Toward the Development of New Textile/Plastic Electrochromic Cells Using Triphenylamine-Based Copolymers

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We report the preparation and characterization of new electrochromic polymers containing a 4-butyltriphenylamine (BuTPA) unit on the main chain. All polymers were obtained through the Suzuki−Miyaura cross-coupling reaction between 4-butyl-*N*,*N*-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-4-phenyl)aniline) and several aryl dibromide molecules to modulate the electronic properties of the resulting copolymers. 2,5-Dibromothiophene, 2,5-dibromo(3,4-ethylenedioxythiophene), 3,6-dibromo-*N*-octylcarbazole, bis(6-bromo-*N*-octylcarbazol-3-yl), and 2,7-dibromo-3,6-dimethoxy-9,9-dihexylfluorene were used as comonomers and led to five new copolymers, PT(BuTPA), PE(BuTPA), PC(BuTPA), PCC(BuTPA), and PF(BuTPA). These polymers are readily soluble in many common organic solvents, which make them suitable for spray-coating film deposition. Electrochromic cells with the following configuration were assembled: ITO-coated glass or plastic/electrochromic polymer/gel electrolyte/ITO-coated glass or plastic or conducting textile. These copolymers exhibit good optical and electrochemical properties for military camouflage needs with color transition from pale yellow to green, transparent to khaki, or pale green to reddish-brown. Electrochemistry, spectroelectrochemistry, and colorimetric measurements of the devices were examined.

Introduction

Electrochromism is known as the reversible change of the color resulting from the oxidation or the reduction of the material by electrochemical means. This interesting property led to the development of many technological applications such as automatic anti-glazing mirror,[1] smart windows,[2] electrochromic displays,[3,4] and chameleon materials.[5−7] Hitherto, a wide variety of electrochromic materials have been developed, which can be classified into four distinct families. The first family of electrochromic materials includes the widely used metal oxides such as tungsten trioxide (WO_3) or iridium dioxide (IrO_2).[8] The second family is composed of mixed-valence metal complexes such as Prussian blue.[9] The third one includes small organic molecules such as viologens and phthalocyanines, while the fourth family is composed of side-chain-substituted polymers or main-chain fully conjugated polymers.[10−13] Among all of these electrochromic materials developed over the past few years, conjugated polymers such as poly(3-alkylthiophene)s, poly(3,4-alkylenedioxythiophene)s, and poly(pyrazine)s derivatives have emerged as promising candidates for large and flexible electrochromic devices.[14−23] Like inorganic and organic compounds, these materials show high coloration over a wide range, good coloration efficiency, low operation voltage, and fast switching abilities (for displays applications), but the most exciting properties are the fine-tuning of the color transition through chemical structure modification of the conjugated backbone and the multichromism. Studies from Reynolds et al.[24−29] have shown a wide variety of conjugated polymers with color changes that cover the

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entire visible spectrum. However, few electrochromic polymers have been obtained by means other than electropolymerization or oxidative polymerization.[16−18,29] These polymerization methods have several inherent drawbacks such as the lack of film uniformity over large surface, low material recovery, or even irregular linkages within the polymer backbone. Moreover, due to the intrinsic properties of conjugated polymers, these electrochromic materials are often highly colored in their neutral state.

Electron-rich triarylamines are known to be easily oxidized to form stable polarons, and the oxidation process is always associated with a noticeable change of the coloration. Furthermore, triarylamine-based polymers are widely used as the hole-transport layer in electroluminescent diodes, but they also show interesting electrochromic behavior.[30−35] The scope of this work is to obtain electrochromic polymers with color tones that fit either desert or forest background for military camouflage. We report the preparation and the characterization of five new triphenylamine-containing polymers through the Suzuki−Miyaura cross-coupling reaction. We have been able to modulate the electronic properties of the materials by varying the comonomer used along with the 4-butyltriphenylamine unit. The resulting copolymers, PT(BuTPA), PE(BuTPA), PC(BuTPA), PCC(BuTPA), and PF(BuTPA), were readily soluble in most common organic solvents such as chloroform, dichloromethane, toluene, and tetrahydrofuran. All-solid-state electrochemical cells were prepared by spray-coating the copolymers onto ITO-coated glass or ITO-coated PET anodes using polymer gel as electrolyte. Finally, we have fabricated hybrid plastic/textile electrochromic cells using a conducting textile as cathode. We report here color changes from pale yellow to green, transparent to khaki, and pale green to reddish-brown.

Experimental Section

Chemicals. All chemical were purchased from Aldrich Chemical. Tetrahydrofuran was distilled over a potassium/benzophenone system. Toluene, acetonitrile, and propylene carbonate (99.7% anhydrous) were distilled over calcium hydride before use.

Instrumentation. NMR spectra were recorded on a Bruker AMX300 in deuterated chloroform at ambient temperature. Number-average (M_n) and weight-average (M_w) molecular weight were determined by size exclusion chromatography (SEC) with an HPLC pump using a Waters 515 differential refractometer. THF (HPLC grade, Aldrich) was the eluting solvent at a flow rate of 1 mL/min. The calibration curve was made with a series of polystyrene standards. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TG50 under a heating rate of 20 °C/min and a nitrogen flow rate of 200 mL/min.

Electrochemical measurements were carried out using a Solartron model 1287 potentiostat. A two-compartment cell using a three-electrode assembly was used to record cyclic voltammetry. The working electrode was either platinum button or ITO-coated glass. The counter electrode was a platinum wire, and 0.01 M Ag/AgNO$_3$ (Ag/Ag$^+$) was used as the reference electrode. The electrolyte used was 0.1 M TBABF$_4$ in acetonitrile. Spectroelectrochemistry data of the polymers films were recorded on Hewlett-Packard diode-array spectrophotometer (model 8452A). The measurements were accomplished using films spray-coated onto previously cut ITO-coated glass slides (10 × 75 × 1.1 mm, 30−60 Ω/square, SPI Supplies) using the same electrode setup used for cyclic voltammetry. Spectroelectrochemical data of the all-solid-state electrochromic cells were recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A) using an Instek GPS-3303 laboratory DC power source to fix the potential between the two ITO electrodes of the device.

Electrochromic polymers films were produced by spraying solutions of the polymers (5 mg/mL in tetrahydrofuran) using a Paasche airbrush nozzle (pressure fixed at 12 psi) onto a ITO-coated glass substrate (25 × 75 × 0.7 mm, 15−25 Ω/square, Delta Technologies Ltd.). The polymers were spray-coated onto an active surface of 2 × 2 cm using a mask. A gel electrolyte based on PMMA (MW: 120 000) and LiClO$_4$ was plasticized with propylene carbonate to form a highly transparent and conductive gel. PMMA (7 g) was dissolved in dry acetonitrile (70 g). LiClO$_4$ (3 g) was added to the solution as supporting electrolyte. Finally, propylene carbonate (20 g) was added as plasticizer. The whole mixture was then slowly heated until gelation. The gel electrolyte was spread on the polymer-coated side of the electrode, and the electrodes were sandwiched under atmospheric conditions. An epoxy resin was used to seal the device.

Colorimetry measurements were obtained using a Datacolor Mercury 2000 portable spectrophotometer. The color coordinates are expressed in the CIE 1931 Yxy color spaces. A Canon (Canon A95) digital camera was used to take photographs of the polymer electrochromic device at high resolution.

Monomer Syntheses. The following starting materials were prepared according to literature procedures: 2,5-dibromo-3,4-ethylenedioxythiophene,[36] 3,6-dibromo-*N*-octylcarbazole,[37] bis(6-bromo-*N*-octylcarbazol-3-yl),[38] 2,7-dibromo-3,6-dimethoxy-9,9-dihexylfluorene,[39] 4-butyl-*N*,*N*-diphenylaniline,[40] and 4-butyl-*N*,*N*-bis(4-bromophenyl)-aniline.[41] All of the monomers were carefully purified prior to use in the polymerization reaction.

4-Butyl-*N*,*N*-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-4-phenyl)-aniline. To a solution of 4-butyl-*N*,*N*-bis(4-bromophenyl)-aniline (7.86 g, 17.1 mmol) in anhydrous THF (170 mL) at −78

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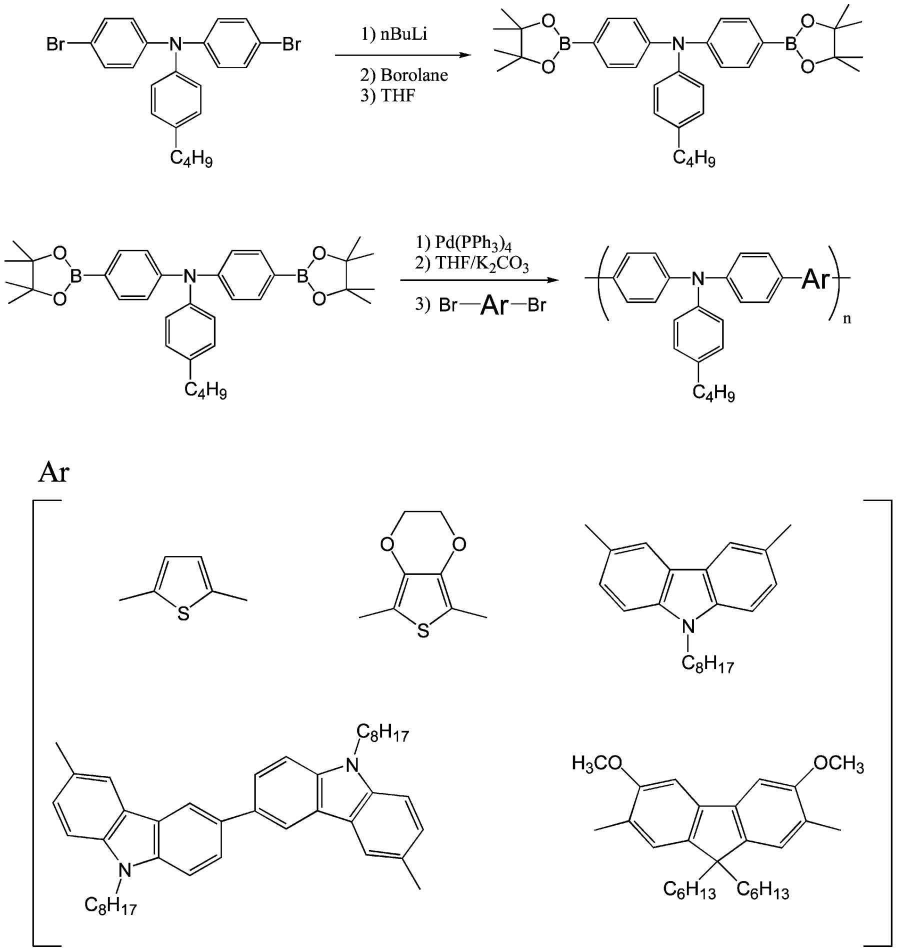
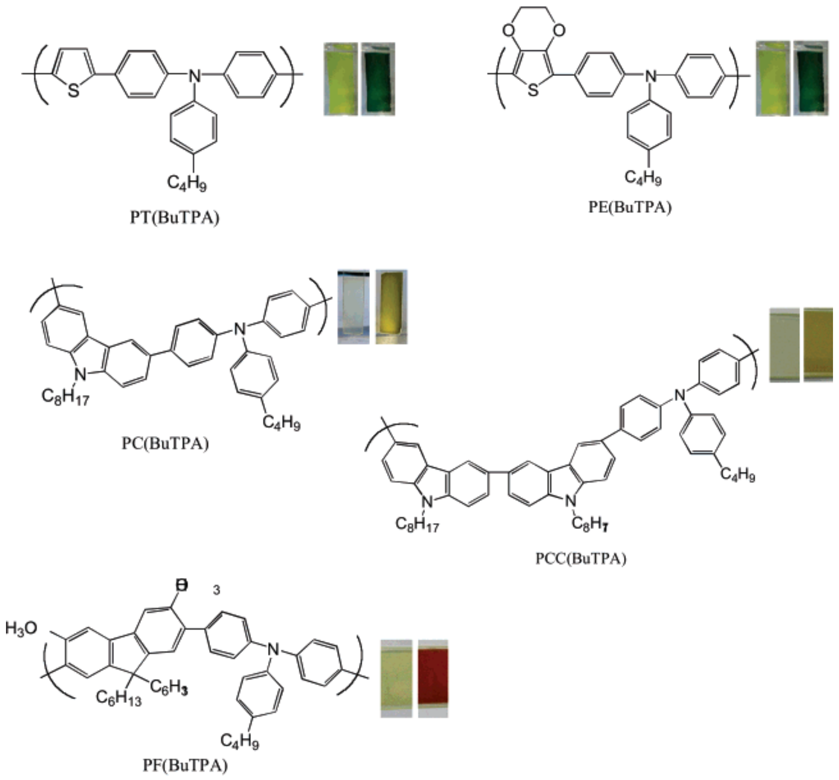
Scheme 1. Synthesis of 4-Butyltriphenylamine-Based Copolymers



Scheme 2. Chemical Structure and Color Transitions of the Copolymers



°C was added *n*-butyllithium (17.1 mL, 43.1 mmol, 2.5 M in hexane). The mixture was stirred at −78 °C for 45 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.5 mL, 51.3 mmol) was added rapidly to the solution. The mixture was stirred

Table 1. SEC and TGA Data of Poly(4-butyltriphenylamine) Derivatives

polymer	M_n	M_w	PDI	T_d (°C)
PT(BuTPA)	10 600	27 000	2.5	466
PE(BuTPA)	9000	23 000	2.6	278
PC(BuTPA)	6200	15 000	2.4	440
PCC(BuTPA)	4900	9500	1.9	448
PF(BuTPA)	16 000	43 000	2.7	300

for 2 h at −78 °C. The mixture was poured into water and extracted with diethyl ether. The organic extracts were combined and washed with brine. The solvent was removed under reduced pressure, and the crude product was purified by recrystallization from methanol to afford the title product as a pale yellow solid (5.35 g, 56%). mp 204−206 °C. ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 150.3, 144.6, 138.9, 135.9, 129.4, 125.9, 122.4, 83.6, 35.1, 33.6, 24.9, 22.5, 14.0. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.66 (d, J = 8.5 Hz, 4H), 7.06 (m, 8H), 2.58 (t, J = 7.6 Hz, 2H), 1.63−1.56 (m, 2H), 1.41−1.33 (m, 26H), 0.94 (t, J = 7.6 Hz, 3H). HRMS: calcd for $C_{34}H_{45}B_2NO_4$, 553.3534; found, 553.3539

Copolymers Syntheses. The chemical structure and the synthetic route to the new poly(4-butyltriphenylamine) derivatives are depicted in Schemes 1 and 2. All of the copolymers were synthesized using the Suzuki−Miyaura cross-coupling reaction using this typical procedure: To a mixture of dibromide compound (1.00 equiv), 4-butyl-*N*,*N*-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-4-phenyl)-aniline (1.00 equiv), and freshly prepared Pd(0)$(PPh_3)_4$ was added a deoxygenated mixture of THF ([monomer = 0.25 M]) and aqueous 2 M K_2CO_3 (3/2 in volume). The mixture was vigorously stirred at 85−90 °C for 48−72 h. After the solution was cooled, the whole mixture was poured slowly into a cold mixture of methanol/deionized water (10/1 in volume). The polymer was collected by filtration and washed with methanol. The solid was then washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The polymer was further purified by redissolving in chloroform and then precipitated from cold methanol prior to drying at room temperature under high vacuum.

Results and Discussion

All of the polymers were obtained in good yield (50−90%). PT(BuTPA) and PE(BuTPA) were obtained as yellow powders. PC(BuTPA) and PCC(BuTPA) were obtained as beige powders, while PF(BuTPA) was obtained as a pale yellow powder. All of these polymers were readily soluble in chloroform, toluene, or tetrahydrofuran, which make them suitable for spin or spray-coating techniques. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the soluble fraction of the copolymers range from 4900 to 16 000 and 9500 to 43 000, respectively, with polydispersity indexes ranging from 1.9 to 2.7. These data are summarized in Table 1. Heeger et al.[31] have reported for a similar copolymer, poly(*N*-(4-butyl-phenyl)imino(1,1′:4′,1″-terphenyl-4′,4″-ylene)) (PBPITP), a number-average molecular weight (M_n) of 6400 with a polydispersity index of 1.75. Uniform, free-standing, dry, and highly flexible films can be obtained from slow evaporation of a concentrated solution. This mechanical property is important for the further development of flexible electrochromic devices. The thermal stability of the polymers was evaluated by thermogravimetric analyses (TGA) under a nitrogen atmosphere. The data are summarized in Table 1. Most copolymers exhibit very good thermal stabilities, losing less than 5% of their weight well above 400 °C.

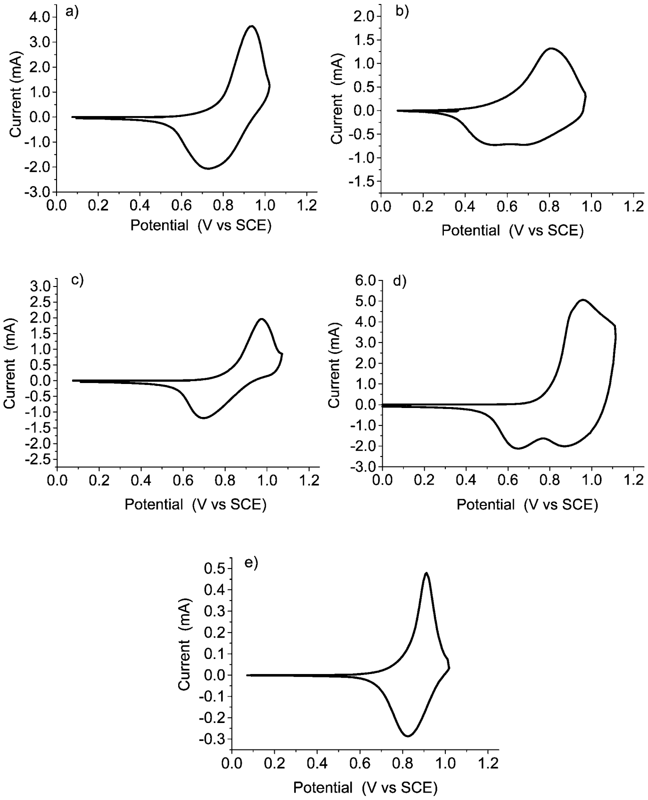


Figure 1. Cyclic voltammograms on platinum button of (a) PT(BuTPA), (b) PE(BuTPA), (c) PC(BuTPA), (d) PCC(BuTPA), and (e) PF(BuTPA).

Films of poly(4-butyltriphenylamine) derivatives were deposited onto ITO-coated glass or ITO-coated poly(ethylene-terephthalate) (PET) substrates following the spray-coating technique reported by Reynolds et al.,[17] leading to uniform polymeric layers (Scheme 2). The UV−vis and colorimetric data of those films are summarized in Table 2. PT(BuTPA) and PE(BuTPA) show absorption in the visible range with maxima of absorption of 416 and 418 nm, respectively, leading to a yellow polymer layer with corresponding 1931

Table 2. Optical, Electrochemical, and Colorimetric Data of Copolymers

					CIE 1931 coordinates			
			color transition		neutral		oxidized	
polymers	abs[a] (nm)	$E_{ox}{}^b/E_{ox}{}^c$ (V vs SCE)	neutral	oxidized	*x*	*y*	*x*	*y*
PT(BuTPA)	416	0.94/1.19	yellow	green	0.39	0.45	0.32	0.41
PE(BuTPA)	418	0.81/0.95	yellow	green	0.42	0.47	0.32	0.42
PC(BuTPA)	344	0.98/1.16	colorless	khaki	0.31	0.33	0.35	0.38
PCC(BuTPA)	342	0.95/1.16	colorless	khaki	0.32	0.35	0.40	0.42
PF(BuTPA)	380	0.92/1.19	pale green	reddish-brown	0.33	0.37	0.40	0.36

[a] Absorption of film of electrochromic polymer. [b] Oxidation potential (film on platinum button). [c] Oxidation potential (film on ITO).

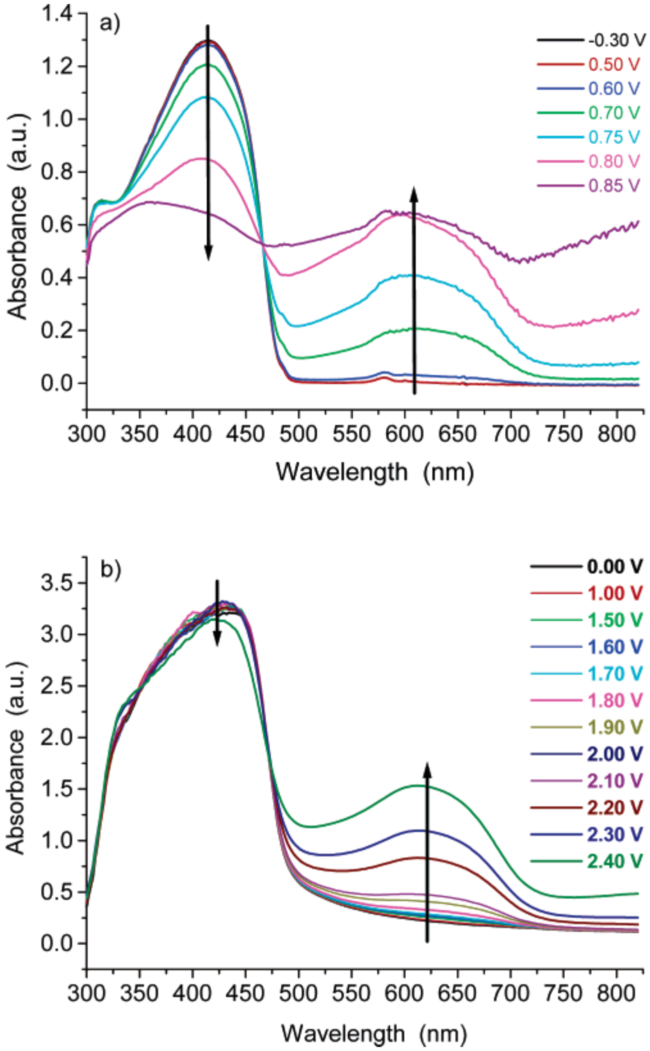


Figure 2. Spectroelectrochemistry of (a) PT(BuTPA) film on ITO immerged in 0.1 M TBABF$_4$/acetonitrile vs Ag/Ag$^+$ and (b) PT(BuTPA) all-solid-state EC using gel electrolyte.

CIE coordinates reported in Table 2. We note an important red shift of the maximum of absorption of PT(BuTPA) and PE(BuTPA) when they are compared to the maximum of absorption of PBPITP synthesized by Heeger et al.[31] The substitution of the phenyl group in PBPITP by a five-membered ring such as thiophene or EDOT unit should give a more planar structure with a better $\pi-\pi^*$ overlap between the phenyl group of the triarylamine unit and the comonomer. While PT(BuTPA), PE(BuTPA), and PBPITP are slightly colored in their neutral state, PC(BuTPA) and PCC(BuTPA) show a maximum of absorption outside of the limit of the visible domain, at 344 and 342 nm, respectively, leading to colorless polymers in the neutral state (Scheme 2). This is an interesting property because only few electrochromic polymers are colorless in their neutral state. The 3,6-linked carbazole unit acts as a conjugation break, leading to a discrete chromophore within the polymer backbone. Finally, as expected, the maximum of absorption of PF(BuTPA) is significantly red-shifted when compared to the maximum of absorption of PC(BuTPA) and PCC(BuTPA).

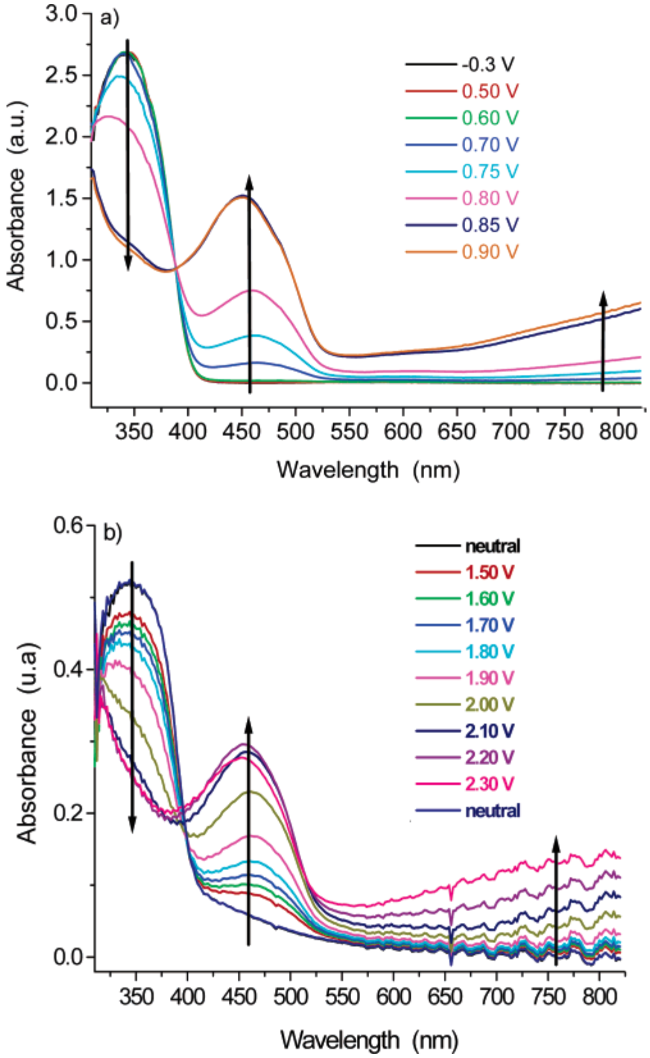
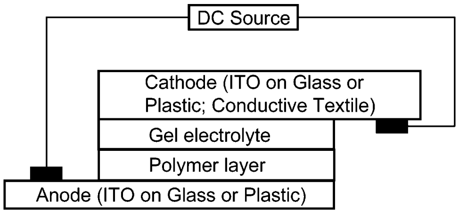


Figure 3. Spectroelectrochemistry of (a) PC(BuTPA) film on ITO immerged in 0.1 M TBABF$_4$/acetonitrile vs Ag/Ag$^+$ and (b) PC(BuTPA) all-solid-state EC using gel electrolyte.

The electrochemical data of the five new polymers are reported in Table 2. Cyclic voltammograms were obtained by casting films of polymers onto a platinum wire or by spray-coating films of polymers onto an ITO-coated glass. As shown in Figure 1, all polymers are stable upon oxidation with potential of oxidation ranging from 0.81 to 0.95 V vs SCE, which make them stable against air oxidation. For all polymers developed here, a change of coloration is associated with the oxidation process (Scheme 2). For PT(BuTPA) and PE(BuTPA), three colors states are observed: yellow to green to black. For our experiments, we have controlled the potential of the electrode to observe the neutral and the intermediate color of those two materials. Moreover, to investigate the influence of the material used as anode in electrochromic cells (ITO-coated glass or ITO-coated PET electrodes), cyclic voltammetry measurements were performed on films of spray-coated polymers (CV not shown here). For all polymer films, a shift of about +210 mV is observed between oxidation potential of the films on the ITO-coated glass electrodes versus the platinum button. This can be attributed to the difference of conductivities between the platinum and the ITO-coated glass. The cycling stability of all polymers films on ITO-coated glass anode was also investigated. For PT(BuTPA), PE(BuTPA), and PF(BuTPA), 1000 redox cycles at 50 mV/s were performed without significant changes. However, the stability of PC(BuTPA)

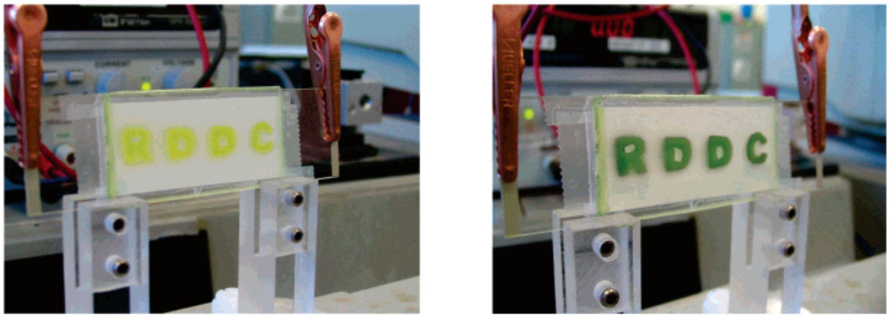
Scheme 3



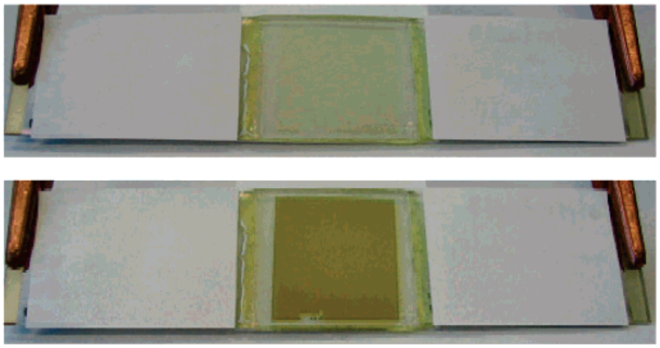
and PCC(BuTPA) was not as good as the other polymers. After 500 redox cycles at 50 mV/s, we have observed that the films become detached from the substrate so they could not be returned to their neutral state. This phenomenon is not surprising because these two copolymers are poorly conjugated (giving a large band gap) and should therefore be poorly conducting.

Spectroelectrochemical measurements were performed on films of polymers spray-coated onto ITO/glass slides. The coated electrodes were immerged in 0.1 M $TBABF_4$/acetonitrile electrolyte solution. As a typical experiment, we report two spectroelectrochemical spectra of PT(BuTPA) and PC(BuTPA), and the results are shown in Figures 2a and 3a. For all polymers, the films were conditioned by applying potentials between the reduced and the oxidized states. The color of both states is shown in Scheme 2. For PT(BuTPA), the potential of the working electrode was set at −0.3 V vs Ag/Ag^+ to ensure that the polymer was fully reduced. As shown in Figure 2a, the onset of the color change was observed at 0.6 V vs Ag/Ag^+. From the reduced (neutral) yellow color, the film of PT(BuTPA) has changed to green (oxidized) within 200 mV range. At 0.85 V vs Ag/Ag^+, the

a) PT(BuTPA) as active layer



b) PC(BuTPA) as active layer



c) PF(BuTPA) as active layer

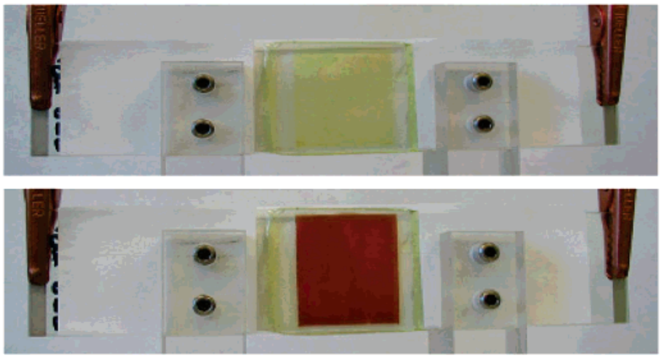


Figure 4. Photos of sandwich-type ITO-coated glass electrochromic cells: (a) PT(BuTPA) as active layer; (b) PC(BuTPA) as active layer; and (c) PF(BuTPA) as active layer.

a) PT(BuTPA)

b) PF(BuTPA)

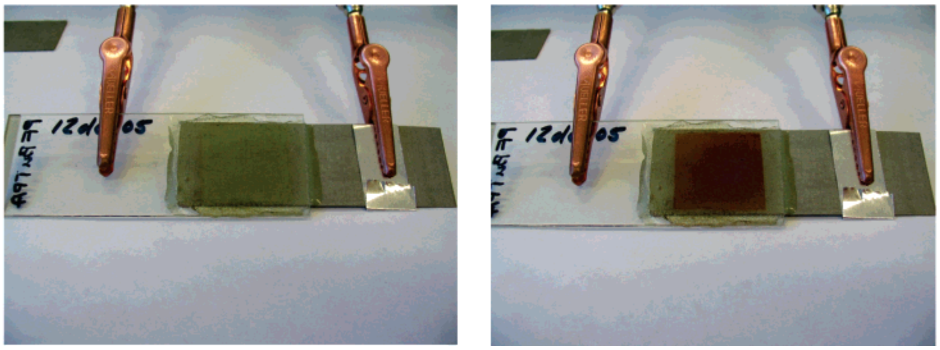


Figure 5. Photos of hybrid ITO-coated PET/textile electrochromic cells: (a) PT(BuTPA), (b) PF(BuTPA).

film was black. We have observed a similar behavior for PE(BuTPA). The second spectroelectrochemical spectrum (Figure 3a) stands for PC(BuTPA). Like the previous experiment, the PC(BuTPA) film was conditioned by applying −0.3 V vs Ag/Ag$^+$ at the working electrode to ensure that the polymer film fully reduced. At this potential the film is colorless. As shown in Figure 3a, the onset of the color change was observed at 0.7 V vs Ag/Ag$^+$. By increasing the potential in a stepwise manner, the color change was observed over a range of 200 mV. The khaki color was uniform over the surface of the working electrode, and the film can be reduced without the loss of the colorless neutral state. The same results were obtained with PCC(BuTPA). Photos of the layers of the neutral and the oxidized states of the five polymers are shown in Scheme 2.

Because the electrochromic switching time and the coloration efficiency are not issues for camouflage applications, we have fabricated as preliminary investigations single layer electrochromic cells (Scheme 3). The polymer films were spray-coated either onto ITO-coated glass or onto ITO-coated PET and then dried. Afterward, the gel electrolyte was spread on the polymer-coated side of the electrode and the electrodes were sandwiched under atmospheric condition. To prevent leakage, an epoxy resin was applied to seal the device. As typical examples, spectroelectrochemical data of the electrochromic cells based on PT(BuTPA) and PC(BuTPA) are reported. Figure 2b shows the spectroelectrochemical spectrum of PT(BuTPA) at a DC voltage fixed between 0.0 and 2.4 V. When the voltage of 0.0 V was applied, the polymer is neutral and yellow. When the voltage applied was increased (to a maximum of 2.4 V), the color changed from yellow to green, the same as was already observed for the solution spectroelectrochemistry experiments. However, we observed that the absorption peak in the all-solid-state electrochromic cell was broader than the one observed in the solution electrochromic cell. Moreover, we did not find a noticeable decrease of the band centered at 416 nm. These effects can be due to the layer thickness and the diffusion effect of the polymer layer. Despite those observations, the color change is uniform, as can be seen in Figure 4a where the letters RDDC were written by spray-coating PT(BuTPA) solution over a stencil. The neutral state (left) is yellow, while the oxidized state (right) is green. The 1931 CIE coordinates are reported in Table 2. Figure 3b shows the spectroelectrochemical spectrum of PC(BuTPA) at a DC voltage fixed between 0.0 and 2.3 V. When a voltage of 0.0 V was applied, the polymer was neutral and colorless. When the voltage applied was increased (to a maximum of 2.3 V), the color changed from colorless to khaki, as was already observed for the solution spectroelectrochemistry experiments. The color change was uniform as can be seen in Figure 4b where the neutral and oxidized states are shown. The 1931 CIE coordinates are reported in Table 2. All-solid-state electrochromic cells using PE(BuTPA), PCC(BuTPA), and PF(BuTPA) were studied (not shown here) using the same device configuration. The color transition from the neutral to oxidized states and 1931 CIE coordinates are reported in Table 2. Figure 4c shows an electrochromic cell using PF(BuTPA) as the active layer.

Finally, the needs for a flexible, lightweight, and wearable adaptive camouflage led us to the fabrication of hybrid plastic/textile electrochromic cells. The polymer films were spray-coated onto ITO-coated PET and further dried. Afterward, the gel electrolyte was spread on the polymer-coated side of the electrode to cover the entire surface. A conductive textile (Shield Super, LessEMF, Inc.) was used as cathode and was applied over the gel electrolyte (Scheme 3). The electrochromic cell was allowed to dry 24 h to let the gel electrolyte seal the devices. Figure 5a and b shows the hybrid electrochromic cells based on PT(BuTPA) and PF(BuTPA), respectively. The behavior of the electrochromic cells was the same as the one reported for the ITO-coated glass electrochemical cell. For PT(BuTPA), the polymer layer was neutral and yellow (Figure 5a, left) when the voltage applied between the two electrodes was fixed at −1.0 V. When the potential was increased stepwise up to 2.0 V, the polymer layer turns green (Figure 5a, right). The reduction of the polymer layer was achieved by applying a negative potential of −1.1 V. The conductive textile did not support any lower potential. For PF(BuTPA), the polymer layer was neutral and pale green (Figure 5b, left) when the voltage applied between the two electrode was fixed at −1.0 V. When the potential was increased stepwise up to 2.2 V, the polymer layer turns reddish-brown (Figure 5b, right). The polymer layer was reduced by applying a negative potential of −1.1 V. The preliminary results for the switching time reveal that these hybrid plastic/textile electrochromic cells fulfill the needs for adaptive camouflage but they are too slow for fast displays devices.

Conclusion

Five soluble, processable, and electrochromic poly(4-butyltriphenylamine) derivatives were prepared using the Suzuki−Miyaura cross-coupling reaction. Interestingly, among these new copolymers, PC(BuTPA) and PCC(BuTPA) are colorless in their neutral states and show reversible color transition from colorless to khaki. Moreover, all-solid-state electrochromic cells fabricated have shown color transitions like those found in natural vegetation such as yellow, green, khaki, and reddish-brown. Finally, to the best of our knowledge, we report for the first time flexible hybrid electrochromic cells using ITO-coated plastic and conductive textile as electrodes, which show interesting features for adaptive camouflage.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of 4-butyl-*N*,*N*-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-4-phenyl)aniline (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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