polymer poly(4-[*tert*-butoxycarbonyl)oxy]styrene) even when exposed to X-ray doses which were more than 100% higher than those used to develop images in the least sensitive PTBSS copolymer.

For the PTBSS copolymers, the X-ray response was shown to be a function of copolymer composition and independent of molecular weight. It was observed that increasing the sulfur dioxide content enhanced the resist sensitivity.

The X-ray-induced reaction mechanism is proposed to be initiated via copolymer main-chain scission. At the scission sites, radical species are produced which in turn are responsible for the formation of acidic moieties. Such moieties may exist as either sulfinic or sulfonic acid end groups of the fragmented polymer chain. Likewise, it is reasonable to assume that the acidic moieties may exist as free molecules such as sulfurous or sulfuric acid. The ratio of G(acid) to that for G(scission) has shown that approximately 50% of all scission sites produce an acid moiety which is subsequently used during the deprotection reaction.

Preliminary lithographic evaluation of these materials demonstrated that for a 1.75:1 TBS:SO_2 copolymer, the X-ray dose necessary to resolve 0.5-μm features is 10 mJ/cm^2 and is independent of the initial film thickness of the resist. Approximately 90° pattern profiles are observed for these features, and this is largely attributable to the extremely high contrast (>6) of these materials. High contrast is postulated to result from the fact that dissolution in the aqueous base developer does not occur until at least 95% of *t*-BOC groups have been removed. It can therefore be expected that the dependence of line width on development conditions will be minimized or that changing the normality of the developer or increasing the development time should have little or no effect on line width.

Further studies elucidating the structure of the acid species will be conducted, and the knowledge gained will be applied to resist formulations used in photolithographic technologies.

Acknowledgment. We thank Paula Trevor for X-ray fluorescence measurements, Hampshire Instruments technical and engineering support staff for X-ray exposures and resist process development, and Dave Mixon, Mike Bohrer and Ed Chandross for many helpful discussions.

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Use of Rutherford Backscattering Spectroscopy To Investigate Anion Exchange Constants of Protonated Poly(4-vinylpyridine)

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Rutherford backscattering spectroscopy (RBS) can be used to measure the competitive electrostatic binding of two anionic metal complexes in protonated poly(4-vinylpyridine), $(\mathrm{VPyH^+})_n$. RBS was done using a 2–3-MeV He^+ or He^{2+} ion beam from a tandem accelerator. The elemental composition was measured for polymer films of <0.5-μm thickness coated onto carbon substrates. Anions such as $\mathrm{Fe(CN)_6^{4-}}$, $\mathrm{Mo(CN)_8^{4-}}$, and $\mathrm{IrCl_6^{3-}}$ can be persistently electrostatically bound into the $(\mathrm{VPyH^+})_n$, and the resulting polymer films can be quantitatively analyzed by RBS. The equilibrium constants for the equilibria between two metal complexes in the solution and in the polymer, as expressed by the equations

$$[\mathrm{4VPyH^+ \cdot Fe(CN)_6^{4-}}]_n + n\mathrm{Mo(CN)_8^{4-}} \overset{K_1}{\rightleftharpoons} n\mathrm{Fe(CN)_6^{4-}} + [\mathrm{4VPyH^+ \cdot Mo(CN)_8^{4-}}]_n$$

$$4[\mathrm{3VPyH^+ \cdot IrCl_6^{3-}}]_n + 3n\mathrm{Fe(CN)_6^{4-}} \overset{K_2}{\rightleftharpoons} 4n\mathrm{IrCl_6^{3-}} + 3[\mathrm{4VPyH^+ \cdot Fe(CN)_6^{4-}}]_n$$

$$3[\mathrm{4VPyH^+ \cdot Mo(CN)_8^{4-}}]_n + 4n\mathrm{IrCl_6^{3-}} \overset{K_3}{\rightleftharpoons} 3n\mathrm{Mo(CN)_8^{4-}} + 4[\mathrm{3VPyH^+ \cdot IrCl_6^{3-}}]_n$$

can be determined using RBS analysis of surface composition and knowledge of the solution concentrations of metal complexes used to modify the surface. The product $(K_1{}^3K_2K_3)$ of the three measured constants is very close to the expected value of 1. RBS data correlate well with polymer composition established by electrochemical measurements, but RBS data are more quantitative. The electrochemical data are not as reliable, due to overlapping electrochemical responses of the anionic metal complexes.

We wish to report use of Rutherford backscattering spectroscopy (RBS) to establish essential features of the composition of polycationic films on carbon substrates. In particular, we demonstrate use of RBS to measure the relative concentration of anionic metal complexes in protonated poly(4-vinylpyridine), $(\mathrm{VPyH^+})_n$. The data are useful for determining equilibrium constants for anion exchange processes such as those shown in eqs 1–3. The

$$[\mathrm{4VPyH^+ \cdot Fe(CN)_6^{4-}}]_n + n\mathrm{Mo(CN)_8^{4-}} \overset{K_1}{\rightleftharpoons} n\mathrm{Fe(CN)_6^{4-}} + [\mathrm{4VPyH^+ \cdot Mo(CN)_8^{4-}}]_n \quad (1)$$

$$4[\mathrm{3VPyH^+ \cdot IrCl_6^{3-}}]_n + 3n\mathrm{Fe(CN)_6^{4-}} \overset{K_2}{\rightleftharpoons} 4n\mathrm{IrCl_6^{3-}} + 3[\mathrm{4VPyH^+ \cdot Fe(CN)_6^{4-}}]_n \quad (2)$$

$$3[\mathrm{4VPyH^+ \cdot Mo(CN)_8^{4-}}]_n + 4n\mathrm{IrCl_6^{3-}} \overset{K_3}{\rightleftharpoons} 3n\mathrm{Mo(CN)_8^{4-}} + 4[\mathrm{3VPyH^+ \cdot IrCl_6^{3-}}]_n \quad (3)$$

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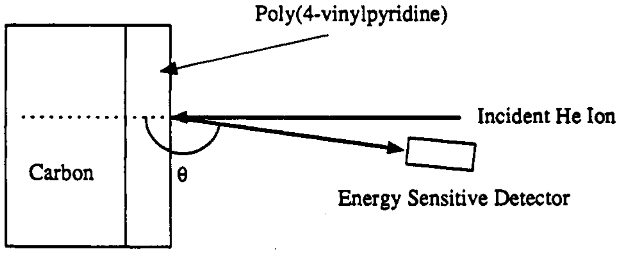
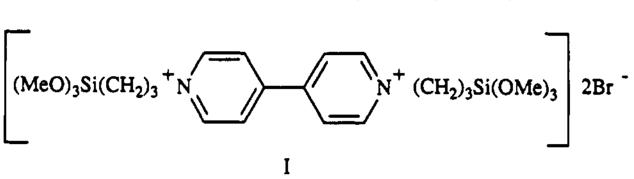
Scheme I. Layout of RBS Experiment



validity of the equilibrium constant measurements can be checked by the fact that the three equilibrium constants are not independent. The product $(K_1{}^3K_2K_3)$ should be close to unity as shown in the Appendix.

The electrochemistry of anions bound in $(VPyH^+)_n$ has been widely studied.[1-7] Such redox-active materials may be used in electrocatalysis,[8-10] photoelectrochemistry,[11,12] batteries,[13,14] and microelectrochemical devices.[15] The electrochemistry of anions bound in $(VPyH^+)_n$ depends on the charge propagation via the electrochemically active anions electrostatically incorporated into the polymer. The majority of the previous work concerning anions bound in $(VPyH^+)_n$ has focused on investigations of the mechanism of charge propagation and the associated diffusion constants of metal complexes bound in the polymer. The present work establishes methodology for quantitative assessment of the binding constants for anions in $(VPyH^+)_n$. Quantitative understanding of the competitive binding is very important in situations where two or more anionic species are present in the solution, as in the case of detecting two or three electroactive, anionic metal complexes using a microelectrochemical device based on competitive, electrostatic binding of the analyte.[16]

By employing electrochemical techniques, Martin measured the binding constants for cations in Nafion films on electrodes.[17] By employing electrochemical techniques and Auger spectroscopy, previous work in this laboratory has established the qualitative binding order of a few anionic species in the polycation formed from hydrolysis of I.[18] In another study, by employing electrochemical techniques, binding of Cl^- and $Fe(CN)_6{}^{4-}$ in the polymer from II has been quantitatively studied.[19] Our new work shows RBS to be a highly quantitative technique which could be applied to a variety of polymer systems.



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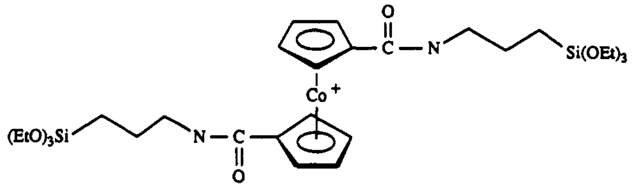

II

RBS is widely used in characterization of semiconductor and ceramic materials.[20-24] RBS is suitable for establishing composition of sufficiently thin polymer samples (<1 μm), and the technique is thus applicable to polymer-modified electrodes. Unlike surface analytical techniques (X-ray photoelectron spectroscopy, Auger spectroscopy, and secondary ion mass spectroscopy), RBS can give the composition of the entire thickness of a thin polymer film rather than that of only the first few monolayers. Importantly, the backscattering of He ions is insensitive to the chemical state of the elements present. Thus, RBS can provide reliable measures of elemental composition for a variety of polymer material systems. Recently, RBS has emerged as a useful tool to study diffusion of iodine and iodoalkanes in polystyrene.[25-27] In connection with studies of diffusion, RBS is useful because one can determine the composition of the polymer as a function of depth with a resolution of about 10 nm. In our work, we show RBS to be useful for electrodes modified with thin films where the composition is expected to be uniform.

We now give a brief summary of the principles of RBS[20] relevant to this work. The experimental arrangement is shown in Scheme I. The elemental information comes from measurement of the number of backscattered He ions (He^+ or He^{2+}) as a function of energy, E, given in eq 4,

$$E = KE_0 \qquad (4)$$

where E is the energy of the surface backscattered He ions, E_0 is the incident He ion energy, and K is the kinematic factor given by eq 5. In eq 5, M_1 and M_2 are the masses of the incident ion and the target nucleus, respectively, and θ is the backscattering angle. It should be noted that the

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$$K = \left\{\frac{[1 - (M_1/M_2)^2 \sin^2 \theta]^{0.5} + (M_1/M_2) \cos \theta}{1 + (M_1/M_2)}\right\}^2 \qquad (5)$$

elemental information of thin films may be lost if the masses of the substrate nuclei are larger than the elements to be analyzed. This difficulty is circumvented in analyzing polymer-modified electrodes by using carbon as the substrate. In principle, any element with a mass larger than carbon can thus be analyzed. In RBS studies of thin polymer films on a carbon substrate, each element heavier than carbon will give a peak in the spectrum. The position of each peak on the energy axis of the spectrum depends on the mass of the element investigated, the value of E_0, and the incident ion mass, eqs 4 and 5. Generally, calibration standards are used to establish the peak positions for the elements under the conditions used in analysis. For sufficiently thin films the peak positions are independent of the film thickness. The minimum width of the peak for each element is governed by the resolution of the detector, but in our polymer films the width is governed by the thickness, density, and distribution of elements in the films. To avoid element peaks that overlap with each other, we have typically used films of <0.5 μm. Flat substrates are best for RBS investigation because a film of uniform thickness is easy to obtain on a flat surface. For a homogeneous film, the width of the RBS peak for an element in the film can be used to determine film thickness.

Quantitative information regarding composition from RBS is obtained from the relative area of the peaks for each element. The Rutherford scattering cross section, σ, is given by eq 6, where Z_1 and Z_2 are the atomic numbers

$$\sigma = (Z_1Z_2e^2/4E_0)^2 \, [\sin^{-4} (\theta/2) - 2(M_1/M_2)^2 + ...] \qquad (6)$$

of the incident ion and target nucleus, respectively. The cross section given by eq 6 shows that RBS is very sensitive for heavy elements and not very sensitive for light elements (C, N, O, and F). However, for high-energy incident beams, the cross section for light elements may be increased owing to the fact that the helium ion can penetrate the nucleus and resonances occur. For instance, the cross section for O is anomalously increased at 3.04 MeV due to nuclear resonance.[28] In the case of $(VPyH^+)_n$, where we are interested in the element nitrogen, each polymer repeat unit contains one nitrogen atom. Thus, the amount of nitrogen in the polymer is high. The lower sensitivity of nitrogen is therefore not a significant problem. The measurement of heavy elements, e.g., Fe (atomic number 26), Mo (atomic number 42), and Ir (atomic number 77), for the anions in eqs 1–3 is relatively easy, since σ varies with the square of the atomic number.

Experimental Section

Chemicals. Poly(4-vinylpyridine) of molecular weight 200 000 daltons was used as received from Reilly Tar and Chemical Co., Indianapolis. $K_4Mo(CN)_8$ was available from a previous study.[29] Omnisolv H_2O was used. Vitreous carbon plates were received from Atomergic Chemetals. Alumina and diamond polish compounds and polish cloth were received from Buehler Analyst. All other chemicals were used as received from Aldrich Chemicals.

Electrochemistry. All electrochemistry was carried out in 0.2 M $NaCOOCF_3/HCOOCF_3$ (pH = 1.5) aqueous solution at 25 °C. The counter electrode was a Pt flag electrode, and the reference electrode was a saturated calomel electrode, SCE. All electrochemical experiments were carried out in a single-compartment cell under N_2. Cyclic voltammetry was done using a Pine Instruments Model RDE-4 bipotentiostat and cyclic voltammograms were recorded with a Kipp and Zonen BD 91 X–Y recorder.

Sample Preparation. Pieces of vitreous carbon (1 × 1 cm squares of 0.4-cm thickness for RBS analysis and 0.5 × 0.5 cm squares of 0.4-cm thickness for electrochemical analysis) were cut from vitreous carbon plate and were polished sequentially with 3-, 1-, and 0.25-μm diamond polish compound. The polish clothes used were Texmet (for 3- and 1-μm diamond polish compounds) and Rayvel (for 0.25-μm diamond compounds). The final polished samples had almost no detectable features by optical microscopy. Carbon electrodes were constructed by connecting a copper wire to the vitreous carbon pieces by means of silver epoxy. The copper wires were passed through Pyrex tubing. The edges and back of the electrodes were completely sealed with white epoxy, leaving only the surface of the carbon exposed.

Poly(vinylpyridine) was coated onto vitreous carbon electrode surfaces by micropipetting 2–3 μL of 0.25% w/v poly(4-vinylpyridine) in CH_3OH containing 0.6 mM 1,6-dibromohexane. The electrodes were allowed to dry at room temperature for 10 min. The electrodes were then heated at 80 °C for 5 h to promote cross-linking via the solid-state alkylation reaction of the 1,6-dibromohexane with the pyridyl nitrogen.[8] Samples for RBS analysis were prepared in a similar fashion.

Incorporation of metal complexes was brought about by dipping the carbon electrodes and RBS samples coated with poly(4-vinylpyridine) into the deoxygenated electrolyte containing the desired metal complexes for at least 30 min. A loading time of 30 min ensures that equilibrium is reached between metal complexes in solution and in $(VPyH^+)_n$, as evidenced by the constancy of cyclic voltammetry waves for the bound metal complexes after exposure to the loading solution for greater than 30 min. The carbon electrodes were held at 0 V during the loading process to ensure that all metal complexes were in their reduced forms. The electrodes and RBS samples were then washed thoroughly with deoxygenated pure electrolyte and either examined by cyclic voltammetry or dried in air and analyzed by RBS.

RBS Experiments. A beam of He^+ or He^{2+} (2 or 3 MeV) from a tandem accelerator (General Ionex Corp. Model 4117) was focused on a 1 mm^2 spot of sample. The backscattered He^{2+} at 176° were analyzed by a silicon-charged particle radiation detector (EG&G ORTEC) with a solid angle of 10.30 msr. The detector resolution was 30 keV. The output of the detector was amplified and fed into a multichannel analyzer. The charge collected was between 5 and 10 μC. The instrument was calibrated with a Si sample coated with Au and Cr.

Results and Discussion

Anionic metal complexes electrostatically bind to $(VPyH^+)_n$.[1–7] The binding of metal complexes becomes competitive when two or more anionic metal complexes are in the solution. For electroactive anionic metal complexes the competition can be assayed by electrochemical methods. Figure 1 shows the cyclic voltammetry for three $(VPyH^+)_n$-coated carbon disk electrodes into which redox-active anions have been incorporated. The cyclic voltammetry waves are due to the electrostatically bound complexes, since $(VPyH^+)_n$ alone exhibits no electrochemical response in the potential region shown. Incorporation of the metal complexes was brought about by dipping (for 30 min) the electrodes into a deoxygenated electrolyte containing a 1:1 ratio of two anionic metal complexes. The electrodes were then examined by cyclic voltammetry in pure electrolyte solution containing no redox-active molecules. The loss of metal complexes to the pure electrolyte is very slow, as evidenced by the constancy (for >30 min) of cyclic voltammetry waves for the bound metal complexes. Figure 1, parts a and c, show $Mo(CN)_8^{4-}$ to be selectively bound by $(VPyH^+)_n$-coated electrodes compared to either $Fe(CN)_6^{4-}$ and $IrCl_6^{3-}$, respectively. The selectivity is established by the relative

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Table I. Binding of Metal Complexes in Protonated Poly(4-vinylpyridine) from Electrochemical Measurements

	equilibration solution[a]			film composition[b]			
electrode no.	$[Fe(CN)_6^{4-}]$	$[Mo(CN)_8^{4-}]$	$[IrCl_6^{3-}]$	$[Fe(CN)_6^{4-}]$	$[Mo(CN)_8^{4-}]$	$[IrCl_6^{3-}]$	equilibrium const[c]
1	10.4	0.967		0.16	0.092		$K_1 = 6.3$
2	10.4	0.967		0.15	0.10		$K_1 = 7.6$
3	10.5	0.725		0.16	0.090		$K_1 = 8.2$
							av $K_1 = 7.3$
4	5.49		5.13	0.10		0.19	$K_2 = 3.3 \times 10^{-3}$
5	5.02		4.86	0.11		0.19	$K_2 = 4.8 \times 10^{-3}$
6	4.92		4.29	0.12		0.18	$K_2 = 4.8 \times 10^{-3}$
							av $K_2 = 4.3 \times 10^{-3}$
7		1.45	9.15		0.092	0.21	$K_3 = 1.1$
8		1.53	7.85		0.090	0.21	$K_3 = 2.7$
9		1.65	8.12		0.090	0.21	$K_3 = 2.9$
							av $K_3 = 2.2$

[a] Concentrations of anionic complexes in millimolar. [b] Concentrations of redox-active anions in $(VPyH^+)_n$ expressed as ratios of each metal complex to pyridinium subunit. [c] Equilibrium constants are calculated according to eqs 1–3.

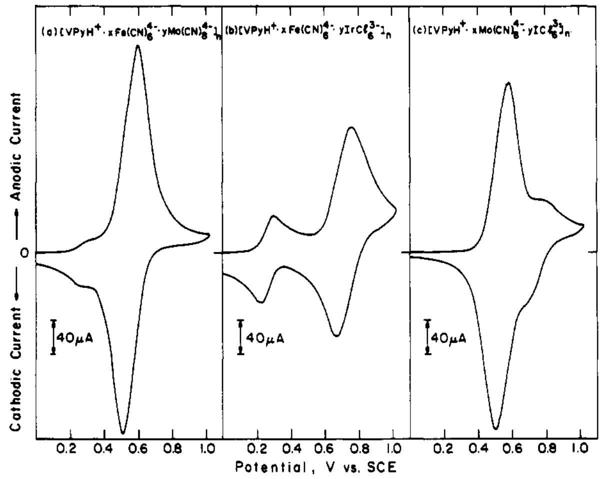

Figure 1. Cyclic voltammograms of $C/(VPyH^+)_n$ electrodes in 0.2 M $Na[CF_3COO]/CF_3COOH$ (pH = 1.5) aqueous electrolyte. (a, left) Electrode taken from a loading solution of 1 mM $Fe(CN)_6^{4-}$ and 1 mM $Mo(CN)_8^{4-}$. (b, center) Electrode taken from a loading solution of 1 mM $Fe(CN)_6^{4-}$ and 1 mM $IrCl_6^{3-}$. (c, right) Electrode taken from a loading solution of 1 mM $Mo(CN)_8^{4-}$ and 1 mM $IrCl_6^{3-}$. Sweep rates are 100 mV/s, and the total coverage of $VPyH^+$ unit is 10^{-7} mol/cm^2. These data establish the following qualitative order of binding: $Mo(CN)_8^{4-} \gg IrCl_6^{3-} > Fe(CN)_6^{4-}$. The $E_{1/2}$ values for the Fe, Mo, and Ir complexes are ~+0.25, ~+0.55, and +0.72 V vs SCE, respectively.

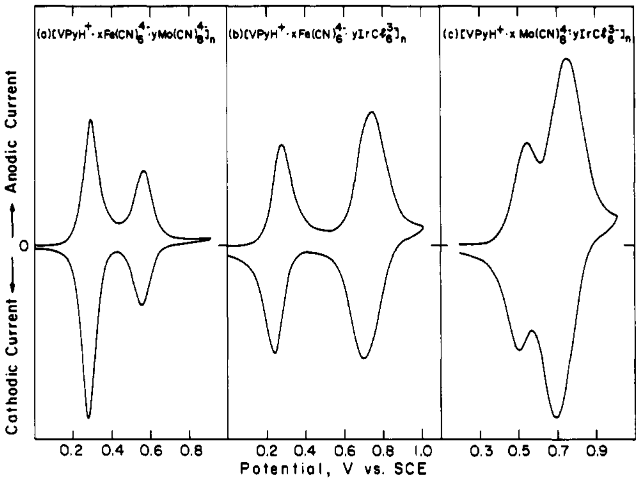

Figure 2. Cyclic voltammograms of $C/(VPyH^+)_n$ electrodes in 0.2 M $Na[CF_3COO]/CF_3COOH$ (pH = 1.5) aqueous electrolyte. (a, left) Electrode taken from a loading solution of 1 mM $Fe(CN)_6^{4-}$ and 0.1 mM $Mo(CN)_8^{4-}$. (b, center) Electrode taken from a loading solution of 1 mM $Fe(CN)_6^{4-}$ and 1 mM $IrCl_6^{3-}$. (c, right) Electrode taken from a loading solution of 0.1 mM $Mo(CN)_8^{4-}$ and 1 mM $IrCl_6^{3-}$. Sweep rates are 10 mV/s, and the total coverage of $VPyH^+$ unit is 10^{-7} mol/cm^2. These data allow integration of the waves to establish relative surface concentrations of the redox-active anions. The $E_{1/2}$ values for the Fe, Mo, and Ir complexes are ~+0.25, ~+0.55, and ~+0.72 V vs SCE, respectively.

area of cyclic voltammetry waves for the various complexes. Figure 1b shows that $Fe(CN)_6^{4-}$ and $IrCl_6^{3-}$ bind to $(VPyH^+)_n$ similarly, with $IrCl_6^{3-}$ binding somewhat more strongly than $Fe(CN)_6^{4-}$.

Qualitative data establish the binding order of $Mo(CN)_8^{4-} \gg IrCl_6^{3-} > Fe(CN)_6^{4-}$ in $(VPyH^+)_n$. The binding can be quantitatively assessed experimentally. Consider the equilibria represented by eqs 1–3. When $(VPyH^+)_n$ is immersed in the loading solution for more than 15 min, the two metal complexes in the solution equilibrate in $(VPyH^+)_n$. We assume that the equilibrium condition is reached after 15 min, since the cyclic voltammetry waves for surface-bound species do not change with longer equilibration times. The charges of the anionic metal complexes are considered in expressing the equilibrium, because the anionic metal complexes are electrostatically bound in $(VPyH^+)_n$. This electrostatic nature is evidenced by two facts: (1) cationic metal complexes are not bound in $(VPyH^+)_n$;[16] (2) the amount of anionic metal complex bound in $(VPyH^+)_n$ roughly equals the amount required to totally charge compensate the cationic polymer (vide infra).

Figure 2 shows slow scan cyclic voltammetry waves for anionic metal complexes bound in $(VPyH^+)_n$ electrodes. Such cyclic voltammetry is used to quantitatively assay the relative surface concentrations of bound complexes. The electrodes were first loaded with various metal complexes by dipping in buffered (pH = 1.5) electrolyte containing 1 mM $K_4Fe(CN)_6$ and 0.1 mM $K_4Mo(CN)_8$; 1 mM $K_4Fe(CN)_6$ and 1 mM K_3IrCl_6; or 1 mM K_3IrCl_6 and 0.1 mM $K_4Mo(CN)_8^{4-}$ for 30 min. The electrodes were then transferred to pure electrolyte to be examined by cyclic voltammetry. For Figure 2 the concentration of $Mo(CN)_8^{4-}$ in the loading electrolyte is 1 order of magnitude smaller than that of the two other metal complexes, to ensure not only that $Mo(CN)_8^{4-}$ is bound in $(VPyH^+)_n$ but also that a significant amount of $Fe(CN)_6^{4-}$ or $IrCl_6^{3-}$ is bound in $(VPyH^+)_n$. Table I summarizes the electrochemically assayed concentrations and the calculated equilibrium constants for the equilibria 1–3. The amount of metal complex bound in $(VPyH^+)_n$ is determined from integration of the anodic cyclic voltammetry wave for the metal complex. The concentrations of the metal complexes bound in the polymer are expressed as the mole ratios of metal complex to pyridinium subunit of the polymer. Every pyridine unit in the polymer is assumed to be protonated and to be totally charge compensated by the anionic metal complexes. The equilibrium constants obtained from cyclic

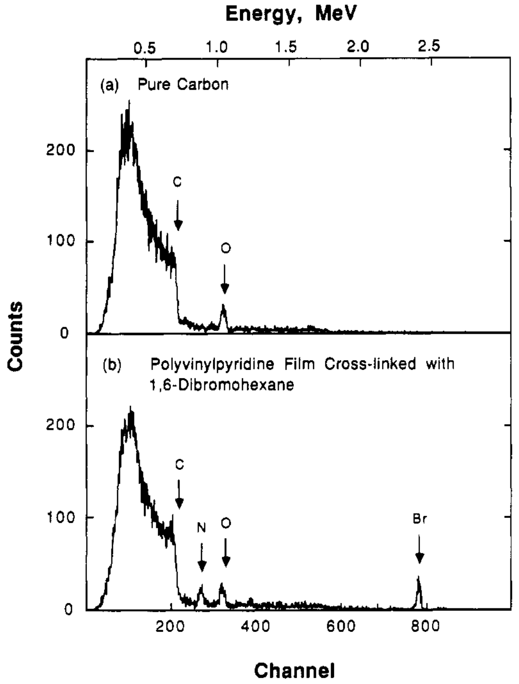

Figure 3. (a) RBS of a polished vitreous carbon sample. (b) RBS of poly(4-vinylpyridine) coated onto a vitreous carbon substrate. The incident ion beam is 3-MeV He^{2+}.

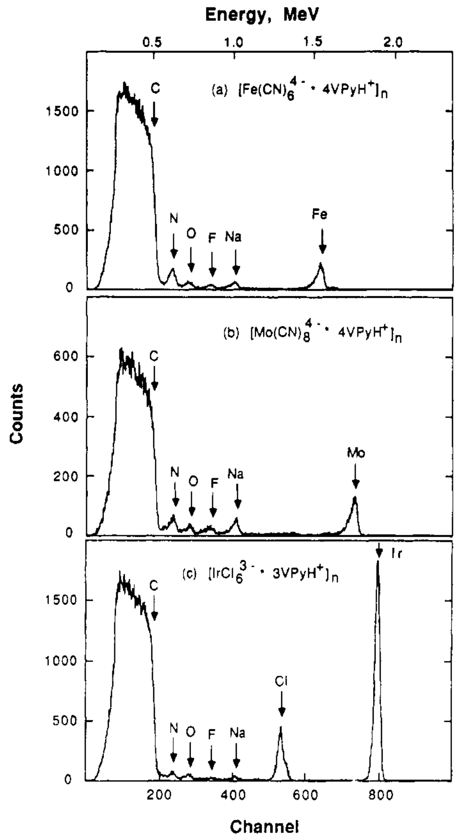

Figure 4. RBS of $(VPyH^+)_n$ loaded with (a, top) $Fe(CN)_6^{4-}$, (b, middle) $Mo(CN)_8^{4-}$, and (c, bottom) $IrCl_6^{3-}$. The incident ion beam is 2-MeV He^+.

voltammetry do have errors owing to problems with baseline subtraction and overlapping cyclic voltammetry waves. More accurate equilibrium constants can be obtained by RBS, as presented below, and RBS can be useful when the bound species are not redox active.

Figure 3a shows the RBS of a naked carbon sample. Only the elements C and O are detected. No N, Cl, or metal elements are detected. The point is that when elements other than C or O are observed for polymer-coated carbon substrates, they are solely due to the presence of elements unique to the polymer films. Figure 3b shows the RBS of freshly prepared, nonprotonated poly(4-vinylpyridine) film on carbon without any bound metal complex. Two extra elements, N and Br, are observed, in addition to C and O. Br comes from the dibromohexane cross-linking reagent. As described in the Experimental Section, a small amount of dibromohexane is mixed with the polymer during the film-casting procedure. One unfortunate aspect is that we cannot distinguish the C in the polymer from the carbon substrate. However, the N peak can be used to gauge the amount of $(VPyH^+)_n$ in the analysis of the amount of metal complex bound in $(VPyH^+)_n$ films.

Figure 4 shows RBS of $(VPyH^+)_n$ films loaded with $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, or $IrCl_6^{3-}$. The spectra show all of the expected elements. In addition, Na and F are observed. These are due to unremoved supporting electrolyte from the loading procedure which concludes with rinsing the electrodes with the $Na[CF_3COO]$ buffer and then drying. Presumably, some $Na[CF_3COO]$ remains on the surface. The Br peak we observed for freshly prepared polymer film is extremely small or nonevident. This loss of the Br signal indicates that there is little if any unreacted dibromohexane that remains in the cross-linked film and that the anionic metal complexes replace the Br^- in the films.

Before quantitative analysis is attempted, one point should be considered regarding the applicability of RBS in quantitative analysis of polymer films. It has been noted that O loss occurs during RBS analysis of polymer samples containing O.[21] The O presumably escapes from the polymer samples as gas because of the radiation damage of the polymer samples induced by the high-energy ion beam. The O signal is relatively uninteresting, because we cannot distinguish the O in the polymer from the O of the carbon substrate. However, we do find that loss of N occurs during RBS experiments. At normal (10 nA) or extremely low (0.3 nA) beam currents, the loss of N amounts to 5–20% during the measurements. This N loss could not be prevented by liquid nitrogen cooling of the sample, although it has been reported[21,23] that liquid nitrogen cooling of the sample can prevent O loss during RBS experiments. At high beam currents (>40 nA, He^+), the N loss is reduced to less than 10% during the time required to record useful data. The smaller N loss at high beam current may be attributed to the fact that less time is required to obtain a RBS spectra at high beam current than at normal (10 nA) beam current. We have also found that the loss of N is less without $Fe(CN)_6^{4-}$ or $Mo(CN)_8^{4-}$ in the polymer. With only $IrCl_6^{3-}$ or no metal complex in $(VPyH^+)_n$, the loss is less than 5% at high beam current. It seems, therefore, that N of the CN group is the most labile N of the $(VPyH^+)_n$-containing cyanometallates. The amount of N inside the polymer may be underestimated by 0–10% when $Fe(CN)_6^{4-}$ or $Mo(CN)_8^{4-}$ is bound into $(VPyH^+)_n$ or 0–5% when $IrCl_6^{3-}$ is bound into the polymer.

The amount of each element in the polymer, N_i (atoms/cm^2), can be calculated from the total number of counts integrated over the region of interest, A_i, as expressed by eq 7, where σ_i is the cross section calculated

$$N_i = A_i/(\sigma_i \Omega Q) \qquad (7)$$

from eq 6, Ω is the detector solid angle, and Q is the amount of charge collected during the measurement. The key element ratios of the three $(VPyH^+)_n$ films characterized by RBS data in Figure 4 are given in Table II. The

Table II. Compositions of Pure Anionic Metal Complex in $(VPyH^+)_n$ Films As Measured by RBS[a]

nominal sample	key element ratio	measured composition
$[4VPyH^+ \cdot Fe(CN)_6^{4-}]_n$	N:Fe = 9.86:1	$[3.77VPyH^+ \cdot Fe(CN)_6^{4-}]_n$
$[4VPyH^+ \cdot Mo(CN)_8^{4-}]_n$	N:Mo = 12.2:1	$[4.21VPyH^+ \cdot Mo(CN)_8^{4-}]_n$
$[3VPyH^+ \cdot IrCl_6^{3-}]_n$	N:Ir:Cl = 3.11:1:5.96	$[3.11VPyH^+ \cdot IrCl_6^{3-}]_n$

[a] Samples were prepared from 0.2 M $Na[CF_3COO]/CF_3COOH$ (pH = 1.5) aqueous solution containing 1 mM metal complex.

RBS data are very close to the ratios expected for complete charge compensation of $(VPyH^+)_n$ by $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, or $IrCl_6^{3-}$. Considering some uncertainty in the estimation of the amount of *N*, we estimate that the pyridinium units of $(VPyH^+)_n$ are at least 90% charge compensated by the anionic metal complexes. Specifically, we find little or no charge compensating anion other than the metal complex anions.

The competitive binding of anionic metal complexes in $(VPyH^+)_n$ can be studied when the loading solutions contain two anionic metal complexes. Figure 5 shows the RBS of three polymer films into which two metal complexes are bound. Again, the spectra show all the expected elements. The peak separations between each key element are excellent, allowing quantitative analysis of the composition of the polymer samples. The key element ratios of the polymer films obtained from these RBS data are given in Table III. Again pyridinium units of the polymer are nearly totally charge compensated by the anionic metal complexes. The higher percentage of the lower atomic number metal complex in the polymer has been intentionally obtained by adjusting the concentrations of metal complexes in the loading solution, in order to give better RBS data for the lower atomic number elements (the cross section is proportional to the square of the atomic number, eq 6).

Analysis of the competitive binding of the anionic metal complexes in $(VPyH^+)_n$ films is based on the assumption that the ratio of the two anionic metal complexes bound in the dry polymer films represents the equilibrium ratio of the two metal complexes bound in $(VPyH^+)_n$ when immersed in the loading solutions. The equilibrium constants of equilibra 1–3 are calculated from the data of atomic ratios of the two metal complexes bound in $(VPyH^+)_n$ as summarized in Table IV. The concentrations of metal complexes bound in the polymer films are calculated as mole ratios of metal complexes to pyridinium subunit of the polymer backbone, assuming that the anionic metal complexes completely charge compensate the polycation.

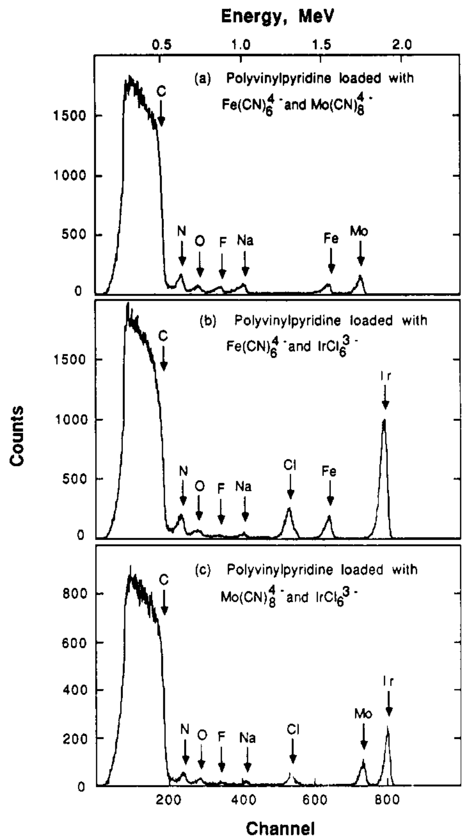

Figure 5. RBS of $(VPyH^+)_n$ loaded with (a) $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$, (b) $Fe(CN)_6^{4-}$ and $IrCl_6^{3-}$, and (c) $Mo(CN)_8^{4-}$ and $IrCl_6^{3-}$. The incident ion beam is 2-MeV He^+.

Table III. RBS Measurements of Competitive Binding of Two Metal Complexes in $(VPyH^+)_n$ Films

loading solution[a]	key element ratio	measured composition
17 mM $Fe(CN)_6^{4-}$ + 2 mM $Mo(CN)_8^{4-}$	N:Fe:Mo = 29.5:1.78:1	$\{VPyH^+ \cdot 0.16[Fe(CN)_6^{4-}] \cdot 0.09[Mo(CN)_8^{4-}]\}_n$
6.9 mM $Fe(CN)_6^{4-}$ + 3.3 mM $IrCl_6^{3-}$	N:Fe:Ir:Cl = 16.2:1.38:1:5.95	$\{VPyH^+ \cdot 0.17[Fe(CN)_6^{4-}] \cdot 0.13[IrCl_6^{3-}]\}_n$
2.6 mM $Mo(CN)_8^{4-}$ + 4.2 mM $IrCl_6^{3-}$	N:Mo:Ir:Cl = 22.2:1.58:1:6.02	$\{VPyH^+ \cdot 0.17[Mo(CN)_8^{4-}] \cdot 0.10[IrCl_6^{3-}]\}_n$

[a] The electrolytes were 0.2 mM 0.2 M $Na[CF_3COO]/CF_3COOH$ (pH = 1.5) aqueous solutions.

Table IV. Summary of RBS Measurements of the Equilibrium Constants of the Competitive Binding of Metal Complexes in Protonated Poly(4-vinylpyridine)

	equilibration solution[a]			film composition[b]			
beam, MeV	$[Fe(CN)_6^{4-}]$	$[Mo(CN)_8^{4-}]$	$[IrCl_6^{3-}]$	$[Fe(CN)_6^{4-}]$	$[Mo(CN)_8^{4-}]$	$[IrCl_6^{3-}]$	equilibrium const[c]
2	16.6	1.89		0.160	0.0899		$K_1 = 4.9$
2	9.61	0.947		0.170	0.0800		$K_1 = 4.8$
3	11.2	0.886		0.181	0.0686		$K_1 = 4.8$
3	9.09	0.967		0.163	0.0868		$K_1 = 5.0$
							av $K_1 = 4.9$
2	6.87		3.26	0.162		0.118	$K_2 = 7.7 \times 10^{-3}$
2	8.29		3.87	0.159		0.121	$K_2 = 7.3 \times 10^{-3}$
3	5.21		1.80	0.183		0.0896	$K_2 = 7.0 \times 10^{-3}$
							av $K_2 = 7.4 \times 10^{-3}$
2		2.58	4.17		0.170	0.107	$K_3 = 1.5$
2		2.34	4.25		0.167	0.110	$K_3 = 1.2$
3		1.13	2.30		0.168	0.109	$K_3 = 1.6$
							av $K_3 = 1.4$

[a] Concentrations of anionic metal complexes in millimolar. [b] Concentrations of redox active anions in $(PVyH^+)_n$ expressed as ratio of each metal complex to pyridinium subunit. [c] Equilibrium constants are calculated according to equations 1, 2, and 3.

It should be noted that different exponential powers of the concentrations of metal complexes are involved in expressing the equilibrium constants for binding differently charged anions in the $(\text{VPyH}^+)_n$. To illustrate the situation, the equilibrium constant involving $IrCl_6^{3-}$ and $Mo(CN)_8^{4-}$, which is close to 1, does not mean that $IrCl_6^{3-}$ and $Mo(CN)_8^{4-}$ bind to $(\text{VPyH}^+)_n$ in equal amounts when their solution concentrations are equal.

The equilibrium constants obtained from RBS, Table IV, are slightly different from those obtained from the electrochemical technique, Table I. In general, the constants obtained from RBS are more accurate for two reasons. First, in analyzing electrochemical data, large errors are introduced in the baseline subtractions and the resolution of overlapping cyclic voltammetry waves. Second, in electrochemical experiments, we are not certain that all of the redox active anionic metal complex inside the polymer films are electrochemically accessible on the time frame of the measurement. An internal check of the measured constants K_1, K_2, and K_3 can be obtained by taking advantage of the fact that the three equilibrium constants are not independent. They are interrelated by the cycle of equilibria shown in the Appendix. If activity coefficients of the metal complexes inside the polymer films and in the solution are ignored, the three equilibrium constants should obey eq 8. The equilibrium constants

$$K_1{}^3K_2K_3 = 1 \tag{8}$$

found from RBS give a value of 1.22, while the electrochemical measurement gives a value of 3.7. Thus, while the RBS and electrochemical methods are in qualitative agreement, the RBS method is more quantitative. The RBS method can obviously be applied when the anions are not electroactive, and our data provide a demonstration of the viability of using RBS as a technique for establishing composition of thin films of polyelectrolytes on surfaces.

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Appendix

For equilibrium between $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ inside the polymer and in solution, the following equilibrium can be written:

$$Fe(CN)_6{}^{4-}{}_{\text{poly}} + Mo(CN)_8{}^{4-}{}_{\text{soln}} \underset{}{\overset{K_1}{\rightleftharpoons}} Fe(CN)_6{}^{4-}{}_{\text{soln}} + Mo(CN)_8{}^{4-}{}_{\text{poly}}$$

If the activity coefficients can be neglected, then the chemical potentials of each term can be written as

$$\mu_{Fe(CN)_6{}^{4-}{}_{\text{poly}}} = \mu^0{}_{Fe(CN)_6{}^{4-}{}_{\text{poly}}} + RT \ln C_{Fe(CN)_6{}^{4-}{}_{\text{poly}}}$$

$$\mu_{Mo(CN)_8{}^{4-}{}_{\text{soln}}} = \mu^0{}_{Mo(CN)_8{}^{4-}{}_{\text{soln}}} + RT \ln C_{Mo(CN)_8{}^{4-}{}_{\text{soln}}}$$

$$\mu_{Fe(CN)_6{}^{4-}{}_{\text{soln}}} = \mu^0{}_{Fe(CN)_6{}^{4-}{}_{\text{soln}}} + RT \ln C_{Fe(CN)_6{}^{4-}{}_{\text{soln}}}$$

$$\mu_{Mo(CN)_8{}^{4-}{}_{\text{poly}}} = \mu^0{}_{Mo(CN)_8{}^{4-}{}_{\text{poly}}} + RT \ln C_{Mo(CN)_8{}^{4-}{}_{\text{poly}}}$$

At equilibrium, the difference of chemical potentials is zero:

$$0 = (\mu_{Fe(CN)_6{}^{4-}{}_{\text{soln}}} + \mu_{Mo(CN)_8{}^{4-}{}_{\text{poly}}}) - (\mu_{Fe(CN)_6{}^{4-}{}_{\text{poly}}} + \mu_{Mo(CN)_8{}^{4-}{}_{\text{soln}}})$$

So

$$\ln K_1 = \ln \frac{C_{Fe(CN)_6{}^{4-}{}_{\text{soln}}} C_{Mo(CN)_8{}^{4-}{}_{\text{poly}}}}{C_{Fe(CN)_6{}^{4-}{}_{\text{poly}}} C_{Mo(CN)_8{}^{4-}{}_{\text{soln}}}} = \left[\left(\mu^0{}_{Fe(CN)_6{}^{4-}{}_{\text{poly}}} + \mu^0{}_{Mo(CN)_8{}^{4-}{}_{\text{soln}}}\right) - \left(\mu^0{}_{Fe(CN)_6{}^{4-}{}_{\text{soln}}} + \mu^0{}_{Mo(CN)_8{}^{4-}{}_{\text{poly}}}\right)\right] \Big/ RT \tag{9}$$

For equilibrium between $Fe(CN)_6^{4-}$ and $IrCl_6^{3-}$ inside the polymer and in solution, the following equilibrium can be written:

$$4IrCl_6{}^{3-}{}_{\text{poly}} + 3Fe(CN)_6{}^{4-}{}_{\text{soln}} \overset{K_2}{\rightleftharpoons} 4IrCl_6{}^{3-}{}_{\text{soln}} + 3Fe(CN)_6{}^{4-}{}_{\text{poly}}$$

If the activity coefficients can be neglected, then the chemical potentials of each term can be written as

$$\mu_{IrCl_6{}^{3-}{}_{\text{poly}}} = \mu^0{}_{IrCl_6{}^{3-}{}_{\text{poly}}} + RT \ln C_{IrCl_6{}^{3-}{}_{\text{poly}}}$$

$$\mu_{Fe(CN)_6{}^{4-}{}_{\text{soln}}} = \mu^0{}_{Fe(CN)_6{}^{4-}{}_{\text{soln}}} + RT \ln C_{Fe(CN)_6{}^{4-}{}_{\text{soln}}}$$

$$\mu_{IrCl_6{}^{3-}{}_{\text{soln}}} = \mu^0{}_{IrCl_6{}^{3-}{}_{\text{soln}}} + RT \ln C_{IrCl_6{}^{3-}{}_{\text{soln}}}$$

$$\mu_{Fe(CN)_6{}^{4-}{}_{\text{poly}}} = \mu^0{}_{Fe(CN)_6{}^{4-}{}_{\text{poly}}} + RT \ln C_{Fe(CN)_6{}^{4-}{}_{\text{poly}}}$$

At equilibrium, the difference of chemical potentials is zero:

$$0 = (4\mu_{IrCl_6{}^{3-}{}_{\text{soln}}} + 3\mu_{Fe(CN)_6{}^{4-}{}_{\text{poly}}}) - (4\mu_{IrCl_6{}^{3-}{}_{\text{poly}}} + 3\mu_{Fe(CN)_6{}^{4-}{}_{\text{soln}}})$$

So

$$\ln K_2 = \ln \frac{(C_{IrCl_6{}^{3-}{}_{\text{soln}}})^4 (C_{Fe(CN)_6{}^{4-}{}_{\text{poly}}})^3}{(C_{IrCl_6{}^{3-}{}_{\text{poly}}})^4 (C_{Fe(CN)_6{}^{4-}{}_{\text{soln}}})^3} = \left[\left(4\mu^0{}_{IrCl_6{}^{3-}{}_{\text{poly}}} + 3\mu^0{}_{Fe(CN)_6{}^{4-}{}_{\text{soln}}}\right) - \left(4\mu^0{}_{IrCl_6{}^{3-}{}_{\text{soln}}} + 3\mu^0{}_{Fe(CN)_6{}^{4-}{}_{\text{poly}}}\right)\right] \Big/ RT \tag{10}$$

For equilibrium between $Mo(CN)_8^{4-}$ and $IrCl_6^{3-}$ inside the polymer and in solution, the following equilibrium can be written:

$$3Mo(CN)_8{}^{4-}{}_{\text{poly}} + 4IrCl_6{}^{3-}{}_{\text{soln}} \overset{K_3}{\rightleftharpoons} 3Mo(CN)_8{}^{4-}{}_{\text{soln}} + 4IrCl_6{}^{3-}{}_{\text{poly}}$$

If the activity coefficients can be neglected, then the chemical potential of each term can be written as

$$\mu_{Mo(CN)_8{}^{4-}{}_{\text{poly}}} = \mu^0{}_{Mo(CN)_8{}^{4-}{}_{\text{poly}}} + RT \ln C_{Mo(CN)_8{}^{4-}{}_{\text{poly}}}$$

$$\mu_{IrCl_6{}^{3-}{}_{\text{soln}}} = \mu^0{}_{IrCl_6{}^{3-}{}_{\text{soln}}} + RT \ln C_{IrCl_6{}^{3-}{}_{\text{soln}}}$$

$$\mu_{Mo(CN)_8{}^{4-}{}_{\text{soln}}} = \mu^0{}_{Mo(CN)_8{}^{4-}{}_{\text{soln}}} + RT \ln C_{Mo(CN)_8{}^{4-}{}_{\text{soln}}}$$

$$\mu_{IrCl_6{}^{3-}{}_{\text{poly}}} = \mu^0{}_{IrCl_6{}^{3-}{}_{\text{poly}}} + RT \ln C_{IrCl_6{}^{3-}{}_{\text{poly}}}$$

At equilibrium, the difference of chemical potentials is zero:

$$0 = (4\mu_{IrCl_6{}^{3-}{}_{\text{poly}}} + 3\mu_{Mo(CN)_8{}^{4-}{}_{\text{soln}}}) - (4\mu_{IrCl_6{}^{3-}{}_{\text{soln}}} + 3\mu_{Mo(CN)_8{}^{4-}{}_{\text{poly}}})$$

$$\ln K_3 = \ln \frac{(C_{IrCl_6{}^{3-}{}_{\text{poly}}})^4 (C_{Mo(CN)_8{}^{4-}{}_{\text{soln}}})^3}{(C_{IrCl_6{}^{3-}{}_{\text{soln}}})^4 (C_{Mo(CN)_8{}^{4-}{}_{\text{poly}}})^3} = \left[\left(4\mu^0{}_{IrCl_6{}^{3-}{}_{\text{soln}}} + 3\mu^0{}_{Mo(CN)_8{}^{4-}{}_{\text{poly}}}\right) - \left(4\mu^0{}_{IrCl_6{}^{3-}{}_{\text{poly}}} + 3\mu^0{}_{Mo(CN)_8{}^{4-}{}_{\text{soln}}}\right)\right] \Big/ RT \tag{11}$$

Combine the three equations together, we obtain

$$3 \ln K_1 + \ln K_2 + \ln K_3 = 0$$

or

$$K_1{}^3K_2K_3 = 1 \tag{8}$$

Registry No. Fe, 7439-89-6; Mo, 7439-98-7; Ir, 7439-88-5; VPy-1,6-dibromohexane (copolymer), 43048-47-1.