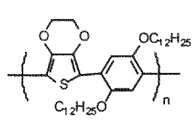
Multiple Colors and High Coloration Efficiencies in Electrochromic Heterocyclic Conductive Polymers

Fei Wang and R. David Rauh
EIC Laboratories, Inc.
111 Downey Street
Norwood, MA 02062

John R. Reynolds
Department of Chemistry
University of Florida
Gainesville, FL 32611

Electrochromism is a common feature of conductive polymers that, as films on electrodes, can be reversibly cycled electrochemically between doped and undoped states. Conjugated polymer systems have been identified that can provide two and three color modulation, some with high contrast or with colorless to absorbing electrochromic transitions.

In this paper, we describe the electrochromic properties of a broad range of conjugated polymers with respect to the spectroscopy of the redox states, the relation between structure and coloration efficiencies, and cyclability. An extensive "toolbox" of heterocyclic conjugated polymers has been synthesized and characterized. These materials include derivatives of polythiophenes and polypyrroles as well as polymers with alternating chromophore groups, such as poly(ethylenedioxythiophene-didodecyloxybenzene) (PEB).



PEB

The spectra of the polymers have several interesting features. The undoped states are characterized by transitions in the mid-visible, which dictate the color. The polythiophenes and pyrroles all have absorptions in these regions, although the degree of vibronic structure varies widely. An example is shown for PEB in Figure 1. On oxidation, the mid-visible absorption decreases and is replaced by a broad band red-shifted absorption, probably arising from quinoid-like structures with long-range planarity and delocalization. If the band is shifted completely into the mid-infrared, the material appears colorless in the doped conductive state, a desirable property for many practical applications.

Conductive polymers with these basic spectroscopic properties are characterized by a high color contrast when the absorption spectra of the two forms occur in complementary regions of the spectrum. For PEB, for example, there is a dramatic red-blue transition. In addition, the extinction coefficients of the neutral forms can be quite large due to significant intramolecular charge transfer character of the lowest energy absorption transitions. In the case of PEB, a coloration efficiency of >1200 cm^2/C has been measured at 552 nm [1]. that can provide improved properties compared to the usual linear polymer structures. The approach entails attaching linear polymer arms to a centrosymmetric core, so the arms radiate in three dimensions. Conductive polymers made in this way produce highly smooth and adherent thin films when cast from solution. More importantly, the cycle life of these films may be observed to increase dramatically, as we have demonstrated for PEB in a star geometry [2].

PEB and other high coloration efficiency polymers can be combined with WO_3, a well-characterized electrochromic oxide, to form charge-balanced variable transmission electrochromic window structures. The coloration efficiency of WO_3 is greater than 10 times less than most of the polymers characterized, so its contribution to the absorption of the device is negligible. The spectra of such a device in Figure 1 are almost totally due to the PEB component.

Stacking electrochromic window devices covering different regions of color space can give access to two-dimensional surfaces in color space [1]. A two layer or three layer system can, in principal, provide the "Holy Grail" of electrochromics-i.e., a fully color tunable pixel element. Also possible are separately addressed patterns of red-green-blue micropixels on a single substrate, similar to present display technology.

ACKNOWLEDGEMENT:

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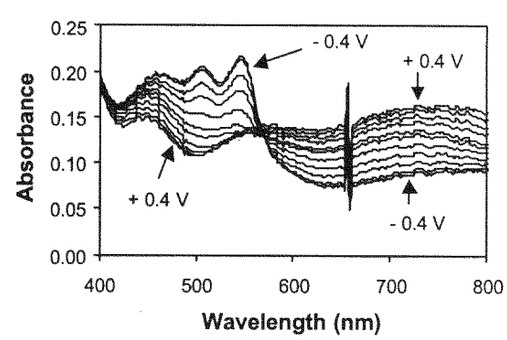

Figure 1. Spectroelectrochemistry of PEB/WO_3 cell as a function of the applied voltage: at 700 nm from bottom