

## References and Notes

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## Solid-State Spectroelectrochemistry of Cross-Linked Donor Bound Polymer Films<sup>1</sup>

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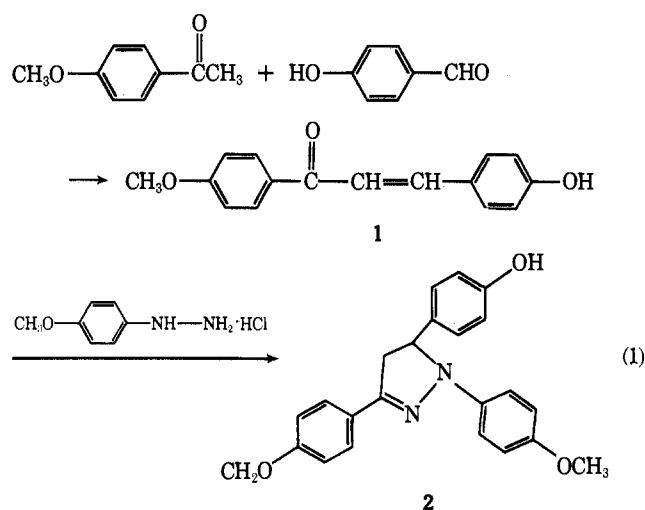
**Abstract:** A new electroactive material has been prepared by attaching the potassium salt of 1,3-di(*p*-methoxyphenyl)-5-(*p*-hydroxyphenyl)- $\Delta^2$ -pyrazoline to cross-linked chloromethylated polystyrene resins. The polymer can be readily coated from benzene suspensions onto metallic electrodes. At these modified electrodes, electrochemical charge transfer reactions are accompanied by large optical changes as pyrazoline cations are formed through the film bulk. Studies of the electrochemical and optical changes as a function of sweep rate and time indicate that electrons are transferred between monomeric pyrazoline species, and that the polymer matrix is characterized by a considerable degree of donor site flexibility.

### Introduction

Recently the surface modification of electrode properties has attracted considerable attention. Most work has centered on the covalent binding of electroactive molecules to electrode surfaces,<sup>2</sup> a method which requires chemical pretreatment of the electrode surface and the use of special analytical techniques to characterize the small amounts (monolayer coverage or less) of material involved. In an alternate approach, films of electroactive polymers<sup>3,4</sup> have been physically adsorbed onto untreated electrode surfaces with the subsequent observation of electrochemical charge transfer. So far these polymeric films<sup>3,4</sup> have been kept *thin* (200 Å or less) to ensure efficient electronic and (charge compensating) ionic transport through the films. However, in this communication we describe a new class of electroactive donor materials based on porous, cross-linked polymer resins which provide a new means of modifying the electrochemical properties of electrodes. Since these materials are porous and can be readily coated onto substrates to form relatively thick films, the electrochemical charge-transfer processes are accompanied by easily detectable optical changes which are used to provide information on the mechanism of electron transport through these films.

### Results

The electroactive material was prepared by attaching a suitably functionalized organic  $\pi$  donor of the triaryl  $\Delta^2$ -pyrazoline class to a cross-linked polymer resin. The pyrazoline  $\pi$  donor was chosen because of its known ability<sup>5</sup> to be reversibly oxidized to stable, colored radical cations. The pyrazoline selected for attachment to the polymer resin was prepared<sup>6</sup> in two steps involving initial aldol condensation of *p*-methoxyacetophenone with *p*-hydroxybenzaldehyde to give a 4-hydroxy-4'-methoxychalcone (**1**). The chalcone is then reacted with *p*-methoxyphenylhydrazine hydrochloride to yield 1,3-di(*p*-methoxyphenyl)-5-(*p*-hydroxyphenyl)- $\Delta^2$ -pyrazoline (**2**) (see eq 1). The potassium salt of pyrazoline **2** was coupled



to S-X1 chloromethylated polystyrene resin (5.4 mequiv/g, 1% cross-linked)<sup>7</sup> in refluxing dioxane-ethanol (4:1) under N<sub>2</sub>. After reaction, about 85% of the chloromethylated sites were reacted<sup>8</sup> (i.e., 72% of the phenyl groups of the polystyrene resin have been coupled to pyrazoline). Spectroscopic measurements (IR and UV-vis: KBr) gave absorptions which were identical with those of the starting pyrazoline (**2**). In the IR, no alcohol absorption of monomer **2** was seen indicating that all of the donor pyrazoline was covalently bound to the polymer chain, and not present as the unreacted monomer.

Although this functionalized polymer is insoluble in common organic solvents by virtue of the internal cross-links present, it was discovered that films of the material could be cast onto a variety of substrates from a suspension in a swelling solvent such as benzene. The films were heterogeneous in character owing to the particulate nature of the polymer, porous, with a high surface area as observed by scanning electron microscopy, and with an average thickness<sup>9</sup> of 5–10  $\mu$ . When films of the pyrazoline copolymer coated onto Pt electrodes were examined for electrochemical response via cyclic voltamme-

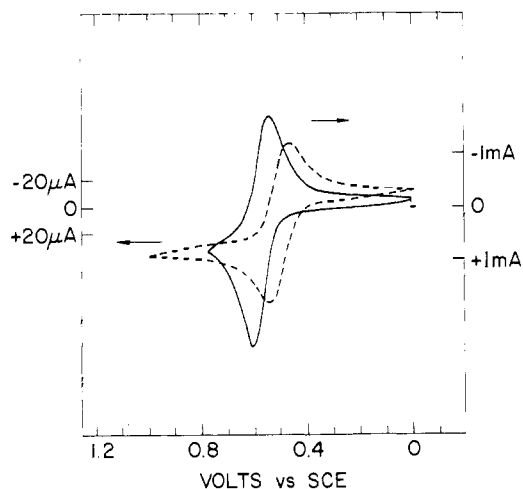


Figure 1. Cyclic voltammograms of pyrazoline polymer bead film (solid curve) and pyrazoline monomer (dashed curve) with  $\text{CH}_3\text{CN}$  solvent (0.1 N TEAP, Pt, 10 mV/s vs. SCE).

try<sup>10</sup> ( $\text{CH}_3\text{CN}$ , 0.1 N TEAP, 10 mV/s vs. SCE), the solid curve in Figure 1 was obtained. In addition, it was observed during the course of the cyclic experiments that *the films changed color* uniformly from yellow to dark green and back again as the voltage was swept through the oxidizing and reducing waves. With care in preparation, films could be cycled without evidence of degradation or loss of surface adhesion.

The polymeric film was found to have a cyclic voltammogram that is slightly shifted to more anodic potentials, with a narrower peak shape than the curve for the monomer (Figure 1, dashed line), but with similar peak to peak separation ( $E_p \sim 60$  V). At slow sweep rates (100 mV/s)  $i_p$  was proportional to the sweep rate. At faster sweep rates, however, the voltammograms become broader, peak splittings approached 300 mV, and  $i_p$  was not proportional to the sweep rate. In addition, a distinct asymmetry was seen in the cyclics with  $i_p^c/i_p^a = 0.6$ , although the integrated peak areas were equal. Similar results were obtained for electrodeposited films of poly(vinylferrocene) reported by Merz and Bard,<sup>3</sup> except for the narrow peak shape and  $E_p \sim 0$  found for the thin films (200 Å) of this homopolymer.

To further characterize the electrochemical properties of these films, the optical changes which occur as a consequence of the electrochemical charge transfer processes were studied by preparing films on optically transparent Pt electrodes.<sup>11</sup> The absorption spectrum of an oxidized film (Figure 2, solid line) shows absorptions at 425, 525, 660 (sh), and 730 nm, very similar to the spectrum of a solution of the monomer pyrazoline cation ( $2^+$ ) generated electrochemically.<sup>12</sup> Since it was found that these spectra were stable, it was possible to study the optical changes as a function of potential in the electrochemical experiments. Spectra taken as a function of potential in the cyclic voltammetry experiments showed that only two species, i.e., neutral donor and donor cation, were involved.

The amount of each of these species present could be conveniently monitored via the intensity of the 725- and 425-nm absorptions.<sup>14</sup> In the cyclic voltammetry experiments at slow sweep rates (100 mV/s) it was found that approximately half of the total available film equivalents<sup>14</sup> were oxidized. Exhaustive controlled potential electrolysis experiments (1 V vs. SCE) confirmed that only half of the bound donors were available for electrochemical oxidation. At faster sweep rates, however, it was observed that the percent film oxidation was reduced to limiting values as low as 10% at 500 mV/s. In addition, from OD vs. time plots in the cyclic experiments it was seen that the rate of production (change in OD per unit time) of the cation was always at least five times faster than the

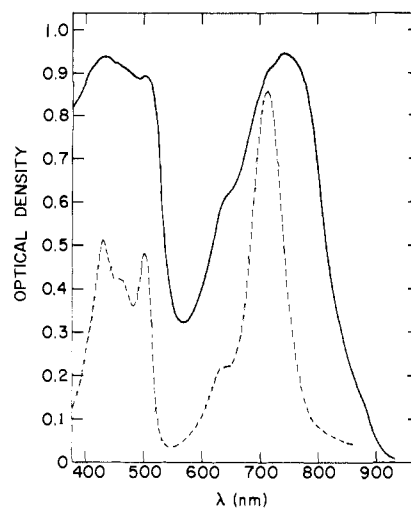


Figure 2. Absorption spectra of oxidized polymer bead film (solid curve) and pyrazoline monomer cation in  $\text{CH}_3\text{CN}$  (dashed curve).

subsequent reduction process, indicating a fundamental asymmetry in the film oxidation-reduction process even at the slowest sweep rates studied.

## Discussion

The spectroelectrochemical experiments on the pyrazoline copolymeric films suggest that electrons and appropriate counterions for charge neutrality can move through the polymer matrix in response to changes in applied potential. Efficient diffusion of solvent and electrolyte through these polymer matrices should be possible owing to the porous character of the polystyrene bead.<sup>15</sup> In fact, films made from polymers subjected to longer reaction times, conditions which are known to degrade the cross-linked structure, were considerably less active electrochemically, suggesting a logical relationship between polymer film porosity and electrochemical activity.

Electronic charge transport through the films could take place by means of mixed valence interactions which are known<sup>16</sup> to give rise to high conductivities in a number of cation radical organic solids. However, from the optical data on the films it is apparent that there is no spectral evidence for the mixed valence aggregates that are the structural-electronic prerequisites<sup>17</sup> for the electrical conductivity in these materials. This is important because it suggests a site-site molecular requirement for electron transport in polymer films that is considerably less specific than mixed valence, a point that is consistent with the observation of film electron transport for other electroactive groups, i.e., ferrocene<sup>3</sup> and nitrobenzene,<sup>4</sup> that are not expected<sup>18</sup> to show mixed valence effects.

We propose that the important requirement for charge transport in these materials is the mobility of electroactive groups attached to the polymer chain. It has been previously shown<sup>19</sup> via a number of physical techniques that solvents impart a considerable degree of flexibility to pendant groups in polymeric matrices of this type. Furthermore, it has been well established<sup>20</sup> that the resulting mobility of the molecular groups in such lightly cross-linked polystyrene leads to significant chemical reactions between the sites. In the present donor copolymeric films, we observe significant electron transfer reactions (rather than chemical reactions) between the interacting sites. In addition, there are also noninteracting sites present in the material which do not take part in the electrochemistry. Some isolated sites can be expected owing to the copolymeric<sup>21</sup> nature of the material, the heterogeneous, particulate character of the films, and the use of  $\text{CH}_3\text{CN}$ , a solvent that is likely to be of relatively nonswelling<sup>19</sup> character for the polymer. In this interpretation, the relatively broad

cyclic peak shape with nonzero  $\Delta E_p$  can be ascribed to the considerable degree of bound donor site flexibility and to the heterogeneous distribution of intersite distances that is expected<sup>22</sup> for these copolymeric films. The observed sweep rate dependence and asymmetry in oxidation-reduction rates then would result from mass transport limitations between these sites for electron and/or ionic flow in the neutral vs. the oxidized polymer. Experiments designed to test this hypothesis by variation of the interdonor distance and the matrix rigidity are currently in progress.

### Experimental Section

**Synthesis of 1,3-Di(*p*-methoxyphenyl)-5-(*p*-hydroxyphenyl)- $\Delta^2$ -pyrazoline (2).** *p*-Methoxyacetophenone (15 g, 0.1 mol) and 12.2 g of *p*-hydroxybenzaldehyde (0.1 mol) were added to a solution containing 75 mL of H<sub>2</sub>O, 25 mL of EtOH, and 5 g of NaOH. The mixture was heated to 70 °C for 2 h with stirring under N<sub>2</sub> and then allowed to stir at room temperature overnight. The reaction mixture was diluted with H<sub>2</sub>O and neutralized with aqueous HCl. An orange-brown oil formed, which was crystallized from EtOH to give 15 g of 4-hydroxy-4'-methoxychalcone (1) as yellow crystals; mp 177–179 °C; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>) 3205 (br, s), 1640 (m), 1590 (s), 1570 (s), 1550 (s), 1500 (s), 1340 (m), 1275 (s), 1210 (s), 1160 (s), 1035 (m), 1015 (m), 970 (m), 830 (m).

The chalcone (4 g) and *p*-methoxyphenylhydrazine hydrochloride (3 g) were refluxed in 125 mL of absolute EtOH for 24 h with stirring under N<sub>2</sub>. To the resulting red-brown solution was added H<sub>2</sub>O and the aqueous layer extracted with ether until it was colorless. The ether layer was dried (MgSO<sub>4</sub>) and the solvent removed to yield an oily, yellow product. Crystallization from EtOH-H<sub>2</sub>O gave 5 g of pyrazoline 2 as a fluorescent, pale yellow solid. Further purification was carried out by recrystallization from toluene; mp 178–180 °C; IR (KBr, cm<sup>-1</sup>) 3190 (br, s), 1605 (m), 1495 (s), 1415 (w), 1380 (w), 1235 (s), 1170 (m), 1125 (w), 1095 (w), 1030 (m), 870 (w), 825 (s), 785 (w). Anal. Calcd: C, 74.01; H, 5.63; N, 7.50. Found: C, 73.80; H, 5.85; N, 7.29.

**Polymer Attachment.** Pyrazoline 2 (1.5 g) was treated with 1 equiv of KOH (0.24 g) in 50 mL of 4:1 dioxane-ethanol under N<sub>2</sub> and refluxed for 0.5 h. Then 370 mg of SX-1 chloromethylated cross-linked polystyrene (1% cross-linked with divinylbenzene, chloromethylation 5.4 mequiv/g, purchased from Bio-Rad Laboratories) was added to the reaction mixture and the solution refluxed for 4 days with stirring under N<sub>2</sub>. The extent of reaction was evaluated by titrating the amount of chloride liberated, by measuring weight gain of the polymer and by elemental analysis.

The chloride concentration was determined as follows. The solution was vacuum filtered and the polymer resin washed with EtOH, H<sub>2</sub>O, and dioxane. These washings and the mother liquor were combined and evaporated to dryness. H<sub>2</sub>O was added, and the solution was filtered. This aqueous solution was then titrated by the Vollard method<sup>23</sup> to determine the amount of chloride produced during the reaction.

The polymer resin, after the initial washings, was further washed repeatedly with the solvent sequence MeOH, H<sub>2</sub>O, MeOH, THF, CH<sub>2</sub>Cl<sub>2</sub>, ether. The polymer was then dried in a vacuum oven for 24 h at 70 °C under N<sub>2</sub> to give 965 mg of light yellow polymer. The IR spectrum (KBr, difference spectrum relative to an equivalent amount of the starting polymer) was identical with the starting pyrazoline, except for the absence of the hydroxyl absorption: 1610 (m), 1500 (s), 1410 (w), 1385 (w), 1235 (s), 1170 (m), 1125 (w), 1095 (w), 1040 (m), 875 (w), 830 (s), 790 (w). Anal. C, 77.27; H, 6.03; N, 4.95; Cl, 1.36. The percent of chloromethyl groups that reacted to give polymer-bound pyrazoline was determined to be 86.5% by chloride titration, 88% based on weight gain, and 85.3% based on elemental analysis for nitrogen. Since 84% of the initial polymer resin was functionalized with chloromethyl groups, the percent pyrazoline covalently attached along the polymer backbone is ~72%.

**Electrochemical Measurements.** The polymer films for electrochemical measurements were prepared by first suspending the polymer in benzene solvent (1:30 w/w) and stirring via a magnetic stirrer for ~15 min. Then a drop of the suspension was applied to the substrate (~80 Å evaporated Pt,<sup>11</sup> ultrasonically cleaned with DMF, acetone, CH<sub>2</sub>Cl<sub>2</sub>) from a pipet. The film was allowed to air dry, followed by 30 min of evacuation under vacuum. Electrochemical measurements were performed on an electrochemical cell equipped with quartz windows which fit into the sample compartment of a Cary 14 spectrometer. The cell (CH<sub>3</sub>CN, 0.1 N TEAP vs. SCE) employed three electrode (Pt auxiliary electrode) potentiostatic control. A Tacussell PRT potentiostat and PAR Model 175 signal generator were used for the measurements.<sup>10</sup>

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- (9) Determined using a Taylor Hobson Talysurf probe.
- (10) Luggin capillary and positive feedback technique used to compensate for solution and film resistance effects.
- (11) 80 Å Pt electron beam evaporated onto 30 Å Nb.
- (12) Exhaustive controlled potential electrolysis (1 V vs. SCE) in CH<sub>3</sub>CN (0.1 N TEAP).
- (13) OD ratios were used to correct for scattering effects and to conveniently monitor unreacted monomer concentration.
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