer Mass Spectrometry (LDFTMS). The LDFTMS spectrum for polymeric vbpy is shown in Figure 1. Analysis of a neat sample desorbed from the probe shows that the predominant polymeric component is the seven-unit polymeric vbpy chain. Additionally, a polydispersity value of 1.07 ± 0.01 was obtained, strongly indicating a radical intermediate polymerization mechanism.

Examination of the spectrum between 1380 and 1460 amu (Figure 2) indicates the presence of two and possibly three identifiable species labeled a, b, and c. Species a corresponds in mass to the intact seven-unit polymeric vbpy (Figure 3a). Species b may be identified as the eight-unit polymeric vbpy fragmented at the terminal vinyl carbon (Figure 3b). Species c may be identified as the eight-unit polymeric vbpy fragmented at the terminal bipyridine (Figure 3c). Due to the repeating-unit nature of the polymer, the indicated molecular structures are not the sole possibilities. The general formulas for each of the respective species are as follows:

$$\text{a:}\quad (197.1)_2 + (196.1)_n + (23 \text{ or } 39)$$

$$\text{b:}\quad (197.1)_2 + (196.1)_n + 15 + (23 \text{ or } 39)$$

$$\text{c:}\quad (197.1)_2 + (196.1)_n + 29 + (23 \text{ or } 39)$$

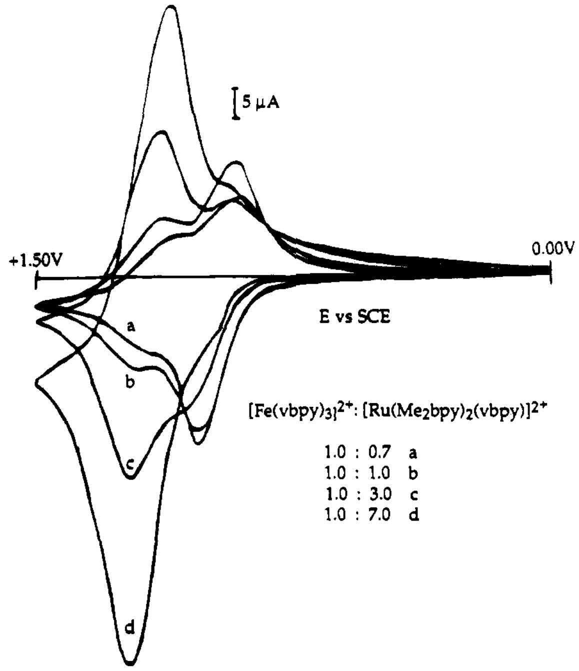

Figure 4. Cyclic voltammograms of copolymer films formed from solutions containing the corresponding monomer in the ratios indicated (see text for details).

For each species noted, the intensity of peaks at one or more atomic mass units (amu) above the noted species formula mass may be accounted for through the contribution of atomic isotopes. For example, the high-intensity peak at 1399 amu is the result of an 86% probability that the seven-unit polymer will contain at least one ^{13}C. Contributions from ^{2}H and ^{15}N isotopes also add intensity. The Na^+ and K^+ attachment ion peaks appear in a 1:2.7 intensity ratio, separated by 16 amu (^{39}K–^{23}Na), consistently throughout the spectrum.

The Copolymer $[Ru(Me_2bpy)_2(vbpy)]^{2+}$-*co*-$[Fe(vbpy)_3]^{2+}$. Copolymer films were formed from solutions containing both $[Ru(Me_2bpy)_2(vbpy)]^{2+}$ and $[Fe(vbpy)_3]^{2+}$ in order that we might study the relative incorporation rates of the two complexes. Figure 4 shows the anodic potential scan cyclic voltammograms of a series of these copolymer films. The $[Fe(vbpy)_3]^{3+/2+}$ redox couple at +0.97 V and the $[Ru(Me_2bpy)_2(vbpy)]^{3+/2+}$ couple at +1.17 V are clearly distinguishable except in the case where one of the species is at a much greater concentration than the other. Table I lists the normalized relative charge due to each type of complex (i.e. Fe or Ru) deposited in the polymer as determined by integration of the current. At a 1:1 ratio, the composition of the film is approximately 2:1 Fe to Ru. Statistically, a 3:1 ratio is expected. At the maximum relative concentrations of the ruthenium complex studied (1 mM Fe:7 mM Ru) the polymer film composition is approximately 1:6 Fe to Ru. Additionally, in the case of the 1:7 ratio, the absolute amount of mono(vinylbipyridine) complex ($[Ru(Me_2bpy)_2(vbpy)]^{2+}$) incorporated in a given copolymer film is significantly enhanced over that formed in a solution of the pure (no $[Fe(vbpy)_3]^{2+}$ present) mono(vinylbipyridine) complex at the same absolute concentration.

Discussion

The LDFTMS results leave little doubt that the electropolymerization of $[Fe(vbpy)_3]^{2+}$ is primarily, if not exclusively, via a normal polyvinyl-type mechanism. Given the similarities in structure, it is likely that this mechanism may be extended to other vbpy metal complexes (Fe, Os, and Ru). As pointed out earlier, several investigators have examined the electropolymerization of these and/or similar complexes and, primarily on the basis of electrochemical evidence, have arrived at the conclusion that hydrodimerization is the major mechanism for polymer formation. It is instructive, in light of our new electrochemical data, to reexamine the previous results and the arguments that led to the conclusion that hydrodimerization predominates in the mechanism of polymerization.

The studies most directly relevant to our present work are those involving Fe, Ru, and Os complexes ligated by only 2,2′-bipyridine derivatives. In complexes of the form $[M(L)_3]^{2+}$, where L = a substituted 2,2′-bipyridine ligand, reduction of the complex results in the addition of the electrons to π^* orbitals primarily localized on the bipyridine ligands.[17,18] Furthermore, each added electron is localized on a single bipyridine ligand within the complex. The exact nature of the reduced form a complex of the general structure MLL′L″ (where M = Fe, Os, or Ru, and the L's refer to different substituted bipyridines) depends on the identity of the various bipyridine ligands; more specifically, it depends on their respective reduction potentials. Since the polymerization efficiency of a complex containing vbpy should depend on the amount of radical-anion character which is experienced by the vinyl-containing bipyridine (irrespective of which of the two mechanisms is in force), it will also depend on the exact nature of the all of the ligands bound to the central metal. Unsubstituted 2,2′-bipyridine (bpy) bound to either ruthenium, osmium, or iron is about 100 mV easier to reduce than is the corresponding 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy).[19,20] Likewise, 4-methyl-4′-vinyl-2,2′-bipyridine is also significantly more difficult to reduce than is bpy, but less so than Me_2bpy.[19,20] This fact is true irrespective of the formal oxidation state of the overall complex; for example, when a complex such as $[Ru(bpy)_2(vbpy)]^{2+}$ is electrochemically reduced by two electrons, these electrons are largely (ca. 90%)[20] localized on the two bpy ligands, and not on the vbpy ligand. Therefore, vinylbipyridine has only marginal anion-radical character. It is for this reason that we have chosen to use $[Ru(Me_2bpy)_2(vbpy)]^{2+}$ rather than $[Ru(bpy)_2(vbpy)]^{2+}$ in our mixed-complex studies. Since the vinyl group is slightly electron withdrawing, the vbpy should be marginally easier to reduce than the Me_2bpy ligands; therefore the vbpy ligand should have significant anion-radical character when $[Ru(Me_2bpy)_2(vbpy)]^{2+}$ is reduced by one or more electrons.

This fact is borne out by a comparison of the composition of our mixed-complex polymers with those reported by Murray and co-workers.[2] In the previous studies, where $[Ru(bpy)_2(vbpy)]^{2+}$ was employed, only a small quantity of this complex was incorporated into copolymer films. In our case, using $[Ru(Me_2bpy)_2(vbpy)]^{2+}$, a nearly statistical composition results once a correction is made for the number of vinyl groups present per complex. The fact that copolymer films of $[Fe(vbpy)_3]^{2+}$ and $[Ru(Me_2bpy)_2(vbpy)]^{2+}$ contain a larger absolute amount of Ru complex than do films formed from solutions of pure Ru complex is also consistent with previous observations. For the pure Ru complex, linear polymers are formed, most likely containing seven or fewer monomer units. The lack of cross-linking would likely result in material that is soluble and that would not deposit on the electrode.

Another observation that has previously been made is that most of these vinyl-containing pyridine and bipyridine complexes polymerize much more rapidly and efficiently (often by more than a factor of 10) when the respective complex is reduced by two electrons rather than one. This fact has been used to bolster arguments favoring the hydrodimerization mechanism, since only a single reducing electron should be necessary to initiate a radical-chain or anionic polymerization. One point that has been overlooked in these discussions, however, is the potential effect of electrostatic interactions in the polymer-forming process. In our systems and the large majority of systems studied previously, the monomer possesses a formal 2+ charge prior to any electrochemical reduction. When reduced by one electron, these complexes are still positively charged, whereas, when reduced by two electrons, they are formally neutral. One would not expect a significant electrostatic work term to result from the dimerization of two formally 1+ charged complexes of this type if they were to simply approach one another, form a single linkage through two vinyl groups, and then remain in a fully extended conformation. For such a arrangement, the metal centers would be separated by more than 15 Å and the electrostatic work term is calculated to be only a few millivolts.[21] However, in order for chain propagation to continue, the two initially dimerized complexes cannot remain in a fully extended conformation. They must approach each other to a distance of ca. 7–8 Å (metal–metal); furthermore, as the third complex approaches, it will experience electrostatic repulsion from both of the original two complexes. We have observed in previous studies that the electrostatic work term for a pair of formally 1+ tris(bipyridine)iron centers held at 7.6 Å is ca. 84 mV.[21] It therefore seems reasonable to postulate that at least part of the reason that the doubly reduced complexes polymerize more rapidly and efficiently than their singly reduced counterparts is simply electrostatic in origin; namely, the doubly reduced complexes are, overall, electrically neutral.[22]

Finally, for cases where the non-vinyl-containing ligands are not 2,2′-bipyridines or where the vinyl-containing ligands are not vbpy, the relevance of the present study is less direct. In cases where the overall charge on the original complex is 2+, for example $[Ru(phen)_2(vbpy)]^{2+}$ (phen = 9,10-phenanthroline), the electrostatic arguments are still valid, and thus doubly reduced complexes should polymerize better, irrespective of the mechanism. It seems likely to us that, in cases where one or more vbpy ligands are present in the complex, the chain propagation mechanism should participate to a significant degree in polymer formation, at least in the absence of other mechanisms that would form polymer at a significantly more rapid rate. In the case of vinylpyridine (as opposed to vbpy) complexes, there are no steric considerations that can be used to argue against a chain propagation mechanism. We thus speculate that such a mechanism is likely to be of significant importance in the formation of most, if not all, of these polymers as well.

Acknowledgment. We thank the U.S. Department of Energy Office of Basic Energy Sciences (Grant No. DE-FGO2-81ER13666) for support of this work.

Registry No. $[Fe(vbpy)_3](PF_6)_2$, 81315-18-6; $[Ru(Me_2bpy)_2(vbpy)](PF_6)_2$, 124355-13-1; $[Fe(vbpy)_3](PF_6)_2$ (homopolymer), 81315-15-3; $Ru(Me_2bpy)_2Cl_2$, 124355-11-9; vbpy, 74173-48-1; $FeSO_4$, 7720-78-7; NH_4PF_6, 16941-11-0; $([Fe(vbpy)_3](PF_6)_2)([Ru(Me_2bpy)_2(vbpy)](PF_6)_2)$ (copolymer), 124355-15-3.

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(22) Note added in proof: One reviewer found the arguments presented here relating formal change to polymerization rate to be "plausible, but...not convincing". Subsequently, we have examined the polymerization rates of several additional vbpy-containing ruthenium complexes. The results from two of these complexes bear directly on the point at hand; the relevant complexes are $Ru(vbpy)_2(CN)_2$ and $Ru(vbpy)_2(Mcbpy)^+$, where Mcbpy is the formally 1− charged ligand 4-methyl-4′-carboxylato-2,2′-bipyridine. Attempts to polymerize the formally neutral $Ru(vbpy)_2(CN)_2$ complex produced very little polymer irrespective of whether the polymerization was carried out at the first or second bipyridine reduction. In this instance, the charges on the respective reduction products would be formally 1− and 2−. Most significant to the present argument, however, is the result obtained with the monocationic complex $Ru(vbpy)_2(Mcbpy)^+$. In this case, for identical constant-potential polymerization times, significantly *more* polymer is deposited by reduction at the first peak (producing a formally neutral species) than is deposited by reduction at the second peak (producing a formally 1− species). This result is exactly what is predicted from our charge-repulsion argument. The details of this study will appear elsewhere, but we do not know of a single example, from our own work, or that of others, where an electrochemical polymerization of a vinylbipyridine-containing metal complex is *inconsistent* with the charge-repulsion arguments we have developed here.