POLY (2,2' - BITHIOPHENE) : AN ELECTROCHROMIC CONDUCTING POLYMER

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POLY(2,2'-BITHIOPHENE) : AN ELECTROCHROMIC CONDUCTING POLYMER

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Résumé- Nous avons étudié les propriétés optiques du polymère poly (2,2' bithiophène) et avons démontré que ce matériau a des propriétés électrochromiques.

Abstract - We present the optical properties of poly (2,2' bithiophene) and show that this material exhibits electrochromic behavior.

Currently much work is devoted to the synthesis of conducting polymers for use in a variety of applications. Polyacetylene, the prototype conducting polymer, has been successfully demonstrated to be useful in constructing p-n heterojunctions,[1] Schottky barrier diodes,[2] liquid junction photoelectrochemical solar cells,[3] and more recently as the active electrode in polymeric batteries.[4] Research on poly (p-phenylene) has demonstrated that this polymer can also be utilized in polymeric batteries.[5]

The improved electrochemical synthesis[6] of poly (pyrrole) has led to its use as a coating for the protection of n-type semiconductors against photocorrosion in photoelectrochemical cells.[7] Recently it was announced that pyrrole was not the only five-membered heterocyclic aromatic ring compound to undergo simultaneous oxidation and polymerization. Thiophene, furan, indole, and azulene all undergo electrochemical polymerization and oxidation to yield oxidized polymers of varying conductivities (5×10^{-3} to 10^{2} $\Omega^{-1}cm^{-1}$).[8] The purpose of our research was to investigate the optical properties of the as-formed oxidized poly (2,2' bithiophene) and the neutral poly (2,2' bithiophene). During the course of this research, we discovered that this material is electrochromic, i.e., a reversible color change occurs when it is switched between the oxidized and neutral states.

Thin films of poly (2,2' bithiophene) perchlorate were grown on SnO_2 coated glass slides using galvanostatic conditions. The electrode was anodically polarized using a current density of 100 $\mu A/cm^2$. for *ca* 6 min. A nickel foil was used as the counter electrode and the solution was 0.1 M $LiClO_4$ and 0.01 M 2,2' bithiophene in acetonitrile. The color of the resulting film was green. The thickness of the film can be controlled by varying the current density and/or the electrolysis time. Typically passage of 35 mC/cm^2 yields a film thickness of 4000 A. The as-grown oxidized film may be reduced to the neutral polymer in a solution containing 0.1 M $LiClO_4$ in acetonitrile. The resulting red film has the absorption spectrum shown in figure 1(a). The peak at 480 nm can be attributed to a π-π^* transition of the aromatic rings. It should be noted that in going from 2,2' bithiophene to 2,2'-5,2" terthiophene, the resulting π-π^* transition shifts from 301 nm to 350 nm.[9] Therefore it is not unreasonable to assume that the peak at 480 nm is assignable to the π-π^* transition of the polymer. The absorption spectrum in figure 1(b) is obtained by anodically passing 10 mC/cm^2. During this process the film changes in color from red to green. It is interesting to note that the peak

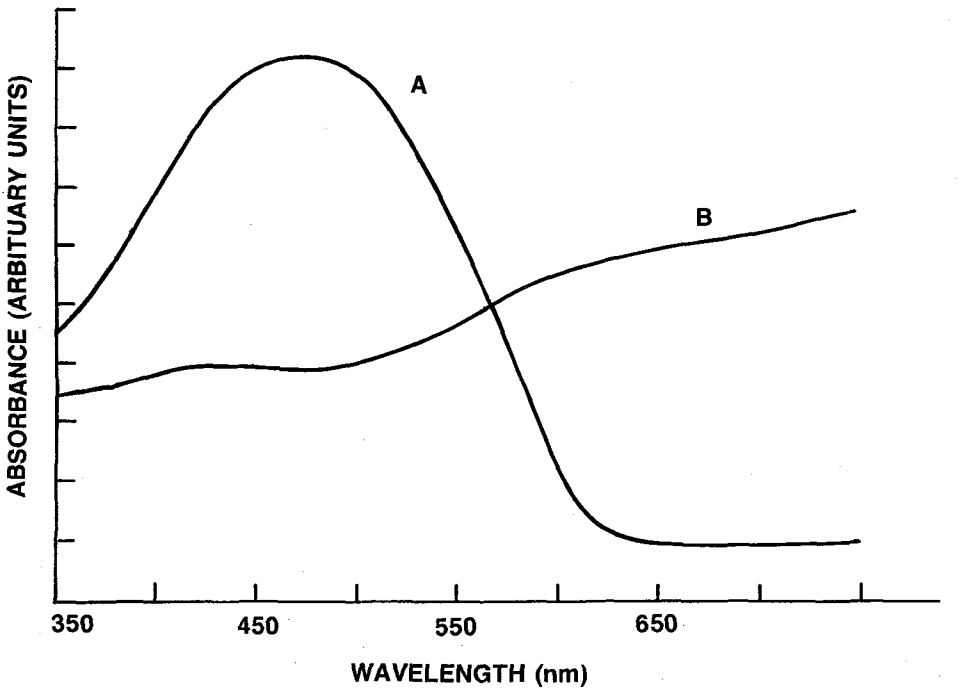

Figure 1: In situ visible absorption spectra of (a) neutral and (b) oxidized poly (2,2' bithiophene).

at 480 nm, corresponding to the interband transition, decreases considerably in going from the neutral polymer to the oxidized polymer. This suggests the near closing of the band gap. In a separate experiment it was observed that the oxidized polymer exhibited free-carrier absorption beginning at 1100 nm and extending to at least 1800 nm. The absorption at 750 nm for the oxidized polymer is in the same region as a peak assigned to charge transfer in complexes of 2,2' bithiophene and TCNE.[10] By stepping between 0.0 V and +1.0 V vs Ag/Ag^+ for a 1 sec pulse duration and then returning to 0.0 V, the film may be made to switch from red to green and back to red.

The response time was measured in situ by measuring the transmission at 640 nm. Figure 2 shows this response. The upper signal corresponds to the applied voltage switching from 0.0 V vs Ag/Ag^+ to +1.0 V vs Ag/Ag^+. The lower signal represents the transmission as detected by the photodiode. As the applied voltage changes from 0.0 V to +1.0 V, the film changes from red to green and the optical response represents the change in the amount of transmitted light. As illustrated in figure 2 (for an electrode surface 2.4 cm^2 and 4200 A thickness) switching speeds of 500 msec are obtainable. The response time of an electrochromic display has been shown to be dependent on the surface area of the active electrode.[11] Larger surface areas result in slower response times. As observed by scanning electron microscopy, the surface of poly(thiophene) films are very globular.[8] Thus, the films may have high surface area, and given that the area of the electrode is

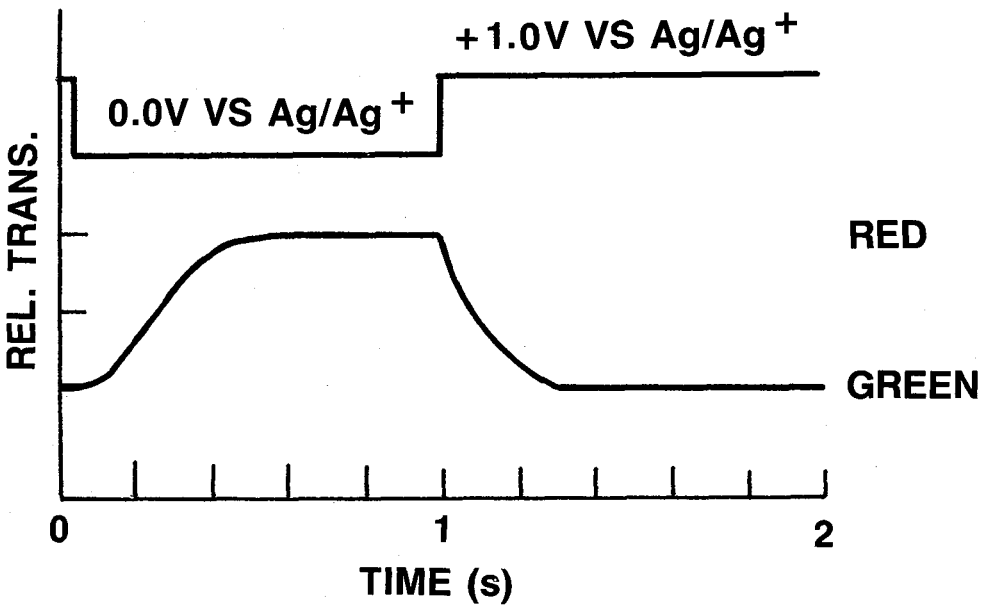

Figure 2: In situ response time of poly(2,2' bithiophene). Relative transmission at 640 nm vs time.

2.4 cm^2, the switching speed of 500 msec is not unexpected. Presumably faster switching speeds could be realized with smaller electrode areas.

In conclusion, we have shown that films of poly (2,2' bithiophene) possess interesting optical properties and therefore may be candidates for elements in electrochromic displays.

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