Electrochromic Polymers for Easily Processed Devices

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Conjugated electroactive polymers offer a broad set of new materials for electrochromic applications. These polymers exhibit ease of processability and useful mechanical properties (e.g. flexibility). However, the major strength of these organic-based materials is that their electrochromic properties (switching speed, contrast ratio, and color) can be tuned through structural modification.[1]

In our group, we have carried out extensive studies on the design and synthesis of poly(3,4alkylenedioxythiophene) (PXDOT), and poly(3,4alkylenedioxypyrrole) (PXDOP) based polymers for electrochromic applications. [2,3] Through structural modification, we have diversified the electrochromic properties accessible and, in some instances, improved upon the already excellent properties displayed by the parent PEDOT.

Here, we present our recent accomplishments in the preparation and characterization of the newest members of this class of electrochromic polymers. We will discuss several approaches to structural modification and the effects on properties in both solution cast and electrodeposited films. We have found through variation of the size of the alkylene bridge and the nature of the alkylene substituent in PXDOT derivatives, that the contrast ratio and switching times can be greatly enhanced. For example, with the dibutyl derivative of poly(3,4-propylenedioxythiophene) (PProDOT-Bu₂), contrast ratios of greater than 75% at λ_{max} can be achieved with one-second switches. [4] In addition, with PProDOT-Me₂, optical contrasts of greater than 60% are observed based on changes in the colorimetrically measured relative luminance. [5] In a second approach, the synthesis of EDOT based comonomers with pyridine derivatives leads to n and p-dopable materials that exhibit multi-color states. [6] The electrochromic properties can also be further tuned via copolymerization as will be shown with copolymers of 3,6-bis(2-EDOT)-N-methyl carbazole and BiEDOT. Finally, an entire family of PXDOP derivatives have been synthesized which show many useful electrochromic properties including red and orange neutral states which become highly transmissive upon oxidation.

The polymers described above have been incorporated into electrochromic devices demonstrating their potential for a variety of useful applications such as multicolored displays and switchable mirrors. We will present on the design, fabrication, and characterization of sandwich type EC devices based on dual conducting polymers. Transmissive/absorptive devices are assembled using optically transparent electrodes and combining two complementary electrochromic polymeric materials. In one example, we use a cathodically coloring, substituted

poly(3,4 -propylenedioxythiophene) (PProDOT-Me₂) and an anodically coloring, N-propyl sulfonated poly(3,4 propylenedioxypyrrole) (PProDOP-N-PS). These devices exhibit high optical contrast (Δ %T = 65% at 580 nm) and a luminance change of 55% measured by colorimetric analysis. [7]

Reflective/absorptive devices have been assembled using thin films of electrochemically deposited PProDOT-Me₂ on gold coated Mylar[™] substrates and been shown to switch between deep blue and reflective gold states. These devices also allow for electrochromism in the NIR and mid-IR with reflectance data showing ΔR >90% at 1.8 µm. [8]

Finally, we report on the construction of laterally configured EC devices using patterned electrodes. Such patterns are achieved by selective removal of ITO from the substrate (transmissive devices) and by region specific metallization (reflective devices) using either metal vapor deposition or electroless plating of metal on line patterned surfaces.

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