

Electrochemical and optical properties of an azo dye based conducting copolymer

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The electrochemical and optical properties of a novel conducting copolymer called poly(2,5'-dimethyl-[4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenyl]azobenzene-co-(3,4-ethylenedioxythiophene)) (poly(1-co-EDOT)) are reported. Electrochemically synthesized poly(1-co-EDOT) based on the azo dye has a well-defined and reversible redox couple (0.37 V vs. Ag/AgCl) with good cycle stability. The copolymer film exhibits high conductivity (13 S/cm) as well as electrochromic behavior (magenta when neutralized and transmissive sky blue when oxidized). Furthermore, electro-optically active copolymer film has a low band gap of 1.79 eV with a $\pi - \pi^*$ transition at 555 nm.

Key Words: Conducting polymers, copolymers, dithienylpyrrole, azobenzene, EDOT

Introduction

Conducting polymers continue to be a subject of great interest due to their potential applications in the development and the construction of new advanced materials including photovoltaic devices,¹ field effect transistors,² light emitting diodes,³ displays and electrochromic devices,⁴⁻⁶ and so forth.⁷ The reason behind this interest in conducting polymers is that their intrinsic properties (i.e. stability, conductivity, electronic and optical behaviors, etc.) can easily be tuned by the modification of their starting materials. For example, the attachment of electron donating ethylenedioxy substituents to thiophene leads to an electron-rich monomer

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called 3,4-ethylenedioxythiophene (EDOT) of which the polymer poly(3,4-ethylenedioxythiophene) (PEDOT) became a low potential, low band gap (1.6-1.7 eV),⁸ and highly conductive material when compared to thiophene.^{9,10} In a similar vein, it may also be possible to combine substances bearing different functionalities and/or properties in a single compound in order to obtain multifunctional materials. For example, chromophoric units can be incorporated into the polymer backbone and this may cause the derivatization of the electrical, optical, (photo)chromic, and nonlinear optical (NLO) properties. Based on this phenomenon, the incorporation of azobenzene units into the polymer backbone would be quite promising due to their reversible trans-cis photoisomerization, photochromic properties, and second order NLO properties.¹¹⁻¹³ However, there are, to our knowledge, only a few reports concerning the polymerization of thiophenes and pyrroles functionalized with diazobenzene appendages.¹⁴⁻¹⁷

Recently, we synthesized novel compounds based on dithienylpyrrole and diazobenzene units that could easily be polymerized by electrochemical means to give stable, processable, electrochromic, and electroactive materials.¹⁸ Unfortunately, one of these compounds, 2,5'-dimethyl-[4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenyl]azobenzene (**1**), provided the corresponding polymer film only with a limited thickness probably due to the poor solubility in LiClO₄/ethanol electrolyte solution. In this paper, we solved this problem by turning the spotlight on the synthesis of a novel conducting copolymer that was based on dithienylpyrrole, diazobenzene, and EDOT units, namely poly(2,5'-dimethyl-[4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenyl]azobenzene-co-(3,4-ethylenedioxythiophene)) (poly(**1**-co-EDOT)). This unique combination was amplified to create an environmentally stable, free-standing, electrochromic, and highly conducting polymeric film with desired thickness.¹⁹⁻²¹ Furthermore, electrochemical and optical properties of the conducting copolymer film were elucidated in comparison with P1 and PEDOT.

Experimental

Tetrabutylammonium hexafluorophosphate (TBAH) (Fluka) and EDOT (Aldrich) were used as received and monomer **1** was synthesized as previously described.¹⁸ Dichloromethane (DCM) was freshly distilled over CaH₂ under N₂ atmosphere. Electrolyte solution of 0.1 M TBAH dissolved in DCM was used for the electrocopolymerization of **1** and EDOT. Copolymer films were successfully synthesized via repetitive cycling or constant potential electrolysis using a 3-electrode system containing a platinum disk (0.02 cm²) and a platinum wire as working and counter electrodes, respectively, as well as Ag/AgCl in 3 M NaCl(aq) solution as a reference. The electrochemical and optical properties of obtained polymer films were investigated in monomer-free electrolyte solution after washing the coated working electrode with solvent (DCM) to remove the unreacted monomers and oligomeric species. For spectro-optical studies, indium-tin oxide (ITO, Delta Tech. 8-12 Ω, 0.7 cm × 5 cm) electrodes were coated with the polymer film. A platinum wire as counter electrode and a Ag wire as a pseudo-reference electrode (calibrated externally using a solution of ferrocene/ferrocenium couple) were used. The polymer films were switched between their redox states several times in monomer-free electrolyte solution in order to obtain reproducible results by equilibrating the redox behavior of the polymer films.

A 4-probe technique was used to measure the conductivity of the polymer films. The conductivity (σ) of these films was calculated from the relation $\sigma = (IL)/(Vwt)$, where L is the length between the contact on the film, w is the width and t is the thickness of the film.

Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat-galvanostat. The electro-optical spectra were measured on a Hewlett–Packard 8453A diode array spectrometer. NMR and FTIR spectra were recorded on a Bruker NMR Spectrometer (DPX-400) and a Bruker Vertex 70 Spectrophotometer, respectively. Photographs of the polymer films were taken using a Canon (PowerShot A75) digital camera.

Results and discussion

Redox Behavior of **1** and Its Electro-copolymerization with EDOT

Electrochemical behavior of **1** was investigated via cyclic voltammetry. During the first anodic scan **1** exhibited two oxidation peaks (Figure 1). The first oxidation peak at 0.75 V was ascribed to the radical cation formation of dithienylpyrrole system^{18,22,23} whereas the second one (1.37 V) was ascribed to the azo chromophore.¹⁶ Moreover, monomer **1** represented a quasi-reversible reduction peak with a half peak potential of -1.35 V due to the formation of radical anion in the azo chromophore.¹⁶

Monomer **1** was highly soluble in DCM and unfortunately no film formation on the electrode surface was observed via repetitive cycling or a prolonged anodic electrolysis due to the dissolution of the oligomeric species in the electrolyte solution.

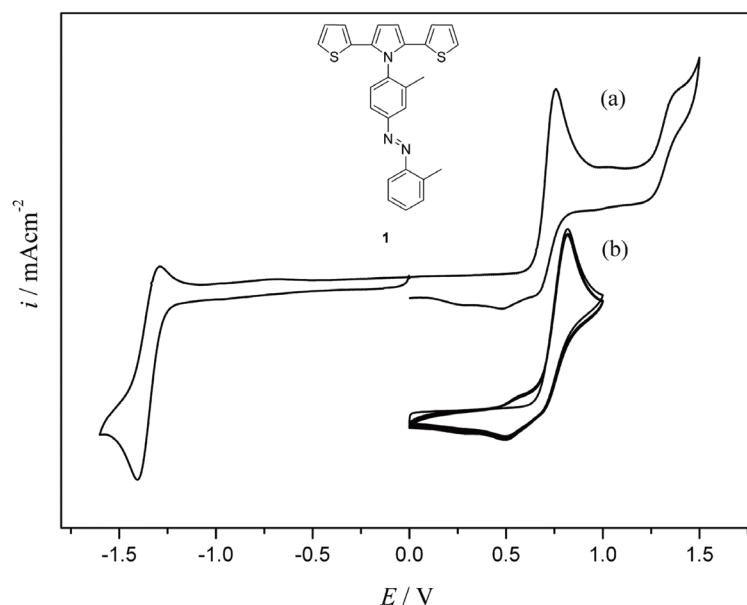


Figure 1. (a) Cyclic voltammogram of 2.5×10^{-3} M of **1** and (b) its repeated cyclic voltammogram in 0.1 M TBAH/DCM vs. Ag/AgCl at a scan rate of 100 mV/s.

In order to overcome this problem, the copolymerization of **1** and EDOT was attempted under similar conditions. Initially, a 1:4 monomer feed ratio of **1** and EDOT, respectively, was taken in order to obtain the electrogenerated copolymer film of poly(**1**-co-EDOT) via cyclic voltammetry and then the results were compared with PEDOT, which was obtained by repetitive cycling. As depicted in Figure 2a, the polymer film can easily

be electrogenerated by scanning the potential between -0.5 V and 1.2 V. A plausible working mechanism can be suggested as the attack of radical cation of monomer **1** on the neutral EDOT. The comparison of repetitive cyclic voltammogram of co-monomers and EDOT²⁴ (Figure 2b) clearly showed striking differences. After a certain number of cycles in the same potential range, the growth of the copolymer on the electrode surface was evident with 3 well-defined reduction peaks as shown in Figure 3. While the peaks at -0.28 V and 0.13 V can be attributed to the reduction of deposited PEDOT polymer film after the nucleation process,^{8,25} the third at 0.47 V can be ascribed to the P1.

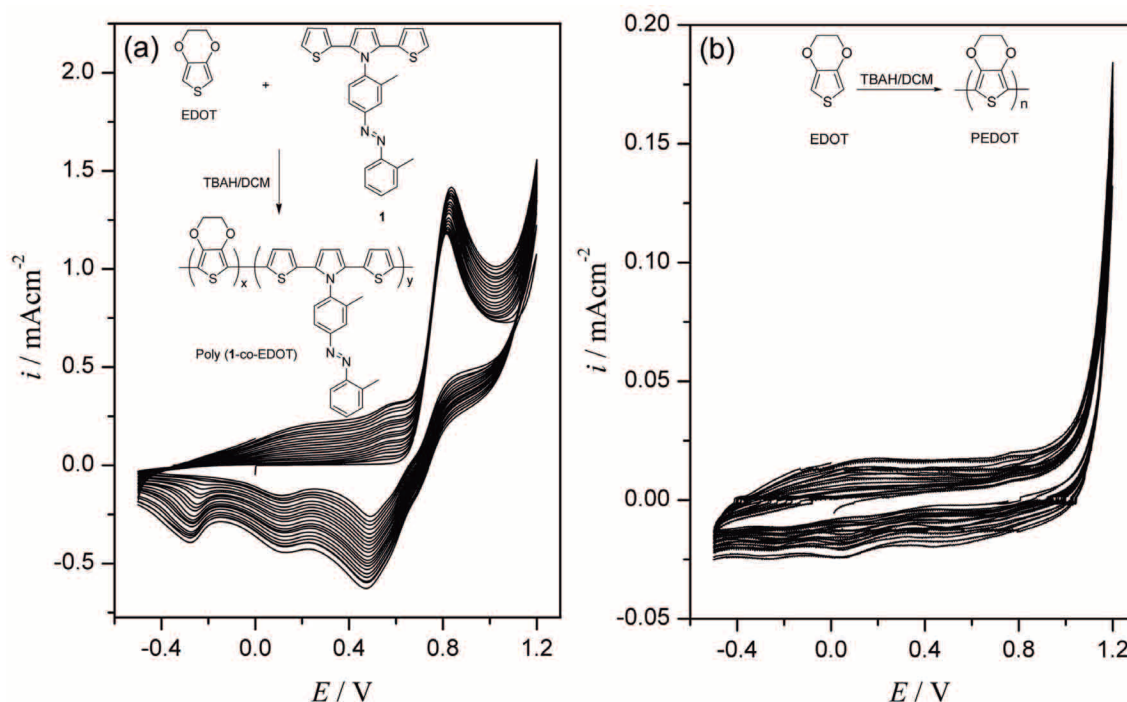


Figure 2. Repeated scan electropolymerization of (a) 2.5×10^{-3} M of **1** and 1.0×10^{-2} M of EDOT (1:4 feed ratio) and (b) 1.0×10^{-2} M of EDOT in 0.1 M TBAH/DCM vs. Ag/AgCl at a scan rate of 100 mV/s.

Figure 3b explicitly demonstrated the differences in electroactivity and redox behavior of the polymer films (poly(**1-co-EDOT**) and PEDOT). It was found that the reversible redox couple of copolymer film ($E_{p,a} = 0.43$ V and $E_{p,c} = 0.31$ V) was shifted to a higher potential value when compared to PEDOT ($E_{p,a} = 0.15$ V and $E_{p,c} = 0.07$ V) and it was shifted to lower potential when compared to P1 ($E_{p,a} = 0.66$ V and $E_{p,c} = 0.49$ V),¹⁸ which indicates the formation of the copolymer since the redox couple of the copolymer was observed between those of its homopolymers as expected (see Table).

The copolymer film was environmentally robust and retained its reversible and well-defined redox couple even after hundreds of cycles and/or at high scan rates. The linearity between peak currents and scan rates indicates the formation of a well-adhered polymer film on the electrode surface as well as a non-diffusional redox process.

The conductivities of the poly(**1-co-EDOT**) and PEDOT at room temperature were found to be 13 S/cm and 19 S/cm, respectively.^{9,10} It can be concluded that due to the insertion of dithienylpyrrole units bearing

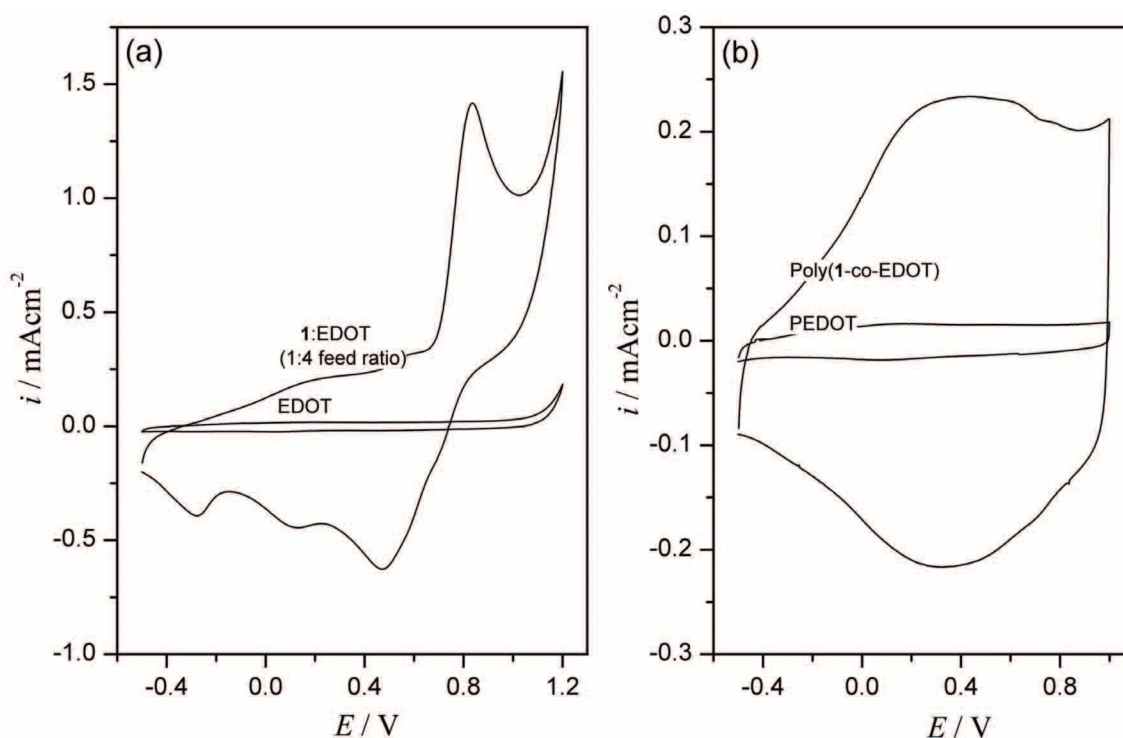








Figure 3. (a) Cyclic voltammograms of the 20th cycle of **1** and EDOT comonomer and EDOT, separately and (b) poly (**1-co-EDOT**) and PEDOT films obtained after 20th cycle repeated electropolymerization in 0.1 M TBAH/DCM vs. Ag/AgCl at a scan rate of 100 mV/s.

Table. Electrochemical and optical data for P1, PEDOT and poly(**1-co-EDOT**).

Polymer	$E_{ox,1/2}(V)^a$	λ_{max} (nm)	E_g (eV)	σ (S/cm)	Neutral State	Oxidized State
P1	0.58	435	2.31	-		
Poly(1-co-EDOT)	0.37	555	1.79	13		
PEDOT	0.11	592	1.66	19		

^aCyclic voltammograms were recorded at 100 mV/s vs. Ag/AgCl.

azo dyes, which affects the conjugation of the polymer backbone, the conductivity of the copolymer is somewhat smaller than that of PEDOT. On the other hand, no appreciable change was observed in the conductivity of copolymer even after standing at ambient conditions for a prolonged period of time (1 month or more).

Electro-optical Properties of Poly(1-co-EDOT)

Electro-oxidation behavior of **1** was monitored via in situ UV-vis spectrophotometry. The absorption of the electrogenerated oligomeric species was intensified at 780 nm and 860 nm. Unfortunately, these oligomeric species were highly soluble in the electrolyte solution and could not be deposited on the ITO electrode surface. To our delight, however, electrodeposition became possible when a mixture of **1** and EDOT was electropolymerized to give poly(**1**-co-EDOT) (Figure 4a).

The absorption bands at 775 nm and 867 nm definitely confirmed the presence of both **1** and EDOT in the polymer backbone (Figure 4). In order to probe the electro-optical properties, attempts were made to neutralize the copolymer film at -0.5 V where 3 absorption bands were observed at 555 nm, 775 nm, and 867 nm. Unfortunately, the copolymer film could not be neutralized fully since the absorption bands attributed to charged oligomeric **1** species were not diminished even at higher negative potentials. Therefore, it can be safely concluded that the absorption band at 555 nm can be ascribed to the $\pi - \pi^*$ transition and by the onset of this band the optical band gap (E_g) was found to be 1.79 eV, which is between the E_g values of P**1** (2.31 eV)¹⁸ and PEDOT (1.66 eV).

Upon oxidation, the absorption band at 555 nm decreased whereas the absorption bands at 775 nm and 867 nm started to intensify simultaneously due to the polaron formation. Upon further oxidation, the $\pi - \pi^*$ transition band was shifted to a higher energy level and diminished completely with a concomitant increase in the intensity of 1100 nm due to the bipolaron formation. Based on these findings, it can be safely noted that the copolymer film exhibited quite different electro-optical behavior when compared to that of PEDOT and P**1**.¹⁸

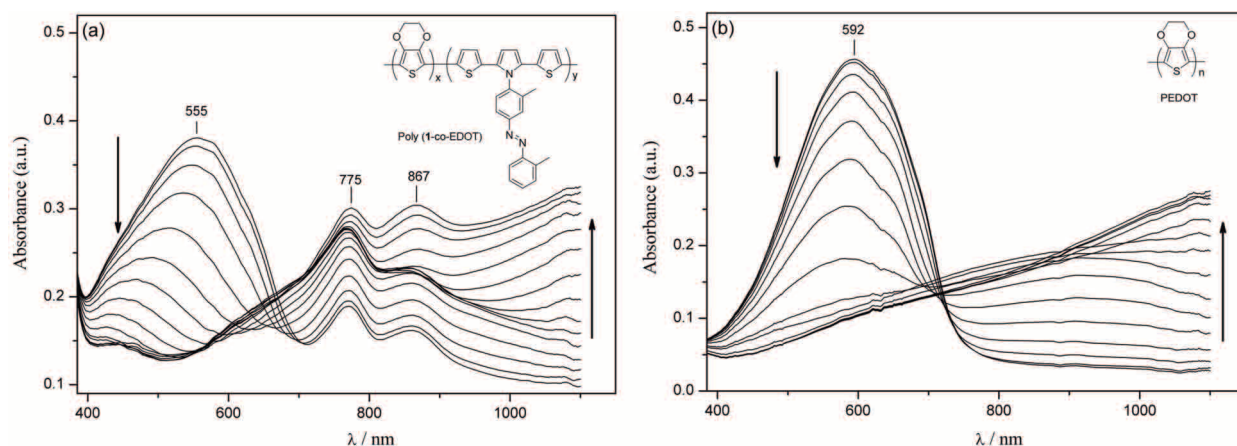


Figure 4. Electronic absorption spectra of (a) poly(1-co-EDOT) from -0.5 V to 1.0 V and (b) PEDOT from -1.0 to 1.0 V vs. Ag wire in 0.1 M TBAH/DCM.

Furthermore, the copolymer film exhibited a color change from magenta to transmissive sky blue (Table) and these colors are completely different than those of P1 and PEDOT. For example, yellow-green and blue colors were observed at the neutral state of P1 and PEDOT, respectively (Table). It is noteworthy that the color change from magenta to sky blue is also a quite significant trait in CMY (cyan, magenta, yellow) colors, which makes the copolymer amenable for use in electrochromic devices and/or displays along with the magenta color of the neutral state.

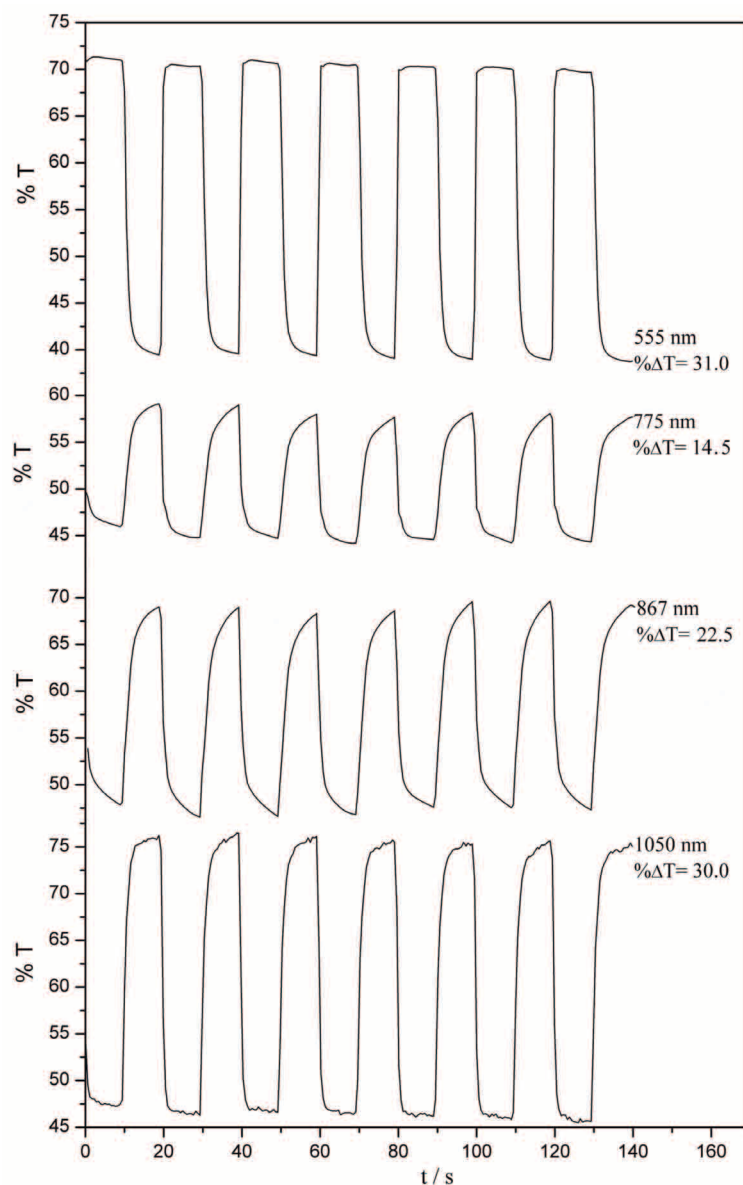


Figure 5. Chronoabsorptometry experiment for poly(1-co-EDOT) on ITO in 0.1 M TBAH/DCM while it is switched between -0.5 V and 1.0 V vs. Ag wire with a residence time of 10 s at each potential.

In addition, a square wave potential step method was used in order to investigate the stability and the electro-optical responses during switching between the redox states (the neutral and oxidized states). As shown in Figure 5, the percentage transmittance change ($\% \Delta T$) at 555 nm is 31% and the switching abilities of the copolymer film occur with a response time of 1.0 s from the neutral to the oxidized states and 2.8 s for the reverse process. Moreover, the copolymer film exhibited long-term stability; it does not completely lose its electro-optical properties after 1000 cycles.

Conclusion

In summary, a novel conducting copolymer based on dithienylpyrrole, azobenzene, and EDOT units was successfully synthesized by electrochemical means and characterized. Poly(1-co-EDOT) exhibited a well-defined reversible redox couple and high stability. The conductivity and the band gap of poly(1-co-EDOT) were found to be 13 S/cm and 1.79 eV, respectively. Furthermore, the copolymer showed multielectrochromic behavior. The incorporation of azo dyes into the conducting polymer certainly provided striking electrochemical and optical properties, which made it amenable for use in material science as electrochromic devices and displays. Further extension of this work to optical data storage media and NLO devices by means of photoisomerization is now in progress and the results will be reported in due course.

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