

Synthesis and Characterization of Poly(thiophen-3-yl acetic acid 4-pyrrol-1-yl phenyl ester-co-*N*-methylpyrrole) and Its Application in an Electrochromic Device

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ABSTRACT: Copolymer of thiophen-3-yl acetic acid 4-pyrrol-1-yl phenyl ester (TAPE) with *N*-methylpyrrole (NMPy) was synthesized by potentiostatic electrochemical polymerization in acetonitrile–tetrabutylammonium tetrafluoroborate solvent–electrolyte couple. The chemical structures were confirmed via Fourier transform infrared spectroscopy (FTIR), cyclic voltammetry (CV), and UV–vis spectroscopy. Electrochromic and spectroelectrochemical properties of poly(TAPE-co-NMPy) [P(TAPE-co-NMPy)] were investigated. Results showed that the copolymer revealed color change between light yellow and green upon doping and dedoping of the copolymer, with a moderate

switching time. Furthermore, as an application, dual-type absorptive/transmissive polymer electrochromic device (ECD) based on poly(TAPE-co-NMPy) and poly(3,4-ethylene dioxythiophene) (PEDOT) have been assembled, where spectroelectrochemistry, switching ability, stability, and optical memory of the ECD were investigated. Results showed that the device exhibited good optical memory and stability with moderate switching time. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1988–1994, 2006

Key words: dual-type electrochromic device; electropolymerization; electrochromic polymers

INTRODUCTION

Intense research has been carried out recently to find out new electrochromic polymeric materials to be used in devices. Electrochromic devices (ECDs) attract great interest because of their potential use in various applications, such as information display and storage, automotive industry (rear-view mirrors and visors), and architecture (“smart windows” to save energy in buildings through the control of sunlight transmission).¹ ECDs based on conducting polymers have become a recent focus of research because they are electroactive and potentially electrochromic materials, and offer the advantage of high degree of color tailorability.²

An ECD is essentially a rechargeable battery in which the electrochromic material is separated by a suitable solid or liquid electrolyte from a charge balancing counter electrode, and it changes its color upon charging and discharging with applied potential of a few volts.³ The use of polymeric electrolyte has the advantages of preventing leaking, eliminating the need for sealing, since no solvent evaporation takes

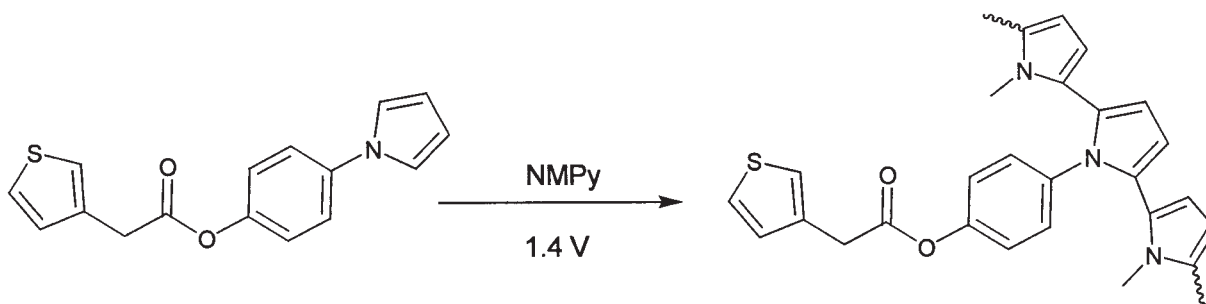
place, all of which occur when liquid electrolyte is used to assemble an ECD.^{4,5} The color change is commonly between a transparent (bleached) state and a colored state, or between two colored states, which results from generation of different visible region in the electronic absorption bands upon switching.^{6–7}

The ability to tune color constitutes an important goal in the design of ECDs. There are three major strategies to control the color of electrochromic polymers. The polymer’s band gap is directly related to the relative energies of HOMO and LUMO. By substituting the polymer’s repeat unit, the electrochromic properties can be controlled by the induced steric and electronic effects.⁸ These substituents determine the effective conjugation length and electron density in the polymer backbone. Copolymerization or homopolymerization can lead to an interesting combination of the properties. The color of copolymers based on carbazole, thiophene, and pyrrole derivatives can be controlled by altering the ratio of the respective monomer.⁹ Blends, laminates, and composite offer a third method. The use of two polymers covering different color regions is a simple way to achieve multicolor ECDs.¹⁰

Electrochemical techniques such as cyclic voltammetry (CV), coulometry, chronoamperometry, and spectroscopic measurements are used for characterization of both single polymer electrode and ECD, which enables us to decide whether they are suitable for

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Scheme 1. Synthesis route of P(TAPE-co-NMPy).

commercial purposes. The requirements for high-performance ECD are high coloration efficiency, short response time, good stability, optical memory, optical contrast, and color uniformity.¹¹

In a previous publication, we described the synthesis and characterization of thiophen-3-yl acetic acid 4-pyrrol-1-yl phenyl ester (TAPE), its homopolymer, and its copolymers with pyrrole and bithiophene.¹² Moreover, the characteristics of dual-type ECD based on poly(TAPE-co-BiTh) and poly(3,4-ethylenedioxythiophene) (PEDOT) were reported. With the help of CV, the route of polymerization, namely through pyrrole moiety, was determined. Attempts to use thiophene as a comonomer required higher applied potentials which in return led to overoxidation of pyrrole unit. This causes a decrease in the electroactivity of TAPE as determined by multiscan voltammograms. Thus, the use of comonomers having an oxidation potential comparable to bithiophene will make sense; hence, the choice of *N*-methylpyrrole (NMPy) is based on this fact.

In this work, we report our research efforts focused on the synthesis and characterization of new copolymers of TAPE with an *N*-substituted pyrrole to be used as anodically coloring electrode in the construction of a dual-type ECD. PEDOT was selected as the cathodically coloring electrode, which exhibits high electrochromic contrast, low oxidation potential, and high conductivity as well as good electrochemical and thermal stability.¹³

EXPERIMENTAL

Materials

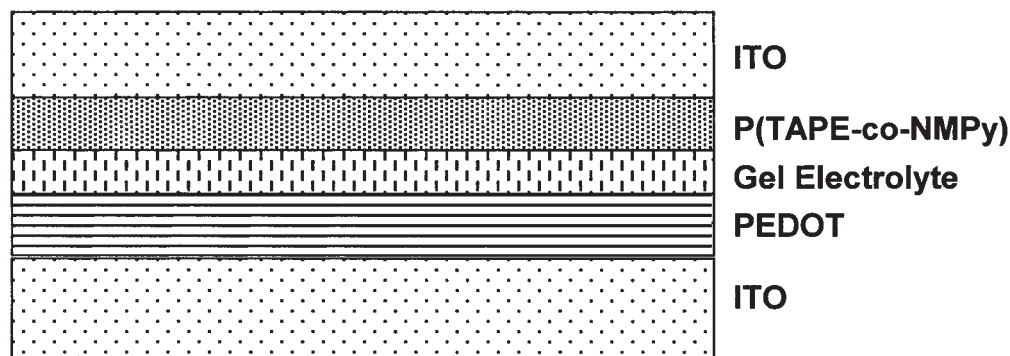
N-Methylpyrrole (NMPy), tetrabutylammonium tetrafluoroborate (TBAFB), propylene carbonate (PC), poly(methyl methacrylate) (PMMA), 3,4-ethylenedioxy thiophene (EDOT), and triethylamine were purchased from Aldrich and used as-received. Acetonitrile (ACN) and dichloromethane were obtained from Merck and distilled prior to use.

Cyclic voltammetry

The oxidation/reduction behavior of homopolymer of TAPE (PTAPE) with a solution of 0.025M TAPE in the presence of 0.0125M NMPy was investigated by CV using ACN-TBAFB solvent-electrolyte couple between 0 and 1.6 V. Experiments were carried out in a three electrode system with Pt as the counter electrode, Ag/Ag⁺ as the reference electrode, and indium tin oxide (ITO)-coated glass as the working electrode. The potential control was achieved by means of a Solartron 1285 model potentiostat/galvanostat. Polymer growth of P(TAPE-co-NMPy) was recorded in a solution containing 0.0125M NMPy and 0.025M TAPE over a potential range 0.0–1.6 V with a scan rate of 250 mV/s.

Synthesis of copolymers of tape with NMPy

Synthesis of TAPE monomer was reported earlier¹² via the esterification reaction of thiophen-3-yl-acetyl chloride with 4-pyrrol-1-yl-phenol in the presence of triethylamine in dichloromethane at 0°C. Copolymer of TAPE in the presence of NMPy was synthesized via constant potential electrolysis (Solartron 1285 potentiostat/galvanostat) in a one compartment cell. Pt buttons were used both as working and counter electrodes and Ag/Ag⁺ was the reference electrode. A solution of 0.025M TAPE and 0.0125M NMPy was prepared. TBAFB (0.1M) was used as the supporting electrolyte and the electrolysis was performed at 1.4 V. Synthesis route is shown in Scheme 1. Films were washed to remove the unreacted monomer and supporting electrolyte, and later characterized by FTIR, which was recorded on a Nicolet 510 FTIR spectrometer. To investigate the electrochromic properties of the copolymer, same procedure was applied during synthesis, with the exception of using ITO as working electrode. The electrochromic properties of the copolymer were investigated by spectroelectrochemical and kinetic studies, which are performed with Agilent 8453 UV-vis spectrophotometer.



Scheme 2. Schematic representation of the ECD.

Gel electrolyte preparation

The gel electrolyte for ECD based on PMMA was plasticized using 1,2-PC to form a highly transparent and conductive gel. A high vapor pressure solvent (ACN) was used to dissolve the PMMA and TBAFB, and to allow an easy mixing of the gel components. After stirring and heating, PC was added. The composition of casting solution (by weight ACN : PC : PMMA : TBAFB) was 70 : 20 : 7 : 3.⁴

Device assembly and characterization

The synthesis of anodically coloring polymer was achieved under the same conditions used for the synthesis of the copolymer. The cathodically coloring polymer (PEDOT) was potentiostatically deposited onto the ITO-coated glass at 1.5 V from a 0.1M EDOT solution. In both cases, 0.1M TBAFB/ACN was used as the electrolyte-solvent couple. The redox sites of these polymer films were matched by stepping the potentials between -0.8 and $+1.6$ V for copolymer and -1.0 and $+1.2$ V for PEDOT. The copolymer-coated electrode and the PEDOT-coated electrode were polarized at $+1.6$ and -1.0 V versus Ag/Ag⁺, respectively, in ACN/TBAFB (0.1M) solvent-electrolyte couple. Afterwards, the films were coated with gel until the entire polymer surface was covered with a uniform, thin layer of gel electrolyte and sealed in sandwich configuration and allowed to dry under atmospheric conditions. The construction of an absorption/transmission-type device is depicted in Scheme 2. The spectroelectrochemical, kinetic, open circuit studies of the device were performed with Agilent 8453 UV-vis spectrophotometer. Colorimetry measurements were done with a Coloreye XTH Spectrophotometer (GretagMacbeth). In both colorimetry and spectroscopic studies, a background measurement was taken using a blank device containing two ITO electrodes held together by the gel electrolyte. A single ITO electrode was used as the blank during the colorimetry studies of copolymer.

RESULTS AND DISCUSSION

Cyclic voltammetry

The polymer growth behavior of homopolymer (PTAPE) and copolymer (P(TAPE-co-NMPy)) was investigated by CV on ITO electrodes at room temperature. Cyclic voltammogram of TAPE in 0.1M TBAFB/ACN revealed oxidation and reduction peaks at 0.95 and 0.70 V versus Ag/Ag⁺, respectively. The current response of this redox process continues to increase in intensity upon additional cycling, consistent with the deposition of an electroactive polymer onto the surface of the working electrode. Figure 1(a) shows the multiple runs for electropolymerization of TAPE on ITO electrode.

After the addition of NMPy to the system, a reduction peak appeared at $+0.4$ V, and the oxidation peak, though not well-defined, shifts to right upon successive runs. This redox behavior was different than that of both homopolymer and PNMPy [Fig. 1(b,c)] in terms of the increase in the increments between consecutive cycles and the oxidation reduction potentials of the material. This difference in CVs may indicate an interaction between TAPE and NMPy, possibly a copolymer formation (Fig. 1).

FTIR spectra

The FTIR spectrum of the electrochemically synthesized P(TAPE-co-NMPy) shows the presence of C=O and C—O—C stretching vibrations at 1752 and 1116 cm⁻¹ respectively, which are the characteristic functional groups of monomer. Besides, the peak at 2983 cm⁻¹ is due to C—H stretching vibrations of methyl group, the shoulder at 1438 cm⁻¹ may be attributed to out-of-plane bending of C=C—C in the ring and inter rings, the peak at 1321 cm⁻¹ may be due to C—C and C—N stretching vibrations. The presence of C=C—N, C=C—C, and C—N—C are indicated by the absorption at 1193 cm⁻¹.¹⁴ Moreover, the peak at 1082 cm⁻¹ revealed the presence of dopant ion in the structure, which confirms that the polymerization has occurred.

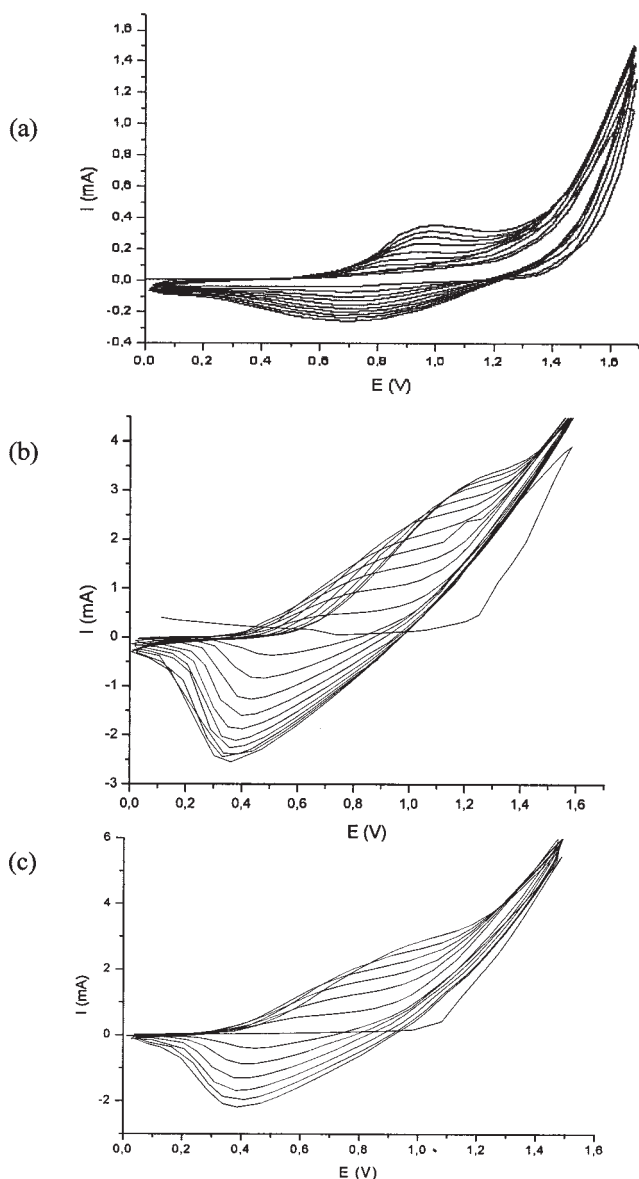


Figure 1 Cyclic voltammograms of (a) TAPE, (b) P(TAPE-co-NMPy), and (c) P(NMPy).

Spectroelectrochemistry of P(TAPE-co-NMPy)

The change in optical properties that accompany the redox switching of conjugated polymers can be examined through spectroelectrochemistry. Spectroelectrochemistry experiments reveal key properties of conjugated polymers such as band gap (E_g) and the intergap

TABLE I
Conductivity Values of the Polymers

Sample	Conductivity (S/cm)
P(TAPE)	2×10^{-10}
P(TAPE-co-NMPy)	5×10^{-7}
PNMPy	2.5×10^{-6}

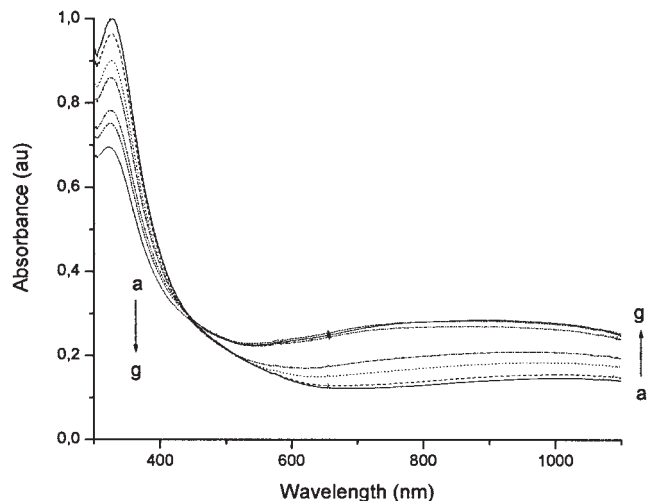


Figure 2 Optoelectrochemical spectrum of poly(TAPE-co-NMPy) at applied potentials: (a) -0.8 V, (b) -0.4 V, (c) 0 V, (d) 0.4 V, (e) 0.8 V, (f) 1.2 V, and (g) 1.6 V.

states that appear upon doping.¹⁵ To study the optical properties of the copolymer, we potentiostatically deposited the film (1.4 V versus Ag/Ag^+) onto ITO-coated glass slides. The coated electrodes were placed in a monomer free electrolyte solution in a quartz cuvette. Figure 2 illustrates the optoelectrochemical spectrum of P(TAPE-co-NMPy) while changing the applied potential between -0.8 and 1.6 V. At the lowest applied potential, the polymer was in its reduced state revealing an absorption due to π - π^* transition with a λ_{max} value for 341 nm. The electronic band gap, which is defined as the onset energy for the π - π^* transition, was determined as 2.7 eV for the copolymer. Upon increase in the applied potential, evolution of new band beyond 600 nm was observed due to formation of charge carrier bands, which was followed by the depletion of the absorption at λ_{max} . These data were different than that of pure PNMPy, having λ_{max} at 335 nm and a band gap of 2.0 eV. The color of the copolymer changes between green and light yellow, whereas that of PNMPy changes from transparent to brown¹⁶ at oxidized and reduced states, respectively.

Switching of P(TAPE-co-NMPy)

To investigate the electrochromic switching properties of the copolymer, a film was prepared on ITO under same conditions as for spectroelectrochemistry. The film was switched between 0.0 and 1.6 V in monomer-free ACN/TBAFB ($0.1M$) solvent-electrolyte couple. Figure 3 shows the percent transmittance variations of this film at the wavelength of maximum contrast while applying a square wave potential with a residence time of 5 s. Results imply that the copolymer has a optical contrast of 15.5 with a switching time of

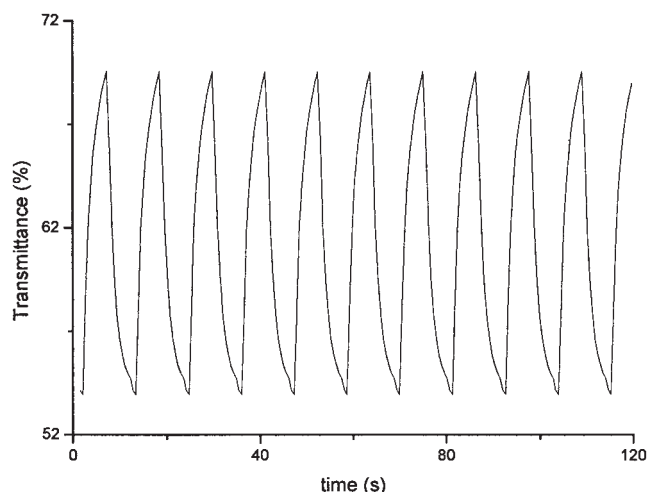


Figure 3 Optical switching of P(TAPE-co-NMPy) monitored at 800 nm between -0.8 and 1.6 V.

3.9 s. The polymer's switching time was calculated at 95% of the full switch because it is difficult to perceive any further color change with the naked eye beyond this point.¹⁷

Electrochromic device application

During construction of the ECD it was important to balance the charge capacities of the electrochromic layers, before assembling the devices. Uneven balancing would result in incomplete electrochromic reaction and residual charges will remain during the coloring/bleaching processes. This will lead to residual coloration of the ECD in the bleached state. To minimize the effect of charge imbalances in ECD, we matched the redox charges of the two complementary polymer films by chronocoulometry and we provided a balanced number of redox sides for switching. Before sealing the ECD, anodically coloring polymer film (the copolymer) was fully reduced and the cathodically coloring polymer (PEDOT) was fully oxidized to achieve complementary operating conditions.

Spectroelectrochemistry of device

Spectroelectrochemistry studies were carried out to elucidate variations of the electronic transitions of P(TAPE-co-NMPy)/PEDOT, upon incremental increase in the applied potential. Figure 4 represents the absorption spectrum of P(TAPE-co-NMPy)/PEDOT, recorded by application of different voltages between -0.4 and 1.6 V. At -0.4 V (bias to the copolymer layer), the copolymer layer was in its neutral state, where the absorption at 330 nm was due to $\pi-\pi^*$ transition of the copolymer. At this potential, PEDOT was in oxidized state revealing no pronounced absorption at the UV-vis region of the spectrum, thus

the color of the device was light yellow. As the applied potential increased the copolymer layer started to oxidize, and a decline in the intensity of the absorption was observed. Meanwhile, PEDOT layer was in its reduced state, which was followed by the appearance of the new absorption at 610 nm and dominated the color of the device as blue.

Switching of device

Response time is one of the most important characteristics of ECD's, which is defined as time required for switching between two colored states. The variation in % transmittance (% T) at the wavelength of maximum contrast was monitored using a UV-vis spectrophotometer, while applying a square wave potential (-0.5 and 1.5 V) with a residence time of 5 s to analyze the switching characteristics of the ECD. The maximum contrast of transmittance was 26% at 600 nm (Fig. 5). The switching time for P(TAPE-co-NMPy)/PEDOT was experimentally determined to be 2.8 s, where the switching time was calculated at 95% of the full switch because it is difficult to perceive any further color change with the naked eye.

Open circuit stability

The optical memory of an ECD is defined as the time during which the material retains its color with no applied potential (open circuit).¹⁸ This effect was studied by polarizing the device between two states and by measuring its spectra under open circuit at regular time intervals (Fig. 6). Initially, the device was polarized by the application of 1.5 V for 1 s and subsequently the circuit held disconnected for 200 s. Mean-

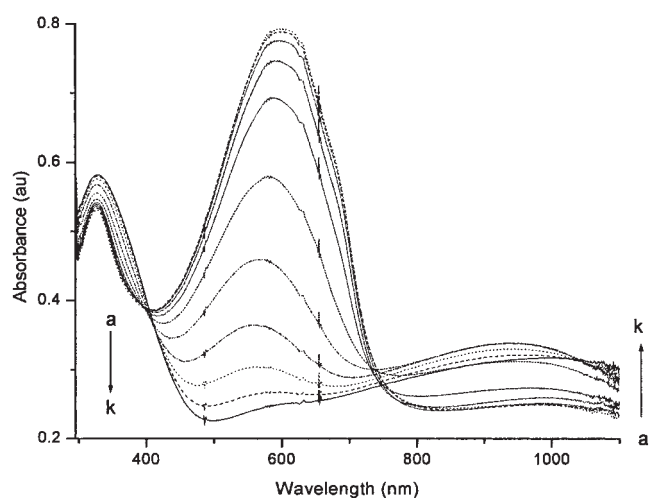


Figure 4 Optoelectrochemical spectrum of poly(TAPE-co-NMPy)/PEDOT device at applied potentials: (a) -0.4 V, (b) -0.2 V, (c) 0 V, (d) 0.2 V, (e) 0.4 V, (f) 0.6 V, (g) 0.8 V, (h) 1.0 V, (i) 1.2 V, (j) 1.4 V, and (k) 1.6 V.

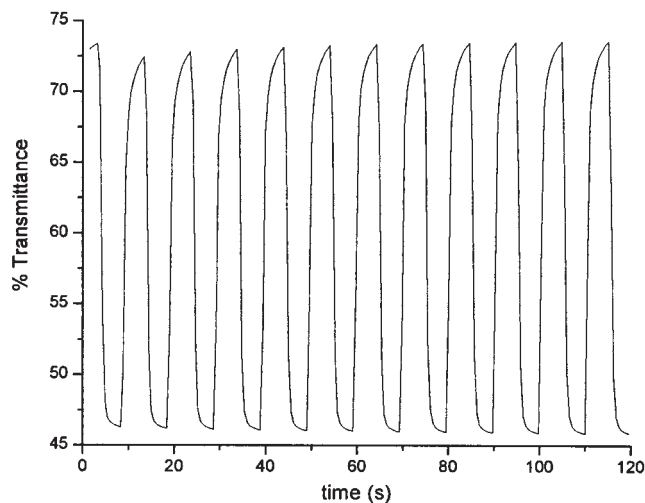


Figure 5 Optical switching of P(TAPE-co-NMPy)/PEDOT monitored at 600 nm with potential stepped between -0.5 V and 1.5 V (5 s each).

while the transmittance was recorded as a function of time. The same procedure was repeated with -0.5 V. Both blue and green states are highly stable, which revealed almost no % T loss. The color persistence in the ECDs is an important feature because it is directly related to aspects involved in its maintenance without decomposition and energy consumption during use.¹⁹ Thus, P(TAPE-co-NMPy)/PEDOT is astonishingly well performing at open circuit conditions, which might be very useful in many applications, like polymeric memory devices.

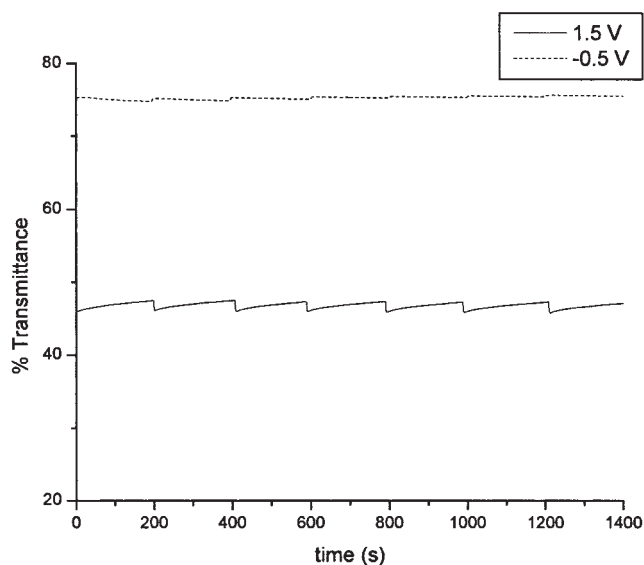


Figure 6 Open circuit memory of P(TAPE-co-NMPy)/PEDOT device monitored by single wavelength absorption spectroscopy at 600 nm by application of -0.5 and 1.5 V pulses for 1 s for every 200 s.

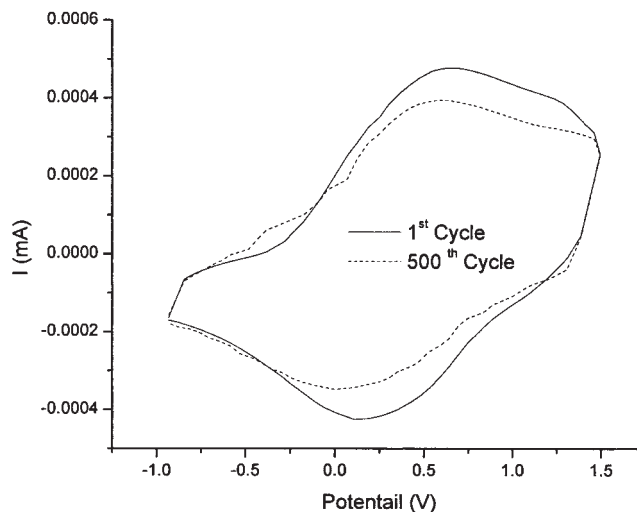


Figure 7 Stability of P(TAPE-co-NMPy)/PEDOT ECD, which was investigated via continuous scanning by CV at scan rate 500 mV/s.

Stability

The stability of bleached and colored states toward multiple redox switches often limits the utility of electrochromic materials in ECD applications. Main reasons for device failure are different electrochemical windows and/or environmental requirements of the complementary materials. The oxidation process of the anodic material should coincide with the reduction process of the cathodic electrochromic material to maintain charge balance within the ECD.²⁰ The long-term stability of P(TAPE-co-NMPy)/PEDOT device was monitored by CV. P(TAPE-co-NMPy)/PEDOT device shows a good redox stability upon sweeping between -1.0 and 1.5 V (Fig. 7) with a scan rate of 500 mV/s. There is only limited decrease in current response between 1st and 500th cycles, indicating good stability for the device.

Colorimetry

Color measurements of P(TAPE-co-NMPy), pure P(NMPy), and P(TAPE-co-NMPy)/PEDOT device were performed at the extreme states of the electrochromic material. L (luminance), a (hue), b (saturation) values are tabulated in Table II. $L \times a \times b$ values of the pure P(NMPy) and the copolymer were different from each other, which could be considered as another proof of copolymerization. The copolymer revealed a light yellow color and green color in its reduced and oxidized states. Consecutively, the device switches color between light yellow and blue.

CONCLUSIONS

In this study, a new copolymer of TAPE, poly(TAPE-co-NMPy), was synthesized successfully. Investigation

TABLE II
Electrochromic Properties of Electrochromic Materials

Electrochromic material	λ_{\max} (nm)	E_g (eV)	Color		Oxidation			Reduction		
			Oxidation	Reduction	<i>L</i>	<i>a</i>	<i>b</i>	<i>L</i>	<i>a</i>	<i>b</i>
P(TAPE- <i>co</i> -NMPy)	341	2.7	Light yellow	Green	48	-11	-10	62	6	14
PNMPy	335	2	Transparent	brown	63	-8	4	70	-4	7
P(TAPE- <i>co</i> -NMPy)/PEDOT	—	—	Light Yellow	Blue	37	-1	22	60	-5	5

of electrochromic properties of the copolymer via spectroelectrochemistry and colorimetry studies and evaluation of its switching ability were also achieved. Colorimetry and kinetic studies showed that the resulting conducting copolymer switch between light yellow and green colors with moderate switching time. An ECD composed of P(TAPE-*co*-NMPy), PEDOT, and a gel electrolyte was assembled, and its electrochromic and spectroelectrochemical features were analyzed. The device exhibited a good optical contrast with $\Delta T_{600 \text{ nm}} = 26\%$, with an optical response time of 2.8 s. The device has a significantly good optical memory in both states and highly stable between -0.5 and 1.0 V.

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