Electrochromic and Conductivity Behavior of Tris[Ester-Substituted Bipyridine]Ruthenium[II] Polymers on Electrodes

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ELECTROCHROMIC AND CONDUCTIVITY BEHAVIOR OF TRIS(ESTER-SUBSTITUTED BIPYRIDINE)RUTHENIUM(II) POLYMERS ON ELECTRODES

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ABSTRACT

Complexes of ruthenium with 2,2'-bipyridines having electron-withdrawing ester functions in the 5,5' positions have been prepared, and they are polymerizable. Films can be cast on electrodes from solutions of the monomer and then polymerized thermally. Once formed, the films are electroactive and quite stable in the absence of O_2. The ruthenium complexes in this polymer have a rich electrochemistry and can exist in seven stable oxidation states. The spectral properties of the polymer are such that, as the oxidation state of the complex is changed successively from 2+ to 4-, the polymer undergoes vivid changes in color. The material is thus of interest as an electrochromic material. Additionally, when the polymer is reduced to the formal zero-valent form it becomes an ohmic conductor with semiconductorlike properties.

INTRODUCTION

Electrochemically active polymer films can be coated on electrode surfaces in a number of ways and for a number of reasons [1]. Often, the motive for modifying an electrode surface with an electroactive polymer is to alter the

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chemical or physical properties of the electrode in some desirable way. Sometimes, however, modifying an electrode with a film of the polymer simply provides an especially convenient way to study the redox properties of the polymer.

Types of electrochemically active polymers that have been used to modify electrode surfaces vary widely; frequently, however, the site of redox activity in the polymer is a transition metal complex of some sort. The metal complex may make up part of the backbone of the polymer [2], it may be appended covalently to side chains on the polymer [3], or it may be held in the polymer only by electrostatic interactions [4]. Many examples of electrodes modified with polymers containing metal trisbipyridine complexes have been reported in the last 10 years [1, 2, 5]. The ways in which this particular class of complex has been incorporated into various polymers encompass all three types of polymers and modes of bonding described above [1, 2, 5].

The specific reasons for modifying electrodes with electroactive-metal-complex-containing polymers are as varied as the polymers themselves. We report here studies on a polymer film formed by the thermal polymerization of a monomeric complex tris(5,5'-bis[acrylyl-1-propoxycarbonyl] -2,2'-bipyridine)-ruthenium(II) as its tosylate salt, I. Our original reasons for preparing and studying this polymer were that we had previously observed that a solution-soluble analog of I undergoes seven reversible electrochemical oxidation state changes and that the observed color of the complex in each of these oxidation states is distinctly different from its color in each other oxidation state [6, 7]. Thus, there seemed to be some potential interest in polymers of I, hereafter poly-I, as potential electrochromic materials.

During our studies of poly-I we determined that, in addition to its electrochromic properties, this material has conductivity properties that are unusual [8, 9]. Unlike other reported polymers containing metal trisbipyridine complexes [5], poly-I when reduced to the formal zero-valent oxidation state is an ohmic conductor over a wide range of applied potentials and temperatures. This behavior suggests that the mechanism of conduction for zero-valent poly-I is different from that for other poly-trisbipyridine metal complexes and even different from that of poly-I in nonzero formal oxidation states [10].

RESULTS

The details of the preparation of poly-I films on electrodes have been reported elsewhere [6]. Basically, the polymer is prepared by coating a film of monomer I on the surface of the electrode (typically by dip or spin coating)
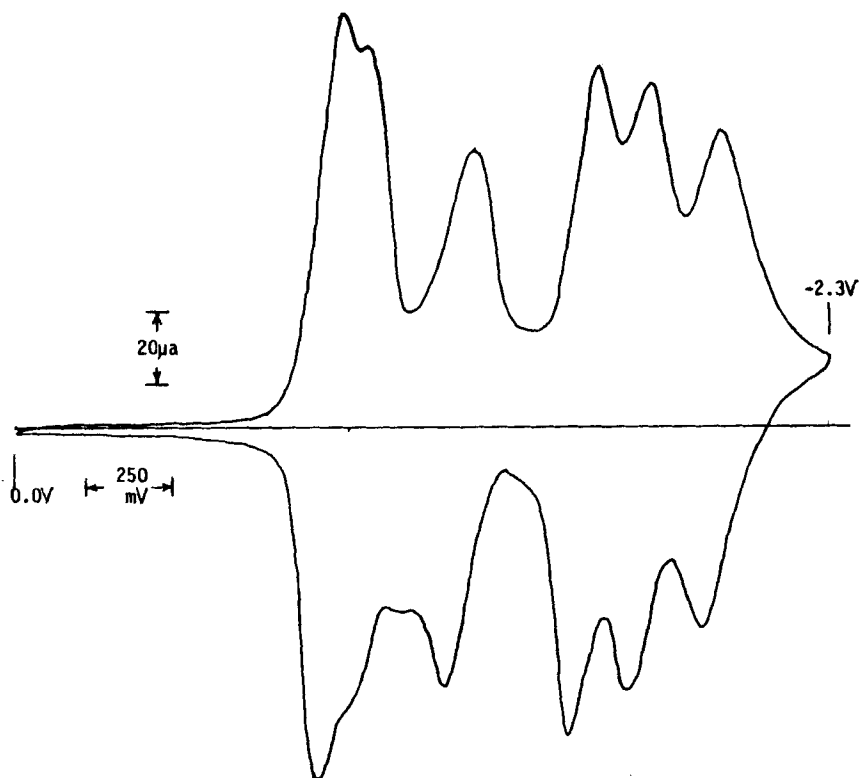
FIG. 1. Cyclic voltammogram of an ~0.4 μm thick film of poly-I on tin oxide. Sweep rate = 50 mV/s. The electrolyte is acetonitrile/0.1 M TBAPF$_6$. E vs Ag/Ag$^+$.

followed by thermal treatment for up to 15 h at 150°C. Figure 1 shows a cyclic voltammogram obtained for a poly-I film on a tin oxide electrode. For films that are at least 0.1 μm thick, one can observe the same series of colors for the polymer as one can observe for solutions of analogous monomers. Table 1 lists the formal oxidation states and the associated colors for poly-I films [6].

Such parameters as response times and "cycle life" are of much concern when considering a material such as poly-I for possible application in device technology. We have previously considered these parameters for relatively thick films on large surface area (1 cm^2) tin oxide electrodes as functions

TABLE 1. Electrochromic Properties of I

Oxidation state	Solution color
+2	Orange
+1	Purple
0	Blue
-1	Green-blue
-2	Brown
-3	Rust
-4	Cherry red

of solvent and electrolyte [6]. More recently we have reexamined these parameters by using small surface area Pt electrodes (5.0×10^{-4} cm^2). The solid curve in Fig. 2 shows the charge/time response for a ~0.2 μm thick virgin poly-I film stepped between -0.60 and -1.1 V (vs Ag/Ag$^+$) in acetonitrile saturated with tetramethylammonium hexafluorophosphate (TMA$^+$PF$_6{}^-$). On the forward step (-0.60 to -1.1 V), the film reaches 90% conversion in 51 ms. On the reverse step (-1.1 to -0.60 V), the response is even more rapid, reaching 90% reoxidation in only 18 ms. The stability of the film in Fig. 2 was tested by repeatedly stepping the potential between -0.6 and -1.1 V for a total of 5×10^5 cycles. Quantitatively, within experimental error, no changes in either the number of coulombs passed per step or the response time for 90% conversion are observed after this extended period of cycling.

For a single potential cycle of a poly-I film out to the 3-/4-redox couple (i.e., a -0.6 to -2.1 V step), 90% oxidation state conversion is achieved in about the same time as above, despite the fact that the transport of both charge type ions are involved in maintaining charge balance for this more negative step. Multiple potential steps, however, to voltages more negative than -1.1 V cause significant changes in the polymer. These changes are reflected in both the cyclic voltammogram and the charge/time response. The dashed curve in Fig. 2 is the charge/time response of the poly-I film after only 5×10^3 potential steps (of 0.1 s duration) between -0.60 and -1.3 V. There is a clear decrease in the charge transfer rate through the film following the multiple steps to -1.30 V. Examination of the cyclic voltammogram of the film before and after the stepping experiment (Fig. 3)
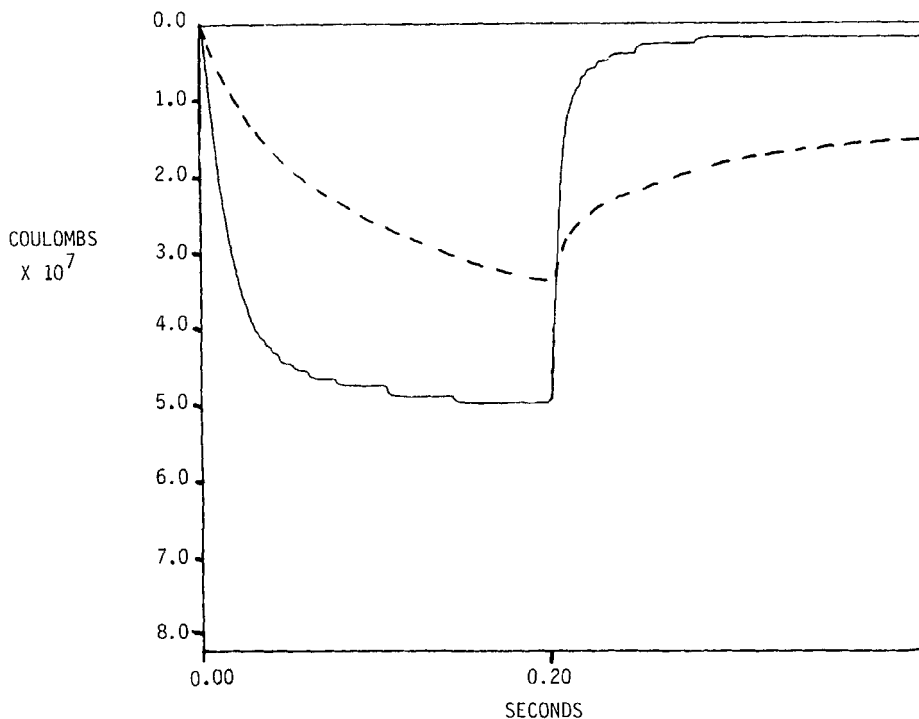
FIG. 2. Charge vs time plot for a ~ 0.2-μm thick poly-I film coated on a 5.0 X 10^{-4} cm^2 Pt electrode stepped from -0.60 to -1.10 V and back to -0.60 V. (——) Virgin film. (- -) Same film after 5000 potential steps between -0.60 and -1.30 V. Volts are vs Ag/Ag$^+$, electrolyte is acetonitrile saturated with TMAPF$_6$.

suggests that the changes in response time are probably not due to electrochemical degradation of the ruthenium sites in the polymer but rather to an electrochemically induced additional crosslinking of the poly-I film. Significant similarities exist between the voltammograms after cycling past -1.1 V and those of films of poly-I that have been heated for extended times or heated at higher than normal polymerization temperatures. This interpretation, if correct, may suggest methods of extending the cycle life and improving the response time of poly-I films.

In addition to the rather unusual optical and electrochemical properties of poly-I films, we have observed and reported previously that poly-I films,
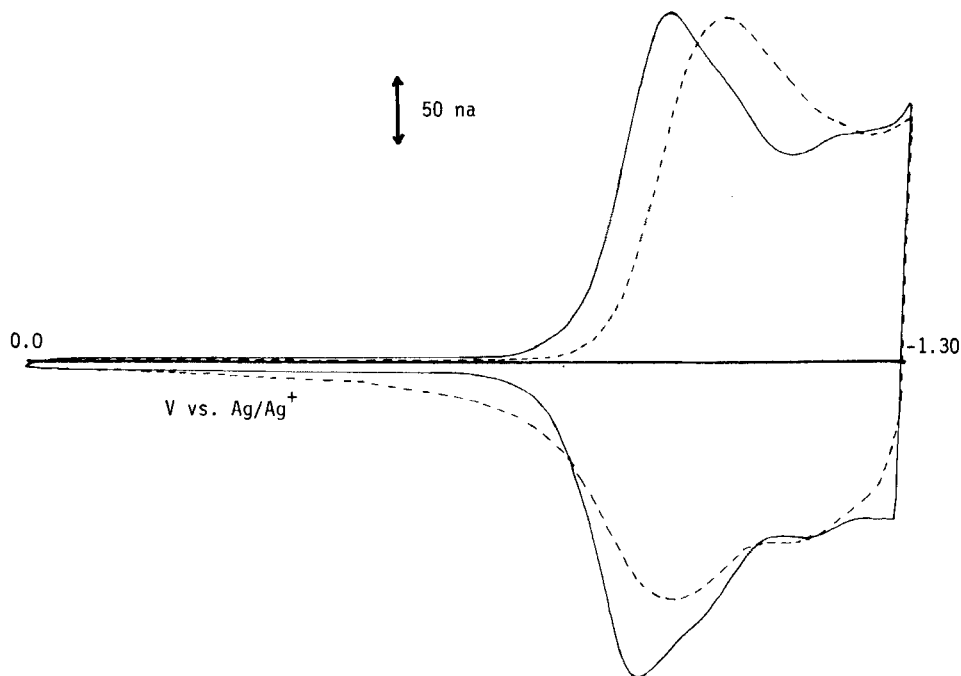
FIG. 3. Cyclic voltammograms of the film in Fig. 2. Solid and dashed lines correspond to the same films as in Fig. 2.

when reduced to the formal zero-valent oxidation state, are ohmic conductors [8-10]. By employing an electrolyte in solution for which one of the ions is sterically too large to enter the poly-I film, one can block the film in the zero-valent form. We have previously reported results using a polycationic electrolyte, trapping the film in the zero-valent form at negative potentials [9]. It is also possible to trap the film in the zero-valent form at positive potentials by first reducing the film at negative potentials in an electrolyte which has sterically large anions. The electrolyte employed in these studies has been the tetrabutylammonium salt of tetra-(p-sulfonatophenyl)porphyrin. The large tetra-anion cannot reenter the poly-I film upon reoxidation after its reduction to a negatively charged form; thus the polymer remains in the conductive zero-valent form at positive potentials.

The magnitude and temperature dependence of the resistance of zero-valent poly-I are semiconductorlike. Once reduced to the zero-valent form, the poly-

mer can be removed from solution and its conductivity properties examined in the dry, nonsolvent swollen form. By using a so-called sandwich electrode configuration [11], the resistance of films of poly-I can be examined in or out of solution in any state of reduction or oxidation desired. With a polycationic electrolyte, films of poly-I were reduced in sandwich-electrode configuration and removed from solution. Then their conductivity was measured as a function of temperature and frequency. Table 2 presents some of the data from these measurements. The dc resistance measured at room temperature is significantly larger than the low-frequency ac values obtained at the same temperature. This dc measurement is somewhat unstable and may not be meaningful. In any event, we have no good explanation at present as to why the two measurements should yield different values. Excluding the dc value, as the ac frequency is increased, the resistance of the poly-I at both temperatures listed in Table 2 decreases slightly up to about 10 kHz, where a significant drop occurs. Based on measurements of standard resistors under identical conditions, we feel at present that the decrease in resistance is real. Generally, a wide variety of models of polymer conduction predict decreases in resistance with increasing frequency. Probably the most notable fact about the data in Table 2 is that the frequency dependence of the resistance up to ~10 kHz is fairly weak.

In contrast to the weak frequency dependence, the low-frequency resistance of poly-I is a strong function of temperature. The dc resistance is exponentially dependent on temperature over at least the range from room temperature down to ~-120°C. Consideration of these results will follow after a discussion of the possible mechanism for conduction in zero-valent poly-I.

Zero-valent poly-I differs in a number of ways from other electronically conducting polymers: 1) It is amorphous and probably highly crosslinked; 2) it contains no extended conjugation; 3) at least in a formal sense, it is not mixed valence. This latter point, while true in the macroscopic sense, is probably not true on the microscopic level. Consideration of the Nernst equation shows that, if roughly the same separation in potentials is assumed to exist between the 1+/0 and 0/1- couples for the polymer as for the solution-soluble monomer, then the zero-valent state of poly-I should be disproportionated to about 5% into the 1+ and 1- forms at room temperature. The zero-valent poly-I is thus, in actuality, a mixed-valent material. Unlike other mixed-valence polymers, however, the degree of mixed valence character is not determined by dopant concentrations. The population of the 1+/1- state is thermally induced, and thus the concentration of the 1+/1- charge carriers is temperature dependent in a Boltzmann fashion. Reduced poly-I, like an intrinsic semiconductor, has an equal concentration of positive and

TABLE 2. Resistance Values of Zero-Valent Poly-I Films as a Function of Temperature and Frequency

Temperature, °C		Frequency, Hz					
		0	10	100	1K	10K	100K
22	Resistance (Ω)	54	23	23	19	19	—
	Phase angle (degree)	—	—	+20	-10	-40	—
-30	Resistance (Ω)	—	2400	2400	2300	2050	1400
	Phase angle (degree)	—	-5	-5	-10	-30	-65

negative charge carriers whose concentration is exponentially dependent on the absolute temperature. Extending this analogy further, the separation between the 1+/0 and 0/1- potentials is analogous to a semiconductor band-gap energy [10]. There is, however, no evidence to suggest that reduced poly-I has any long-range electron delocalization analogous to a band structure [10].

The data in Table 2 can now be considered in light of the conduction model developed previously and described above. First, as stated above, the population of 1+ and 1- charge carriers is expected to decreases approximately exponentially with T^{-1}. Second, the barrier to electron self-exchange between 1+ and 0 sites and 0 and 1- sites should be activational in nature. For low concentration of charge carriers, both processes are expected to contribute to the measured resistance. This model is thus consistent with the experimental temperature dependence of the resistance of poly-I. The weak frequency dependence of the resistance is consistent with an activational hopping mechanism where the "attempt rate" of electron hopping is high relative to the frequency [12]. A more detailed explanation of the frequency dependence of the conductivity will, however, require further data.

Another factor which appears to be of importance in the consideration of the conductivity behavior of zero-valent poly-I is the absence of nonelectroactive ions in the polymer. Since ions of both charge type can move by electron exchange in zero-valent poly-I, the potential wells localizing the charges seem to be shallower than would otherwise be the case. Comparisons between the conductivity of the formal 1+ form of the polymer with that of the zero-valent form support this explanation. Based solely on the degree of mixed valent nature (and thus the number of charge carriers), and 1+ form should be the significantly better conductor than the zero-valent form; in fact, it is at least a factor of 5 times more resistive. Nonelectroactive anions must be present in the 1+ form for charge balance; consequently, the barrier to electron exchange is raised because the electrostatic potential wells localizing the positive charges are deeper than for the ion-free zero-valent material.

SUMMARY

Polymer films of I have a wide range of reversible reduction electrochemistry. The fixed sites are stable in oxidation states that range form the formal 2+ to 4- forms. Over this range of oxidation states the polymer changes through an array of colors. Additionally, because the fixed sites change formal charge, the film can be either a cation exchanger, a neutral polymer, or an anion exchanger, depending upon the applied voltage. Making use of this

potential-dependent ion exchange property by employing a soluble carionic polymer as the solution electrolyte, films of poly-I can be sterically blocked from reducing beyond the formal zero valent form. In the zero-valent form the polymer is an ohmic conductor both in solution and dry. A model has been proposed which describes the conductivity of the polymer and, in part, accounts for its ohmic nature and semiconductorlike temperature dependence.

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